Methane Activation

Deutsche Ausgabe: DOI: 10.1002/ange.201606707
Internationale Ausgabe: DOI: 10.1002/anie.201606707

Hidden Hydride Transfer as a Decisive Mechanistic Step in the Reactions of the Unligated Gold Carbide $[AuC]^+$ with Methane under Ambient Conditions

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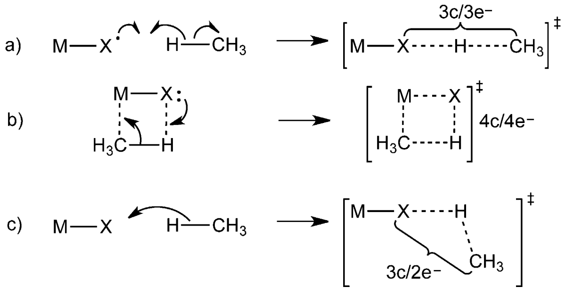
Dedicated to Professor Diethard K. Böhme on the occasion of his 75th birthday

Abstract: *The reactivity of the cationic gold carbide $[AuC]^+$ (bearing an electrophilic carbon atom) towards methane has been studied using Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS). The product pairs generated, that is, Au^+/C_2H_4, $[Au(C_2H_2)]^+/H_2$, and $[C_2H_3]^+/AuH$, point to the breaking and making of C–H, C–C, and H–H bonds under single-collision conditions. The mechanisms of these rather efficient reactions have been elucidated by high-level quantum-chemical calculations. As a major result, based on molecular orbital and NBO-based charge analysis, an unprecedented hydride transfer from methane to the carbon atom of $[AuC]^+$ has been identified as a key step. Also, the origin of this novel mechanistic scenario has been addressed. The mechanistic insights derived from this study may provide guidance for the rational design of carbon-based catalysts.*

Despite its structural simplicity, it remains a challenge to selectively activate methane's C–H bonds under ambient conditions.[1] Quite some attention has been paid to elucidate mechanistic aspects pertinent to the cleavage of this thermodynamically strong and kinetically inert bond.[2] In fact, well-designed, state-of-the-art mass spectrometry (MS) experiments in conjunction with high-level quantum-chemical (QC) calculations have permitted the identification of the elementary steps at a molecular level and provided valuable mechanistic insights.[2a–d] For example, spin density has been identified to play a crucial role in the hydrogen atom transfer (HAT) from methane to a suitable hydrogen atom acceptor; typical examples include cluster oxides possessing a terminal oxyl group in the active site ($O_t^{\bullet}$).[3] Mechanistic studies revealed that a three-center/three-electron (3c/3e⁻) transition state constitutes the rate-determining step in HAT, and a singly occupied, nonbonding orbital with a node on the hydrogen atom in transit is present (Scheme 1 a).[3c,4] Additionally, as shown recently under certain conditions, even closed-shell clusters, lacking unpaired high spin-density at the active site, can effectively activate methane under ambient, single-collision conditions.[5] Furthermore, and as shown for the $[Al_2O_2]^+/CH_4$ couple, a proton-coupled electron transfer (PCET) mechanism instead of the conventional HAT can bring about thermal cleavage of the C–H bond of methane.[4a] This is due to the strong electrophilic, Lewis acidic site of the aluminum of $[Al_2O_2]^+$, which cleaves the C–H bond heterolytically while the hydrogen is transferred as a proton to the basic oxygen atom. The corresponding transition state for this C–H bond cleavage has been classified as a 4c/4e⁻ transition state (Scheme 1 b).[3c,4a]



Scheme 1. Simplified mechanistic scenarios for the participation of M-X/CH_4 couples in a) a HAT process, b) a PCET reaction, and c) a hydride transfer process. M = metal, X = hydrogen acceptor.

While quite a few unexpected mechanistic variants have been identified recently in the context of thermal methane activation,[1a,2d,3a,5a–e,6] to the best of our knowledge, C–H bond cleavage by a positively charged ligand (X) of a complex $[M\text{-}X^{\delta+}]^+$, in which X serves as the hydrogen acceptor, has not yet been reported. Herein, we describe our findings on the reaction of the cationic gold carbide $[AuC]^+$ with methane, as derived from a combined experimental/computational approach.

