J. Am. Chem. Soc. **1991**, *113*, 833–839

The Gas-Phase Chemistry of Fe^+ with *n*-Pentanenitrile: A Seemingly Simple System?

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Revised Manuscript Received August 3, 1990

Abstract: The reactions of gas-phase Fe^+ with *n*-pentanenitrile and several deuterium-labeled isotopomers have been studied together with low-energy collision-induced dissociation (CID) of $Fe(C_4H_9CN)^+$ complexes, employing Fourier transform ion cyclotron resonance (FTICR) spectrometry. While loss of H_2 is due to *remote functionalization*, ethylene is produced from *internal* positions, generating $CH_3–Fe^+–CH_2CN$, an isomer of $Fe(CH_3CH_2CN)^+$. Loss of propene is also observed in low abundance, producing an iron–acetonitrile complex. All three processes are in competition with the formation of the ferracyclobutane complex $\overline{Fe(CH_3)(CN)CH_2CH_2CH_2}^+$, which, upon reopening, brings about equilibration of the α and $(\omega - 1)$ positions, thus affording a specific, degenerate isomerization of the $Fe(C_4H_9CN)^+$ collision complex. Collision-induced dissociation experiments with isotopomeric reaction products were performed, which provided structural information and revealed the positions of the deuterium atoms after the degenerate isomerization.

Introduction

The ability to active C–H or C–C bonds in organic substrates is a prerequisite for the functionalization of alkanes. Despite the many improvements that have been made recently, our knowledge on the mechanistic details, and the electronic/steric requirements that have to be met in order to design proper catalysts for such reactions, is still rather poor.[1,2] Gas-phase studies with bare transition-metal ions are therefore conducted to improve our understanding of the *intrinsic* metal properties, such as bond dissociation energies, without the necessity to account for all the complications that arise from the presence of solvent, additional ligands, and counterions in the condensed phase.[3] The isolated metal ions offer the opportunity to probe the principal ability of certain transition-metal-containing complexes for oxidative additions to C–H or C–C bonds, or for the formation of some reaction intermediates that might not be detectable under the reaction conditions of ordinary catalytic studies due to rapid decomposition. We believe that for a better understanding of the gas-phase reactions it is vital to deconvolute the instrumental influence (sector versus ICR, for example) as much as possible to obtain the inherent chemistry of the systems under investigation.

We have already shown that two completely different approaches such as ion/molecule reactions of bare metal ions M^+ with neutral substrates S in a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer[4] and metastable or collision-induced decompositions of adduct complexes $M(S)^+$ in a sector-field instrument can indeed be compared if some restrictions are kept in mind.[5,6] This first study, a more general comparison of several different metal ions with various substrates, was later deepened by a detailed examination of the branching ratios that are observed in the case of labeled compounds. Good to excellent agreement between both instrumental approaches could be noted for the label distributions of individual neutral losses even in cases where differences in the branching ratios for competing reaction channels were present.[7] Still, different research groups, active in the field of organometallic chemistry, might not only arrive at slightly divergent results due to the instruments used, but also because of different operating conditions which may arise out of some habits that are not recognized as such. Only if the same results are obtained in different approaches, can one feel more convinced that, e.g., the metal ions are in their electronic ground state and are kinetically not excited. A further comparison was therefore initiated whereby instruments of the same principle, viz two FTICR spectrometers, were employed. The FTICR in Purdue

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Table I. Products That Arise from the Reaction of Fe^+ with *n*-Pentanenitrile (**1**)[a]

instrumental method	H_2	C_2H_4	C_3H_6
TU Berlin FTICR	76	23	1
Purdue FTICR	80	20	<1
MI of **1**-$Fe^{+\,b,c}$	75	21	<1

[a] Data are given in Σ products = 100%. [b] For experimental data, see ref 9. [c] In addition, 4% ligand detachment (Fe^+) are also observed.

is of conventional design, while the Berlin group uses an instrument with an external ionization source so that a comparison deemed appropriate. We also wanted to further the comparison between FTICR and sector-field instruments, metastable ion yields, and low-energy collision-induced dissociation (CID) results, and hence a system was chosen for study that seemed well-understood.

