On the Reactions of $Fe(CH_2)^+$ with 1,7-Octadiene in the Gas Phase

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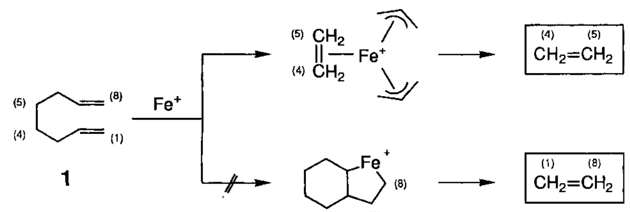
In contrast to the reactions of "bare" Fe^+ with 1,7-octadiene (**1**), the chemistry of $Fe(CH_2)^+$ with **1** represents a "textbook" example for a gas-phase metathesis process to generate in a clean fashion $Fe(C_2H_4)^+$. Similarly, for the formation of $Fe(C_6H_6)^+$ a mechanism is suggested which is in keeping with the experimental findings. In contrast, the reactions of $Fe(CH_2)^+$ with **1** leading to $Fe(C_3H_4)^+$ and $Fe(C_4H_6)^+$ are so complex that a coherent description is not yet possible.

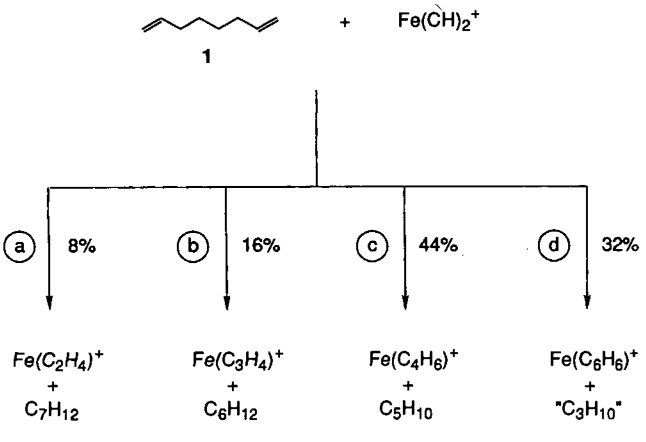
As demonstrated recently[1], the gas-phase chemistry of 1,7-octadiene (**1**) with "bare" transition-metal cations M^+ (M = Fe, Co, Ni) is quite distinct from that of simple alkenes. For example, the mechanistic details (i.e. β- versus γ-hydrogen transfer) of the metal-ion-mediated generation of propene from **1** is strongly affected by the nature of M^+[1a]. Similarly, the course of C_2H_4 formation from **1** also is determined by the metal ion. Most interesting – and unprecendented – is the observation that the Fe^+-induced generation of C_2H_4 from **1** involves to more than 90% the *internal* C(4)/C(5) methylene units instead of the familiar metathesis-like coupling of the terminal C(1)/C(8) groups (Scheme 1)[2–4].

Scheme 1



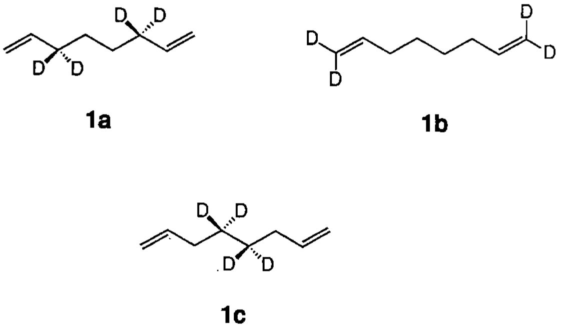
We wondered if this unexpected behavior also prevails when $Fe(CH_2)^+$, the direct gas-phase analogue of Grubb's carbene complexes $M(L)CH_2$[3], rather than "bare" Fe^+ is treated with **1** in the gas phase. To this end, Fourier transform ion cyclotron resonance (FT-ICR) experiments were conducted[5], and the products described in Scheme 2 are formed. Although we did not determine the absolute rate constant for the reaction of $FeCH_2^+$ with **1**, a comparison with the rate constant for the reaction of FeO^+ with **1** – which occurs at collision rate[6] – indicates that the former proceeds with half the collision rate.

Scheme 2



While a proper structural characterization of the species – and, on principal grounds, this holds true in particular for the neutral products generated in ion/molecule reactions – described in Scheme 2 is not yet feasible, the study of the D-labeled isotopomers **1a**–**1c** (Scheme 3) as well as the reaction of **1** with $Fe(CD_2)^+$ in conjunction with thermochemical data[13] reveal some unexpected findings.

