Gas-Phase Reactions

DOI: 10.1002/anie.200605145

Thermal Activation of Methane by Group 10 Metal Hydrides MH^+: The Same and Not the Same**

*Maria Schlangen and Helmut Schwarz**

Dedicated to Professor Roald Hoffmann on the occasion of his 70th birthday

Well-designed gas-phase reactions of transition-metal fragments using advanced mass-spectrometric techniques in conjunction with theoretical studies have greatly helped in uncovering mechanistic aspects underlying metal-mediated bond activation, in particular that of saturated hydrocarbons.[1] While factors like the significant energies required for both homolytic and heterolytic C–H bond cleavage, negligibly small (if not negative) electron affinities, large ionization energies, and extremely high pK_a values of the organic substrates[2] make the selective activation of, for example, methane, quite difficult, there is compelling evidence that transition-metal complexes help to surmount some of the obstacles.[2,3]

For *thermal* gas-phase reactions of transition-metal ions with methane, two strategies have proven useful: 1) In the spontaneous dehydrogenation of CH_4 by "bare" atomic or cluster metal ions [Eq. (1)], advantage is taken of the huge

$$M^+ + CH_4 \rightarrow M(CH_2)^+ + H_2 \tag{1}$$

relativistic stabilization exhibited by 5d transition-metal cations in forming metal–carbon bonds.[1h] 2) Ligand effects have been employed either to alter the electronic structure of the metal-ion core or to prepare reactive centers, which are then capable to bring about homolytic C–H bond cleavage. As an example of the former category, diatomic metal-hydride cations MH^+ serve as an illustrative case. Whereas the naked 3d metal ions M^+ (M = Fe, Co, Ni) do not bring about thermal C–H bond activation, the corresponding MH^+ ions give rise to efficient H/CH_3 ligand exchange [Eq. (2)],

$$MH^+ + CH_4 \rightarrow [M(CH_3)]^+ + H_2 \tag{2}$$

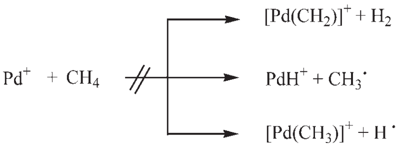
with reactivities increasing from FeH^+ to NiH^+.[4]

As to the second option, some binary (and higher order) metal oxides, in contrast to their metal cations, often exhibit room-temperature H-abstraction reactivity [Eq. (3)]; this is

$$MO^{\cdot+} + CH_4 \rightarrow [M(OH)]^+ + CH_3^{\cdot} \tag{3}$$

because the presence of an oxygen-centered radical in the oxide as well as significant O–H bond energies in the product provide sufficient kinetic and thermodynamic driving forces.[1e,5] For example, Mn^+ is the least reactive 3d transition-metal cation toward alkanes, whereas MnO^+ is the most reactive one,[6a] and other efficient systems include FeO^+,[6b] MgO^+,[6c] MoO_3^+,[6d] ReO_3^+,[6e] OsO_4^+,[6e] and $V_4O_{10}^+$;[6f] the latter serves as a rare example for a highly reactive cluster oxide cation radical.

Much less is known about the potential role of 4d transition-metal systems in thermal activation of methane, and the prospects have been judged as less promising. For example, atomic Pd^+ is extremely unreactive in the gas phase owing to the inability of its ground state to undergo oxidative insertion, and its lowest excited quartet state is much too high in energy to engage in thermal bond activation;[1c] in fact, none of the processes summarized in Equation (4) occur.[7]



$$Pd^+ + CH_4 \not\rightarrow \begin{cases} [Pd(CH_2)]^+ + H_2 \\ PdH^+ + CH_3^{\cdot} \\ [Pd(CH_3)]^+ + H^{\cdot} \end{cases} \tag{4}$$

However, Pd^{II} species exhibit contrasting behavior in their gas-phase reactivity; for example, while Pd^+ reacts only sluggishly even with the otherwise rather reactive substrate CH_3I, the Pd^{II} alkyl complex $[Pd(CH_3)]^+$ undergoes bond activation with collision efficiency at room temperature [Eq. (5)], thus pointing to an enhanced reactivity of this oxidation state.[8,9]

$$[Pd(CH_3)]^+ + CH_3I \rightarrow [Pd(CH_2I)]^+ + CH_4 \tag{5}$$

This observation and the previous findings that the Group 10 metal–hydride cations NiH^+[4] and PtH^+[10] activate methane at low temperature [Eq. (2)] prompted us to extend our earlier studies[4d,10] to PdH^+. While the latter hydride has been characterized computationally at great length,[11] to the best of our knowledge its chemical reactivity toward C–H bond activation has not been reported.