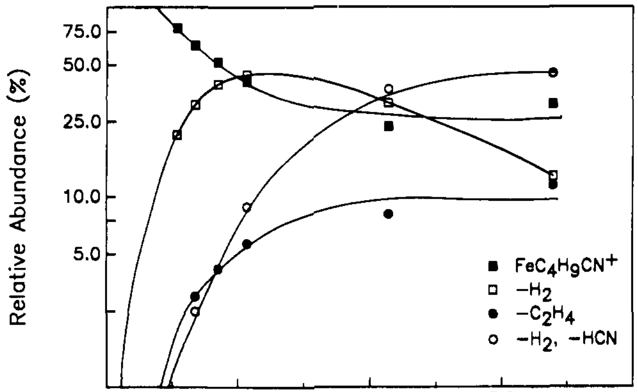

Figure 1. Collision-induced dissociation of $Fe(n\text{-}C_4H_9CN)^+$ (**1**-Fe^+) with continuous ejection of Fe^+ as a function of center-of-mass energy.

Chart I

$CH_3CH_2CH_2CH_2CN$
1

$CH_3CH_2CH_2CD_2CN$
1a

$CH_3CH_2CD_2CH_2CN$
1b

$CH_3CD_2CH_2CH_2CN$
1c

$CD_3CH_2CH_2CH_2CN$
1d

In gas-phase organometallic chemistry, *model systems* are employed that can be systematically varied so that the influences of the metal ion itself, or of substituents as well as further functionalities in the substrate, can be distinguished. Probably one of the best studied systems is that of nitriles and their reactions with bare metal ions,[3k-m,7-11] and it is only for this system that the variation principle has been consequently applied and a large amount of data has been collected. Especially the behavior of *linear* nitriles was thought to be well understood as these compounds represent the starting point of our efforts with the nitrile model system at the TU Berlin. It seemed therefore obvious to choose an example from the *n*-alkanenitriles for the purpose of the comparison. In the course of these studies, we then came across some rather unexpected findings that resulted exclusively from the chemistry of the model system chosen and that represent important observations in their own right. Two hidden degenerate isomerizations were discovered, and one proceeds via a ferracyclobutane intermediate. As metallacyclobutanes are proposed as intermediates for olefin metathesis,[12] for the cyclopropanation of alkenes,[13] in transition-metal-catalyzed rearrangements of strained carbocyclic rings,[14] and for the polymerization of alkenes by Ziegler–Natta catalysts,[15] the principal ability of iron (formally Fe^V in the proposed structure) to form such a metallacycle may give some useful hints that might reach far beyond the particular example discussed in the following.[16] For example, the existence of *positively charged ferracyclobutane intermediates* in alkene cyclopropanations with $[Cp(CO)_2Fe{=}CRR']^+$ has not unambiguously been determined or ruled out. They may or may not be involved albeit *after* the transition state,[13a] although recent results favor "backside closure" of the cyclopropane ring and, hence, would argue against their being involved.[13b,c] Ferracyclobutanes have also been invoked in the Fischer–Tropsch