Scheme 3



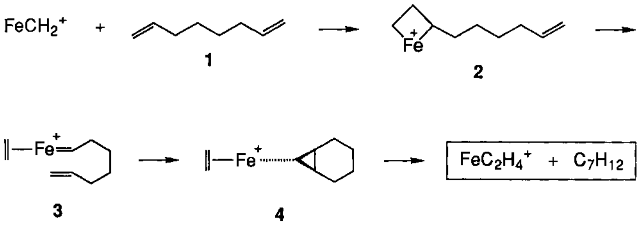
The interpretation of the data (Table 1) for reaction ⓐ is straightforward, in that the $Fe(C_2H_4)^+$ complex generated contains exclusively the methylene unit of $Fe(CH_2)^+$ and a *terminal* methylene group of **1** and its isotopomers. The reaction is neither preceded by a carbene exchange process nor a metal-mediated, degenerate isomerization of **1**–**1c**. The results can be accounted for in terms of a well-knwon[4] gas-phase metathesis reaction involving exclusively the terminal double bond. With regard to the neutral C_7H_{12}, which escapes experimental identification, thermochemical considerations[14] demonstate that numerous isomers are possible. However, olefins like 1,6-heptadiene, isomeric ethylcyclopentenes or methylcyclohexenes, and vinylcyclopentane, respectively, can be discarded on the ground that their binding energy to Fe^+ exceeds that of $Fe(C_2H_4)^+$ [13a,c]. Consequently, these molecules should give rise to the product combination $Fe(C_7H_{12})^+/C_2H_4$ rather than $Fe(C_2H_4)^+/C_7H_{12}$; however, as shown in Scheme 2, this is not observed experimentally. In analogy to a well-studied metal-carbene isomerization in solution[15], we suggest that in the reaction of $Fe(CH_2)^+$ with 1,7-octadiene the neutral C_7H_{12} corresponds to bicyclo[4.1.0]heptane. The latter may emerge from the intermediate **3**, and due to the smaller binding energy of a bicycloalkane in comparison to ethylene, the metal ion in the resulting complex **4** upon further dissociation retains the olefine. An oversimplified mechanism, ignoring several other conceivable intermediates, is given in Scheme 4.

Table 1. Labeling distribution for the reactions of $Fe(CX_2)^+$ (X = H, D) with 1,7-octadiene isotopomers[a]

	$Fe(CH_2)^+$/**1a**	$Fe(CH_2)^+$/**1b**	$Fe(CH_2)^+$/**1c**	$Fe(CD_2)^+$/**1**
$Fe(C_2H_4)^+$	100	–	100	–
$Fe(C_2H_2D_2)^+$	–	100	–	100
$Fe(C_3H_4)^+$	27	32	37	72
$Fe(C_3H_3D)^+$	30	28	35	8
$Fe(C_3H_2D_2)^+$	43	40	28	20
$Fe(C_4H_6)^+$	–	34	–	75
$Fe(C_4H_5D)^+$	40	28	24	3
$Fe(C_4H_4D_2)^+$	60	38	40	22
$Fe(C_4H_3D_3)^+$	–	–	19	–
$Fe(C_4H_2D_4)^+$	–	–	17	–
$Fe(C_6H_6)^+$	– (2)[b]	47 (52)	–	100 (100)
$Fe(C_6H_5D)^+$	12 (15)	39 (34)	– (4)	–
$Fe(C_6H_4D_2)^+$	69 (66)	14 (14)	73 (82)	–
$Fe(C_6H_3D_3)^+$	19 (15)	–	27 (12)	–
$Fe(C_6H_2D_4)^+$	– (2)	–	– (2)	–

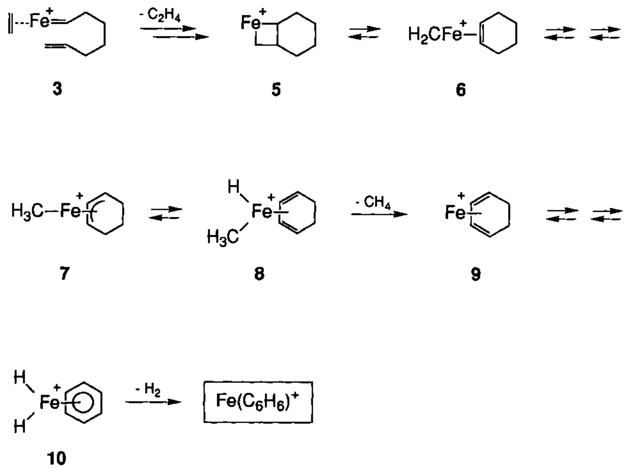
[a] Intensities are normalized to 100% for a given ionic product. – [b] Data given in parentheses correspond to calculated labeling distributions; for details, see text.

