Methane Activation

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Efficient Room-Temperature, Au^+-Mediated Coupling of a Carbene Ligand with Methane To Generate C_2H_x ($x = 4$, 6)

*Shaodong Zhou, Jilai Li, Xiao-Nan Wu, Maria Schlangen, and Helmut Schwarz**

Dedicated to Professor Bärbel Friedrich on the occasion of her 70th birthday

Abstract: *The thermal reactions of the closed-shell, "naked" gold–carbene complex $[Au(CH_2)]^+$ with methane have been explored by using FTICR mass spectrometry complemented by quantum chemical (QC) calculations at the CCSD(T)//BMK level of theory. Mechanistic aspects for this unprecedentedly efficient carbene insertion in the C–H bond of methane have been addressed and the origin of the counterintuitive high reactivity of $[Au(CH_2)]^+$ towards this most inert hydrocarbon is discussed.*

In addition to the vast amount of literature on condensed-phase studies of metal carbenes, there also exists a considerable number of reports dealing with various aspects of gaseous metal–carbene complexes.[1] The reactions observed in these studies can be classified into four different types: 1) metathesis processes;[1a,c,e,o] 2) mechanistic aspects of stepwise versus concerted carbene transfer to produce cyclopropane derivatives;[1r,u] 3) metal–carbene complexes that participate in C–N and C–O coupling;[1l–n] and 4) extrusion of a carbon atom from halobenzenes and its coupling with a methylene unit to form C_2H_2.[1v]

Here we report the efficient, room-temperature coupling of the methylene ligand of $[Au(CH_2)]^+$ ($^1A_1$) with CH_4 to form C_2H_4 and C_2H_6 [Eq. (1)].[2]

$$[Au(CH_2)]^+ + CH_4 \longrightarrow Au^+ + C_2H_6 \quad 16\% \quad (1a)$$

$$[Au(CH_2)]^+ + CH_4 \longrightarrow [Au(C_2H_4)]^+ + H_2 \quad 84\% \quad (1b)$$

Although the thermal reactions of CH_4 with the open-shell cluster carbenes $[Pt_n(CH_2)]^+$ [Eq. (2)] have been studied previously, only the dehydrogenation [Eq. (2)] was observed for $n = 1$ and 5. The reaction pair $[Pt(CH_2)]^+/CH_4$ did in fact result in the formation of C_2H_4, but with a rather low efficiency ($\phi = 2\%$). The efficiency with $[Pt_5(CH_2)]^+/CH_4$ was higher at $\phi = 26\%$, but the dehydrogenation occurred without carbon–carbon bond formation.[1l,3] Fischer—Tropsch-type coupling of methylene units has also been reported for the gas-phase reactions of atomic Ta^+, W^+, Ir^+, and Os^+ with CH_4 [Eq. (3)].[1d,4]

$$[Pt_n(CH_2)]^+ + CH_4 \longrightarrow [Pt_n,C_2,H_4]^+ + H_2 \quad (2)$$

$$[M]^+ + nCH_4 \longrightarrow [M(CH_2)_n]^+ + nH_2 \quad (3)$$

M = Ta, W, Ir, Os; $n \leq 8$

"Naked" $[Au(CH_2)]^+$ has been generated in the reaction of Au^+ with CH_3Cl, as described previously,[5] and further experimental details are given in the Supporting Information. Mass-selected and thermalized $[Au(CH_2)]^+$, when treated with CH_4, produced the products shown in Equation (1) with an efficiency of 29%, relative to the collision rate;[6] the rate constant amounts to $k = 2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. Although collision-induced dissociation (CID) of the product ion $[Au(C_2H_4)]^+$ at collision energies up to $E_{coll} = 3.0$ eV (given in the center-of-mass frame) liberates the C_2H_4 ligand, double resonance experiments demonstrate that $[Au(C_2H_4)]^+$ does not serve as the precursor in the thermal reaction of $[Au(CH_2)]^+$ with CH_4 to form Au^+. Labeling studies provide further mechanistic details: in the reaction of $[Au(CH_2)]^+$ with CD_4, the loss of D_2/HD/H_2 occur in a ratio of 2:6:1, and when $[Au(CH_2)]^+$ is reacted with CH_2D_2 it amounts to 1:7:9. Clearly, dehydrogenation involves both the carbene ligand and the incoming hydrocarbon substrate, and the reaction is accompanied by H/D exchange. For complete H/D scrambling, ignoring the operation of kinetic isotope effects, one would expect a ratio of 6:8:1 for the $[Au(CH_2)]^+/CD_4$ couple and 1:8:6 for the $[Au(CH_2)]^+/CH_2D_2$ system (Figure 1).