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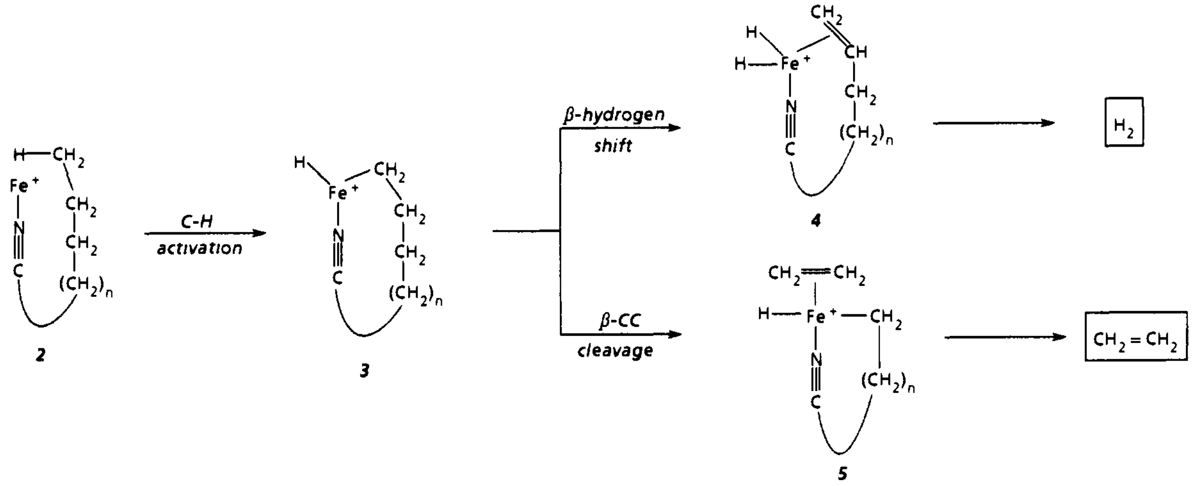
Scheme I



synthesis,[17] and recently, the preparation of the perfluorinated complex $\overline{Fe(CO)_4CF_2CF_2CF_2}$ could be accomplished.[18]

Results and Discussion

The reaction of bare Fe^+ with n-C_4H_9CN (1) gives rise to three ionic products by losses of H_2, C_2H_4, and C_3H_6 (eq 1).

$$Fe^+ + \underset{1}{n\text{-}C_4H_9CN} \longrightarrow \begin{cases} FeC_5H_7N^+ + H_2 & \text{(1a)} \\ FeC_3H_5N^+ + C_2H_4 & \text{(1b)} \\ FeC_2H_3N^+ + C_3H_6 & \text{(1c)} \end{cases}$$

The agreement between the results obtained from the two different FTICR spectrometers is excellent and needs no further comment (Table I). Similarly satisfying results were gained from the deuterium-labeled isotopomers of n-C_4H_9CN, **1a–d** (Chart I), so with a view to greater clarity average values are given in the following, and we note that the precision is in most cases better than ±3% absolute.

The product distributions observed were found to be quite dependent on background argon pressure. With no argon present, 40% of the products are due to dehydrogenation, 60% due to the loss of ethylene, and <1% due to the elimination of propene. With argon present during the reaction, a shift is observed in the products formed (60% H_2, 40% C_2H_4, and <1% C_3H_6). However, when a cooling period for the Fe^+ is inserted prior to the reaction, an even larger change is apparent. The ratios given in the tables correspond to conditions whereby at higher pressures or longer cooling times no further changes in the product distribution are observed. These results indicate that the Fe^+ is initially formed with excess energy, and, when argon is present, the Fe^+ undergoes thermalizing collisions. This effect is already obvious when argon is present, but no cooling time is used, so that Fe^+ is only partially cooled during the isolation/reaction. These experiments illustrate that caution must be exercised when studying laser desorbed metal ions.

Low-energy CID was also performed on Fe(pentanenitrile)$^+$ complexes which were formed in secondary reactions by ligand displacement. Loss of the intact ligand is the major CID product. Therefore, Fe^+ was continuously ejected during the CID process to increase the sensitivity to other fragments. As shown in Figure 1, at low kinetic energies, only dehydrogenation is observed. As the energy is increased, in addition, loss of ethylene is observed. $FeC_4H_6^+$ is also formed by the dehydrogenation product subsequently losing HCN (see below) and arises due to multiple collisions during the CID process. At higher energies, Fe^+–CH_3 is also formed, and this product is the result of the $FeC_3H_5N^+$ ion fragmenting further (see below). Loss of propene was not observed to occur above 1%. The CID results may indicate that the dehydrogenation represents the lowest energy decomposition pathway; this would be entirely consistent with the observed argon cooling effect on the ion/molecule reaction product distribution discussed above.

