

70. Site-Specific, Oxidative Addition of C–C Bonds by ‘Anchored’ Bare Fe(I) Cations Prior to C–H Bond Activation

Preliminary Communication

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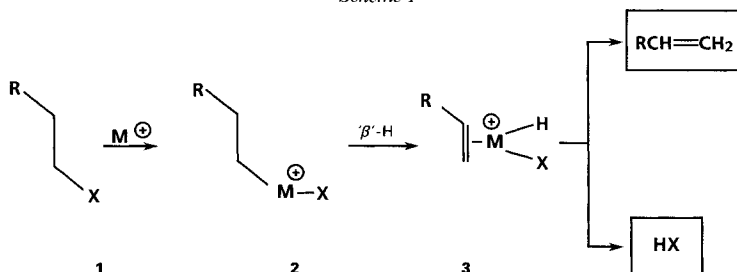
Dedicated to Dr. Günther Ohloff on the occasion of his 65th birthday

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Evidence is presented for the first time that ‘naked’ Fe^+ ions, complexed to the NH_2 group of primary amines, are capable of intramolecularly activating C–C bonds in a highly specific mode without preceding C–H activation.

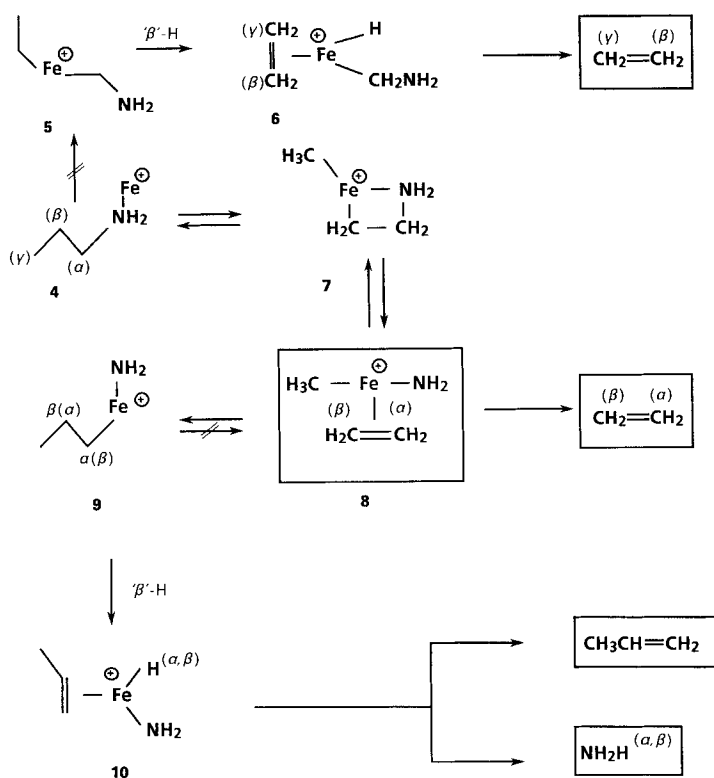
Several reactions of ‘naked’ transition-metal ions M^+ with substituted alkanes RX in the gas phase can be described by a mechanism reported for the first time by Allison and Ridge [1]. Oxidative addition of the polar C–X bond to M^+ (Scheme 1: **1** $\rightarrow$ **2**) is followed by a β -H transfer, and the so-formed bidentate complex **3** undergoes competitive ligand detachment ($\rightarrow \text{RCH}=\text{CH}_2$) or reductive elimination of HX .

Scheme 1



In the reactions of Fe^+ with $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$, the major process was ascribed [2] to an insertion of Fe^+ into the central C–C bond to generate **5** (Scheme 2). This species was assumed to serve as initial intermediate for the eventual generation of C_2H_4 containing $\text{C}(\beta)$ and $\text{C}(\gamma)$ as building entities. However, a detailed labeling study led to a revision and modification of this mechanism [3]; it was demonstrated that *i*) the $\text{CH}_2=\text{CH}_2$ molecule contains exclusively the α - and β - CH_2 groups, and *ii*) the α - and β - CH_2 groups undergo a positional ‘equilibration’ prior to the β -H transfer to generate **10**. The mechanism depicted in Scheme 2, with complex **8** as the central intermediate, accounts for all experimental findings.

Scheme 2



Here, we describe an unprecedented site-specific oxidative addition of a C–C bond to bare Fe^+ , ‘anchored’ at the NH_2 function of 2-ethylbutylamine (**11**). In addition, we shall present evidence that C–C bond activation can be achieved without activation of C–H bonds which is usually considered to precede the former. The metastable-ion (MI) mass spectrum of **11**- Fe^+ (Scheme 3) contains only two signals; these are attributable to the losses of H_2 (87%) and C_4H_8 (13%). The study of the isotopomers **11a–d** (Table 1) reveals a clear-cut pattern from which the origin of the neutral species can be traced. We first discuss the mechanism for loss of C_4H_8 and later the Fe^+ -mediated dehydrogenation of **11**.

