Methane Conversion

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Thermal Methane Conversion to Formaldehyde Promoted by Single Platinum Atoms in $PtAl_2O_4^-$ Cluster Anions**

*Yan-Xia Zhao, Zi-Yu Li, Zhen Yuan, Xiao-Na Li, and Sheng-Gui He**

Abstract: *Identification and mechanistic study of thermal methane conversion mediated by gas-phase species is important for finding potentially useful routes for direct methane transformation under mild conditions. Negatively charged oxide species are usually inert with methane. This work reports an unexpected result that the bi-metallic oxide cluster anions $PtAl_2O_4^-$ can transform methane into a stable organic compound, formaldehyde, with high selectivity. The clusters are prepared by laser ablation and reacted with CH_4 in an ion trap reactor. The reaction is characterized by mass spectrometry and density functional theory calculations. It is found that platinum rather than oxygen activates CH_4 at the beginning of the reaction. The $Al_2O_4^-$ moiety serves as the support of Pt atom and plays important roles in the late stage of the reaction. A new mechanism for selective methane conversion is provided and new insights into the surface chemistry of single Pt atoms may be obtained from this study.*

Direct and selective transformation of methane into value-added chemicals under mild conditions is of great importance.[1–4] However, CH_4, a highly symmetric molecule, has a high C–H bond energy, a large ionization energy, and a huge HOMO–LUMO gap, so selective methane conversion is challenging and has attracted interests of researchers from most of the disciplines within chemistry.[1–5] Discovery of gas-phase species that can react with CH_4 under thermal collision conditions serves as a first step to find useful mechanisms to transform methane under mild conditions.[2–4]

Oxides are an important type of catalytic materials and many metal and metal-free oxide species have been identified to be able to react under thermal collision conditions with CH_4 in the gas phase. These gas phase oxides include not only diatomic and tri-atomic ions (FeO^+,[6] CuO^+,[7] SO_2^+,[8] and so on)[2,3] but also polyatomic cluster species such as $(V_2O_5)_n^+$ ($n=1$–5),[9] $V_2O_5(SiO_2)_n^+$ ($n=1$–4),[10] $V_xP_{4-x}O_{10}^+$ ($x=0$, 2, 3),[11] $V_xY_{4-x}O_{6+x}^+$ ($x=1$–3),[12] and many others.[2–4,13] Most of these oxides activate methane through oxygen-centered radicals ($O^{\bullet-}$) to generate methyl radicals, which was also proposed for oxidative coupling of methane in the condensed-phase studies:[2c,14]

$$O^{\bullet-} + CH_4 \rightarrow OH^- + CH_3^{\bullet} \quad (1)$$

Only a few oxide species such as FeO^+,[6,15] CoO^+,[16] and NiO^+[17] can react with methane to produce stable C_1 oxygenates methanol and formaldehyde.[2,3] It is noteworthy that in addition to oxides, oxygen-free species including atomic transition metal ions,[18] Au_2^+,[19] MoC^+,[20] and so on[3,21] can also react with methane to generate stable molecules such as C_2H_4 and H_2.

To the best of our knowledge, all of the reported gas phase ions that can react with CH_4 under thermal collision conditions to generate stable organic compounds are positively rather than negatively charged species.[4,22,23] It was reported that the anions are mostly inert or react very slowly with methane.[2–4,22] Herein, we report an unexpected result that oxide cluster anions $PtAl_2O_4^-$ with single platinum atoms can react with methane quite efficiently to generate the stable organic compound formaldehyde.

Platinum has been extensively studied for methane activation. The neutral, cationic, and anionic Pt atomic and cluster species Pt_n ($n=1$–24),[24] Pt_n^+ ($n=1$–21),[23,25] and Pt_n^- ($n=2$–5, 7, 11, 12)[23,25] all can activate methane in the gas phase, for example:[26,27]

$$Pt^q + CH_4 \rightarrow [HPtCH_3]^q \quad (2a)$$

$$[HPtCH_3]^q \rightarrow [PtCH_2]^q + H_2, \quad q = 0 \text{ and } +1 \quad (2b)$$

In addition, Pt-containing organic compounds[1c,28] and supported Pt nanoparticles[29] are also effective catalysts for methane conversion. Recently, single-atom catalysts which contain isolated Pt atoms[30] dispersed on supports such as metal oxides, have been developed in order to maximize the effective use of the noble metal atoms and offer great potential for achieving high activity and selectivity. As a result, it is important to study the reactivity of heteronuclear oxide clusters with single Pt atoms in CH_4 activation in order to find potentially useful mechanisms of methane conversion. In this study, the Pt-Al-O heteronuclear cluster anions $PtAl_xO_y^-$ are prepared and reacted with CH_4. Once a reactive cluster is experimentally identified, it is very interesting to investigate whether the Pt atom or the usually identified $O^{\bullet-}$ radical[2,4,31] is the active center for C–H bond activation of CH_4. It is noteworthy that aluminium oxide is an important catalyst-support material and study of $PtAl_xO_y^q$ clusters also