Here we will describe experiments with a quadrupole-based mass spectrometer equipped with an electrospray ionization (ESI) source (for details, see the Experimental Section). Upon ESI of a solution of $PdCl_2$ in CH_3OH, under

---

[*] M. Schlangen, Prof. Dr. H. Schwarz
Institut für Chemie
Technische Universität Berlin
Strasse des 17. Juni 135, 10623 Berlin (Germany)
Fax: (+49) 30-314-21102
E-mail: helmut.schwarz@mail.chem.tu-berlin.de

[**] Financial support of this work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is acknowledged. We thank Dr. Detlef Schröder for helpful suggestions and the reviewers for insightful comments.

harsh ionization conditions (cone voltage ca. 80 V) one can generate PdH^+ in yields sufficient to permit reactivity studies of mass-selected ions with methane. In distinct contrast to completely inert atomic Pd^+, the cationic palladium hydride undergoes at room temperature a H/CH_3 ligand exchange (Figure 1) with an efficiency of 120% (relative to the rate of methane activation by NiH^+).

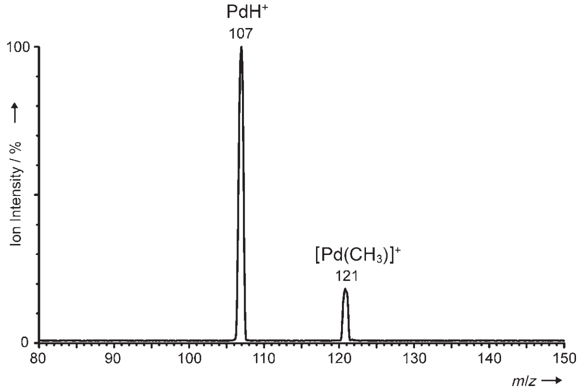
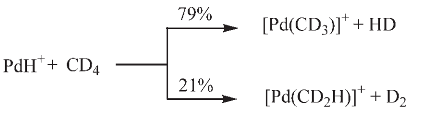


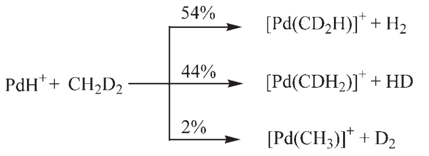
Figure 1. Ion–molecule reaction of thermalized mass-selected PdH^+ with CH_4 at $E_{lab} = 0$ eV.

As to the specificity of the ligand-exchange process [Eq. (6)], isotopic-labeling experiments with the couples described in Equations (7a–7d) are quite revealing.

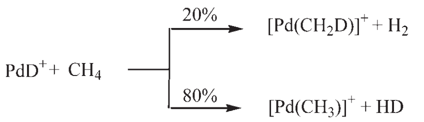
$$PdH^+ + CH_4 \rightarrow Pd(CH_3)^+ + H_2 \qquad (6)$$



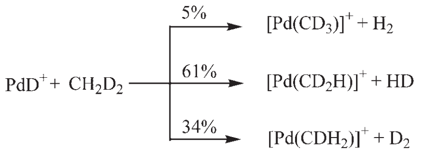
$$PdH^+ + CD_4 \begin{cases} \xrightarrow{79\%} [Pd(CD_3)]^+ + HD \\ \xrightarrow{21\%} [Pd(CD_2H)]^+ + D_2 \end{cases} \qquad (7a)$$



$$PdH^+ + CH_2D_2 \begin{cases} \xrightarrow{54\%} [Pd(CD_2H)]^+ + H_2 \\ \xrightarrow{44\%} [Pd(CDH_2)]^+ + HD \\ \xrightarrow{2\%} [Pd(CH_3)]^+ + D_2 \end{cases} \qquad (7b)$$



$$PdD^+ + CH_4 \begin{cases} \xrightarrow{20\%} [Pd(CH_2D)]^+ + H_2 \\ \xrightarrow{80\%} [Pd(CH_3)]^+ + HD \end{cases} \qquad (7c)$$



$$PdD^+ + CH_2D_2 \begin{cases} \xrightarrow{5\%} [Pd(CD_3)]^+ + H_2 \\ \xrightarrow{61\%} [Pd(CD_2H)]^+ + HD \\ \xrightarrow{34\%} [Pd(CDH_2)]^+ + D_2 \end{cases} \qquad (7d)$$

