1. Unparalleled, Enormous Metal–Carbon Bond Strength in $PdCH_2I^+$

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Dedicated to *Albert Eschenmoser* on the occasion of his 70th birthday

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Thermalized Pd^+ cations activate methyl iodide by selective cleavage of a C–H bond under formation of $PdCH_2I^+$ and an H-atom. This finding implies that the interaction energy between the metal cation and the CH_2I fragment and thus the metal–carbon bond strength exceeds 103 kcal/mol. Theory predicts that the energetically most favorable isomer of this ion exhibits the $Pd^+–CH_2–I$ structure, which is stabilized by an unprecedented bridging interaction between the two heavy atoms Pd and I.

Due to its high-lying excited quartet state [1], Pd^+ is one of the least reactive 'bare' transition-metal cations in the gas phase [2]. Under thermal conditions, it is unreactive with methane[1]) and methyl halides CH_3X for X = F, Cl, and Br. Surprisingly, under the conditions of *Fourier-Transform* ion cyclotron resonance mass spectrometry [4], thermalized Pd^+ cations react with CH_3I (*Fig. 1*) under formation of $PdCH_2I^+$ concomitant with loss of an H-atom (*Eqn. 1*).

$$Pd^+ + CH_3I \rightarrow PdCH_2I^+ + H^{\cdot} \qquad (1)$$

Eqn. 1 is most notable from an energetic point of view, because instead of the weak C–I bond (bond dissociation energy, *BDE:* 56.4 kcal/mol[2])), the strong C–H bond (*BDE:* 103.3 kcal/mol [6]) of CH_3I is cleaved selectively. The Pd^+ cations were produced by Nd:YAG-laser desorption/laser ionization of a metallic Pd target and thermalized with both pulsed-in Ar (maximum pressure 10^{-5} mbar for 0.5 s) and Ar buffer gas present at a stationary pressure of $1.5 \cdot 10^{-7}$ mbar in all experiments. The thermochemical implication of the observed reaction is that the net interaction energy between the $CH_2I^{\cdot}$ radical and Pd^+ is ≥ 103 kcal/mol, because only more or less thermoneutral or exothermic processes can occur under these experimental conditions. A bond strength of more than 100 kcal/mol for a metal–carbon single bond is very unusual, and must be due to an effect of the I-atom in $PdCH_2I^+$, if the CH_2I moiety remains intact in $PdCH_2I^+$. The integrity of the CH_2I group is a reasonable assumption on the basis of the $4d^95s^0$ (^2D) ground state of Pd^+

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[1]) Extensive theoretical studies demonstrate that there is not even an insertion minimum $H–Pd^+–CH_3$ on the $[Pd,C,H_4]^+$ potential-energy surface. See [13].

[2]) If not otherwise indicated, all theochemical data are taken from [5].

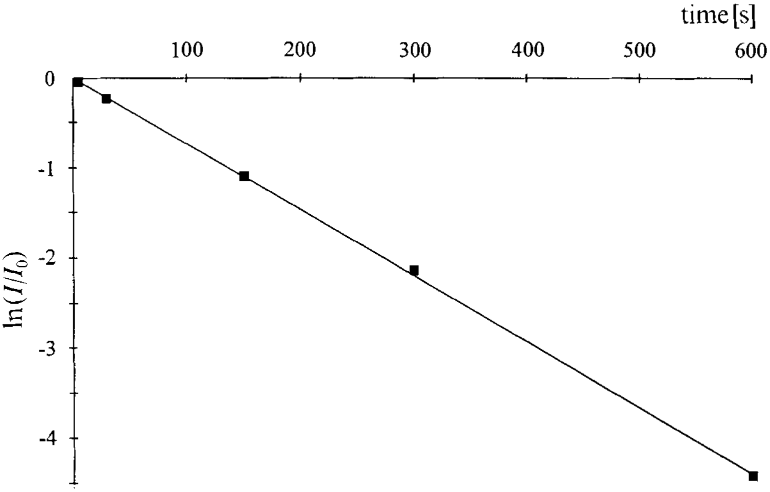

Fig. 1. *First-order decay of intensity (*I*) of* Pd^+ *in the reaction with* CH_3I ($p = 2 \cdot 10^{-8}$ mbar)

and the high d→s promotion energy to the lowest quartet state such that formation of other inserted structures than $Pd^+{-}CH_2I$ is unlikely [1]. However, the genuine Pd–C single- and double-bond strengths (0-K values) in the cationic species $PdCH_3^+$ and $PdCH_2^+$ amount to only 59 ± 5 [7a] and 71 ± 2 kcal/mol, respectively [7b].