[*] Dr. Y.-X. Zhao, Z.-Y. Li, Z. Yuan, Dr. X.-N. Li, Prof. Dr. S.-G. He
Beijing National Laboratory for Molecular Science, State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Institute of Chemistry, Chinese Academy of Sciences
Beijing 100190 (P.R. China)
E-mail: shengguihe@iccas.ac.cn

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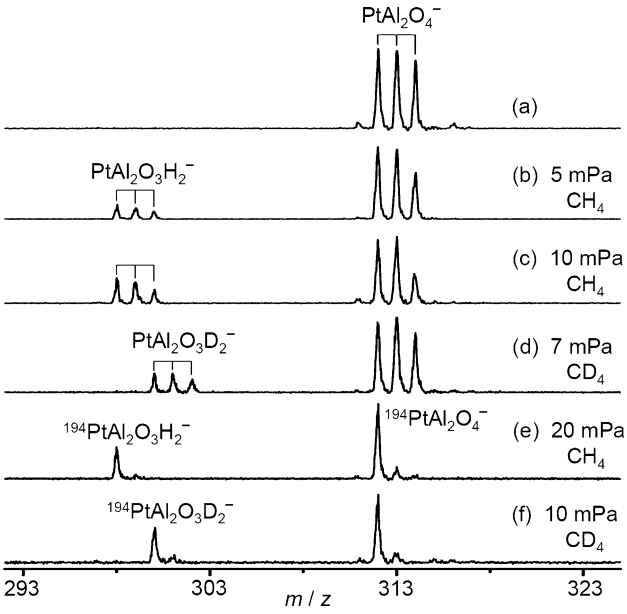

Figure 1. TOF mass spectra for the reactions of mass selected $PtAl_2O_4^-$ with CH_4 (b, c, e) and CD_4 (d, f). The maximal reactant gas pressures[32] are shown. The reaction times are 1.6 ms for (b–e) and 5.6 ms for (f).

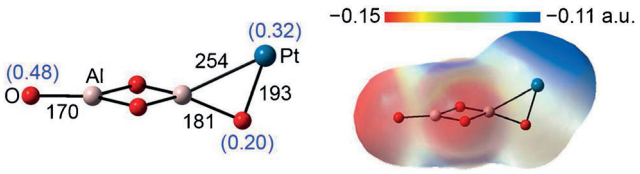

Figure 2. DFT-calculated structure (left, C_s, $^2A''$) and electrostatic potential map (right) of $PtAl_2O_4^-$. Bond lengths (in pm) and natural spin densities (in μ_B and listed in the parentheses) are shown.

serves as a bottom-up strategy to understand single platinum atom catalysis over Al_2O_3 supports.

The $PtAl_xO_y^-$ cluster anions are generated by laser ablation, mass-selected, thermalized, and then interacted with CH_4 or CD_4 in an ion trap reactor.[32] Pt has six stable isotopes: ^{190}Pt (0.014 %), ^{192}Pt (0.782 %), ^{194}Pt (32.967 %), ^{195}Pt (33.832 %), ^{196}Pt (25.242 %), and ^{198}Pt (7.163 %).[33] Figure 1 a presents the time-of-flight (TOF) mass spectrum for the three major isotopomers of $PtAl_2O_4^-$ (^{194}Pt, ^{195}Pt, and ^{196}Pt). Upon the interactions with 5 mPa CH_4 for about 1.6 ms, product peaks that can be assigned as $PtAl_2O_3H_2^-$ are observed (Figure 1 b). The magnitudes of the $PtAl_2O_3H_2^-$ product peaks increase as the CH_4 pressure increases (Figure 1 c), which suggests the following reaction generating formaldehyde:

$$PtAl_2O_4^- + CH_4 \rightarrow PtAl_2O_3H_2^- + HCHO \quad (3)$$

The above reaction is confirmed by using the isotopic labelling experiment with CD_4 (Figure 1 d) as well as the experiments by mass-selecting the cluster ions with a single isotope of platinum (^{194}Pt, Figure 1 e,f).