The observed products were not altogether unexpected as it was already known from sector-field studies[8,9] that hydrogen and ethylene were produced from this particular nitrile. Loss of propene was not observed before, which can be attributed to the much better sensitivity of the FTICR instrument. The **1**-Fe^+ complexes formed in the ion source of the sector-field instrument are of only moderate abundance so that the signal-to-noise ratio of the spectra was not very good. However, careful reexamination of the previously reported metastable ion (MI) spectrum[9] of **1**-Fe^+ revealed a tiny bump in the baseline for the loss of propene which was not recognized as a peak before. Data for the MI spectrum of **1**-Fe^+, calculated under inclusion of the propene loss, are also given in Table I and here as well, very good agreement can be noted.

For the primary products from eq 1, secondary and tertiary reactions were observed as well, eq 2–4. Except for eq 2b these

$$FeC_3H_5N^+ + \underset{1}{n\text{-}C_4H_9CN} \longrightarrow \begin{cases} \xrightarrow{0.84} FeC_5H_9N^+ + [C_3H_5N] & \text{(2a)} \\ \xrightarrow{0.01} FeC_6H_{12}N^+ + [C_2H_2N] & \text{(2b)} \\ \xrightarrow{0.15} FeC_8H_{14}N_2^+ & \text{(2c)} \end{cases}$$

$$FeC_5H_7N^+ + \underset{1}{n\text{-}C_4H_9CN} \longrightarrow \begin{cases} \xrightarrow{0.16} FeC_5H_9N^+ + [C_5H_7N] & \text{(3a)} \\ \xrightarrow{0.84} FeC_{10}H_{16}N_2^+ & \text{(3b)} \end{cases}$$

$$FeC_5H_9N^+ + \underset{1}{n\text{-}C_4H_9CN} \longrightarrow FeC_{10}H_{18}N_2^+ \qquad (4)$$

reactions represent simple additions or ligand-switching processes. This interpretation is also in line with the results from the labeled compounds, and we therefore will not discuss these reactions further. We will, however, come back to eq 2b after the discussion of the $FeC_3H_5N^+$ product.

Loss of H_2 and C_2H_4 is also observed for the higher homologues of **1**, and labeling studies[8] had revealed that the formation of these products could best be described by a mechanism which was termed *remote functionalization*, in analogy to the studies of Breslow on biomimetic systhesis.[19] This mechanism, given in Scheme I, has since then been found to be quite generally applicable as it is operative for a large variety of other substrates as well.[20] The metal ion is complexed to the cyanide group (or

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Table II. Products That Arise from the Reaction of Fe^+ with Labeled *n*-Pentanenitriles (**1a–d**)[a]

product	$CH_3CH_2CH_2CD_2CN$ (**1a**)	$CH_3CH_2CD_2CH_2CN$ (**1b**)	$CH_3CD_2CH_2CH_2CN$ (**1c**)	$CD_3CH_2CH_2CH_2CN$ (**1d**)
H_2	81	100	29	<2
HD	19		71	>98
C_2H_4	73	4	25	94
$C_2H_2D_2$	27	96	75	6
C_3H_6	83		28	
C_3H_5D	17		72	
$C_3H_4D_2$		100	*b*	
$C_3H_3D_3$				100