The gas-phase reactions were performed using Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) under single-collision conditions (see the Experimental Section in the Supporting Information for details). The FT-ICR mass spectra (Figure 1) show the reactions of mass-selected, thermalized $[AuC]^+$ ions ($m/z = 209$) with isotopologues of methane. To clearly differentiate between reactions of the parent ion with background gases, reference spectra with argon have been recorded as well.

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Supporting information for this article can be found under: http://dx.doi.org/10.1002/anie.201606707.

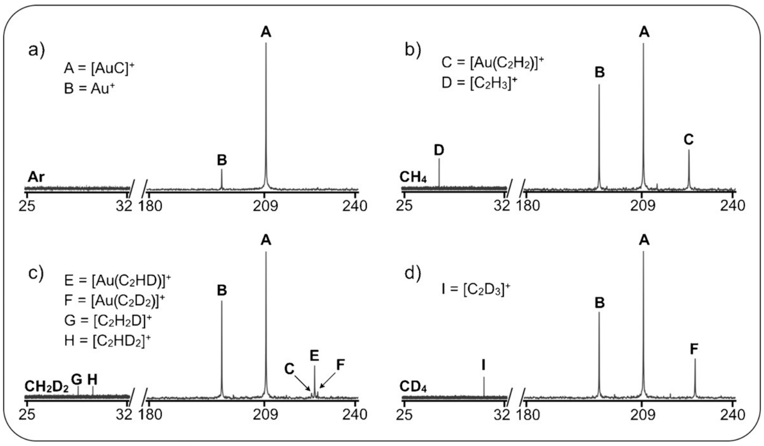

Figure 1. Mass spectra for the thermal reactions of $[AuC]^+$ with a) argon, b) CH_4, c) CH_2D_2, and d) CD_4 at a pressure of 4.0×10^{-9} mbar after a reaction time of 5 s. The unit for the x axes is m/z.

As indicated in the reference spectrum (Figure 1 a) $[AuC]^+$ reacts by carbon atom transfer (CAT) to the background gases. However, when CH_4, CH_2D_2, or CD_4 are admitted to the cell (Figures 1 b–d) the signal corresponding to CAT is significantly enhanced (Equation (1)). Moreover, a new signal appears, representing the formal uptake of a carbene unit from methane accompanied by the concomitant liberation of H_2 (Equation (2)). Furthermore, a signal is present at the lower mass range which has been assigned to $[C_2H_3]^+$ (Equation (3)).

$$[AuC]^+ + CH_4 \rightarrow Au^+ + C_2H_4;\ 51\,\% \tag{1}$$

$$[AuC]^+ + CH_4 \rightarrow [Au(C_2H_2)]^+ + H_2;\ 28\,\% \tag{2}$$

$$[AuC]^+ + CH_4 \rightarrow [C_2H_3]^+ + AuH;\ 21\,\% \tag{3}$$

In addition to exact mass measurements, the identity of the product species in the observed reactions has been confirmed by labeling experiments. For example, Au^+ and the ions $[Au(C_2D_2)]^+$ and $[C_2D_3]^+$ are generated in the reaction of $[AuC]^+$ with CD_4 (Figure 1 d). The $[AuC]^+/CH_2D_2$ couple gives rise to charged products $[Au(C_2H_2)]^+$, $[Au(C_2HD)]^+$, $[Au(C_2D_2)]^+$, $[C_2H_2D]^+$, and $[C_2HD_2]^+$; they are formed with a ratio of 1.2:5.4:1 and approximately 1:1, respectively (Figure 1 c).

The rate coefficient for the reaction, $k([AuC]^+/CH_4)$, is estimated to be $2.2\times10^{-11}\ cm^3\,molecule^{-1}\,s^{-1}$, corresponding to a collision efficiency of 22 % relative to the collision rate.[7] The intermolecular kinetic isotope effect (KIE) derived from the $[AuC]^+/CH_4/CD_4$ couples amounts to $KIE_{C\text{-}H/C\text{-}D} = 1.3$ after considering the contribution of the reactions with background gases.