A detailed model[12] of the labeling distributions for these four couples demonstrates that the direct hydrogen/methyl ligand exchange amounts to 70%, and 30% of all hydrogen/deuterium atoms undergo scrambling prior to loss of molecular hydrogen (and its isotopic variants). For the direct reaction an averaged kinetic isotope effect of KIE = 1.6 and for the latter process an averaged KIE = 1.2 are derived, thus suggesting that breaking of the Pd–H(D) and C–H(D) and forming the H–H(D) bonds contribute slightly to the rate of the overall process. Given the limited set of data, a further decomposition of the KIEs to individual components is not warranted.

Insight into the mechanistic details of the C–H bond activation of methane by PdH^+ has been obtained by B3LYP calculations (for computational details, see the Experimental Section). Coordination of the alkane with the cation is associated with a relatively large gain of energy, −84 kJ mol⁻¹ (Figure 2), resulting in η^2 coordination between the palladium atom and a C–H bond of the incoming hydrocarbon. Next, this encounter complex **1** proceeds via a properly characterized, σ-metathesis-like transition structure (TS **1/2**): The formal oxidation state of Pd^{II} is retained in the $[Pd(CH_3)(H_2)]^+$ intermediate **2** from which, in a barrier-free process, molecular hydrogen is liberated with an overall exothermicity of −21 kJ mol⁻¹ relative to the reactants. As the transition structure TS **1/2** is located energetically below the entrance and exit channels and rotation around the $(H_2)Pd-(CH_3)^+$ bond in **2** requires at most only a few kJ mol⁻¹, the energy profile depicted in Figure 2 also explains qualitatively the occurrence of hydrogen/deuterium scrambling processes [Eq. (7a–7d)].[13] Inspection of the geometric details (Table 1) of the species involved in reaction (6) reveals a smooth breaking and making of carbon–hydrogen, palladium–hydrogen, and hydrogen–hydrogen bonds, respectively. We note in particular the features of the transition structure TS **1/2** in which the migrating hydrogen atom H2 interacts with three centers simultaneously, that is, the carbon, palladium, and hydrogen H(1) atoms. As required for a σ-metathesis process, in TS **1/2** the atoms H1, H2, Pd, and C are coplanar; based on internal reaction coordinate calculations,[14] rotation of the orthogonal Pd–H1 and C–H2 vectors in the encounter complex $[Pd(H)(CH_4)]^+$ (**1**) en route to the transition structure occurs smoothly with a small rotational barrier (< 6 kJ mol⁻¹); the latter does not contribute to the overall

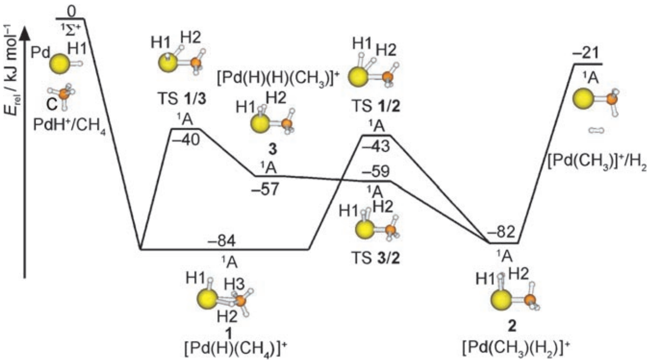


Figure 2. Energy diagram (in kJ mol⁻¹) for the reaction of PdH^+ and methane. The values are relative to the entrance channel and corrected for zero-point vibrational energies.

Table 1: Relevant bond lengths (in Å) of B3LYP-calculated geometries of the species involved in the reaction: $Pd(H)^+ + CH_4 \rightarrow [Pd(CH_3)]^+ + H_2$.