In addition to $PtAl_2O_3H_2^-$, minor products $PtAl_2O_4H_2O^-$, PtO^-, and $Al_2O_4^-$ of which the summed intensity amounts to 3 % of the total ion intensity and 11 % of the product ion intensity also appear in $PtAl_2O_4^- + CH_4$ (Figure S2 in the Supporting Information (SI)). It turns out that these products are due to reactions of $PtAl_2O_4^-$ with residual water [$PtAl_2O_4^- + H_2O \rightarrow PtAl_2O_4H_2O^- \rightarrow PtO^- + Al_2O_2(OH)_2$] and oxygen ($PtAl_2O_4^- + O_2 \rightarrow Al_2O_4^- + PtO_2$) in the ion trap (see SI). It can be concluded that the production of formaldehyde is the sole channel for $PtAl_2O_4^- + CH_4$. The pseudo first-order rate constant (k_1) of Reaction (3) is estimated to be (7.3 ± 3.6) $\times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, corresponding to a reaction efficiency (Φ)[34] of (7.0 ± 3.5) %. The kinetic isotope effect [KIE $= k_1(PtAl_2O_4^- + CH_4)/k_1(PtAl_2O_4^- + CD_4)$] is 2.4 ± 0.7.

Density functional theory (DFT) calculations are performed to understand the mechanisms of Reaction (3). The lowest-energy structure of $PtAl_2O_4^-$ (Figures 2 and S4) is a doublet and the unpaired spin densities are distributed around the Pt and two O atoms. The Pt atom as well as the Pt-O unit with 193 pm bond length is quite strongly bonded with the remaining part of the cluster:

$$PtAl_2O_4^- \rightarrow Al_2O_4^- + Pt, \quad \Delta H_0 = 2.99\ eV \quad (4a)$$

$$PtAl_2O_4^- \rightarrow Al_2O_3 + PtO^-, \quad \Delta H_0 = 5.35\ eV \quad (4b)$$

The natural charge on Pt atom is $-0.06\,|e|$, indicating that the Pt atom in $PtAl_2O_4^-$ cluster is close to a metallic state (Pt^0). The electrostatic potential (ESP) map shown in Figure 2 (right) indicates that the Pt-side of $PtAl_2O_4^-$ is less negatively charged than the other side of the cluster, suggesting that the Pt atom can be the preferred trapping site when the CH_4 molecule approaches $PtAl_2O_4^-$ cluster.

The lowest energy reaction pathway found for Reaction (3) is shown in Figure 3 (see Figure S9 for other reaction paths considered). As predicted by the nature of the ESP map shown in Figure 2, the CH_4 interacts with Pt rather than O or Al atom in the encounter complex (I1) with a binding energy of 0.432 eV. The reaction proceeds through insertion of Pt into one C–H bond (I1→TS1→I2) with a negligible barrier (0.003 eV), resulting in the formation of one Pt–H and one Pt–C bond and the cleavage of one C–H and the Pt–Al bond. The above process follows a mechanism of oxidative addition driven by the strong bond strengths of Pt–C (5.95 eV)[35] and Pt–H (3.44 eV).[36] After the oxidative addition, the H atom can transfer from Pt atom to the "oxide support" to make a chemical bond with a bridging O (I2→TS2→I3) and this step releases additional energy (0.52 eV). More energy (0.83 eV) can be released if the H atom is further transferred to the terminally bonded O atom (I3→TS3→I4). After formation of I4, the system has enough energy (2.10 eV) to transfer a second H atom from the methyl group to Pt atom (I4→TS4→I5) and then from Pt to O (I5→TS5→I6).

After activating two C–H bonds of CH_4 by the Pt atom and accepting two H atoms by the "oxide support", the system is ready to form a C–O chemical bond (I6→TS6→I7), which is the last important step to generate the HCHO moiety. In order to evaporate HCHO molecule, the reaction complex is relaxed (I7→TS7→I8→TS8→I9) so that the Pt atom is