Quantum chemical (QC) calculations have been performed to obtain a refined mechanistic insight into the reactions of $[Au(CH_2)]^+$ with CH_4. The potential-energy surface (PES) and relevant structural information of the most favorable pathways are shown in Figure 2; additional computational details are provided in the Supporting Information. The chemical transformations start from a weakly bound encounter complex **1**, and the initial step corresponds to the insertion of the carbene ligand into the H_3C–H bond via **TS1/2** to form an Au^+–ethane complex **2**. Since the PES is rather flat in this region, a 2D scan of the emerging C–C distance

[*] Dr. S. Zhou, Dr. J. Li, Dr. X.-N. Wu, Dr. M. Schlangen, Prof. H. Schwarz
Institut für Chemie, Technische Universität Berlin
Strasse des 17. Juni 135
10623 Berlin (Germany)
E-mail: Helmut.Schwarz@tu-berlin.de
Dr. J. Li
Institute of Theoretical Chemistry,
Jilin University
Changchun, 130023 (People's Republic of China)

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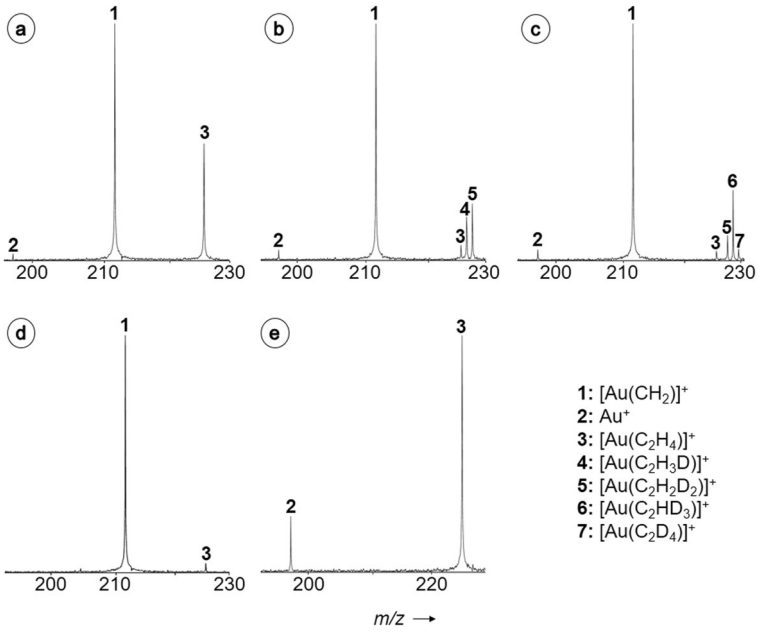

Figure 1. Mass spectra for the reactions of $[Au(CH_2)]^+$ and methane ($p = 3 \times 10^{-9}$ mbar; reaction delay 5 s): a) $[Au(CH_2)]^+/CH_4$; b) $[Au(CH_2)]^+/CH_2D_2$, c) $[[Au(CH_2)]^+/CD_4$, d) $[Au(CH_2)]^+$/He. The signal labeled as **3** is due to the reaction of $[Au(CH_2)]^+$ with residual CH_3Cl; e) CID spectrum of $[Au(C_2H_4)]^+$ with Ar at $E_{coll} = 3.0$ eV.