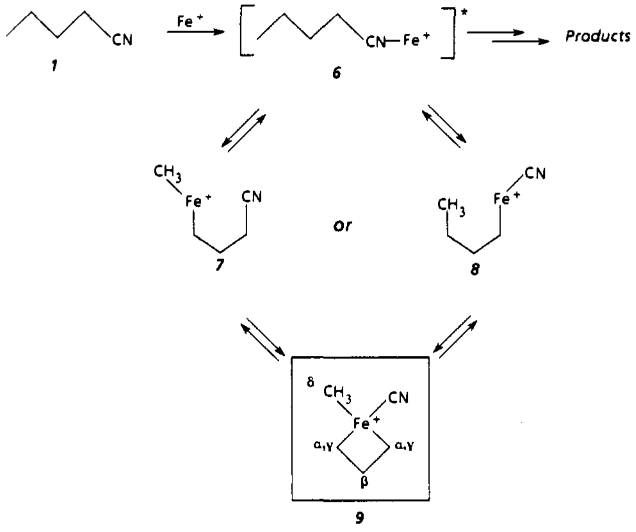
[a] Intensities were normalized to 100% for each neutral. [b] See ref 22.

some other functionality for a different substrate) and is thus only able to reach some remote bonds upon folding back of the alkyl chain. Insertion into a C–H bond of the terminal methyl group generates the intermediate **3**, which undergoes β-cleavage of a C–H or a C–C bond, followed by reductive elimination of H_2 or ethylene detachment. This mechanism is not operative or of minor importance for nitriles with a very short chain length, as the strain induced in **3** would be too high. This can be clearly seen from a comparison of the relative amount of remote functionalization versus simple ligand detachment, i.e., back-dissociation to Fe^+ and the intact substrate, in the MI spectra of the Fe^+ complexes of those nitriles.[3m,9,21]

It seemed natural to assume that in the **1**/Fe^+ system H_2 and C_2H_4 were also produced via remote functionalization, especially as high-energy collision induced dissociation (CID) spectra of **1c**-Fe^+ were already reported[8] to yield exclusively loss of HD and $C_2H_2D_2$, in line with the mechanism in Scheme I. We will show now that, while this assumpion is indeed justified for the dehydrogenation, ethylene is for the special case of *n*-pentanenitrile/Fe^+ produced by a completely different mechanism involving internal positions. The reaction products for the labeled compounds **1a–d** are given in Table II. The labeling distributions found for **1c** are clearly in contrast to the previously published data.[8] Reexamination of the old spectra revealed, however, that, in fact, the reported numbers were incorrect as the CID spectra showed loss of H_2 and C_2H_4 as well. In addition, MI spectra, previously unpublished, prove that losses of H_2, HD, C_2H_4, and $C_2H_2D_2$ are also observed in sector-field studies and that no discrepancy to FTICR data exists. The correct isotopomer ratios, determined from the MI spectra, are 28% H_2, 72% HD, and 31% C_2H_4, 69% $C_2H_2D_2$, in very good agreement with the FTICR data.

It is immediately obvious that while for **1b** and **1d** all reactions are highly specific, with 95–100% production of only one isotopomer, respectivley, for **1a** and **1c** a different behavior can be noted. For each of the three neutrals produced, two isotopomers are formed, a major one that accounts for 70–80% of the products, and a minor one with 20–30% abundance. For **1a**, the minor products correspond to the main products of **1c** and vice versa. *Thus, it inevitably follows that an intermediate must be produced that partly equilibrates the α and γ position of the nitrile and leaves the β and ω position unaffected.* The intermediate **9** in Scheme II fulfills all these requirements. After formation of the collision complex **6** from Fe^+ and **1**, the reaction will in part proceed directly to the products, but in part also to the metallacycle **9**. In **9**, the α and γ positions are indistinguishable, and hence reopening of the ferracyclobutane and the reverse reaction back to **6** serves to equilibrate **1a** and **1c**, thus affording a degenerate isomerization. Whether the formation of **9** is accomplished via **7** or **8** cannot be rigorously decided. An argument in favor of **7** might be that we will use **7** again as an intermediate en route to the loss of ethylene. The very similar branching ratios of products formed *directly* from **6**, and *after passage through* **9**, for the three neutrals, respectively, would on the other hand speak for an independent way to **9**, e.g., via **8**. If **7** were the intermediate to **9** as well, one would expect a somewhat different branching ratio for C_2H_4 compared to H_2 and C_3H_6. As the reopening of **9** proceeds with equal probability to **6a** and **6c**, i.e., with CD_2 in the α or γ position (see Scheme III below), it can be estimated that ca. 50% of the products are formed directly and 50% via **9**, i.e., if a mean value for the labeling distributions of 75 to 25% is used.

