97. Theory-enforced Re-investigation of the Origin of the Large Metal–Carbon Bond Strength in PdCH$_2$I$^+$ and Its Reactions with Unsaturated Hydrocarbons[1])

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Dedicated to Edgar Heilbronner on the occasion of his 75th birthday

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State-of-the-art ab initio studies demonstrate that the reaction Pd$^+$ + CH$_3$I → PdCH$_2$I$^+$ + H$^·$ is endothermic by ca. 20 kcal/mol, which translates into a bond dissociation energy (BDE) of ca. 83 kcal/mol for the Pd$^+$–CH$_2$I bond. This figure is in agreement with an experimental bracket of 68 kcal/mol < BDE(Pd$^+$–CH$_2$I) < 92 kcal/mol. Based on these findings, the previously studied Pd$^+$/CH$_3$I system was re-investigated, and double-resonance experiments demonstrate that the formation of PdCH$_2$I$^+$ occurs stepwise via PdCH$_3^+$ as a reactive intermediate. Further, ion/molecule reactions of PdCH$_2$I$^+$ with unsaturated hydrocarbons are studied, which reveal the formation of carbon–carbon bonds in the gas phase.

In a recent publication [1], we have reported an unusually large bond-dissociation energy (BDE) of 103 kcal/mol for the metal–carbon bond in cationic PdCH$_2$I$^+$. This figure was derived from the occurrence of Reaction 1, when carefully thermalized Pd$^+$ cations are allowed to react with CH$_3$I under the conditions of Fourier-transform ion-cyclotron resonance (FTICR) mass spectrometry.

$$Pd^+ + CH_3I \rightarrow PdCH_2I^+ + H^· \tag{1}$$

This enormous BDE was traced back to an α-agostic interaction between Pd and I in PdCH$_2$I$^+$, as derived from ab initio calculations. The agostic interaction is manifested in a short Pd–I bond (2.58 Å) together with a small Pd–C–I angle (78°) in the MP2-optimized geometry of PdCH$_2$I$^+$ (Fig. 1). However, by means of computational chemistry we were unable to quantitatively reproduce the BDE, and the closest theoretical prediction lead to an endothermicity of 13 kcal/mol for Reaction 1, implying that the BDE(Pd$^+$–CH$_2$I) ≤ 90 kcal/mol.

Thus, there is an obvious discrepancy between experiment and theory, and in our previous paper we argued that this may be due to an incomplete description of the Pd–I interaction in the computational approach used. Here, we describe in detail our further experimental[2]) and theoretical efforts aimed at resolving this discrepancy. In doing so, we

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[1])   In [1], a preliminary account of the reaction of ground-state Pd$^+$ with CH$_3$I is given.
[2])   The experiments were performed in a Spectrospin CMS47X FTICR mass spectrometer in the same manner as reported in [1], and, therefore, we refrain from a further description, except when this is indicated.
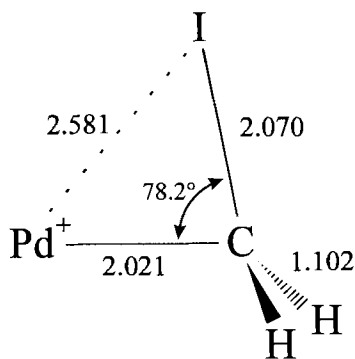
τ(H–C–Pd–I) = 113.9

ω(H–C–Pd) = 110.1

Fig. 1. *Optimized MP2 geometry for PdCH$_2$I$^+$.* For details see text and [1].

will demonstrate that nowadays well chosen theoretical methods[3]) do not only accurately predict energetic features of transition-metal compounds, but also serve to guide experiments [12].

At first, we would like to point out that the calibration of the theoretical approach (*Table 1*) reveals that the experimental reaction energies for the Pd$^+$/CH$_4$ system are well reproduced, thus implying that the Pd–C interaction is reasonably described using this theoretical approach. Following the idea of an insufficient theoretical description of the Pd–I interaction [1], our first approach to the problem was to examine this particular