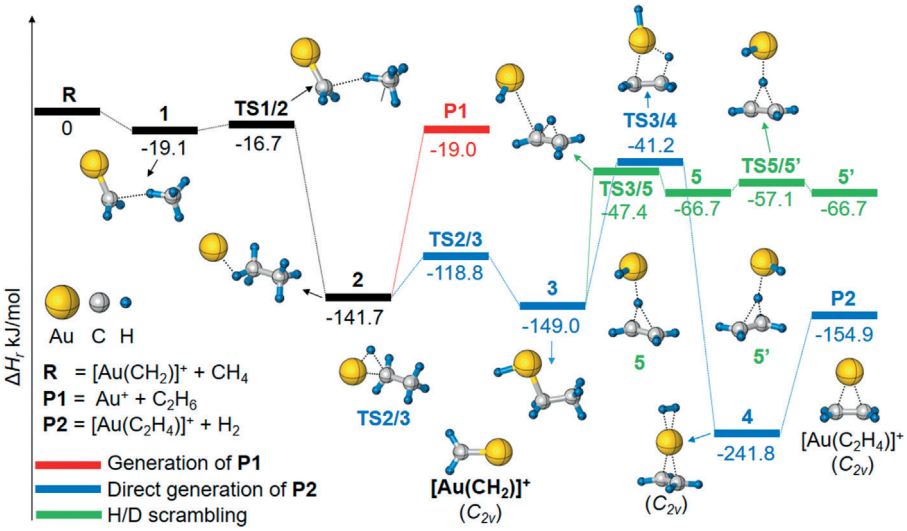

Figure 2. PES for the reactions of $[Au(CH_2)]^+$ ($^1A_1$) with CH_4 calculated at the CCSD(T)/BSI//BMK/BSI level of theory (more structural information of the stationary points are given in Figure S3). Zero-point corrected energies are given in kJ mol^{-1}, and charges are omitted for the sake of clarity.

and a lengthening of the C–H bond of CH_4 was performed to locate **TS1/2** (for more details, see the Supporting Information). Complex **2** can either dissociate directly to Au^+ and C_2H_6 (**P1**), or can be transformed to the insertion intermediate **3**. From **3**, dehydrogenation via **TS3/4** takes place to generate the product complex **4**; this then dissociates to $[Au(C_2H_4)]^+$ and neutral H_2 (**P2**). In addition to the direct dehydrogenation path of **3**, hydrogen atom scrambling can occur via **3**⇌**5**⇌**5′**⇌**5**⇌**3**. As the related transition structures **TS3/5** and **TS5/5′** as well as rotation around the C–C bond of **3** are less energy-demanding than the path **3**→**P**, the experimentally observed H/D scrambling in the reaction of $[Au(CH_2)]^+$ with CD_4 or CH_2D_2 can be explained. To quantitatively analyze the measured D_2/HD/H_2 distribution, the hydrogen atom exchange is treated in a kinetic model[7] as a complete H/D scrambling process; the ratio for a direct molecular hydrogen loss versus H/D scrambling prior to this elimination as well as the operation of an intramolecular kinetic isotope effect (KIE) were then fitted to the experimental data. The best agreement was found for KIE = 2 and a ratio of 2.3:1 in favor of H/D scrambling. As to the branching ratio of the reactions (1a) and (1b), although the generation of **P1** is entropically favored, it is energetically much more demanding compared to the formation of **P2**. Furthermore, in line with previous experimental and computational studies,[8] the dissociation of $[Au(C_2H_4)]^+$ requires 274 kJ mol^{-1}; this implies that the formation of the separated products H_2, Au^+, and C_2H_4 requires 119 kJ mol^{-1} above the entrance channel. Thus, in line with the double-resonance experiment, Au^+ is not generated by dissociation of $[Au(C_2H_4)]^+$. We also note that the liberation of H_2 from complex **4** requires a relatively high amount of energy (87 kJ mol^{-1}), which clearly indicates a strong interaction between H_2 and the Au atom of **4**; similar situations have been noted by Armentrout and co-workers in previous studies.[9]

