$= x$), S_A is the signal intensity due to product A at the m/q value chosen to represent product A, and f_{xA} is the cracking fraction at $m/q = x$ due to product A.

These equations may also be written in matrix form:

$$\begin{bmatrix} f_{1A} & f_{1B} & f_{1C} & f_{1D} \\ f_{2A} & f_{2B} & f_{2C} & f_{2D} \\ f_{3A} & f_{3B} & f_{3C} & f_{3D} \\ f_{4A} & f_{4B} & f_{4C} & f_{4D} \end{bmatrix} \cdot \begin{bmatrix} S_A \\ S_A \\ S_A \\ S_A \end{bmatrix} = \begin{bmatrix} s_1 \\ s_2 \\ s_3 \\ s_4 \end{bmatrix} \qquad (20)$$

The 4 × 4 matrix contains the cracking fractions determined experimentally by desorbing multilayers of authentic compounds into the same mass spectrometer used for the TPRS experiments. By multiplying both sides of eq 20 by the inverted matrix, we obtain a set of equations for the signals of interest. Solving these equations gives signal intensities for four individual products.

The experimental TPRS data consists of a series of measurements of signal intensities vs time. The experimental curves are decomposed into product desorption curves by solving the $N \times N$ set of equations for each point in time. These curves are then multiplied by a correction factor (Table IV) so that the relative peak heights of the TPRS spectra represent the relative yields of products. Correction factors were determined based on the masses chosen to represent each compound as previously described.[12,23,24] Figure 8 shows the raw data of Figure 1 prior to the corrections for the cracking functions. It can be seen that the major effects are to reduce the H_2 peak and eliminate the sharp feature on m/q 57 due to the propanal (m/q 58).

(24) UTI 100C Precision Mass Analyzer Operating and Service Manual, Appendix B.

Oxidative Addition of the Carbon–Hydrogen Bond Is Not the Rate-Determining Step in the Remote Functionalization of Nitriles by Bare Fe(I) Ions[†]

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Abstract: The study of D-labeled 5-cyanononane isotopomers in the gas phase provides evidence that the Fe^+-mediated remote functionalization of nitriles, resulting in the regiospecific generation of H_2 and C_2H_4 from the ω and ($\omega - 1$) positions of the alkyl chain, can be described as follows: (i) Oxidative addition of a methyl C–H bond is not rate limiting. For the generation of $C_2H_{4-x}D_x$ it is the elimination of the olefin which is associated with kinetic isotope effects comparable to the ones reported earlier for other systems. (ii) The generation of $H_{2-x}D_x$ is affected by two isotope effects. One concerns the β-hydrogen transfer ($k_H/k_D = 1.59$) and the other the reductive elimination of hydrogen ($k_{H_2}/k_{HD} = 1.70$ and $k_{HD}/k_{D_2} = 1.44$).

The selective functionalization of C–H bonds remains one of the major focuses of catalytic and organic chemistry. High selectivity is often achieved by the presence of activating groups which induce the reactivity of the neighboring C–H bonds. The functionalization of *remote* C–H bonds, i.e., several carbon atoms away from the activating group, represents a great challenge. While such reactions are common to enzymes which coordinate a functional group and *geometrically* select a specific site of the substrate, only a few cases in solution chemistry are reported[1] where a similar principle seems to be operative. Breslow[1c] has coined the term "remote functionalization" for this kind of coordination of a functional group followed by selective reactions at sites away from the complexed functionality. We have recently demonstrated that a similar system exists in the gas phase.[2] The chemistry of the Fe^+ complexes of aliphatic, unbranched, saturated nitriles is very unique, in that selective C–H activation occurs only at positions remote from the cyanide functionality. This unprecedented behavior contrasts with that of other unsaturated systems, such as alkenes[3] and alkynes,[4] where allylic and propargylic activations, respectively, of the C–C and/or C–H bonds are reported to be the major modes of reaction. The primary reason for the unique behavior of nitriles is due to the initial interaction of the cyanide group with Fe^+. The preferred coordination leads to an "end-on" complex 1 characterized by a "linear"[5] —CH_2—$C{\equiv}N$—M^+ entity (M = transition-metal

atom). The linear fragment in turn constrains the remainder of the molecule such that Fe^+ activates C–H bonds while trying to

(1) For selected references, see: (a) Breslow, R. *Chem. Soc. Rev.* **1972**, *1*, 553. (b) Breslow, R.; Maresca, L. M. *Tetrahedron Lett.* **1977**, 623. (c) Breslow, R. *Acc. Chem. Res.* **1980**, *13*, 170. (d) Kerb, U.; Stahnke, M.; Schulze, P. E.; Wiechert, R. *Angew. Chem.* **1981**, *93*, 89.