To obtain mechanistic insight into the $[AuC]^+$ mediated C–H bond activation of methane, high-level quantum mechanical (QM) calculations were carried out. The potential-energy surfaces (PESs) of the most favorable pathways, as well as important structural parameters of key species, are shown in Figure 2 (additional computational details are provided in the Supporting Information).

The reaction of singlet-ground state[8] $[AuC]^+$ with CH_4 starts by the barrier-free, exothermic formation of an encounter complex (**I1**). This step corresponds to an electrophilic attack of methane's C–H bond by the positively charged carbon ligand of $[AuC]^+$. Subsequently, a H-atom is transferred to the AuC moiety via transition state **TS1/2**; the latter is located 39 kJ mol^{-1} below the energy of the separated reactants (**SR**). The so-formed ethylidene intermediate **I2** rearranges further to the η^2-ethylene complex **I3** by a second H-transfer from the CH_3 group in **I2** via transition state **TS2/3. I3**, which represents the global minimum, has two options to react further: it can dissociate into cationic Au^+ and neutral ethylene C_2H_4 (**P1**) or undergoes a double hydrogen atom transfer from the C_2H_4 moiety to the gold atom via the sequence **I3**→**TS3/4**→**I4**→**TS4/5**→**I5**; the latter intermediate dissociates into $[Au(C_2H_2)]^+$ under the evaporation of neutral H_2 (**P2**). Alternatively, intermediate **I4** can directly dissociate into neutral AuH and $[C_2H_3]^+$ (**P3**).

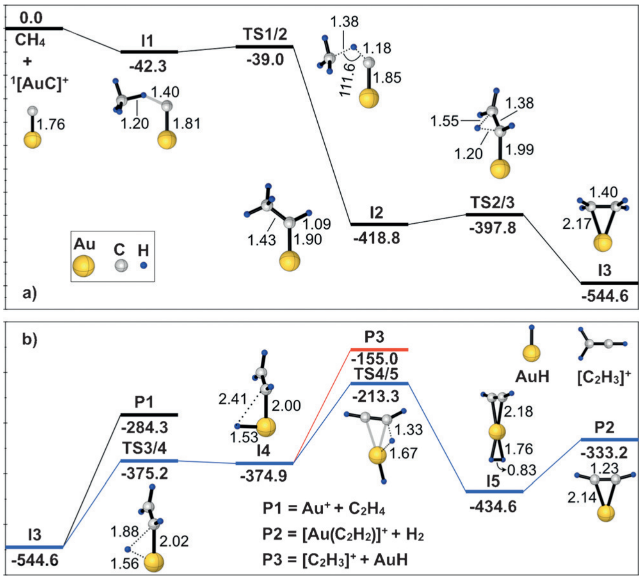

Figure 2. CCSD(T)-REL//B2GP-PLYP-calculated potential energy profile for the reaction of the cationic gold carbide $[AuC]^+$ with CH_4 at the singlet ground-state surface. Key ground-state structures with selected geometric parameters are also provided. The zero-point vibration corrected energies (ΔH_{298K} in kJ mol^{-1}) of the reaction intermediates, transition states, and products with respect to the separated reactants, are given relative to the separated reactants $[AuC]^+$ and CH_4.

For gas-phase reactions under thermal, single-collision conditions, the total energy of the system remains constant. As shown in Figure 2, all the stationary points along the reaction coordinates are located energetically below the reaction entrance; thus, all products **P1**–**P3** are accessible without external energy input. The energetically most demanding step in the overall reaction of CH_4 with $[AuC]^+$ corresponds to transition state **TS1/2**, which, however, is accessible, in line with the experimental results. Furthermore, as the channel leading to the products **P1** is both entropically and energetically favored as compared with generation of **P2** and **P3**, respectively, a branching ratio in favor of **P1** is expected. Again, this is observed experimentally. Actually, when **P1** is generated independently from Au^+ and C_2H_4, the products **P2** and **P3** are not formed. Rather, upon collisional activation decomposition back to Au^+ and C_2H_4 occurs in line with the PES. It should be mentioned, however, that the branching ratio cannot be predicted by the PES alone but that dynamic factors of the different pathways also have to be taken into account.