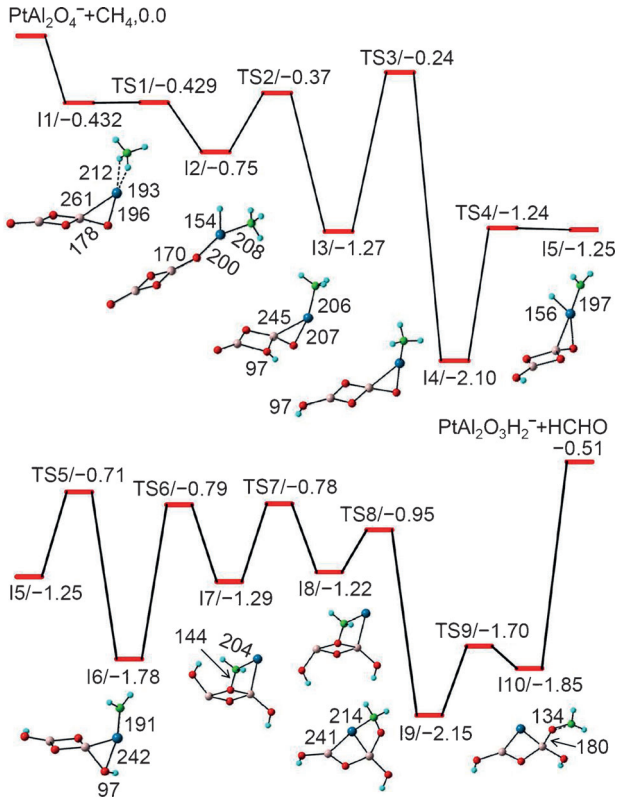

Figure 3. DFT-calculated potential energy profile for Reaction (3). The energies of the reaction intermediates (I1–I10) and transition states (TS1–TS9) with respect to the separated reactants are given in eV. The structures of I1–I10 are plotted and those of TS1–TS9 can be found in the Supporting Information.

bonded with two Al atoms. The cleavage of the Pt-C (I9→TS9→I10) and then Al–O bond (I10→$PtAl_2O_3H_2^-$ + HCHO) evaporates HCHO. The reaction intermediates, transition states, and products are all lower in energy than the separated reactants, so the DFT calculations are consistent with the experimental observation of gas-phase Reaction (3).

Oxide cluster anions are usually inert with methane and it has been only recently identified that $La_6O_{10}^-$ and $La_8O_{13}^-$ anions can activate CH_4 through the $O^{\bullet-}$ centers to generate CH_3 [Reaction (1)] under thermal collision conditions whereas the reaction efficiencies are quite low ($\Phi = 0.02$–$0.03\,\%$),[22] in sharp contrast to the good efficiency of (7.0 ± 3.5) % for $PtAl_2O_4^-$ with CH_4. This also implies that methane activation by $PtAl_2O_4^-$ follows a different mechanism. In the DFT calculations for Reaction (3), in addition to the facile oxidative addition of C–H bond to Pt atom ($PtAl_2O_4^-$ + CH_4→I1→I2 in Figure 3), direct C–H activation by the terminal O atom with the unpaired spin density of 0.48 μ_B (Figure 2) has also been tested. It turns out that such a process has an overall barrier of 0.25 eV (Figure S10), which means that it cannot happen under thermal collision conditions. Therefore, it is the Pt rather than O atom (or $O^{\bullet-}$ radical)[2,4,31] in $PtAl_2O_4^-$ acting as the active center for C–H activation of CH_4 in the initial stage of Reaction (3).

Methane activation by free Pt atom and Pt^+ ion [Reaction (2)] was extensively studied[26,27] and it has been recently realized that the neutral (Pt) and cationic (Pt^+) reaction systems follow a similar mechanism, in which the oxidative addition of one C–H bond to Pt atom [Reaction (2a)] is facile (barrierless for Pt and a tiny barrier for Pt^+).[27d] The natural charge on the Pt atom in $PtAl_2O_4^-$ is only $-0.06\,|e|$, so the $PtAl_2O_4^-$ cluster can be considered to be composed of a neutral Pt atom and a "support" cluster anion ($Al_2O_4^-$). It turns out that the mechanism of methane activation by the supported Pt atom, the initial stage of Reaction (3), is very similar to that of the free Pt or Pt^+ reaction system: the formation of the oxidative-addition complex ($PtAl_2O_4^-$ + CH_4→I1→I2, Figure 3) is almost barrierless, indicating that the supported Pt atom inherits the high reactivity of free Pt in methane activation. It is noteworthy that the encounter complex I1 in Figure 3 has a large binding energy (0.43 eV) in sharp contrast to small adsorption energies (0.05–0.15 eV) between oxide cluster anions and alkane molecules reported in literature.[22,37,38] The two C–H bonds pointing toward Pt in I1 are significantly activated as the C–H distances are lengthened from 109 pm of free CH_4 to about 113 pm.

The Pt atom plays a crucial role in the activation and cleavage of methane C–H bonds for Reaction (3) on the one hand. On the other hand, formation of HCHO rather than H_2 molecule [as in Reaction (2b)] from $PtAl_2O_4^-$ + CH_4 tells that the "support" cluster should also play important roles. It is noteworthy that free $Al_2O_4^-$ is oxygen-rich[4] and has a high H-atom affinity to abstract an H atom through the $O^{\bullet-}$ center [as in Reaction (1)] from *n*-butane under thermal collision conditions.[38] The high H-atom affinity of $Al_2O_4^-$ is the driving force to transfer the H atom from Pt to the "oxide support" (I2→I3→I4, Figure 3), so that enough energy (2.10 eV) can be released to activate the second C–H bond (I4→I5) and to manage the subsequent transformation to produce HCHO.