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[3]   The all-electron calculations were performed using the MOLCAS-3 program system [2]. Geometries were those determined earlier [1] at the B3LYP level of theory. For single-point energy calculations, a single-reference ansatz was chosen: first, the *Hartree-Fock* self-consistent field (SCF) wave functions were computed, and correlation effects were accounted for by a subsequent modified coupled-pair functional (MCPF) [3] calculation in which the core electrons ([Kr] for Pd; [Kr + 4d^{10}] for I, 1s^2 for C) were kept frozen. First-order estimates for relativistic effects were derived from the mass-velocity and *Darwin* terms [4]. Following a suggestion of *Siegbahn et al.* [5], the relativistically corrected correlation energies were divided by 0.8 and added to the relativistically corrected SCF energies in order to obtain the relativistically corrected PCI-80 energies (PCI80rel). This procedure compensates possible errors made in the MCF calculations due to the truncations of both the one- and *n*-particle space treatments. Corrections for spin-orbit effects were done similarly to related studies of PtCH$_2^+$ [6] [7] and are anyhow minor for the Pd compounds under study (*e.g.* 1.6 kcal/mol for PdCH$_3^+$). The following basis sets were employed in the all-electron calculations: *a*) For palladium, we started with the SCF-optimized primitive (20s14p11d) set according to *Faegri* [8]. This set was augmented by one diffuse s function (exponent: 0.016), two diffuse p functions (exponents: 0.079, 0.025), and one diffuse d function (exponent: 0.06). To cover the higher angular momentum space, the (4f)/[3f] set of *Langhoff et al.* [9] was added. An atomic natural orbital contraction scheme for the spd part of this basis set was generated [10] by using the coefficients of the respective natural MCPF orbitals of Pd(^{1}S) with occupation numbers $> 0.5 \cdot 10^{-5}$ to contract the primitive set (21s16p12d) to [8s7p7d]; *i.e.*, (21s16p12d4f)/[8s7p7d3f] comprising a total of 85 functions (in general, only the spherical harmonic components of the higher angular momentum functions were retained). *b*) For iodine, we started with a (19s15p12d)/[11s9p6d] basis [11], which has been optimized for the description of dipole moments and polarizabilities. The performance of this basis with respect to covalent-bond dissociation energies (*BDE*s) was tested for the I$_2$ molecule: Under the

Table 1. *Reaction Energies* (kcal/mol), *Corrected for Spin-Orbit Effects and Translational, Rotational, and Vibrational Energies at the Indicated Temperatures* T (see text)[a]

		T [K]	MCPF	MCPF +rel.	PCI-80 +rel.	CCSD(T) RECP[b]	Exp.
$Pd^+ + CH_4$	$\rightarrow PdCH_3^+ + H^.$	0	58.4	56.5	49.5	47.4	44 ± 4
$Pd^+ + CH_4$	$\rightarrow PdCH_2^+ + H_2$	0	53.9	44.2	36.9	33.1	39 ± 2
$Pd^+ + CH_3I$	$\rightarrow PdCH_2I^+ + H^.$	298	37.7	31.4	20.6	16.3	23 ± 12
$PdCH_3^+ + CH_3I$	$\rightarrow PdCH_2I^+ + CH_4$	298	−21.2	−25.4	−29.2	−31.4	$−22 \pm 12$
CH_3I	$\rightarrow CH_2I^. + H^.$	298	95.8	96.2	100.6	95.4	103 ± 1

[a]   Ground states: Pd^+ (^2D), $PdCH_3^+$ ($^1A_1$), $PdCH_2^+$ ($^2A_1$), $PdCH_2I^+$ ($^1A'$), and $^.CH_2I$ ($^2B_1$).
[b]   Calculations reported in [1].

interaction in the diatomic species PdI^+. Although the $BDE(Pd^+-I)$ is not precisely known, ion/molecule reactions provide lower and upper limits[4] of 36 kcal/mol $< BDE(Pd^+-I) < 57$ kcal/mol. In fact, at the highest level of theory applied here, the Pd^+-I interaction is underestimated by a few kcal/mol due to incompleteness of the basis sets[5]). However, the analogous underestimation for $BDE(Pd^+-CH_2I)$ is expected to be smaller, because of the secondary Pd–I interaction in $PdCH_2I^+$ as compared to the covalent type in diatomic PdI^+. Thus, in view of the theoretical results[3])[5]) for I_2 and PdI^+, it seems unlikely that levels of theory significantly higher than applied here or even in our earlier work [1] would enlarge $BDE(Pd^+-CH_2I)$ by more than a few kcal/mol. Further, as will be shown next, spin-orbit interaction can be neglected to contribute to an unusual bond strengthening in $PdCH_2I^+$. Using a CAS-SCF wave function (12 active orbitals for 22 active electrons) of $PdCH_2I^+$ in a semiempirical spin-orbit calculation [13][6]), at this level of theory the spin-orbit stabilization of $PdCH_2I^+$ amounts to only 60 cm^{-1} (0.2 kcal/mol) with respect to the spin-orbit-uncoupled picture.

As far as the role of relativistic effects is concerned, all Pd–C bonds are strengthened by scalar relativistic terms. While the effect is only minor (*ca.* 3 kcal/mol) for the single

assumption that spin-orbit interaction affects only the atomic iodine fragment, but that it plays no role at the equilibrium geometry of the ground-state ($^1\Sigma_g^+$) molecule, the BDE for I_2 amounts to 36.0 kcal/mol. With the (19s15p12d)/[11s9p6d] basis, the spin-orbit-corrected BDEs are computed as 20.9 kcal/mol and 25.7 kcal/mol using relativistically corrected MCPF and PCI-80, respectively. To enlarge the treatment of valence correlation effects, a further f exponent of 0.45 was added, leading to $BDE(I-I) = 30.2$ kcal/mol. Preliminary calculations indicate that further augmentation of the basis set together with correlation of the 4d electrons will bring the computed $BDE(I-I)$ to within 3 kcal/mol of the experimental number. c) Carbon and hydrogen were described by valence triple-zeta doubly polarized atomic natural orbital basis sets ((14s9p4d)/[4s3p2d] and (8s4p)/[3s2p], respectively). Note that, in our earlier work, only double-zeta-polarized type basis sets were used for these atoms.