To obtain a more detailed mechanistic view of the reaction of $[AuC]^+$ with methane, we performed an analysis of the quasi-restricted orbitals (QROs) that participate in the initial step of the chemical transformations.[4b,9] Figure 3 shows the detailed evolution of the electronic structures along the reaction coordinates.

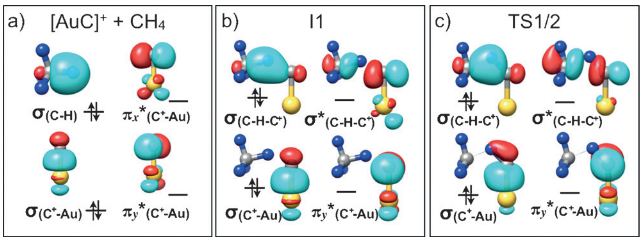

Figure 3. Schematic molecular orbital diagrams as represented by quasi-restricted orbitals. a) Separated reactants $[AuC]^+ + CH_4$; b) encounter complex **I1**; c) transition state **TS1/2**.

As shown in Figure 3a, initially the reactants possess a $\sigma_{(\mathrm{C-H})}$ orbital representing the C–H bond of methane that undergoes C–H bond cleavage, then a doubly occupied $\sigma_{(\mathrm{C^+-Au})}$ orbital that represents the σ-bond of the gold carbide, and finally two unoccupied $\pi_{x/y*(\mathrm{C^+-Au})}$ orbitals are mainly provided by the carbon atom. Notably, these two empty orbitals are relatively low in energy, thus making $[AuC]^+$ highly electrophilic. At the encounter complex **I1** (Figure 3b) a significant electronic reorganization has already taken place. The carbon atom of $[AuC]^+$ interacts with the electron pair residing in the $\sigma_{(\mathrm{C-H})}$ bond of methane, thus resulting in the formation of a doubly occupied three-centered orbital, $\sigma_{(\mathrm{C\text{-}H\text{-}C^+})}$. Correspondingly, the spatially involved empty $\pi_{x*(\mathrm{C^+-Au})}$ orbital is transformed to an antisymmetric orbital ($\sigma^*_{(\mathrm{C\text{-}H\text{-}C^+})}$), which is composed of lobes on H_3C and C of the carbide moiety. The orbitals of $\sigma_{(\mathrm{C^+-Au})}$ and $\pi_{y*(\mathrm{C^+-Au})}$ are not involved in this process. Comparing the electronic structures of **I1** and **TS1/2**, as shown in Figure 3b,c, only relatively minor changes have occurred, even though the hydrogen transfer is almost completed. The interaction between the two carbon atoms increases as the angle of the $C\cdots H\cdots C^+$ triad is considerably bent ($\measuredangle$C-H-$C^+ = 111.6°$ in **TS1/2**). Notably, the lobe of the $\sigma_{(\mathrm{C^+-Au})}$ orbital starts to interact with the transferred hydrogen, but the $\pi_{y*(\mathrm{C^+-Au})}$ orbital still acts as a mere spectator.

Since a singly occupied nonbonding-type orbital with a node on the hydrogen atom in transit does not appear along this process, the reaction cannot be classified as a conventional HAT mechanism.[3] However, as the C–H bond activation step features a two-electron, three-center, bent transition state (**TS1/2**) (Scheme 1c),[10] we speculate that it is rather a hydride transfer; this is, indeed, confirmed by an analysis of the total electron-density evolution of the $[AuC]^+$ moiety along the reaction coordinates (Figure 4).