Scheme 3

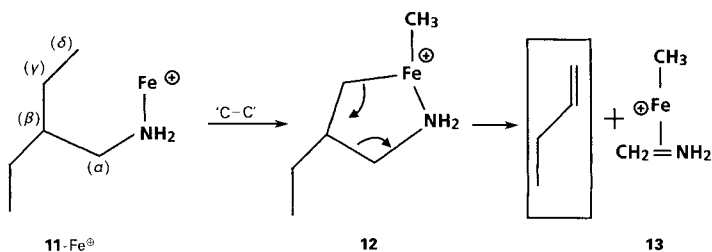


Table 1. *Isotopic Products Formed from Fe⁺ Complexes of 11a–d^{a)}*

	$\begin{array}{c} \text{C}_2\text{H}_5\text{CHC}_2\text{H}_5 \\ \\ \text{CD}_2\text{NH}_2 \\ \mathbf{11a} \end{array}$	$\begin{array}{c} \text{C}_2\text{H}_5\text{CDC}_2\text{H}_5 \\ \\ \text{CH}_2\text{NH}_2 \\ \mathbf{11b} \end{array}$	$\begin{array}{c} \text{CH}_3\text{CD}_2\text{CHC}_2\text{H}_5 \\ \\ \text{CH}_2\text{NH}_2 \\ \mathbf{11c} \end{array}$	$\begin{array}{c} \text{CD}_3\text{CH}_2\text{CHC}_2\text{H}_5 \\ \\ \text{CH}_2\text{NH}_2 \\ \mathbf{11d} \end{array}$
H ₂	100	> 99	75	67
HD		< 1	25	33
C ₄ H ₈	100			30
C ₄ H ₇ D		100		
C ₄ H ₆ D ₂			100	
C ₄ H ₅ D ₃				70

^{a)} Intensities are expressed in % Σ fragments = 100%, for each class of neutral species separately.

The label distribution for C₄H_{8-x}D_x proves that the neutral molecule¹⁾ is generated without any positional exchange processes preceding the elimination step. Neither C(α) nor the NH₂ group provide atoms to the formation of neutral C₄H_{8-x}D_x. The olefin is built up from C(β), C(γ), and C(γ'), and the attached H-atoms. The missing CH₃ group is provided by the intact C(δ)/C(δ') positions of **11**. This isotope-distribution pattern strongly suggests that the formation of the neutral C₄H₈ molecule (presumably but-1-ene¹⁾) commences with an insertion of the 'anchored' Fe⁺ into the C(γ)–C(δ) bond (*Scheme 3*: **11**-Fe⁺→**12**). From the so-formed metallacycle, *via* β-C–C bond cleavage, the neutral species C₄H₈ is detached (**12**→**13**). It remains open to speculation, whether the reaction **12**→**13** proceeds *via* ligated Fe⁺ intermediates. Similarly, the actual structure of the product ion **13** is unknown. With regard to the insertion step **11**-Fe⁺→**12**, the study of **11d** reveals a quite large secondary isotope effect for the 'migration' of CH₃ *vs.* CD₃, favoring the former by a factor of 2.33 (*i.e.* an isotope effect of $k_{\text{H}}/k_{\text{D}} = 1.33$ per D-atom). This value is in the range expected for sp³→sp² hybridization of alkyl groups [5]²⁾.

The mechanism suggested in *Scheme 3* also provides an interpretation of experimental findings on the C₄H₉NH₂/Fe⁺ system (**14**-Fe⁺), which remained unclear for some time. In the MI spectrum of **14**-Fe⁺, we observe signals due to the elimination of H₂ (93%) and C₂H₄ (7%). The labeling data (*Table 2*) demonstrate that C₂H₄ consists to roughly 64% of C(β)/C(γ) and 36% of C(γ)/C(δ). The former combination (allowed for partial H scrambling within the C₂H₅ group) can be accounted for in terms of *Scheme 3* (substitution of H for C₂H₅).

¹⁾ Due to sensitivity limitations, we could not apply the otherwise powerful method of collisionally induced dissociative ionization (CID), a variant of neutralization-reionization mass spectrometry (NRMS), for the characterization of the neutral species generated from the organometallic complexes. For reviews, see [4].

²⁾ R. Keese, Bern, has recently wondered (March 1989), why loss of but-1-ene from **11**-Fe⁺ might not follow the reaction sequence shown in *Scheme 3* but rather commences with a homolytic cleavage of the C(α)–C(β) bond of **11**-Fe⁺ to generate an ion/dipole complex consisting of CH₃CH₂CHCH₂CH₃ and ·CH₂NH₂/Fe⁺. From the so-formed 1-ethylpropyl radical, CH₃ might then be transferred – *via* a β-radical cleavage – to the ionic part, thus, eventually generating but-1-ene. While such a reaction sequence is also likely to be subject to a secondary kinetic isotope effect (for many examples on secondary isotope effects of the same magnitude operative in the losses of methyl and ethyl radicals from radical cations in the gas phase, see [6]), we would find it difficult to provide a rationale for the specific cleavage of the C(α)–C(β) bond, as the difference in ionization energies of Fe (*IE* = 7.87 eV [7]) *vs.* RNH₂ (*IE* = 9.40 eV for R = C₄H₉ [8]) will exclude electron transfer from the amine to Fe⁺. Thus, no amine radical cation is likely to be generated; the latter species would be viewed as a prerequisite for a homolytic cleavage of the C(α)–C(β) bond. In any event, our overall conclusion that but-1-ene loss from **11**-Fe⁺ is *not* preceded by C–H activation is not affected by this consideration. We are very grateful to Prof. Keese for drawing our attention to this aspect.