Bond	PdH^+/CH_4	$[Pd(H)(CH_4)]^+$ **1**	TS **1/2**	$[Pd(CH_3)(H_2)]^+$ **2**	TS **1/3**	$[Pd(H)(H)(CH_3)]^+$ **3**	TS **3/2**	$[Pd(CH_3)]^+/H_2$
Pd–H1	1.477	1.480	1.592	1.731	1.499	1.505	1.527	
Pd–H2		1.946	1.653	1.732	1.531	1.505	1.527	
Pd–H3		2.167						
Pd–C		2.342	2.143	2.015	2.106	2.040	2.035	1.999
C–H1					2.497	2.427	2.474	
C–H2	1.090	1.134	1.550	2.685	1.170	2.427	2.474	
C–H3		1.108						
H1–H2		2.305	1.017	0.838	1.840	1.794	1.391	0.744

barrier. The nascent bond formation between H1 and H2 in TS **1/2** is indicated by a bond length of 1.017 Å;, in the intermediate $[Pd(CH_3)(H_2)]^+$ (**2**) the H1–H2 bond length (0.838 Å) is almost comparable to that in free H_2.

As the σ-metathesis process **1**$\rightleftarrows$**TS1/2**$\rightleftarrows$**2** is rather exceptional for a late-transition metal like palladium,[15] we have searched for alternative routes. In fact, in addition to the direct equilibrium reaction **1**$\rightleftarrows$**2**, an independent oxidative addition-type path exists (**1**$\rightleftarrows$**3**$\rightleftarrows$**2**). At the theoretical level used, the relevant transition structure TS **1/3** is energetically comparable to TS **1/2**. The assignment of a formal oxidation state IV for palladium in intermediate **3** is supported by the rather long H1–H2 distance of 1.794 Å, the short Pd–H bonds (each 1.505 Å), and a Pd–C bond length of 2.040 Å. The subsequent reductive elimination proceeds on a flat potential energy surface via the practically isoenergetic TS **3/2** in a process that is typical and facile for Pd^{IV},[16] to give the complex $[Pd(CH_3)(H_2)]^+$ (**2**) rather than reverting to **1**. Thus, path **1**$\rightleftarrows$**3** does not constitute—as conjectured by a reviewer—an alternative H/D equilibration variant but simply opens up an additional channel to link **1**$\rightleftarrows$**2.**

While the thermal reactions of MH^+ (M = Ni, Pd, Pt)[4,10] with methane have many features in common, fundamental differences exist with regard to the details of the potential energy surfaces and thus to the actual reaction mechanisms: As already shown by Zhang and Bowers,[4c] the Ni-mediated H/CH_3 ligand exchange constitutes a textbook example for the operation of "two-state reactivity" (TSR) [1b,j,17] because crossings between the high-spin and low-spin potential-energy surfaces take place at both the entrance and the exit channels of reaction (2) (M = Ni). Thereby, a pathway is opened up that bypasses an energetically rather unfavorable transition structure associated with a spin-conserving σ-metathesis process on the high-spin ground-state surface. This TSR scenario is favored by the relatively small energy separation ($<100\ kJ\,mol^{-1}$) of the two relevant spin states of NiH^+, that is, ground-state $^3\Delta$ and excited $^1\Sigma^+$. In distinct contrast, the PdH^+/CH_4 couple can be fully explained without invoking a multistate pattern. As the excited states of PdH^+ ($^3\Delta$ and $^3\Pi$) are $>320\ kJ\,mol^{-1}$ higher in energy than the $^1\Sigma^+$ ground state, they are too high in energy to contribute to a TSR scenario; instead, the whole reaction proceeds on the singlet potential-energy surface in a spin-conserving manner. Finally, for the PtH^+/CH_4 system, one encounters yet another electronic situation. Here, the $^1\Sigma^+$ and $^3\Delta$ states are practically isoenergetic[11,18] and spin–orbit coupling for heavy elements is generally rather efficient;[1h,17c,19] thus, a multitude of both single- and multistate reactivity routes are accessible in the course of the platinum-mediated H/CH_3 ligand exchange. Obviously, for the three formally related Group 10 metal-hydride cations in their thermal reaction with methane and with regard to the mechanistic details it seems appropriate to use the phrase "the same and not the same" coined by Hoffmann in a different context.[28]