According to the PES shown in Figure 2, the dehydrogenation of ethane by atomic Au^+ is exothermic and kinetically not hindered by unsurmountable barriers along the reaction path **P1**→**2**→**P2**. To verify this prediction, the reaction of Au^+ with ethane has also been investigated, and the associated mass spectra are provided in the Supporting Information. This reaction takes place with a rate constant of $k = 3.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, which corresponds to an efficiency of $\phi = 40\,\%$. In addition, eliminations of D_2/HD/H_2 were observed in a ratio of 1:11:6 for the Au^+/CH_3CD_3 couple; kinetic modeling studies suggest an average KIE = 3, and a ratio of 2.6:1 in favor of a complete H/D scrambling versus direct elimination of molecular hydrogen was derived.

As mentioned above, there are only a few metal–carbene complexes that, under ambient conditions, react with methane, and the reactivity of these $[M(CH_2)]^+/CH_4$ couples cannot be correlated with either the bond dissociation energy (BDE) of M^+-CH_2 or the charge distribution.[1b,10] What can be concluded is only that third-row transition-metal carbenes

are more prone to react than their lower congeners, and among the former, $[Au(CH_2)]^+$ seems to possess electronic features that are unique compared to other third-row transition-metal carbenes.[4,9a,10a,b,11] As shown below, these properties may be the root cause for its high reactivity toward methane.

For example, the metal–carbene bonds of other third-row elements for which the metal orbitals contribute up to 40% to the σ bond, while the Au^+–CH_2 bond is characterized as a nearly pure dative bond. That is, the $^1A_1$ state of CH_2 donates the lone pair of electrons into the empty 6s orbital of Au^+ to form the σ bond, while the Au^+ 5d orbital contributes more than 80% of the π-backbonding.[10a] This unique character of the Au^+–CH_2 bond originates from the substantial promotion energy (ca. 180 kJ mol^{-1}) to access a high-spin $d^{n-1}s^1$ configuration for Au^+,[10a] which is a prerequisite to form two covalent bonds. These features combined with the rather high electronegativity of Au^+[12] result not only in the relatively moderate BDE(Au^+–CH_2) (357 kJ mol^{-1} [9a]), but also in a reduced electron density of the carbene ligand, that is, the CH_2 moiety is slightly positively charged[10a] (amounting to 0.33 |e| according to our calculations). Both the positive charge of the ligand and the low BDE(Au^+–CH_2) favor accepting electron density from the σ(C–H) bond of the incoming hydrocarbon and the subsequent cleavage of the Au^+–CH_2 bond, thus resulting in the insertion of the methylene ligand in a C–H bond (**1**→**TS1/2**→**2**; Figure 2).[13]

In summary, we have presented the first example of an efficient thermal activation of methane by the closed-shell, "naked" metal–carbene complex $[Au(CH_2)]^+$ and deciphered mechanistic aspects of this insertion/coupling process to eventually generate C_2H_6 and $[Au(C_2H_4)]^+$. The high reactivity of the $[Au(CH_2)]^+/CH_4$ couple can be traced back to the moderate BDE(Au^+–CH_2) and the positively charged methylene ligand.