To further understand the importance of the "oxide support" in methane conversion, the one-oxygen-atom less cluster $PtAl_2O_3^-$ is mass-selected and interacted with CH_4 in the ion trap reactor while no evidence of reaction can be identified (Figure S3). The DFT study indicates that $Al_2O_3^-$, which is oxygen-poor,[4] has a much smaller electron detachment energy than the oxygen rich cluster $Al_2O_4^-$ (3.3 versus 4.4 eV), so the Pt atom in $PtAl_2O_3^-$ (Figure S7) has a large negative natural charge ($-0.55\,|e|$) in contrast to the small charge ($-0.06\,|e|$) on the Pt atom in $PtAl_2O_4^-$. The Pt-insertion step in $PtAl_2O_3^-$ + CH_4 (as I1→TS1→I2 in Figure 3) is subject to an overall barrier of 0.54 eV (Figure S11), which is in line with the result that the free Pt^- anion is inert or reacts very slowly with CH_4.[23] It means that $PtAl_2O_3^-$ cannot transform methane under thermal collision conditions and implies that, in the single-Pt-atom catalysis,[30] the nature of supports and the charge transfers between Pt atoms and supports should play very important roles.

In conclusion, selective conversion of methane to stable organic compounds (formaldehyde) mediated by oxide cluster anions ($PtAl_2O_4^-$) under thermal collision conditions has been identified for the first time. The Pt atom rather than oxygen radical is the active species for methane activation at

the beginning of the reaction. The support cluster $Al_2O_4^-$ accepts two H atoms delivered through Pt atom and plays important roles in the late stage of the reaction. This study provides a new mechanism for selective methane conversion and may serve as a good example to understand surface chemistry of single platinum atoms at a strictly molecular level.

Experimental Section

The $PtAl_xO_y^-$ clusters are generated by laser ablation of a Pt/Al mixed metal disk (mole ratio: Pt:Al = 3:1) in the presence of 0.15% O_2 seeded in 7 atm He carrier gas (Figure S1). The clusters of interest are mass-selected by a quadrupole mass filter (QMF) and enter into a linear ion trap (LIT) reactor, where they are thermalized (see Supporting Information) by collisions with a pulse of He gas and then interacted with a pulse of CH_4 or CD_4 for a period of time. The LIT is formed by a set of hexapole rods and two cap electrodes. A reflectron TOF mass spectrometer is used to measure masses and abundances of the reactant and product ions (see Ref. [32] for experimental details). The QMF can be run with around unit mass resolution (Figure 1 e,f) while in order to enhance the transmittance of the ions, the resolution is decreased to be about 3 amu in most cases (Figure 1 a–d). The slight instability of the radio-frequency potentials that drive the QMF causes the differences of Pt isotopic patterns (the multiple $PtAl_2O_4^-$ peaks) in Figure 1 a–d. Methods of rate constant determination and DFT calculations are described in the Supporting Information.

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[1] a) M. Lin, A. Sen, *Nature* **1994**, *368*, 613 – 615; b) R. H. Crabtree, *Chem. Rev.* **1995**, *95*, 987 – 1007; c) R. A. Periana, D. J. Taube, S. Gamble, H. Taube, T. Satoh, H. Fujii, *Science* **1998**, *280*, 560 – 564; d) A. Holmen, *Catal. Today* **2009**, *142*, 2 – 8; e) R. A. Himes, K. D. Karlin, *Proc. Natl. Acad. Sci. USA* **2009**, *106*, 18877 – 18878; f) M. C. Alvarez-Galvan, N. Mota, M. Ojeda, S. Rojas, R. M. Navarro, J. L. G. Fierro, *Catal. Today* **2011**, *171*, 15 – 23; g) P. Venkata, L. Reddy, K.-H. Kim, H. Song, *Renewable Sustainable Energy Rev.* **2013**, *24*, 578 – 585.

[2] a) D. Schröder, H. Schwarz, *Proc. Natl. Acad. Sci. USA* **2008**, *105*, 18114 – 18119; b) H. Schwarz, *Angew. Chem.* **2011**, *123*, 10276 – 10297; *Angew. Chem. Int. Ed.* **2011**, *50*, 10096 – 10115; c) N. Dietl, M. Schlangen, H. Schwarz, *Angew. Chem.* **2012**, *124*, 5638 – 5650; *Angew. Chem. Int. Ed.* **2012**, *51*, 5544 – 5555.

[3] J. Roithová, D. Schröder, *Chem. Rev.* **2010**, *110*, 1170 – 1211.