Experimental Section

The experiments were carried out using a VG BIO-Q mass spectrometer with QHQ configuration (Q: quadrupole, H: hexapole) equipped with an electrospray ionization source as described in detail previously.[21] In brief, the cations PdH^+ and PdD^+ were formed from a millimolar solution of $PdCl_2$ in CH_3OH and CD_3OD, respectively. The ions containing palladium were readily identified by their characteristic isotope pattern. Experiments with PdH^+ were conducted by mass selection of the isotopomer involving the most abundant ^{106}Pd isotope without isobaric interferences by other isotope compositions. To avoid isobaric overlap, for the experiments with PdD^+ the less abundant isotope ^{105}Pd was employed. After mass selection by means of Q1, the thermalized ions were exposed to react with methane in the hexapole at room temperature and at pressures on the order of 10^{-4} mbar, which is considered to correspond to nearly single-collision conditions, and the ionic products were detected using Q2. Ion-reactivity studies were performed at an interaction energy in the hexapole (E_{lab}) nominally set to 0 eV.[10,22]

In the computational studies the geometries of all species were optimized at the B3LYP level of theory[23] as implemented in the Gaussian 03 program package[24] using basis sets of approximately triple-ζ quality. For H and C atoms these were the triple-ζ plus polarization basis sets (TZVP) of Ahlrichs and co-workers.[25] For palladium, Stuttgart–Dresden scalar relativistic pseudopotentials (ECP28MWB replacing 28 core electrons) were employed in conjunction with the corresponding (8s,7p,6d)/[6s,5p,3d] basis set describing the 4s5s4d valence shell of Pd.[26,27] The nature of the stationary structures as minima or saddle points was characterized by frequency analysis, and internal reaction coordinate calculations were performed to link transition structures with the intermediates shown in Figure 2.[14]

Received: December 20, 2006
Revised: March 7, 2007

Keywords: C–H activation · gas-phase reactions · ligand effects · mass spectrometry · palladium

---

[1] For selected reviews, see: a) P. B. Armentrout, J. L. Beauchamp, *Acc. Chem. Res.* **1989**, *22*, 315; b) P. B. Armentrout, *Science* **1991**, *251*, 175; c) K. Eller, H. Schwarz, *Chem. Rev.* **1991**, *91*, 1121; d) J. C. Weisshaar, *Acc. Chem. Res.* **1993**, *26*, 213; e) D. Schröder, H. Schwarz, *Angew. Chem.* **1995**, *107*, 2126; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1973; f) H. Schwarz, D. Schröder, *Pure Appl. Chem.* **2000**, *72*, 2319; g) P. Chen, *Angew. Chem.* **2003**, *115*, 2938; *Angew. Chem. Int. Ed.* **2003**, *42*, 2832; h) H. Schwarz, *Angew. Chem.* **2003**, *115*, 4580; *Angew. Chem. Int. Ed.* **2003**, *42*, 4442; i) D. A. Plattner, *Top. Curr. Chem.* **2003**, *225*, 153; j) H. Schwarz, *Int. J. Mass Spectrom.* **2004**, *237*, 75; k) D. K. Böhme, H. Schwarz, *Angew. Chem.* **2005**, *117*, 2388; *Angew. Chem. Int. Ed.* **2005**, *44*, 2336.

[2] a) A. A. Fokin, P. R. Schreiner, *Chem. Rev.* **2002**, *102*, 1551; b) G. A. Olah, A. Molnár, *Hydrocarbon Chemistry*, Wiley, New York, **1995**.

[3] For selected reviews, see: a) P. L. Watson, G. W. Parshall, *Acc. Chem. Res.* **1985**, *18*, 51; b) R. H. Crabtree, *Chem. Rev.* **1995**, *95*, 987; c) B. A. Arndtsen, R. G. Bergman, T. A. Mobley, T. H. Peterson, *Acc. Chem. Res.* **1995**, *28*, 154; d) C. Hall, R. N. Perutz, *Chem. Rev.* **1996**, *96*, 3125; e) A. E. Shilov, G. B. Shul'pin, *Chem. Rev.* **1997**, *97*, 2879; f) A. Sen, *Acc. Chem. Res.* **1998**, *31*, 550; g) S. S. Stahl, J. A. Labinger, J. E. Bercaw, *Angew. Chem.* **1998**, *110*, 2298; *Angew. Chem. Int. Ed.* **1998**, *37*, 2180; h) J. H. Lunsford, *Catal. Today* **2000**, *63*, 165; i) W. D. Jones, *Science* **2000**, *287*, 1942; j) R. H. Crabtree, *J. Chem. Soc. Dalton Trans.* **2001**, 2437; k) J. A. Labinger, J. E. Bercaw, *Nature* **2002**, *417*, 507; l) U. Fekl, K. I. Goldberg, *Adv. Inorg. Chem.* **2003**, *54*, 259; m) J. A. Labinger, *J. Mol. Catal. A* **2004**, *220*, 27; n) M. Lersch, M. Tilset, *Chem. Rev.* **2005**, *105*, 2471; o) B. L. Conley, W. J. Tenn III, K. J. H. Young, S. G. Ganesh, S. K. Meier, V. R. Ziatdinov, O. Mironov, J. Oxygaard, J. Gonzales, W. A. Goddard III, R. A. Periana, *J. Mol. Catal. A* **2006**, *251*, 8; p) for a thorough theoretical study, see: A. Paul, C. B. Musgrave, *Organometallics* **2007**, *26*, 793.