Scheme II



In condensed-phase organometallic chemistry an ever-increasing number of metallacyclobutanes has been isolated and characterized since the discovery of the first platinacyclobutanes,[23] and today examples are known for several different metals.[24,25] This con-

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(21) A more general discussion of this point can be found in: Eller, K.; Schwarz, H. *Chem. Ber.* **1990**, *123*, 201.

(22) The spectrum of **1c**, in addition to the losses of C_3H_6 and C_3H_5D, also contains a signal for $FeC_2H_3N^+$, which formally corresponds to loss of $C_3H_4D_2$, the inclusion of which would result in a labeling distribution of 17% C_3H_6, 44% C_3H_5D, and 39% $C_3H_4D_2$. Two strong arguments let us believe, however, that this signal is due to a trace amount of some impurity in the GC-purified sample. The formation of this ion is observed to be *slower* than the two other propene-loss isotopomers, which rules out a common precursor. Furthermore, if $C_3H_4D_2$ were truely formed from **1c**, this could only be due to an exchange with other positions in the nitrile. Yet, *none* of the three other compounds **1a**, **1b**, or **1d** shows the *corresponding* exchange.

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Table III. CID Spectra of the Isotopomeric Ethylene-Loss Products Generated from Fe$^+$ and **1a–d**

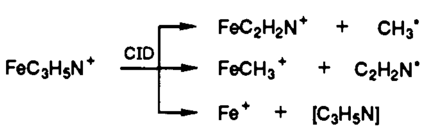
precursor nitrile	ethylene isotopomer lost	ion isolated for CID	observed reactions
$CH_3CH_2CH_2CD_2CN$ **1a**	C_2H_4	$FeC_3H_3D_2N^+$	$FeC_2D_2N^+ + CH_3^\bullet$ $FeCH_3^+ + C_2D_2N^\bullet$ $Fe^+ + [C_3H_3D_2N]$
	$C_2H_2D_2$	$FeC_3H_5N^+$	*a* $FeCH_3^+ + C_2H_2N^\bullet$ $Fe^+ + [C_3H_5N]$
$CH_3CH_2CD_2CH_2CN$ **1b**	$C_2H_2D_2$	$FeC_3H_5N^+$	$FeC_2H_2N^+ + CH_3^\bullet$ $FeCH_3^+ + C_2H_2N^\bullet$ $Fe^+ + [C_3H_5N]$
$CH_3CD_2CH_2CH_2CN$ **1c**	C_2H_4	$FeC_3H_3D_2N^+$	$FeC_2D_2N^+ + CH_3^\bullet$ $FeCH_3^+ + C_2D_2N^\bullet$ $Fe^+ + [C_3H_3D_2N]$
	$C_2H_2D_2$	$FeC_3H_5N^+$	$FeC_2H_2N^+ + CH_3^\bullet$ $FeCH_3^+ + C_2H_2N^\bullet$ $Fe^+ + [C_3H_5N]$
$CD_3CH_2CH_2CH_2CN$ **1d**	C_2H_4	$FeC_3H_2D_3N^+$	$FeC_2H_2N^+ + CD_3^\bullet$ $FeCD_3^+ + C_2H_2N^\bullet$ $Fe^+ + [C_3H_2D_3N]$

[a] The signal-to-noise ratio for this particular spectrum was not sufficient to detect loss of $CH_3^\bullet$, which represents the by far smallest CID product.

trasts the gas-phase organometallic chemistry, where metallacyclobutanes have been invoked frequently as reaction intermediates,[26] although a direct detection is still lacking; in fact, the available evidence for their formation is scarce and relies mainly on indirect information.[27] With the present system we are therefore able to present another indirect demonstration for the viability of bare Fe$^+$ to form ferracyclobutane structures, reaction intermediates that cannot be neglected a priori.