[4] a) Y.-X. Zhao, X.-N. Wu, J.-B. Ma, S.-G. He, X.-L. Ding, *Phys. Chem. Chem. Phys.* **2011**, *13*, 1925 – 1938; b) X.-L. Ding, X.-N. Wu, Y.-X. Zhao, S.-G. He, *Acc. Chem. Res.* **2012**, *45*, 382 – 390.

[5] a) J. A. Labinger, J. E. Bercaw, *Nature* **2002**, *417*, 507 – 514; b) F. Arena, A. Parmaliana, *Acc. Chem. Res.* **2003**, *36*, 867 – 875; c) R. Balasubramanian, A. C. Rosenzweig, *Acc. Chem. Res.* **2007**, *40*, 573 – 580; d) G.-J. Wang, M.-F. Zhou, *Int. Rev. Phys. Chem.* **2008**, *27*, 1 – 25; e) D. Balcells, E. Clot, O. Eisenstein, *Chem. Rev.* **2010**, *110*, 749 – 823; f) A. Caballero, P. J. Péreze, *Chem. Soc. Rev.* **2013**, *42*, 8809 – 8820; g) S. Ma, X. Guo, L. Zhao, S. Scottc, X. Bao, *J. Energy Chem.* **2013**, *22*, 1 – 20.

[6] D. Schröder, A. Fiedler, J. Hrušák, H. Schwarz, *J. Am. Chem. Soc.* **1992**, *114*, 1215 – 1222.

[7] N. Dietl, C. van der Linde, M. Schlangen, M. K. Beyer, H. Schwarz, *Angew. Chem.* **2011**, *123*, 5068 – 5072; *Angew. Chem. Int. Ed.* **2011**, *50*, 4966 – 4969.

[8] G. de Petris, A. Troiani, M. Rosi, G. Angelini, O. Ursini, *Chem. Eur. J.* **2009**, *15*, 4248 – 4252.

[9] a) S. Feyel, J. Döbler, D. Schröder, J. Sauer, H. Schwarz, *Angew. Chem.* **2006**, *118*, 4797 – 4801; *Angew. Chem. Int. Ed.* **2006**, *45*, 4681 – 4685; b) Y.-X. Zhao, X.-N. Wu, Z.-C. Wang, S.-G. He, X.-L. Ding, *Chem. Commun.* **2010**, *46*, 1736 – 1738.

[10] X.-L. Ding, Y.-X. Zhao, X.-N. Wu, Z.-C. Wang, J.-B. Ma, S.-G. He, *Chem. Eur. J.* **2010**, *16*, 11463 – 11470.

[11] a) N. Dietl, M. Engeser, H. Schwarz, *Angew. Chem.* **2009**, *121*, 4955 – 4957; *Angew. Chem. Int. Ed.* **2009**, *48*, 4861 – 4863; b) J.-B. Ma, X.-N. Wu, Y.-X. Zhao, X.-L. Ding, S.-G. He, *Phys. Chem. Chem. Phys.* **2010**, *12*, 12223 – 12228; c) N. Dietl, R. F. Höckendorf, M. Schlangen, M. Lerch, M. K. Beyer, H. Schwarz, *Angew. Chem.* **2011**, *123*, 1466 – 1470; *Angew. Chem. Int. Ed.* **2011**, *50*, 1430 – 1434.

[12] Z.-Y. Li, Y.-X. Zhao, X.-N. Wu, X.-L. Ding, S.-G. He, *Chem. Eur. J.* **2011**, *17*, 11728 – 11733.

[13] a) X.-N. Wu, X.-N. Li, X.-L. Ding, S.-G. He, *Angew. Chem.* **2013**, *125*, 2504 – 2508; *Angew. Chem. Int. Ed.* **2013**, *52*, 2444 – 2448; b) R. Kretschmer, M. Schlangen, H. Schwarz, *Angew. Chem.* **2013**, *125*, 6213 – 6217; *Angew. Chem. Int. Ed.* **2013**, *52*, 6097 – 6101.

[14] a) H.-F. Liu, R.-S. Liu, K. Y. Liew, R. E. Johnson, J. H. Lunsford, *J. Am. Chem. Soc.* **1984**, *106*, 4117 – 4121; b) J. H. Lunsford, *Angew. Chem.* **1995**, *107*, 1059 – 1070; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 970 – 980; c) S. Arndt, G. Laugel, S. Levchenko, R. Horn, M. Baerns, M. Scheffler, R. Schlögl, R. Schomäcker, *Catal. Rev.* **2011**, *53*, 424 – 514.