[4] a) T. J. Carlin, L. Sallans, C. J. Cassady, D. B. Jacobson, B. S. Freiser, *J. Am. Chem. Soc.* **1983**, *105*, 6320; b) L. F. Halle, F. S. Klein, J. L. Beauchamp, *J. Am. Chem. Soc.* **1984**, *106*, 2543; c) Q. Zhang. M. T. Bowers, *J. Phys. Chem. A* **2004**, *108*, 9755; d) M. Schlangen, D. Schröder, H. Schwarz, *Angew. Chem.* **2007**, *119*, 1667; *Angew. Chem. Int. Ed.* **2007**, *46*, 1641.

[5] a) D. Schröder, H. Schwarz, S. Shaik, *Structure and Bonding* (Ed.: B. Meunier), Springer, Berlin, **2000**, S. 97; b) D. Schröder, H. Schwarz, *Top. Organomet. Chem.* **2007**, *10*, 1.

[6] a) M. F. Ryan, A. Fiedler, D. Schröder, H. Schwarz, *J. Am. Chem. Soc.* **1995**, *117*, 2033; b) D. Schröder, H. Schwarz, *Angew. Chem. 107*, 2126; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1973; c) D. Schröder, J. Roithová, *Angew. Chem.* **2006**, *118*, 5835; *Angew. Chem. Int. Ed.* **2006**, *45*, 5705; d) I. Kretzschmar, A. Fiedler, J. N. Harvey, D. Schröder, H. Schwarz, *J. Phys. Chem. A* **1997**, *101*, 6252; e) K. K. Irikura, J. L. Beauchamp, *J. Am. Chem. Soc.* **1989**, *111*, 75; f) S. Feyel, J. Döbler, D. Schröder, J. Sauer, H. Schwarz, *Angew. Chem.* **2006**, *118*, 4797; *Angew. Chem. Int. Ed.* **2006**, *45*, 4681.

[7] a) M. L. Mandich, L. F. Halle, J. L. Beauchamp, *J. Am. Chem. Soc.* **1984**, *106*, 4403; b) M. A. Tolbert, M. L. Mandich, L. F. Halle, J. L. Beauchamp, *J. Am. Chem. Soc.* **1986**, *108*, 5675; c) J. Schwarz, C. Heinemann, D. Schröder, H. Schwarz, J. Hrušák, *Helv. Chim. Acta* **1996**, *79*, 1; d) Y.-M. Chen, M. R. Sievers, P. B. Armentrout, *Int. J. Mass Spectrom. Ion Processes* **1997**, *167*/168, 195.

[8] J. Schwarz, D. Schröder, H. Schwarz, C. Heinemann, J. Hrusák, *Helv. Chim. Acta* **1996**, *79*, 1110.

[9] a) For a review on $\mathrm{Pd^{II}}$ intermediates in coupling reactions in solution and involving C–H bond activation, see: G. Dyker, *Transition Metals for Organic Synthesis*, *Vol. 1* (Eds.: M. Beller, C. Bolm), Wiley-VCH, Weinheim, **1998**, p. 241; b) for aspects on homogeneous alkane oxidations by late-transition-metal complexes, including $\mathrm{Pd^{II}}$, see: [3g]; c) for low-temperature, $\mathrm{Pd^{II}}$-mediated oxidation of methane, see: Z. An, X. Pan, X. Liu, X. Han, X. Bao, *J. Am. Chem. Soc.* **2006**, *128*, 16028.

[10] D. Schröder, H. Schwarz, *Can. J. Chem.* **2005**, *83*, 1936.

[11] a) J. B. Schilling, W. A. Goddard III, J. L. Beauchamp, *J. Am. Chem. Soc.* **1987**, *109*, 5565; b) G. Ohanessian, W. A. Goddard III, *Acc. Chem. Res.* **1990**, *23*, 386, and references therein.