Under consideration of the degenerate isomerization, the interpretation of the dehydrogenation is straightforward. It can be seen from Table II that the hydrogen atoms are exclusively provided by the ω and γ, i.e., the $(\omega - 1)$ position, as was expected from the mechanism of remote functionalization (Scheme I).

A different situation pertains, though, for the loss of ethylene. The degenerate isomerization somewhat hampers the interpretation for **1a** and **1c**, but nevertheless it can be seen that at least 95% of the total ethylene originates from the β and γ position. If remote functionalization also contributes to the production of C_2H_4, it has to be for less than 5%. Before we discuss the mechanism for this process, it is helpful to examine the structure of the ion that results from the ethylene loss, i.e., $FeC_3H_5N^+$. Collision-induced dissociation (CID) experiments[28] were performed with this ion. Only three signals were observed, eq 5. This



$$FeC_3H_5N^+ \xrightarrow{CID} \begin{cases} FeC_2H_2N^+ + CH_3^\bullet \\ FeCH_3^+ + C_2H_2N^\bullet \\ Fe^+ + [C_3H_5N] \end{cases} \qquad (5)$$

spectrum would be in accordance with a $CH_3\text{-}Fe^+\text{-}CH_2CN$ structure. $FeC_3H_5N^+$, produced from the reaction of Fe$^+$ with C_2H_5CN (this is probably a ternary reaction with Ar, as the product is observed only at high pressures and it is formed very slowly) gives a *different* CID spectrum. From this ion, which is presumed to have the structure of the adduct complex, $Fe(CH_3CH_2CN)^+$, the exclusive production of Fe$^+$ is observed. The secondary reaction described in eq 2b can now be better understood. In this reaction, the $CH_3\text{–}Fe^+$ fragment is retained, and only the CH_2CN ligand is lost upon complexation of the pentanenitrile. The small magnitude of this product might point to a slightly endothermic or thermoneutral process, an assumption that seems reasonable for the loss of a radical. It is tempting to interpret the formation of $CH_3\text{–}Fe^+\text{–}CN_2CN$ with an insertion into the $C\text{–}CH_3$ bond, affording **7**, followed by β-cleavage and ethylene detachment. It has to be mentioned, though, that the reversed sequence, insertion into the $C_{(\alpha)}\text{–}C_{(\beta)}$ bond followed by β-cleavage of $C\text{–}CH_3$, affords the same intermediate **10**. It is, however, unlikely that the β-CC-cleavage could compete so effectively with the β-H shift which affords C_3H_6 (see below). To substantiate this proposal, but also to test, if we were able to falsify our earlier conclusions (Popper !), concerning the suggested mechanism for the degenerate isomerization, we also performed similar CID experiments for *all* the ethylene-loss products in this study, except for the very weak ones where experimental difficulties were encountered. The result is presented in Table III, and it is gratifying to see that not a single exception from the predicted pattern can be noted. Scheme III exemplifies the combined