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[1] a) A. E. Stevens, J. L. Beauchamp, *J. Am. Chem. Soc.* **1979**, *101*, 6449–6450; b) D. B. Jacobson, B. S. Freiser, *J. Am. Chem. Soc.* **1985**, *107*, 4373–4378; c) D. B. Jacobson, B. S. Freiser, *J. Am. Chem. Soc.* **1985**, *107*, 2605–2612; d) K. K. Irikura, J. L. Beauchamp, *J. Am. Chem. Soc.* **1989**, *111*, 75–85; e) D. Stöckigt, H. Schwarz, *Chem. Ber.* **1992**, *125*, 2817–2819; f) K. L. Wilson, B. T. Cooper, S. W. Buckner, *Rapid Commun. Mass Spectrom.* **1993**, *7*, 844–847; g) D. Schröder, W. Zummack, H. Schwarz, *J. Am. Chem. Soc.* **1994**, *116*, 5857–5864; h) H. H. Cornehl, C. Heinemann, D. Schröder, H. Schwarz, *Organometallics* **1995**, *14*, 992–999; i) C. A. Schalley, D. Schröder, H. Schwarz, *Organometallics* **1995**, *14*, 317–326; j) Q. Chen, K. J. Auberry, B. S. Freiser, *Int. J. Mass Spectrom.* **1998**, *176-181*, 1–14; k) C. Hinderling, C. Adlhart, P. Chen, *Angew. Chem. Int. Ed.* **1998**, *37*, 2685–2689; *Angew. Chem.* **1998**, *110*, 2831–2835; l) K. Koszinowski, D. Schröder, H. Schwarz, *Organometallics* **2003**, *22*, 3809–3819; m) K. Koszinowski, M. Schlangen, D. Schröder, H. Schwarz, *Int. J. Mass Spectrom.* **2004**, *237*, 19–23; n) K. Koszinowski, D. Schröder, H. Schwarz, *Organometallics* **2004**, *23*, 1132–1139; o) K. Koszinowski, D. Schröder, H. Schwarz, *Organometallics* **2005**, *24*, 2214–2223; p) A. Božović, S. Feil, G. K. Koyanagi, A. A. Viggiano, X. H. Zhang, M. Schlangen, H. Schwarz, D. K. Bohme, *Chem. Eur. J.* **2010**, *16*, 11605–11610; q) A. Fedorov, E. P. A. Couzijn, N. S. Nagornova, O. V. Boyarkin, T. R. Rizzo, P. Chen, *J. Am. Chem. Soc.* **2010**, *132*, 13789–13798; r) A. Fedorov, L. Batiste, A. Bach, D. M. Birney, P. Chen, *J. Am. Chem. Soc.* **2011**, *133*, 12162–12171; s) V. J. F. Lapoutre, B. Redlich, A. F. G. van der Meer, J. Oomens, J. M. Bakker, A. Sweeney, A. Mookherjee, P. B. Armentrout, *J. Phys. Chem. A* **2013**, *117*, 4115–4126; t) L. Batiste, P. Chen, *J. Am. Chem. Soc.* **2014**, *136*, 9296–9307; u) D. H. Ringger, I. J. Kobylianskii, D. Serra, P. Chen, *Chem. Eur. J.* **2014**, *20*, 14270–14281; v) S. Zhou, M. Schlangen, J. Li, X.-N. Wu, H. Schwarz, *Chem. Eur. J.* **2015**, *21*, 9629–9631.

[2] For recent reviews on various aspects of the gas-phase activation of methane, see a) H. Schwarz, *Angew. Chem. Int. Ed.* **2011**, *50*, 10096–10115; *Angew. Chem.* **2011**, *123*, 10276–10297; b) N. Dietl, M. Schlangen, H. Schwarz, *Angew. Chem. Int. Ed.* **2012**, *51*, 5544–5555; *Angew. Chem.* **2012**, *124*, 5638–5650; c) H. Schwarz, *Isr. J. Chem.* **2014**, *54*, 1413–1431; d) H. Schwarz, *Chem. Phys. Lett.* **2015**, *629*, 91–101.

[3] K. Koszinowski, D. Schröder, H. Schwarz, *J. Phys. Chem. A* **2003**, *107*, 4999–5006.

[4] K. K. Irikura, J. L. Beauchamp, *J. Phys. Chem.* **1991**, *95*, 8344–8351.

[5] a) A. K. Chowdhury, C. L. Wilkins, *J. Am. Chem. Soc.* **1987**, *109*, 5336–5343; b) J. R. Brown, P. Schwerdtfeger, D. Schröder, H. Schwarz, *J. Am. Soc. Mass Spectrom.* **2002**, *13*, 485–492; c) T. H. Li, X. Y. Liu, S. W. Yu, N. Zhao, S. Q. Liu, X. Y. Ao, X. G. Xie, *J. Mol. Struct. THEOCHEM* **2009**, *899*, 18–24; d) W. S. Taylor, C. C. Matthews, A. J. Hicks, K. G. Fancher, L. C. Chen, *J. Phys. Chem. A* **2012**, *116*, 943–951.