To substantiate the significance of this experiment, the degree of thermalization (affected by collisions with Ar) of the reactant Pd^+ cations was carefully verified *via* their electron-transfer behavior. It was observed that laser-generated and thermalized Pd^+ ions (ionization energy of Pd, *IE* (Pd) = 8.33 eV) do not undergo electron transfer with neither benzene (*IE*(C_6H_6) = 9.25 eV) nor chinoline (*IE*(C_7H_9N) = 8.62 eV), but rather form the corresponding adduct complexes. Under the reasonable assumption that single-electron transfer in such reactions is not inhibited kinetically, excited states of Pd^+ (*e.g.* the low-lying terms $^2D_{3/2}$ and $^4F_{9/2}$ with excitation energies of 0.44 eV and 3.11 eV, respectively; see [1]) are not populated within the sensitivity of the experiment (< 0.5%)[3]). Involvement of excited Pd^+ states in the observed reaction is also disapproved by the strict pseudo-first-order decay of the Pd^+ intensity over a period of 10 min up to a total conversion of more than 95%. The corresponding rate constant amounts to $k_{exp} = (1.4 \pm 0.5) \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1}, *i.e.*, an efficiency of 2% of the collision limit ($k_c = 8.5 \cdot 10^{-10}$ cm^3 molecule^{-1} s^{-1}) [9][4]). To provide insight into the structure of the $PdCH_2I^+$ ion, we have subjected this species to collision-induced dissociation experiments with Ar: the observed fragmentation channels are elimination of iodine under formation of $PdCH_2^+$ and loss of CH_2I to yield Pd^+ with almost equal intensities over the applied energy range (0–200 eV). On the basis of these results, differentiation between the two most possible structures, the mixed iodo-methylene species $Pd(CH_2)(I)^+$ (**I**) and the

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[3]) For a recent application of this method, see [8].

[4]) In view of the low efficiency of *Reaction 1*, the purity of CH_3I was carefully checked by ^{1}H- and ^{13}C-NMR; in addition, also CD_3I is activated by Pd^+ to yield $PdCD_2I^+$ and D .

$I—\overset{+}{Pd}=CH_2$ **I**

$\overset{+}{Pd}—CH_2I$ **II**

I-substituted cationic methyl-palladium complex $Pd(CH_2I)^+$ (**II**), is impossible, because neither PdI^+ nor CH_2I^+ are observed, which would be indicative for **I** and **II**, respectively.

These findings prompted us to perform a theoretical investigation of the $[Pd,C,H_2,I]^+$ potential-energy surface [10]; here, we will present those details that are relevant for an understanding of the remarkable Pd^+/CH_3I reaction. First of all, let us mention that the low-lying structures on the potential-energy surface are all of singlet multiplicity with considerable (> 50 kcal/mol) excitation energies to the triplet regime. Second, an initial series of calculations (*Hartree-Fock*/DFT hybrid method Becke3LYP/LANL2DZ basis of the GAUSSIAN92 program [11]) indicated a clear energetic preference for structure **II** (> 30 kcal/mol) as compared to **I**. The discussion of the theoretical results is, therefore, restricted to a theoretical prediction of an accurate geometry of **II** and the computation of the reaction enthalpy given by *Eqn. 1, i.e.*, $\Delta H_R(1)$. Along the series X = F, Cl, Br, I, the minimum structures for ions of the composition $PdCH_2X^+$ are characterized by decreasing Pd—C—X angles, which vary, in the B3LYP/LANL2DZ scheme, from 98.1° to 84.2° from X = F–I with concomitant increase of the interaction energies between Pd^+ and the CH_2X moiety. Thus, structurally the chemical nature of the enhanced $Pd^+—CH_2I$ binding energy appears as a *secondary bridging interaction between the two heavy atoms I and Pd.* The nature of this interaction is both charge-induced dipole interaction between the charge formally located on the Pd^+ cation and the polarizable I-atom (estimated as *ca.* 20 kcal/mol for **II**) and some small degree of electron donation from the I lone pairs into the formally empty 5s and 5p orbitals of the Pd-atom (*Mulliken* populations for Pd valence orbitals in **II**: 5s: 0.21e; 5p: 0.13e; 4d: 9.17e; q(Pd) = +0.49; compared to $PdCH_3^+$: 5s: 0.09e; 5p: 0.06e; 4d: 9.17e; q(Pd) = +0.68). Similar interactions are expected to be less prominent for the lighter halogen atoms due to their lower polarizabilities and increasing ionization energies of the $CH_2X^\cdot$ radicals from X = I to X = F [5].