[15] a) D. Schröder, H. Schwarz, *Angew. Chem.* **1990**, *102*, 1468 – 1469; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1433 – 1434; b) D. Schröder, H. Schwarz, D. E. Clemmer, Y. Chen, P. B. Armentrout, V. I. Baranov, D. K. Böhme, *Int. J. Mass Spectrom. Ion Processes* **1997**, *161*, 175 – 191; c) F. Aguirre, J. Husband, C. J. Thompson, K. L. Stringer, R. B. Metz, *J. Chem. Phys.* **2002**, *116*, 4071 – 4078; d) S. G. Ard, J. J. Melko, V. G. Ushakov, R. Johnson, J. A. Fournier, N. S. Shuman, H. Guo, J. Troe, A. A. Viggiano, *J. Phys. Chem. A* **2014**, *118*, 2029 – 2039.

[16] a) Y.-M. Chen, D. E. Clemmer, P. B. Armentrout, *J. Am. Chem. Soc.* **1994**, *116*, 7815 – 7826; b) M. F. Ryan, A. Fiedler, D. Schröder, H. Schwarz, *Organometallics* **1994**, *13*, 4072 – 4081.

[17] D. Schröder, H. Schwarz, *Angew. Chem.* **1995**, *107*, 2126 – 2150; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1973 – 1995.

[18] a) K. K. Irikura, J. L. Beauchamp, *J. Am. Chem. Soc.* **1991**, *113*, 2769 – 2770; b) L. G. Parke, C. S. Hinton, P. B. Armentrout, *J. Phys. Chem. C* **2007**, *111*, 17773 – 17787; c) P. B. Armentrout, L. Parke, C. Hinton, M. Citir, *ChemPlusChem* **2013**, *78*, 1157 – 1173.

[19] S. M. Lang, T. M. Bernhardt, R. N. Barnett, U. Landman, *Angew. Chem.* **2010**, *122*, 993 – 996; *Angew. Chem. Int. Ed.* **2010**, *49*, 980 – 983.

[20] Z.-Y. Li, Z. Yuan, Y.-X. Zhao, S.-G. He, *Chem. Eur. J.* **2014**, *20*, 4163 – 4169.

[21] a) C. J. Cassady, S. W. Mclvany, *J. Am. Chem. Soc.* **1990**, *112*, 4788 – 4797; b) S. M. Lang, A. Frank, T. M. Bernhardt, *J. Phys. Chem. C* **2013**, *117*, 9791 – 9800; c) S. M. Lang, A. Frank, T. M. Bernhardt, *Int. J. Mass Spectrom.* **2013**, *354*, 365 – 371.

[22] J.-H. Meng, X.-J. Deng, Z.-Y. Li, S.-G. He, W.-J. Zheng, *Chem. Eur. J.* **2014**, *20*, 5580 – 5583.

[23] U. Achatz, C. Berg, S. Joos, B. S. Fox, M. K. Beyer, G. Niedner-Schatteburg, V. E. Bondybey, *Chem. Phys. Lett.* **2000**, *320*, 53 – 58.

[24] D. J. Trevor, D. M. Cox, A. Kaldor, *J. Am. Chem. Soc.* **1990**, *112*, 3742 – 3749.

[25] C. Adlhart, E. Uggerud, *Chem. Commun.* **2006**, 2581 – 2582.

[26] a) Ref. [18a]; b) C. Heinemann, R. Wesendrup, H. Schwarz, *Chem. Phys. Lett.* **1995**, *239*, 75 – 83; c) X.-G. Zhang, R. Liyanage, P. B. Armentrout, *J. Am. Chem. Soc.* **2001**, *123*, 5563 – 5575; d) A. Shayesteh, V. V. Lavrov, G. K. Koyanagi, D. K. Bohme, *J. Phys. Chem. A* **2009**, *113*, 5602 – 5611; e) D. J. Harding, C. Kerpal, G. Meijer, A. Fielicke, *Angew. Chem.* **2012**, *124*, 842 – 845; *Angew. Chem. Int. Ed.* **2012**, *51*, 817 – 819.

[27] a) J. J. Carroll, J. C. Weisshaar, P. E. M. Siegbahn, C. A. M. Wittborn, M. R. A. Blomberg, *J. Phys. Chem.* **1995**, *99*, 14388 – 14396; b) M. L. Campbell, *J. Chem. Soc. Faraday Trans.* **1998**, *94*, 353 – 358; c) H.-G. Cho, L. Andrews, *J. Phys. Chem. A* **2008**, *112*, 12293 – 12295; d) M. Perera, R. B. Metz, O. Kostko, M. Ahmed, *Angew. Chem.* **2013**, *125*, 922 – 925; *Angew. Chem. Int. Ed.* **2013**, *52*, 888 – 891.