(2) (a) Lebrilla, C. B.; Schulze, C.; Schwarz, H. *J. Am. Chem. Soc.* **1987**, *109*, 98. (b) Drewello, T.; Eckart, K.; Lebrilla, C. B.; Schwarz, H. *Int. J. Mass Spectrom. Ion Process.* **1987**, *76*, R1. (c) Lebrilla, C. B.; Drewello, T.; Schwarz, H. *Int. J. Mass Spectrom. Ion Process.* **1987**, *79*, 287. (d) Lebrilla, C. B.; Drewello, T.; Schwarz, H. *J. Am. Chem. Soc.* **1987**, *109*, 5639.

(3) (a) Larsen, B. S.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 1912. (b) Peake, D. A.; Gross, M. L.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 4307. (c) Peake, D. A.; Gross, M. L. *Anal. Chem.* **1985**, *57*, 115.

(4) (a) Peake, D. A.; Gross, M. L. *Organometallics* **1986**, *5*, 1236. (b) Schulze, C.; Schwarz, H.; Peake, D. A.; Gross, M. L. *J. Am. Chem. Soc.* **1987**, *109*, 2318. (c) Schulze, C.; Weiske, T.; Schwarz, H. *Chimia* **1986**, *40*, 362. (d) Schulze, C.; Schwarz, H. *Chimia* **1987**, *41*, 29.