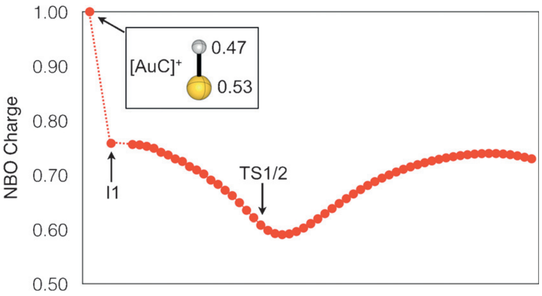

Figure 4. The evolution of the NBO charge of the $[AuC]^+$ moiety along the reaction coordinate of the first C–H bond activation of methane. The inset shows the atomic charges of the $[AuC]^+$ species.

As shown in Figure 4, at the initial stage the carbon atom of $[AuC]^+$ carries a significant positive charge (+0.47), thus serving as a good hydride acceptor. In the course of the formation of **I1**, the positive charge of $[AuC]^+$ diminishes greatly, indicating that electron density has already been transferred from methane to $[AuC]^+$ via the hydrogen in transit. Next to the transition state for C–H bond activation, the positive charge of $[AuC]^+$ continually decreases until the reaction proceeds through the transfer event. In the transition region, the $[AuC]^+$ moiety has a minimum positive charge of +0.59. As the transferred electron density takes the same route with that of the simultaneously transferred hydrogen atom, the C–H bond activation can be described as a hydride transfer mechanism. Additionally, an analysis of the NBO charge variations of the CH_3 moiety and the hydrogen in transit also confirmed this mechanism (Supporting Information, Figure S1). While gas-phase hydride abstraction from larger hydrocarbons ($\geq C_3H_8$) has been observed earlier,[11] the system described here is the very first in which this process involves methane.

In summary, in this study the reactivity and mechanistic details of the reactions of the cationic gold carbide $[AuC]^+$ with methane has been studied by a combined experimental/theoretical approach. $[AuC]^+$ activates methane under thermal, single-collision conditions and three reaction channels have been identified by using FT-ICR-MS; the reaction mechanisms of these reactions are elucidated by detailed high-level QC calculations. A hydride transfer, along with the making of a C–C bond, are key, and account for the rate-limiting step of the C–H bond activation.[12] The existence of a low-energy empty π-orbital on the carbon active site, serving as the hydride acceptor, plays an important role in this transfer step. This novel mechanistic scenario might open up a new view for methane activation by using carbon-based materials in heterogeneous catalysis.[13]

Acknowledgements

This research was sponsored by the Deutsche Forschungsgemeinschaft (DFG); in particular the Cluster of Excellence "Unifying Concepts in Catalysis" (coordinated by the Technische Universität Berlin and funded by the DFG), and the Fonds der Chemischen Industrie. We thank Dr. Caiyun Geng for helpful comments.

Keywords: carbide · C–H bond activation · gas-phase reactions · hydride transfer

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 13072–13075
Angew. Chem. **2016**, *128*, 13266–13269

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[12] Direct transfer of a hydride from CH_4 to form $[CH_3]^+$ and neutral AuCH is, according to our calculations, on the singlet ground state surface very endothermic with $> 190\ \mathrm{kJ\,mol^{-1}}$. The excited triplet state of $[AuC]^+$ is located $> 75\ \mathrm{kJ\,mol^{-1}}$ above the ground state and, therefore, most likely not involved. In line with this finding, in the thermal reaction of $[AuC]^+$ with CD_4 there is no signal at m/z 18.04231 (that is, the exact mass of $[CD_3]^+$) at the detection limit of our FT-ICR instrument. Furthermore, regarding the formation of neutral AuH, the experimental BDE of neutral Au–H amounts to $300.5\ \mathrm{kJ\,mol^{-1}}$ (S. Brutti, G. Balducci, G. Gigli, *Rapid Commun. Mass Spectrom.* **2007**, *21*, 89–98). Thus, if separated Au and hydrogen atoms are formed instead of AuH, the reaction is endothermic by $> 140\ \mathrm{kJ\,mol^{-1}}$ and thus not accessible under thermal conditions.

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Received: July 11, 2016
Revised: August 9, 2016