[4])   The figures for the $BDE(Pd^+-I)$ are derived from the formation of PdI^+ in the reaction of thermalized Pd^+ with elemental iodine ($BDE(I-I) = 36$ kcal/mol; this reaction continues up to the PdI_4^+), and the absence of the PdI^+ product in the reaction of Pd^+ with CH_3I ($BDE(H_3C-I) = 57$ kcal/mol).

[5])   At the highest level of theory (PCI80rel), the $BDE(Pd^+-I)$ was calculated as 39 kcal/mol ($r(Pd-I) = 2.56$ Å). However, corrections for atomic spin-orbit effects reduce this figure to 31 kcal/mol. Still, considering the limitations of the iodine basis set (see above) and the valence-only treatment, this figure compares well with the experimentally determined lower limit $BDE(Pd^+-I) > 36$ kcal/mol.

[6])   This calculation includes all spin-orbit matrix elements between the five lowest singlet and triplet states and effective charges (optimized for atomic spin-orbit effects) are as follows: 240 (Pd), 3.6 (C), 600 (I) and 1 (H).

Pd—C bond in PdCH$_3^+$, it becomes larger for PdCH$_2^+$ (10 kcal/mol). This can readily be explained by the necessity to promote a 4d electron of the Pd$^+$ (^{2}D) ground state into the relativistically stabilized 5s orbital, in order to form a genuine double bond to the CH$_2$ fragment [14]. For PdCH$_2$I$^+$, the relativistic bond strengthening is computed to be *ca.* 7 kcal/mol at the MCPF level of theory. This reflects part of the α-agostic interaction mechanism between the Pd-center and the I-atom as electron donation from the iodine's lone pairs into the formally empty 5s orbital of Pd. However, despite the finding that part of the bond strengthening in PdCH$_2$I$^+$ is due to relativistic effects on the valence orbitals, these can also not account for the discrepancy.

As we have mentioned in [1], another source of error may be due to the use of relativistic effective core potentials in the theoretical approach such that core correlation is underestimated. To this end, we examined *Reaction 1* in an all-electron ansatz^3) and improved basis sets. However, also at this level of theory, *Reaction 1* is definitely predicted to be endothermic (*Table 1*). Considering a typical error of ±6 kcal/mol of the computational aproach used (see *Table 1* and [15]), these results lead to a theoretical prediction of BDE(Pd$^+$—CH$_2$I) = 83 ± 6 kcal/mol. While this figure clearly demonstrates that the Pd—C interaction in PdCH$_2$I$^+$ is significantly larger (> 20 kcal/mol) than in PdCH$_3^+$, thus justifying the title of our earlier paper [1], the substantial discrepancy between experiment and theory remains obvious. In fact, from a theoretical point of view, at these levels of theory no interactions are neglected which can possibly account for the large difference of calculated and experimental results.

Thus, a careful inspection of the experiment was indicated. The first and obvious reason for an experimental overestimation of BDE(Pd$^+$—CH$_2$I) is due to unintentional excitation of the Pd$^+$ reactant. However, as we have demonstrated before [1], even most thorough thermalization of Pd$^+$ does not prevent *Reaction 1* from occurring, and it continues until complete conversion of Pd$^+$, following pseudo-first-order kinetics. What remains somewhat suspicious is the low efficiency (φ) of *Reaction 1* in that the rate constant k_1 amounts to only a percentage of the corresponding collision rate constant k_c [16], *i.e.*, $\phi_1 = k_1/k_c \approx 0.02$. Under the conditions of FTICR mass spectrometry, a low efficiency of a reaction of thermalized ions may be due to the existence of a significant kinetic barrier in the vicinity of the entrance channel (*i.e.*, isolated Pd$^+$ + CH$_3$I), or the reaction is slightly endothermic [17]; assuming *Arrhenius* behavior [18], $\phi_1 \approx 0.02$ leads to a barrier or an endothermicity, respectively, of 2 kcal/mol. Again this figure is much too small to resolve the discrepancy. However, as we have discussed in another context [19], the low-pressure regime under which the FTICR experiments are conducted may lead to artifacts due to unintentional background impurities, and, therefore, it had to be confirmed beyond any doubt that PdCH$_2$I$^+$ does indeed originate from the reaction of Pd$^+$ with CH$_3$I. Therefore, we carefully excluded by GC/MS and NMR that CH$_3$I contains neither methylene iodide, which rapidly reacts with Pd$^+$ to form PdCH$_2$I$^+$, nor any other impurities which would lead to PdCH$_2$I$^+$.