(5) In the present context we use the term "linear" very loosely, as we know little about the energetics and electronics of this coordination. No doubt that depending on the nature of the transition-metal ion M^+ and on the internal energy of 1, deviation from linearity of the —CH_2—$C{\equiv}N$—M^+ unit must occur (see ref 2c for a comparison of Fe^+, Co^+, and Ni^+), which may even result in the formation of a "side-on" complex for M = Cu^+ (Lebrilla, C. B.; Drewello, T.; Schwarz, H. *Organometallics* **1987**, *6*, 2450). A quite interesting case has been reported recently for *unsaturated* aliphatic nitriles (Püsse, T.; Drewello, T.; Lebrilla, C. B.; Schwarz, H. *J. Am. Chem. Soc.* **1989**, *111*, 2857) of the general structure $CH_3(CH_2)_nCH{=}CH(CH_2)_mCN$. Data were reported that strongly suggest that depending on the length of the methylene chain $-(CH_2)_m-$ the bidentate Fe^+ complexes may contain an "end-on" or a "side-on" complexed nitrile function.
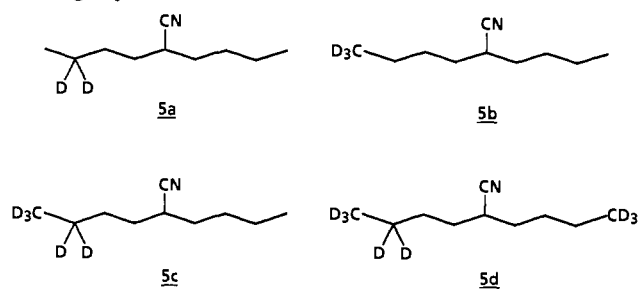
Scheme I
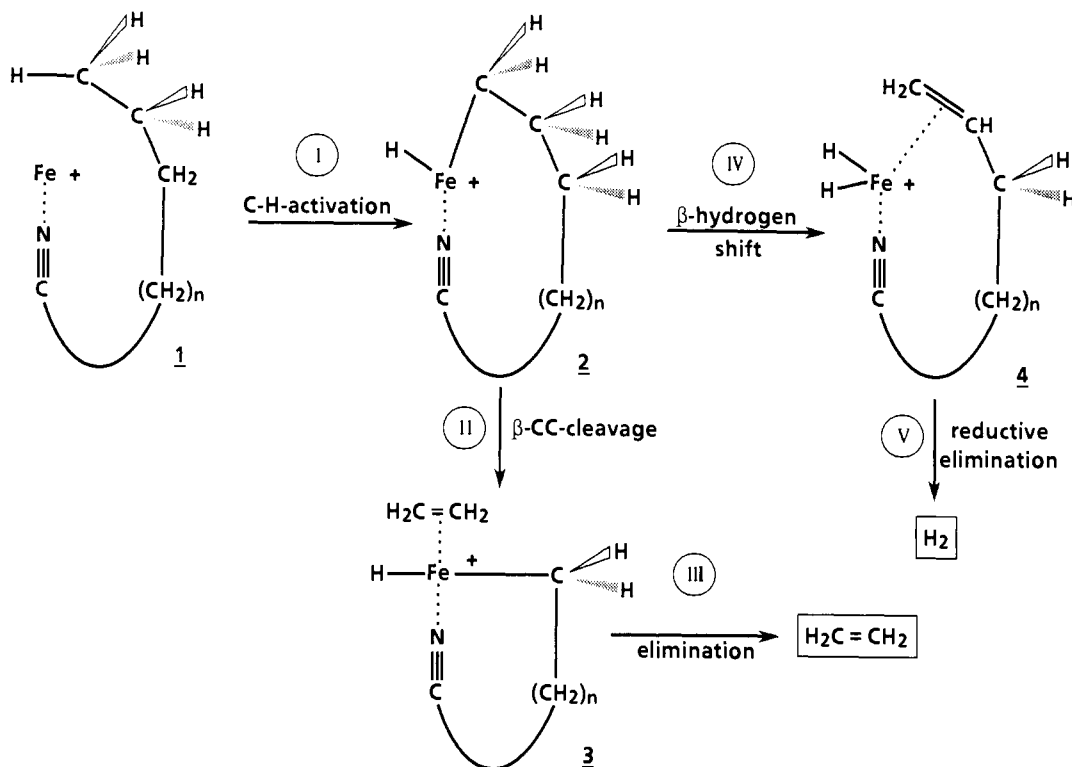
minimize the strain of the intermediate "metallacycles". For nitriles containing four to seven carbon atoms, this deformation results in the exclusive activation of the terminal methyl group by oxidative addition of a methyl C–H bond to the (complexed) Fe^+ (Scheme I: $1 \rightarrow 2$). The insertion is followed by competitive β-cleavage of the C–C bond ($2 \rightarrow 3$) or β-hydrogen shift ($2 \rightarrow 4$) to generate intermediates 3 and 4, from which eventually the neutrals C_2H_4 and H_2, respectively, are eliminated. The high specificity as well as the absence of hydrogen scrambling processes, which are often caused by transition-metal ions,[7] are worth mentioning.

In spite of the advanced understanding of the RCN/M^+ system, there exist pertinent questions that were not yet addressed. For example, an important one concerns the problem of which step is rate-determining in the sequence depicted in Scheme I. In previous studies of $Fe(alkyne)^+$ and $Fe(allene)^+$ complexes,[4b–d,7] we have demonstrated that this crucial information can be provided by the analysis of appropriately labeled, *symmetric* precursors. Not only did the study of these systems prove the origins of the atoms transferred, more importantly, by evaluation of the *intramolecular* kinetic isotope effects the rate-determining step was determined. As this important link in the understanding of metal-ion-induced functionalization of nitriles is yet missing, the isotopomers 5a–d were synthesized, and the unimolecular chem-

Scheme II

Neutral eliminated (%)

H_2	(85)	*(1)*
C_2H_4	(12)	*(2)*
CH_4	(3)	*(3)*
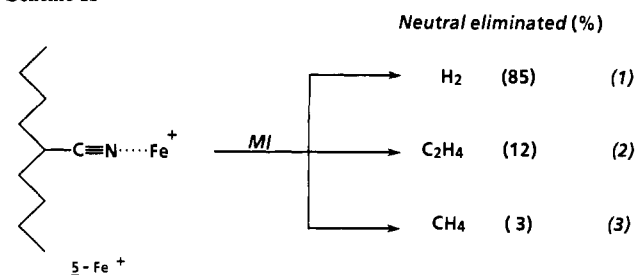
istry of the respective mass-selected Fe^+ complexes was studied in the gas phase.