Scheme 4



The next process to be discussed concerns the formation of $Fe(C_6H_6)^+$, which most likely corresponds to a Fe(benzene)$^+$ complex. The concomittantly formed species "C_3H_{10}" must, by necessity, consist of several hydrocarbons. Based on thermochemical data[13,14] many product combinations are possible; however, the labeling experiments are in favor of the combination $C_2H_4/CH_4/H_2$. The heat of reaction for the generation of these neutrals and $Fe(C_6H_6)^+$ from $Fe(CH_2)^+$ and **1** is estimated to −51 kcal/mol[14]. From the labeling data (Table 1) it follows that the carbene unit of $Fe(CX_2)^+$ (X = H, D) is not retained in the $Fe(C_6H_6)^+$ product ion. This result points to at least one common intermediate for the two processes ⓐ and ⓓ. It is conceivable that **3** (Scheme 4) serves as a branching point in that in competition with the formation of $Fe(C_2H_4)^+$ (reaction ⓐ), neutral C_2H_4 is eliminated. The resulting carbene complex has several options to eventually react to $Fe(C_6H_6)^+$. We have considered *five* different reaction sequences[14], and the best fit (see data in parentheses in Table 1) is obtained for the process depicted in Scheme 5. However, the modeling gave internally consistent results only, if one allows for hydrogen equilibration up to 58%.

Scheme 5



For the processes ⓑ and ⓒ (Scheme 2), we have also performed extensive modeling in order to explain the label distribution associated with the formations of $Fe(C_3H_4)^+$ and $Fe(C_4H_6)^+$, respectively, and to provide some mechanistic insight[14]. However, we did not yet arrive at an unambiguous solvation of the matrix equations for competing mechanisms which would not be in conflict with existing basic concepts of gas-phase organometallic processes. As it looks like, the potential surface is relatively flat in the region which eventually leads to the $Fe(C_3H_4)^+$ and $Fe(C_4H_6)^+$ thus permitting the simultaneous operation of at least three competing pathways the details of which remain to be elucidated.

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[5] Experimental conditions: Fe$^+$ was generated from a stainless-steel target with the aid of an Nd:YAG laser (Spectron systems, λ = 1064 nm) by laser desorption/laser ionization[7] in the external ion source of a Spectrospin CMS 47X mass spectrometer[8]. The metal ions were transferred to the acual ICR cell by a system of electrical potentials and lenses. After deceleration, they were stored in a magnetic field of a superconducting magnet (Oxford Instruments; maximum field strength 7.05 T). The ^{56}Fe$^+$ isotope, as also all other ions in the reactions to be described, were isolated by FERETS[9], and Fe(CX)$_2^+$ (X = H, D) was generated by the reaction sequence (1) Fe$^+$ + N$_2$O $\rightarrow$ FeO$^+$ + N$_2$[10], (2) FeO$^+$ + C$_2$X$_4$ $\rightarrow$ Fe(CX$_2$)$^+$ + CX$_2$O. The neutral gases N$_2$O and C$_2$X$_4$, respectively, were sequentially injected in the ICR cell by means of pulsed valves ($p_{\text{cell,max}} \approx 10^{-6}$ mbar). As Fe(CD$_2$)$^+$ is isobaric with FeO$^+$, high-resolution FTICR experiments had to be conducted to separate the two species[11,14]. To this end, one ejection pulse with a duration of ca. 1.9 ms and a frequency corresponding to FeO$^+$ was applied to the excitation plates in order to eject this ion and to avoid off-resonance excitation of FeCD$_2^+$. The so-formed Fe(CX$_2$)$^+$ ions were re-isolated and treated with **1** and its isotopomers **1a**–**1c**[12], which were present at a constant pressure of $3-8 \times 10^{-9}$ mbar, as measured with an uncalibrated ion gauge (Balzers IMG 070). For collisional cooling of any excited states and removal of kinetic energy remaining from the transfer, argon was present as a buffer gas with a constant pressure (ca. 5×10^{-7} mbar). The absence of excited FeCX$_2^+$ (X = H, D) is indicated by the observation of strictly pseudo first-order kinetics in the ions' reaction with **1**.

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