The solution of the discrepancy became apparent upon a thorough inspection of the products of the reaction of Pd$^+$ with CH$_3$I: As reported before, PdCH$_2$I$^+$ is formed almost exclusively (> 99%), while PdCH$_3^+$ and the adduct complex Pd(CH$_3$I)$^+$ are co-generated in very small fractions (< 1%, see below). For an unambiguous detection of the PdCH$_3^+$ signal, it was necessary to accumulate several hundreds of spectra (high resolution of ^{106}PdCH$_3^+$: m_{exp} = 120.92687 ± 0.00015 amu, m_{th} = 120.92695 amu), and the signal is too

weak to allow for a precise kinetic analysis. At this stage, we, therefore, considered $PdCH_3^+$ as a minor side product in analogy to the $M-CH_3^+$ formation in the reactions of first-row transition-metal ions M^+ with CH_3I [20], and neglected $PdCH_3^+$ as potential intermediate in the formation of $PdCH_2I^+$. However, the discrepancy between experiment and theory as described forced us to revise this (otherwise reasonable) assumption, and we decided to perform a double-resonance experiment on the $PdCH_3^+$ ion formed in the reaction of Pd^+ with CH_3I. In a double-resonance experiment, an ion of interest is continuously ejected from the FTICR cell by irradiation of the appropriate cyclotron frequency [21]. Removal of the ions occurs within a few microseconds such that these ions are not any more available for consecutive ion/molecule reactions.

In fact, the $PdCH_2I^+$ product, which is present when Pd^+ is reacted with CH_3I (*Fig. 2, a*), vanishes completely when $PdCH_3^+$ is ejected from the ICR cell in a double-resonance experiment (*Fig. 2, b*). The only channel present is that of a slow association of Pd^+ and CH_3I ($\phi \approx 10^{-4}$). Thus, we have to conclude that, instead of *Reaction 1*, the sequence of *Reactions 2* and *3* leads to the formation of $PdCH_2I^+$ in the Pd^+/CH_3I system[7]).

$$Pd^+ + CH_3I \rightarrow PdCH_3^+ + I^{\cdot} \qquad (2)$$

$$PdCH_3^+ + CH_3I \rightarrow PdCH_2I^+ + CH_4 \qquad (3)$$
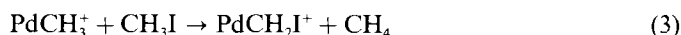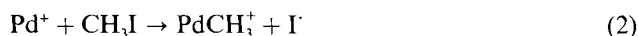
Consequently, the thermochemical arguments used previously about the bond strength in Pd^+-CH_2I are not any more justified; instead, at this stage the occurrence of *Reaction 3* truncates into $BDE(Pd^+-CH_2I) \geqslant BDE(Pd^+-CH_3) = 59 \pm 5$ kcal/mol [22]. Further refinement of the thermochemical estimate for the metal–C bond strength in $PdCH_2I^+$ can be derived from the formation of $PdCH_2I^+$ concomitant with HI in the reaction of PdI^+ and CH_3I, and the absence of $PdCH_2I^+$ in the reaction of Pd^+ with C_2H_5I, leading to a bracketed value of 68 kcal/mol $\leq BDE(Pd^+-CH_2I) \leq 92$ kcal/mol. In fact, these experimental findings do not anymore contradict the theoretical prediction of $BDE(Pd^+-CH_2I) = 83 \pm 6$ kcal/mol (see above).

An obvious question is, of course, why we have not earlier considered the existence of a sequence of *Reactions 2* and *3*, and instead based our (erroneous) conclusion on the direct *Reaction 1*. The reason is related with the efficiences of the ion/molecule reactions. While *Reaction 2* has a very small efficiency ($\phi_2 \approx 0.02$), *Reaction 3* proceeds with unit efficiency ($\phi_3 = 1$) as demonstrated by reacting independently generated, mass-selected $PdCH_3^+$ with CH_3I[7]). Thus, the rate constant of *Reaction 2*, k_2, is ca. 50 times smaller than that of *Reaction 3*, k_3, such that the abundance of $PdCH_3^+$ follows steady-state kinetics. As a consequence, the abundance of $PdCH_3^+$ is always small (ca. 1%) and eventually disappearing in the noise.