Experimental Part

The experimental setup and the machine, a VG Instruments ZAB-HF-3F triple-sector mass spectrometer of B(1)EB(2) configuration, have been described earlier.[2,8] Briefly, in a typical experiment $Fe(CO)_5$ and the nitrile of interest were in an approximate 1:2–5 ratio introduced in the ion source and bombarded with an electron beam of 100-eV kinetic energy. Organometallic ions corresponding to RCN/Fe^+, having 8-keV translational energy, are mass-selected and focused with B(1)E at a resolution sufficiently high to separate the RCN/Fe^+ species from isotobaric interference signals. Unimolecular reactions occurring in the field-free region between E and B(2) were recorded by scanning B(2). To improve the signal-to-noise ratio and the reproducibility. spectra were

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(6) Although labeling experiments clearly reveal the origin of the atoms that are involved in the multistep sequence, there is no doubt that proposed structures are very often hypothetical in mass spectrometric studies. With regard to the detailed mechanism of the generation of RCN/Fe^+ it should be mentioned that according to FTICR studies (Nibbering, N. M. M.; Schwarz, H.; et al., unpublished results) $Fe(CO)_x^+$ ions ($x = 1, 2$) serve as major precursor species. Similar results were obtained by: Allison, J.; Stepnowski, R. M. *Organometallics* **1988**, *7*, 2097. It should be emphasized that double-resonance experiments performed at 10^{-7} Torr give results that may not strictly apply at the high pressure used under chemical ionization conditions. The neutrals formed from the organometallic complexes are not structurally characterized but inferred indirectly from the mass differences between mass-selected precursor and observed daughter ions. On energetic grounds there cannot possibly exist any doubt that mass differences of 2 and 28 must correspond to intact H_2 and C_2H_4 molecules. The generation of an CH_3CH isomer, for example, would be too costly energetically.

(7) For examples and many references, see: Steinrück, N.; Schwarz, H. *Organometallics* **1989**, *8*, 759.

(8) (a) Weiske, T. *Ph.D. Thesis*, Technical University Berlin, D83, 1985. (b) Terlouw, J. K.; Weiske, T.; Schwarz, H.; Holmes, J. L. *Org. Mass Spectrom.* **1986**, *21*, 665.

Table I. Unimolecular Losses of Ethene and Hydrogen from RCN/Fe⁺ Complexes[a]

	precursor[b]			
	5a	**5b**	**5c**	**5d**
C_2H_4	61	61	68	
$C_2H_2D_2$	39	39		60
C_2D_4			32	40
H_2	73	63	79	
HD	27	37		69
D_2			21	31

[a] Data are expressed in %∑neutral = 100% for each class of species formed. [b] $CH_3CD_2(CH_2)_2CH(CN)C_4H_9$ (**5a**); $CD_3(CH_2)_3CH(CN)$-C_4H_9 (**5b**); $CD_3CD_2(CH_2)_2CH(CN)C_4H_9$ (**5c**); $CD_3CD_2(CH_2)_2CH$-$(CN)(CH_2)_3CD_3$ (**5d**).

averaged by using the VG 250/11 data system. All nitriles were synthesized by standard laboratory conditions, purified by GC, and fully characterized by spectroscopic means.

Results and Discussion

The metastable ion (MI) mass spectrum of the Fe⁺ complex of 5-cyanononane (**5**–Fe⁺) contains only signals due to the losses of H_2, C_2H_4, and CH_4 (Scheme II).[9]

The organization of the discussion of the data, given in Table I for the isotopomers **5a–d** of 5-cyanononane, is such that we will first describe the loss of ethylene.

The identical ratio of the losses of C_2H_4 and $C_2H_2D_2$ from both **5a** and **5b** proves already that the oxidative addition of the terminal $CH_3(CD_3)$ group[10] to the metal ion (Scheme I = step I) is *not* rate-limiting. If this would be the case, one should observe a primary kinetic isotope effect, discriminating against D transfer in **5b**–Fe⁺,[11] thus increasing the ratio for loss of $C_2H_4/C_2H_2D_2$.

from **5d**–Fe⁺ in comparison to **5a**–Fe⁺. This is not the case. A kinetic isotope effect is, however, operative in the elimination of $C_2H_{4-x}D_x$ (step III). Loss of C_2H_4 is favored over that of $C_2H_2D_2$ (C_2D_4) by factors of 1.56 in **5a** and **5b** and 2.13 in **5c**, and $C_2H_2D_2$ and C_2D_4 are competitively eliminated in a ratio of 1.50 (**5d**–Fe⁺). Slightly smaller secondary isotope effects were observed for the Fe⁺-induced eliminations of $C_2H_{4-x}D_x$ from Fe(4-octyne)⁺ complexes.[4b,c,12] We note that both ethylene and hydrogen eliminations occur without any scrambling.