Elimination of C_2H_4 , containing the C_2H_5 group of **14**, is another example of the well-established 'remote functionalization' concept operative in organometallic systems in the gas phase [9]. Oxidative addition of a terminal C–H bond to the 'anchored' metal ion generates a metallacycle (*Scheme 4*: **14**– $Fe^+ \rightarrow$ **15**); **15** is able to undergo, in competition, β -H transfer (**15** $\rightarrow$ **16**) or β -C–C cleavage (**15** $\rightarrow$ **17**). The latter path eventually gives rise to the detachment of C_2H_4 , containing $C(\gamma)/C(\delta)$.

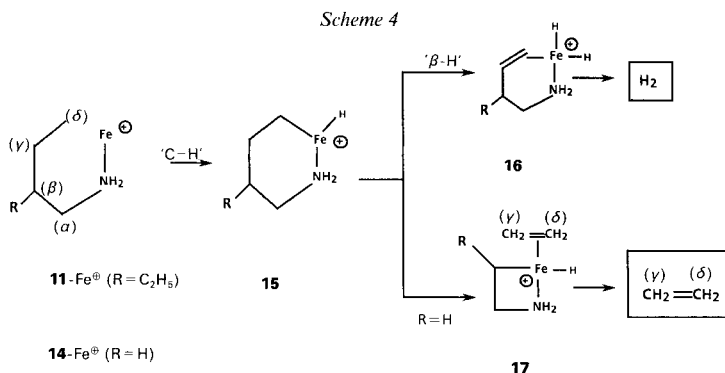


Table 2. Isotopic Products Formed from Fe^+ Complexes of **14a–c**^{a)}

	$C_3H_7CD_2NH_2$ 14a	$C_2H_5CD_2CH_2NH_2$ 14b	$CD_3(CH_2)_3NH_2$ 14c
H_2	100	100	
HD			100
C_2H_4	100	38	64
C_2H_3D		27	
$C_2H_2D_2$		35	36

^{a)} See Footnote of Table 1.

With regard to the Fe^+ -mediated dehydrogenation of **11** and **14**, the labeling data (*Tables 1* and *2*) prove that the reaction is site-specific for either amines; dehydrogenation involves exclusively the C_2H_5 group of the Fe^+ -complexed amines. The reaction constitutes a genuine 1,2-elimination and is not preceded by H scrambling. The data for the isotopomers of **11**– Fe^+ allow for an estimate of the overall isotope effect associated with the dehydrogenation process. Earlier studies on many Fe^+ systems [9] [10] provided evidence that the oxidative addition of the C–H bond to the 'anchored' metal ion is not rate-limiting; however, kinetic isotope effects were observed for both the β -H transfer and the reductive elimination of H_2 . A similar situation pertains for **11**– Fe^+ . The observation that the total losses of H_2 /HD from both **11c** and **11d** are roughly constant, compared to $C_2H_{4-x}D_x$ formation, already indicates that step **14**– $Fe^+ \rightarrow$ **15** is also not rate-limiting ($k_H/k_D \approx 1$) in the present system. With this assumption, the observed overall isotope effects for losses of H_2 /HD of 3:1 (from **11c**) and 2:1 (from **11d**) suggests that the rate-determining step(s) are associated with the rearrangement/dissociation behavior of **15**. The present set of data does not permit a further distinction, though it is tempting to

interpret the different data from **11c** and **11d** as an indication that step **15**→**16** is also subjected to an isotope effect. For the reductive elimination of H₂, earlier studies have already provided ample evidence for the operation of kinetic isotope effects [9].

In conclusion, the present results provide firm evidence that a direct, site-specific C–C activation by transition-metal ions can be achieved *without* preceding C–H activation. This observation is very distinct from the sequence of C–C/C–H activation prevailing in the condensed phase, using ‘conventional’ activating systems; there, C–H bond activation usually precedes the metal-induced cleavage of a C–C bond [11].

Experimental. – The experimental setup has been described earlier [3] [9] [10]. Metal ions were generated by 100-eV electron-impact ionization of Fe(CO)₅ and reacted in the chemical-ionization source of a *VG Instruments ZAB-HF-3F* mass spectrometer³⁾ with the organic substrates. The resulting complexes are accelerated to 8-keV kinetic energy and mass-selected by using BE; the unimolecular reactions (MI spectra) occurring in the field-free region between E and B(2) were recorded by scanning B(2). Signal-averaging techniques were used to increase the signal-to-noise ratio. All compounds were synthesized according to standard procedures, purified, and characterized by established techniques.

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³⁾ For a description of the apparatus and further details, see [12].