In fact, this situation points to the existence of a fundamental problem in studying *slow* ion/molecule reactions by means of mass spectrometry, and it seems indicated to

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[7])   To measure *Reaction 3* independently, $PdCH_3^+$ was generated by reacting kinetically excited Pd^+ with methane [22] [23]. The ion formed was subsequently thermalized by collisions with repeatedly pulsed-in Ar, and *Reaction 3* was then followed using CH_3I as neutral reactant. Note that in the reaction of $PdCH_3^+$ with CD_3I the products $PdCH_2I^+$ and $PdCD_2I^+$ are formed in similar amounts, thus pointing to the operation of two competing multi-center reactions.
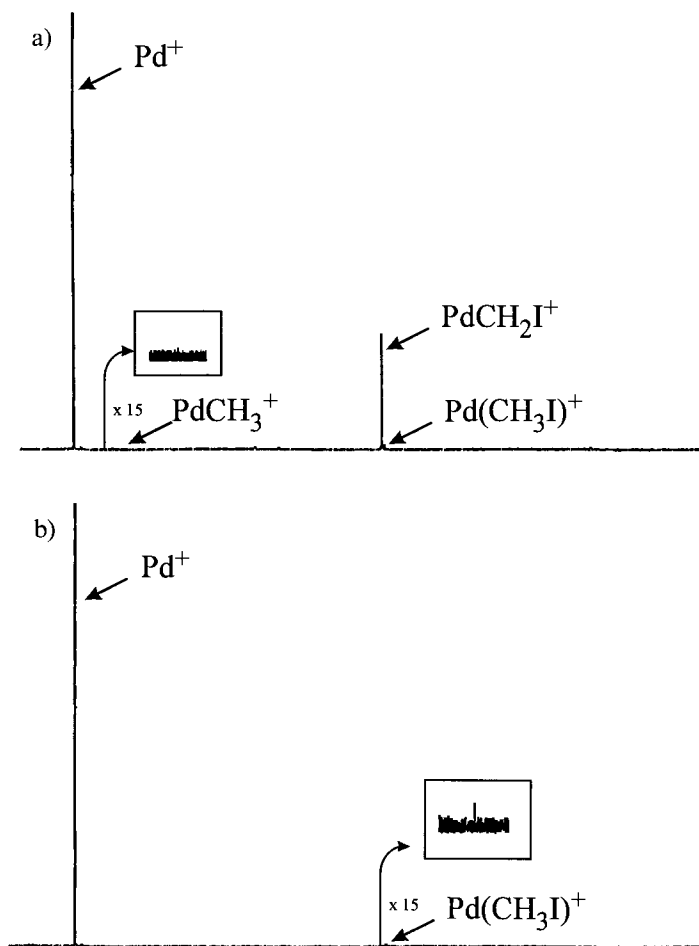
Fig. 2. a) *Reaction of Pd$^+$ with CH$_3$I with a reaction time of 40 s* (p(CH$_3$I) $= 2 \cdot 10^{-7}$ mbar). b) *Double-resonance experiment: reaction of Pd$^+$ with CH$_3$I with a reaction time of 40 s* (p(CH$_3$I) $= 2 \cdot 10^{-7}$ mbar) *and continuous ejection of PdCH$_3^+$*

outline a few more general aspects. Any spectroscopic technique has to deal with limitations due to the signal-to-noise ratio. If a reactive intermediate B is formed under steady-state conditions in a sequence of two consecutive reactions A→B→C, for $k_A \ll k_B$, the signal for B may disappear in the noise and thus escapes experimental detection. With respect to gas-phase ion/molecule reactions conducted under the strictly bimolecular conditions that prevail in an FTICR set-up, one can define a criterion which helps to probe the role of a conjectured intermediate B of a sequence of consecutive reactions with $k_A \ll k_B$, i.e., the signal-to-noise ratio (S/N) must exceed the quotient k_B/k_A at least by a factor of two in order to allow for the experimental observation of B (*Eqn. 4*).

$$\text{Observation of B: S/N} \geqslant 2 \cdot k_B/k_A \qquad (4)$$

Due to the fact that k_A and k_B cannot exceed the collision rate k_c (*i.e.*, $\phi \leq 1$), and the overall rate constant for the disappearance of A is equal to k_A, the assumption of a *direct* reaction $A \rightarrow C$ is justified only, provided no signal for a possible intermediate is observed within a given S/N ratio (*Eqn. 5*).

$$\text{Direct reaction: } A \rightarrow C \quad S/N \geqslant 2/\phi \tag{5}$$
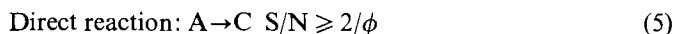
These two equations help to distinguish direct *vs.* multi-step ion/molecule processes. For example, in a reaction with unit efficiency, practically any reactive intermediate would be detected, because S/N must not be larger than 2, whereas for a reaction with $\phi = 0.01$, the signal-to-noise ratio has to exceed 200 in order to conclude that a certain product ion is formed in a direct process without involving a reactive intermediate.