For an accurate determination of $BDE(Pd^+—CH_2I)$, we chose methods which can reliably describe electron correlation, the polarizability of the I-atom, the doublet-quartet excitation energy of Pd^+ as well as relativistic effects[5]. This approach yields accurate C—H as well as $Pd^+—CH_n$ (n = 2,3) *BDE*s[6]. Complete reoptimization at the MP2 level using larger basis sets with inclusion of f-functions for Pd[5] leads to a decrease of Pd—C—I angle to 78.2° (*Fig. 2*). This geometry was used in CCSD(T) calculations which predict

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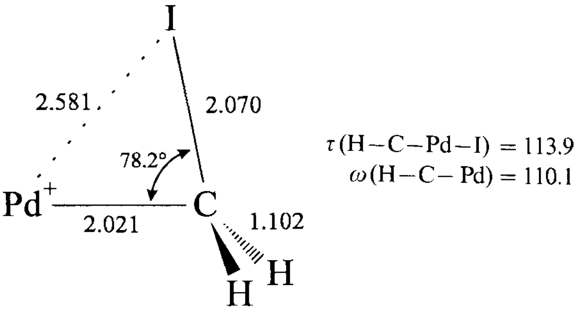
[5] The coupled cluster method including all single and double excitations and a perturbative estimate of the triples contributions (CCSD(T)) was used to calculate total energies (Program system MOLPRO, written by *J. Almlöf, R. D. Amos, M. J. O. Deegan, S. T. Elbert, C. Hampel, W. Meyer, K. Peterson, R. Pitzer, A. J. Stone, P. R. Taylor*). Zero-point vibrational effects and thermal contributions were calculated from harmonic frequencies using B3LYP geometries. Basis sets: Pd: 28-electron quasi-relativistic *ab initio* pseudo-potential and a (8s7p6d)/[6s5p4d] valence basis [12], augmented by a (4f)/[3f] polarization set [13]. CCSD(T) ${}^2D \rightarrow {}^4F$ excitation energy: 2.95 eV (exp. 3.19 eV). I: 46-electron quasi-relativistic *ab initio* pseudo-potential [14] together with the outer (7s5p6d)/[7s5p3d] part of the iodine basis set according to [15]. CCSD(T) Polarizability of the I-atom 4.98 Å^3 (exp. 5.35 Å^3). Other ECPs for Pd and I yield similar results to the ones reported here C, H: cc-pVDZ basis sets from [16]. Spin-orbit effects for $PdCH_2I^+$ were estimated according to a method recently described [17].

[6] Zero-point-corrected 0-K binding energie for $Pd^+—CH_n$: 53 kcal/mol (n = 3), 68 kcal/mol (n = 2). 298 K binding energy $IH_2C—H$: 95 kcal/mol.



II

Fig. 2. *Optimized MP2 geometry for* $PdCH_2I^+$

$\Delta H_R(1) = +12$ kcal/mol at 298 K. After explicit corrections for spin-orbit effects, $\Delta H_R(1)$ increases to +16 kcal/mol.

In view of the complicated electronic situation in $PdCH_2I^+$, it is also instructive to extrapolate the theoretical prediction for $\Delta H_R(1)$ using the PCI-85 scheme as suggested by *Siegbahn et al.* [18]. This procedure reduces the spin-orbit-corrected reaction endothermicity for *Eqn. 1* to $\Delta H_R(1) = +13$ kcal/mol. Likewise, the calculated enthalpies for *Eqns. 2* and *3* (34 and 43 kcal/mol, resp.) agree well with the experimental figures (38 ± 2 and 44 ± 5 kcal/mol, resp.), which lends further support to the applicability of the chosen PCI-85 scheme.

$$Pd^+ + CH_4 \rightarrow PdCH_2^+ + H_2 \tag{2}$$

$$Pd^+ + CH_4 \rightarrow PdCH_3^+ + H^\cdot \tag{3}$$

In conclusion, our best theoretical estimate for $\Delta H_R(1)$ amounts to +13 kcal/mol, which is clearly endothermic. Strinctly speaking, the charge-transfer bracketing experiments³) allow for a maximum reaction endothermicity of 0.29 eV, which means that the disagreement between the best computational result and the experimental observation is at least 6 kcal/mol. More accurate basis sets and correlation-energy treatments will eventually lower $\Delta H_R(1)$, but a relativistic all-electron treatment of both Pd and I is indicated; unfortunately, the computational costs of such an effort seem to be out of proportion. Notwithstanding, the theoretical findings corroborate the observation of a thermal reaction between Pd^+ and CH_3I under formation of $PdCH_2I^+$, which is substantially stabilized by bridging between Pd and I. It is instructive to compare the reaction of Pd^+ with CH_3I to the respective processes for Fe^+, Co^+, and Ni^+ [19]. These 3d-block cations undergo exclusively C–I bond cleavage to yield MCH_3^+ (M = Fe, Co) and MI^+ (M = Fe–Ni). Again, the fundamentally different behavior of Pd^+ can be rationalized by its inability to oxidatively insert into the C–I bond due to the high excitation energy associated with this process; consequently, H-atom loss remains as exclusive reaction channel.

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