[12] For technical details of the modeling, see: a) J. Loos, D. Schröder, W. Zummack, H. Schwarz, R. Thissen, O. Dutuit, *Int. J. Mass Spectrom.* **2002**, *214*, 105; b) C. Trage, D. Schröder, H. Schwarz, *Organometallics* **2003**, *22*, 693; c) M. Schlangen, D. Schröder, H. Schwarz, *Helv. Chim. Acta* **2005**, *88*, 1405; d) B. Butschke, M. Schlangen, D. Schröder, H. Schwarz, *Z. Naturforsch. B* **2007**, *62*, 309.

[13] We note that a *quantitative* discussion of the competition between direct $\mathrm{H/CH_3}$ ligand exchange (70%) versus prior hydrogen exchange (30%) in relation to the energy profile in Figure 2 is not really meaningful without sufficiently detailed trajectory calculations of the ion–molecule reactions based on a potential energy surface calculated at a much higher and more accurate level of theory. These aspects are beyond the scope of this Communication.

[14] a) K. Fukui, *J. Phys. Chem.* **1970**, *74*, 4161; b) K. Fukui, *Acc. Chem. Res.* **1981**, *14*, 363; c) C. Gonzalez, H. B. Schlegel, *J. Phys. Chem.* **1990**, *94*, 5523.

[15] a) "Transition State Modeling for Catalysis": S. Niu, D. L. Strout, S. Zarić, C. A. Bayse, M. B. Hall, *ACS Symp. Ser.* **1998**, *721*, 138; b) S. Niu, M. B. Hall, *Chem. Rev.* **2000**, *100*, 353; c) S. Sakaki, *Top. Organomet. Chem.* **2005**, *12*, 31; d) R. N. Perutz, S. Sabo-Etienne, *Angew. Chem.* **2007**, *119*, 2630; *Angew. Chem. Int. Ed.* **2007**, *46*, 2667.

[16] A. J. Canty, P. R. Traill, R. Colton, I. M. Thomas, *Inorg. Chim. Acta* **1993**, *210*, 91.

[17] a) D. Schröder, S. Shaik, H. Schwarz, *Acc. Chem. Res.* **2000**, *33*, 139; b) R. Poli, J. N. Harvey, *Chem. Soc. Rev.* **2003**, *32*, 1; c) J. M. Mercero, J. M. Matxain, X. Lopez, D. M. York, A. Largo, L. A. Erikson, J. M. Ugalde, *Int. J. Mass Spectrom.* **2005**, *240*, 37; d) I. Rivalta, N. Russo, E. Sicilia, *J. Comput. Chem.* **2006**, *27*, 174.

[18] X.-G. Zhang, R. Liyanage, P. B. Armentrout, *J. Am. Chem. Soc.* **2001**, *123*, 5563.

[19] P. Pyykkö, *Chem. Rev.* **1988**, *88*, 563.

[20] R. Hoffmann, *The Same and Not the Same*, Columbia University Press, New York, **1995**.

[21] D. Schröder, T. Weiske, H. Schwarz, *Int. J. Mass Spectrom.* **2002**, *219*, 729.

[22] a) D. Schröder, T. Weiske, M. Brönstrup, C. Daniel, J. Spandl, H. Hartl, *Int. J. Mass Spectrom.* **2003**, *228*, 743; b) S. Feyel, D. Schröder, H. Schwarz, *J. Phys. Chem. A* **2006**, *110*, 2647.

[23] Gaussian03 (Revision C.02), M. J. Frisch et al., Gaussian, Inc., Pittsburgh, PA, **2004**.

[24] a) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.

[25] A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829.

[26] The basis sets and ECPs correspond to Revision: Fri Jun 27, 1997, of the Stuttgart/Dresden groups.

[27] The present computational treatment of the $\mathrm{PdH^+/CH_4}$ system aims at a qualitative description; for an example of a rigorous ab initio calculations of the gas-phase chemistry of various cationic palladium complexes, see Ref. [8].

[28] Note added in proof: For another example of different mechanistic behaviour of structurally related organometallic systems in the context of the C–H bond activation, see: W. H. Lam, G. Jia, Z. Lin, C. P. Lau, O. Eisenstein, *Chem. Eur. J.* **2003**, *9*, 2775.