In the present example, k_3/k_2 amounts to *ca.* 50 at a reaction efficiency of *ca.* 0.02 which hence requires S/N > 100. On principal grounds, the intensity of Pd^+ is lower than for most other metal ions, because, due to the natural isotope abundances, 75% of the incident Pd^+ cations present are lost in the mass-selection of $^{106}Pd^+$. Nevertheless, $PdCH_3^+$ can still be detected, provided a large enough number of spectra are accumulated (*Fig. 2,a*); however, the signal is still much too weak for a precise inclusion in the kinetic analysis, which led us previously [1] to ignore the role of $PdCH_3^+$ in the formation of $PdCH_2I^+$. One may easily imagine ion/molecule reactions in which the ratio k_B/k_A of two consecutive reactions is even larger, *e.g.*, for $k_B/k_A > 1000$, and it would be hard, if not impossible, to detect the intermediate species. As far as FTICR is concerned, the double-resonance technique, however, can resolve this dilemma, because the time-scale of ion ejection is much shorter (μs) than that of the ion/molecule reactions (typically seconds). Thus, in principle, intermediates can be probed even for ratios of $k_B/k_A \approx 10^6$ with double resonance[8]). There is, however, a fundamental problem, in that, for the worst case of a very slow ion/molecule reaction, none of the intermediates could be detected directly, and hence it would be necessary to perform double-resonance experiments on *all* conceivable intermediates in order to evaluate to what extent consecutive reactions may play a role in the formation of the observed products. While this problem can still be tackled for the system Pd^+/CH_3I, it will become prohibitive for larger substrates; fortunately these objections do only apply for slow ion/molecule processes, *i.e.*, $\phi \ll 1$.

Due to the prominent position of palladium-alkyl species in the *Heck* reaction [24], in the following we address briefly some reactions of $PdCH_2I^+$ with unsaturated hydrocarbons. In fact, $PdCH_2I^+$ reacts with unsaturated hydrocarbons relatively efficiently. For example, in the reaction of $PdCH_2I^+$ with ethene, the cationic palladium-allyl complex $PdC_3H_5^+$ is formed as the exclusive product with $\phi \approx 0.2$ (*Reaction 6*).

$$PdCH_2I^+ + C_2H_4 \rightarrow PdC_3H_5^+ + HI \tag{6}$$
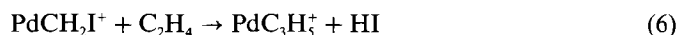
In analogy to the *Heck* reaction, we propose a reaction mechanism (*Scheme 1*) in which in the first step a carbonmetallation takes place such that the reactant $PdCH_2I^+$ adds across the C=C bond of ethene (**1** → **2**). Subsequently, β-H transfer (**2** → **3**) leads to the metalhydrido species **3** which can either undergo isomerization to **5**, **6**, and **7** or

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[8])   In principle, the dynamic range of an FTICR mass spectrometer would allow for the detection of much larger differences in ion intensities. However, for the study of ion/molecule reactions, the background pressure needs to be relatively high, which limits the dynamic range to less than 500.

Scheme 1
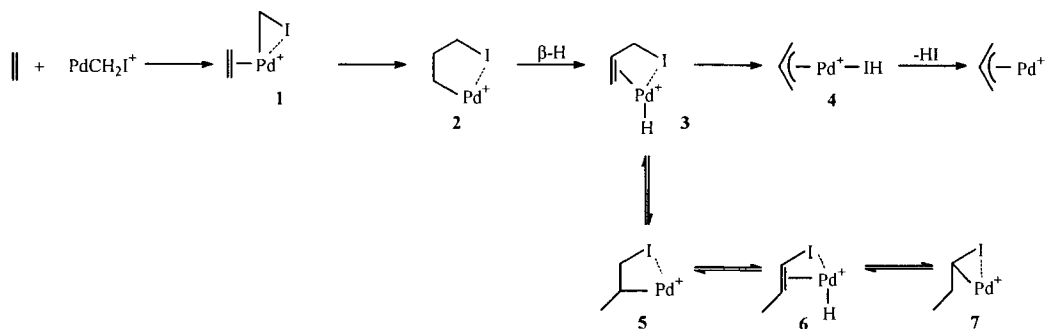
rearrange to the complex **4** which eventually dissociates into $PdC_3H_5^+$ and HI. This mechanism is supported by the observation of partial H/D equilibration in the reaction of D-labeled substrates (*Table 2*). Further, by solving the set of differential kinetic equations[9]), the abundances of HI and DI losses can nicely be modeled, assuming that *i*) the loss of HI/DI is associated with a kinetic isotope effect of $k_H/k_D = 1.5$, and *ii*) 25% of initially formed **3** dissociates directly while the rest undergoes statistical H/D equilibration *via* **5, 6**, and **7** prior to dissociation. Overall, *Reaction 6* can be considered as a formal methylene transfer from the metal to the alkene concomitant with dehydroiodination. As loss of HI is not attractive from a thermochemical point of view, the formation of $PdC_3H_5^+$ seems to provide the driving force for *Reaction 6*. A high stability of $PdC_3H_5^+$ is further indicated by its formation along with the same amount of the $PdC_3H_6^+$ adduct in the

Table 2. *Experimentally Measured and Calculated[a]) Fractions (in %) of HI and DI Losses in the Reactions of Isotopologues of $PdCH_2I^+$ and Ethene (normalized to $\Sigma = 100\%$)*

	−HI		−DI	
	exp.	calc.	exp.	calc.
$PdCH_2I^+ + C_2H_4$	100	100	0	0
$PdCD_2I^+ + C_2H_4$[b])	82	82	18	18
$PdCH_2I^+ + t\text{-}C_2H_2D_2$[b])	71	72	29	28
$PdCD_2I^+ + t\text{-}C_2H_2D_2$[b])	48	47	52	53

[a]) Calculated assuming the kinetic isotope effect associated with HI/DI losses amounts to $k_H/k_D = 1.5$, and that 25% of the reaction occurs *via* direct dissociation of **3**, while 75% are subject to complete H/D equilibration *via* **5/7**.