The hydrogen molecule liberated from **5**–Fe⁺ originates exclusively from the ω and (ω − 1) positions of the alkyl chain, and the neutral is formed in a formal 1,2-elimination. This is convincingly evidenced by the data shown in Table I. As to the rate-limiting step for the generation of hydrogen, we know already from the analysis of the $C_2H_{4-x}D_x$ losses that the insertion step I is *not* rate-determining. This information together with the data for loss of $H_{2-x}D_x$ ($x = 0, 1, 2$) permit us to solve in an unambiguous way the algebraic equations for step IV (k_H/k_D) and step V (reductive eliminations of H_2/HD and HD/D_2, i.e., k_{H_2}/k_{HD} and k_{HD}/k_{D_2}, respectively). The following kinetic isotope effects are obtained, which demonstrate that both the β-hydrogen transfer *and* the reductive elimination of hydrogen are crucial for the product distribution: (i) step IV, $k_H/k_D = 1.59$; (ii) step V, $k_{H_2}/k_{HD} = 1.70$[13] and $k_{HD}/k_{D_2} = 1.44$.

In conclusion the present data provide the missing link in the understanding of the highly remarkable remote functionalization of saturated nitriles by bare Fe⁺ in the gas phase.

(9) In this article we refrain from discussing the mechanistic aspects of CH_4 loss from **5**–Fe⁺. This reaction will be discussed in another context: Czekay, G.; Drewello, T.; Eller, K.; Zummack, W.; Schwarz, H. *Organometallics*, in press.

(10) Insertion of Fe⁺ into a *methylene* CH bond as a reaction-initiating step can be excluded as this would result in the generation not of C_2H_4 but rather of higher alkenes.[2d] These products are, however, not observed for **5**–Fe⁺.

(11) Kinetic isotope effects $2 \leq k_H/k_D \leq 6$ (depending on the excess energy of the chemically activated organometallic compounds) were reported for β-hydrogen (deuterium) transfer by: Bomse, D. S.; Woodin, R. L.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 5503.

(12) Schulze, C.; Weiske, T.; Schwarz, H. *Organometallics* **1988**, *7*, 898.

(13) A similar isotope effect was recently reported[12] for the Cr⁺- and Mn⁺-induced dehydrogeneration of 4-octyne in the gas phase.

Picosecond Infrared Probing of Metal Carbonyl Photodissociation Products

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Abstract: Picosecond time-resolved infrared spectroscopy has been used for the first time to study the spectra and kinetics of the primary products obtained on visible photolysis of [CpFe(CO)₂]₂ (Cp = cyclopentadienyl) in cyclohexane. Observations in the terminal CO stretch region show an initially diffuse spectrum that develops with a rise time of 50 ps into two bands at 1933 and 1926 cm⁻¹. No further spectral changes occur within 4 ns. These observations can be interpreted as the production of a structure with Fe–CO bridge bonds broken, but the formation of CpFe(CO)₂ is not the primary process; alternative interpretations are discussed.

The photochemistry of transition-metal carbonyls has been studied extensively, often because of its relevance to the understanding of the role such systems play in homogeneous catalysis.[1-3]

The aim of such studies is the characterization of both the structures and reactivities of the species produced following photolysis, thereby allowing complete reaction mechanisms to be determined. Several approaches to this problem have been adopted.

The use of low-temperature techniques, including matrix isolation, has allowed the characterization of numerous unstable species since their lifetimes are considerably extended under such

(1) Wrighton, M. S. *Chem. Rev.* **1974**, *74*, 401.
(2) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1978.
(3) Meyer, T. J.; Caspar, J. V. *Chem. Rev.* **1985**, *85*, 187.