[6] M. T. Bowers, J. B. Landenslager, *J. Chem. Phys.* **1972**, *56*, 4711–4712.

[7] a) J. Loos, D. Schröder, H. Schwarz, *J. Org. Chem.* **2005**, *70*, 1073–1076; b) B. Butschke, D. Schröder, H. Schwarz, *Organometallics* **2009**, *28*, 4340–4349.

[8] a) D. Schröder, J. Hrušák, R. H. Hertwig, W. Koch, P. Schwerdtfeger, H. Schwarz, *Organometallics* **1995**, *14*, 312–316; b) R. H. Hertwig, W. Koch, D. Schröder, H. Schwarz, J. Hrušák, P. Schwerdtfeger, *J. Phys. Chem.* **1996**, *100*, 12253–12260; c) D. Schröder, H. Schwarz, J. Hrušák, P. Pyykkö, *Inorg. Chem.* **1998**, *37*, 624–632; d) D. Schröder, R. Wesendrup, R. H. Hertwig, T. K. Dargel, H. Grauel, W. Koch, B. R. Bender, H. Schwarz, *Organometallics* **2000**, *19*, 2606–2615; e) N. J. Barnett, L. V. Slipchenko, M. S. Gordon, *J. Phys. Chem. A* **2009**, *113*, 7474–7481.

[9] a) F.-X. Li, P. B. Armentrout, *J. Chem. Phys.* **2006**, *125*, 133114; b) F.-X. Li, C. S. Hinton, M. Citir, F. Liu, P. B. Armentrout, *J. Chem. Phys.* **2011**, *134*, 024310; c) A. Dorta-Urra, A. Zanchet, O. Roncero, A. Aguado, P. B. Armentrout, *J. Chem. Phys.* **2011**, *135*, 091102.

[10] a) K. K. Irikura, W. A. Goddard, *J. Am. Chem. Soc.* **1994**, *116*, 8733–8740; b) F. Aguirre, J. Husband, C. J. Thompson, R. B. Metz, *Chem. Phys. Lett.* **2000**, *318*, 466–470; c) X. H. Zhang, H. Schwarz, *Chem. Eur. J.* **2010**, *16*, 5882–5888.

[11] C. Heinemann, R. H. Hertwig, R. Wesendrup, W. Koch, H. Schwarz, *J. Am. Chem. Soc.* **1995**, *117*, 495 – 500.
[12] H. Schwarz, *Angew. Chem. Int. Ed.* **2003**, *42*, 4442 – 4454; *Angew. Chem.* **2003**, *115*, 4580 – 4593.
[13] We have also tried to probe the reactions of the other coinage-metal carbene complexes $[M(CH_2)]^+$ (M = Cu, Ag) with methane. However, so far we have not succeeded in generating sufficient amounts of $[M(CH_2)]^+$, which may reflect the rather weak metal–carbon bonds in these systems: $BDE(Cu^+–CH_2) = 267\ kJ\,mol^{-1}$; $BDE(Ag^+–CH_2) \geq 107\ kJ\,mol^{-1}$. References: a) P. B. Armentrout, L. S. Sunderlin, E. R. Fisher, *Inorg. Chem.* **1989**, *28*, 4436 – 4437; b) E. R. Fisher, P. B. Armentrout, *J. Phys. Chem.* **1990**, *94*, 1674 – 1683; c) Y. M. Chen, P. B. Armentrout, *J. Phys. Chem.* **1995**, *99*, 11424 – 11431; d) W. S. Taylor, C. C. Matthews, K. S. Parkhill, *J. Phys. Chem. A* **2005**, *109*, 356 – 365.

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