[b]) Statistical H/D equilibration would lead to the ratios: 67:33, 67:33, and 33:36, respectively.

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[9]) To a first approximation, the ratio of the intensities (*I*) of HI and DI losses can be expressed as: $I(HI)/I(DI) = [n_d(H) \cdot k_d + n_{ex}(H) \cdot k_{ex}]/[n_d(D) \cdot k_d/KIE + n_{ex}(D) \cdot k_{ex}/KIE]$ with n_d: statistical weight for propensity of direct H or D transfer, k_d; rate constant of the direct dissociation, n_{ex}: statistical weight for H- or D-transfer after complete equilibration, k_{ex}: rate constant for dissociation after complete equilibration, *KIE*: kinetic isotope effect associated with HI *vs.* DI losses, *i.e.*, $KIE = k_{HI}/k_{DI}$. For example, the couple $PdCH_2I^+ + t\text{-}C_2H_2D_2$ leads to: $I(HI)/I(DI) = [0.5 \cdot k_d + 0.67 \cdot k_{ex}]/[0.5 \cdot k_d/KIE + 0.33 \cdot k_{ex}/KIE]$ which translates to a result close to the experimental figure for $k_{ex}/k_d = 3$ and $KIE = 1.5$.

Scheme 2

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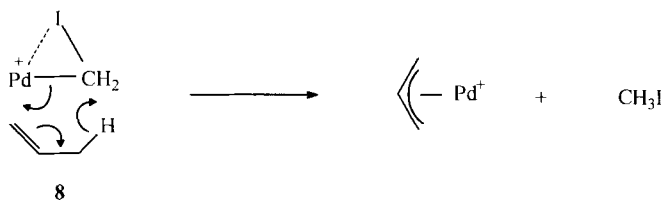
reaction of bare Pd^+ with propene, although Pd^+ was found to be unreactive towards a series of other hydrocarbons [23].

Interestingly, C–C bond formation does not occur with larger alkenes. For example, when $PdCH_2I^+$ is allowed to react with propene ($\phi \approx 0.25$) loss of CH_3I is observed exclusively (*Reaction 7*) while dehydroiodination is suppressed.

$$PdCH_2I^+ + C_3H_6 \rightarrow PdC_3H_5^+ + CH_3I \qquad (7)$$
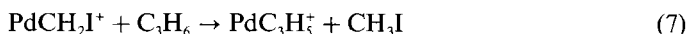
Further, unlike to the reaction of $PdCH_2I^+$ with ethene, H/D equilibration is hardly observed with propene, *i.e.*, 95% loss of CHD_2I as compared to 5% loss of CH_2DI when $PdCD_2I^+$ is used as a reactant. Thus, we propose that the reaction proceeds *via* a six-membered ring transition structure **8** (*Scheme 2*) in which H-transfer occurs directly from one C-atom to the other without involving a metal-hydride intermediate. Presumably, the presence of an activated allylic C–H bond prevents addition of the Pd–C bond across the C=C bond in favor of direct H-transfer to yield the $PdC_3H_5^+$ species.

Benzene ($\phi \approx 0.5$) behaves again quite similar to ethene in its reaction with $PdCH_2I^+$ in that dehydroiodination prevails with concomitant formation of $PdC_7H_7^+$. In addition, a significant amount of the adduct ion $[Pd,C_7H_8,I]^+$ is formed (see *Table 3*) which is not unexpected due to the many degrees of freedom in benzene; in fact, adduct formation is quite common in the gas-phase chemistry of arenes with metal cations [20]. In analogy to *Reaction 6*, methylene transfer from $PdCH_2I^+$ to benzene is associated with significant H/D equilibration (*Table 3*). Further, an intermolecular isotope effect is observed in that

Table 3. *Experimentally Measured and Calculated*[a]) *Fractions* (in %) *of HI and DI Losses in the Reactions of Isotopologues of* $PdCH_2I^+$ *and Benzene* (normalized to $\Sigma = 100\%$)

	Adduct	–HI		–DI	
		exp.	calc.	exp.	calc.
$PdCH_2I^+ + C_6H_6$	25	75	75	0	0
$PdCH_2I^+ + C_6H_3D_3$ [b])	45	41	42	14	13
$PdCH_2I^+ + C_6D_6$ [b])	50	29	28	21	22
$PdCD_2I^+ + C_6H_6$ [b])	60	18	18	22	22
$PdCD_2I^+ + C_6H_3D_3$ [b])	55	8	10	37	35
$PdCD_2I^+ + C_6D_6$	70	0	0	30	30