[28] a) M. Lersch, M. Tilset, *Chem. Rev.* **2005**, *105*, 2471 – 2526; b) O. A. Mironov, S. M. Bischof, M. M. Konnick, B. G. Hashiguchi, V. R. Ziatdinov, W. A. Goddard, M. Ahlquist, R. A. Periana, *J. Am. Chem. Soc.* **2013**, *135*, 14644 – 14658.

[29] a) W. Tang, Z. Hu, M. Wang, G. D. Stucky, H. Metiu, E. W. McFarland, *J. Catal.* **2010**, *273*, 125 – 137; b) P. J. S. Prieto, A. P. Ferreira, P. S. Haddad, D. Zanchet, J. M. C. Bueno, *J. Catal.* **2010**, *276*, 351 – 359; c) D. B. Lukyanov, T. Vazhnova, *J. Mol. Catal. A* **2011**, *342 – 343*, 1 – 5; d) Z. Cheng, C. S. Lo, *Ind. Eng. Chem. Res.* **2013**, *52*, 15447 – 15454.

[30] a) Y. Zhai, D. Pierre, R. Si, W. Deng, P. Ferrin, A. U. Nilekar, G. Peng, J. A. Herron, D. C. Bell, H. Saltsburg, M. Mavrikakis, M. Flytzani-Stephanopoulos, *Science* **2010**, *329*, 1633 – 1636; b) B. Qiao, A. Wang, X. Yang, L. F. Allard, Z. Jiang, Y. Cui, J. Liu, J. Li, T. Zhang, *Nat. Chem.* **2011**, *3*, 634 – 641; c) M. Moses-DeBusk, M. Yoon, L. F. Allard, D. R. Mullins, Z. Wu, X. Yang, G. Veith, G. M. Stocks, C. K. Narula, *J. Am. Chem. Soc.* **2013**, *135*, 12634 – 12645; d) X.-G. Yang, A. Wang, B. Qiao, J. Li, J. Liu, T. Zhang, *Acc. Chem. Res.* **2013**, *46*, 1740 – 1748.

[31] a) M. Nößler, R. Mitrić, V. B. Koutecký, G. E. Johnson, E. C. Tyo, A. W. Castleman, Jr., *Angew. Chem.* **2010**, *122*, 417 – 420; *Angew. Chem. Int. Ed.* **2010**, *49*, 407 – 410; b) H.-J. Zhai, L.-S. Wang, *Chem. Phys. Lett.* **2010**, *500*, 185 – 195; c) A. W. Castleman, Jr., *Catal. Lett.* **2011**, *141*, 1243 – 1253; d) S. Yin, E. R. Bernstein, *Int. J. Mass Spectrom.* **2012**, *321*, 49 – 65.

[32] Z. Yuan, Z.-Y. Li, Z.-X. Zhou, Q.-Y. Liu, Y.-X. Zhao, S.-G. He, *J. Phys. Chem. C* **2014**, DOI: 10.1021/jp5040344.

[33] J. K. Böhlke, J. R. de Laeter, P. De Bièvre, H. Hidaka, H. S. Peiserb, K. J. R. Rosman, P. D. P. Taylor, *J. Phys. Chem. Ref. Data* **2005**, *34*, 57 – 67.

[34] a) The Φ value is calculated as $k_1/k_{calc,}$ where k_{calc} is the theoretical collision rate;[34b,c] b) G. Gioumousis, D. P. Stevenson, *J. Chem. Phys.* **1958**, *29*, 294 – 299; c) G. Kummerlöwe, M. K. Beyer, *Int. J. Mass Spectrom.* **2005**, *244*, 84 – 90.

[35] M. Citir, R. B. Metz, L. Belau, M. Ahmed, *J. Phys. Chem. A* **2008**, *112*, 9584 – 9590.

[36] M. C. McCarthy, R. W. Field, R. Engleman, P. F. Bernath, *J. Mol. Spectrosc.* **1993**, *158*, 208 – 236.

[37] a) Y.-X. Zhao, X.-N. Wu, J.-B. Ma, S.-G. He, X.-L. Ding, *J. Phys. Chem. C* **2010**, *114*, 12271 – 12279; b) J.-B. Ma, X.-N. Wu, Y.-X. Zhao, X.-L. Ding, S.-G. He, *J. Phys. Chem. A* **2010**, *114*, 10024 – 10027; c) Y.-X. Zhao, J.-Y. Yuan, X.-L. Ding, S.-G. He, W.-J. Zheng, *Phys. Chem. Chem. Phys.* **2011**, *13*, 10084 – 10090.

[38] L.-H. Tian, T.-M. Ma, X.-N. Li, S.-G. He, *Dalton Trans.* **2013**, *42*, 11205 – 11211.