[a])   Caculated assuming the kinetic isotope effect associated with HI/DI losses amounts to $k_H/k_D = 1.0$, and that 40% of the reaction occurs *via* direct dissociation, while 60% are subject to complete H/D equilibration.
[b])   Statistical H/D equilibration would lead to the ratio: 63:37, 75:25, 25:75, and 37:63, respectively.

the amount of adduct formation increases with the D-content of the encounter complex. However, semi-quantitative analysis of the labeling distribution similar to that outlined above for the reaction $PdCH_2I^+ + C_2H_4$, reveals that the intramolecular kinetic isotope effect associated with dehydroiodination is more or less negligible in the $PdCH_2I^+/C_6H_6$ system. Thus, we conclude that C–C bond formation in the addition step is rate-determining. With respect to the reaction mechanism, the extensive H/D equilibration indicates that all positions of the aromatic ring are available for bond activation in the course of the reaction. Considering that direct C–H bond activation of benzene (BDE(c-C_6H_5–H) = 110 kcal/mol) is rather unlikely for $PdCH_2I^+$, we propose a multi-center reaction mechanism which involves intermediate formation of a Pd(I)(cycloheptatrien)$^+$ complex (*Scheme 3*). This mechanism implies the formation of Pd(c-C_7H_7)$^+$ as the final reaction product; however, we cannot discriminate between the tropylium complex Pd(c-C_7H_7)$^+$ and the isomeric benzylic species Pd($CH_2C_6H_5$)$^+$ as far as the product structure is concerned[10]).

Scheme 3
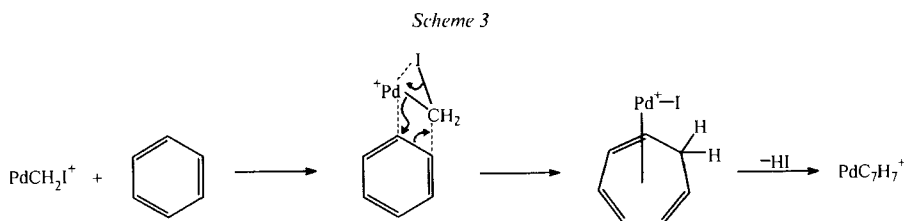
Interestingly, toluene ($\phi \approx 1.0$) behaves similar to propene in that besides adduct formation (15%) only loss of CH_3I is observed to yield $PdC_7H_7^+$ (85%); dehydroiodination does not take place. In perfect analogy to the differences observed in the reactions of $PdCH_2I^+$ with ethene and propene, we propose, therefore, that benzylic C–H bond activation is favored for toluene (*Scheme 4*). This conjecture goes in hand with the observation that H/D equilibration is much less extensive in the reaction of $PdCD_2I^+$ with toluene (CHD_2I/CH_2DI 75:25) as compared to the reaction of $PdCD_2I^+$ with benzene (*Table 3*).

Finally, let us summarize the implications of the present study. To begin with, it has to be stated that the interpretation of the experimental findings is not always that conclusive

Scheme 4

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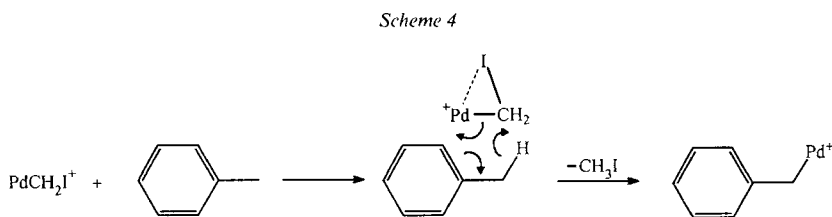
[10]) For a recent survey of the benzylium/tropylium case, see [25].

as they appear to be upon first sight, simply due to limitations in the detection of possible intermediates. Although in FTICR the double-resonance technique can help out to some extent, its application may become prohibited in cases in which too many conceivable intermediates are chemically feasible and need to be considered. Second, though still limited to small systems, nowadays computational methods deserve a high degree of credibility when performed with great care on levels of theory which are appropriate to tackle the problem of interest. Third, although the strength of the metal–C bond in $PdCH_2I^+$ is not that enormous as stated in [1], it is still extraordinarily large (83 kcal/mol) as compared to $PdCH_3^+$ (59 kcal/mol [22]). This enhanced stabilization can be traced back to an α-agostic interaction between Pd and I. Finally, the iodomethyl ligand increases significantly the reactivity of Pd^+ towards hydrocarbons, and the major driving forces of these reactions seem to be due to the formation of conjugated ligand systems, $i.e.$, allyl in $Pd^+–C_3H_5$ and benzyl/tropylium ligand in $Pd^+–C_7H_7$.

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