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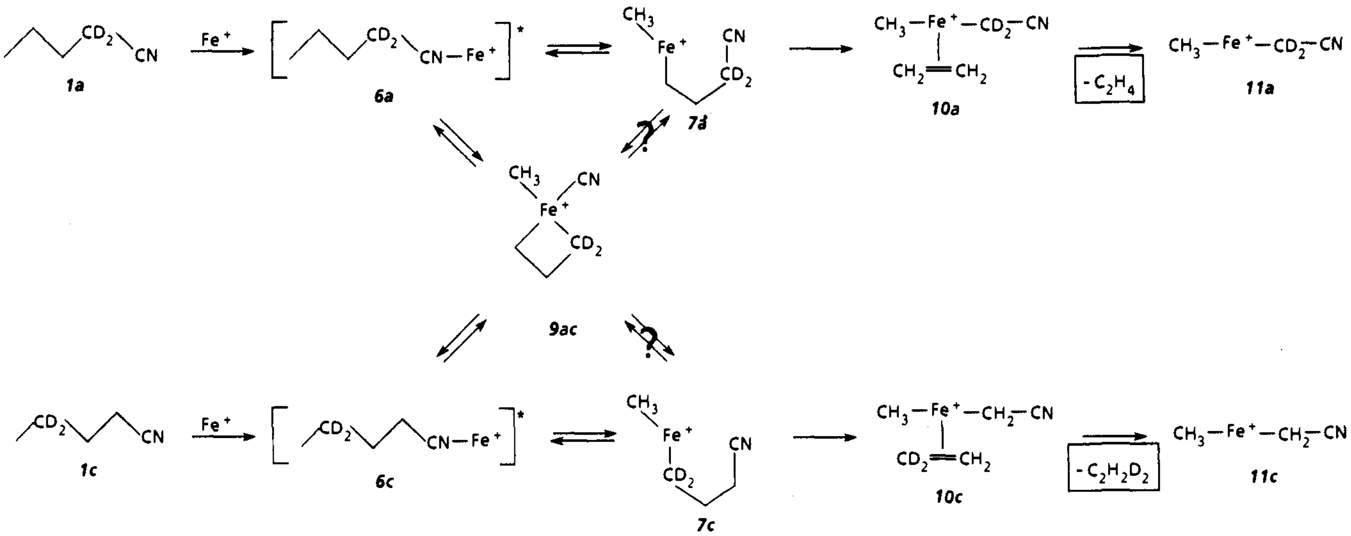
Scheme III



mechanisms for **1a** and **1c** and serves to facilitate the interpretation of Table III.

It is believed that ethylene is generated from **7** and not directly from **9**. Cleavage of **9** to afford ethylene and an alkylidene intermediate, in analogy to conventional organometallic chemistry,[12,24a] is considered less likely for two reasons. First, the same argument that favored **8** as the intermediate from **6** to **9** applies here as well. If ethylene were produced directly from **9**, a 50:50 labeling distribution for C_2H_4:$C_2H_2D_2$ should result from **1a** and **1c**, because a symmetric metallacycle **9ac** is formed in these cases. However, no differences were observed in the labeling distributions between ethylene on the one hand, and H_2 and C_3H_6 on the other hand, for the relative amount of "directly" formed products (see above). Second, any alkylidene intermediate produced from **9** would have to rearrange by a 1,2-cyanide shift to generate the experimentally observed CH_3–Fe^+–CH_2CN structure; this is a step for which no precedent exists.

For what reasons does **1** differ in the mechanism for ethylene loss from its higher homologues, where C_2H_4 is produced via remote functionalization?[8-10] The most likely explanation is in our opinion the ring strain that would be present in **5** (Scheme I), with $n = 1$ for **2** = **6**. Dehydrogenation does not induce a comparable strain and can thus be achieved by remote functionalization. Yet, other reasons might also be feasible for this special behavior of **1**, and we are currently investigating further model compounds to give a conclusive answer.

The loss of propene can be explained by the conventional insertion/β-hydrogen-shift mechanism, once again preceded by a degenerate isomerization **6a** ⇌ **6c**. Insertion into the $C_{(\alpha)}$–$C_{(\beta)}$ bond, followed by a β-hydrogen shift from $C_{(\gamma)}$ generates propene, containing the three terminal carbon atoms. The intensity of the propene-loss product was unfortunately too low to allow a further characterization by CID experiments, but most likely the $FeC_2H_3N^+$ ion has the structure of a Fe^+/acetonitrile complex. Reductive elimination of cyclopropane from **9**, a common decomposition mode for metallacyclobutanes in the condensed phase,[12,24a,29] can be excluded on the basis of the labeling results.

We will finally concern ourselves with the structure of the dehydrogenation product, $FeC_5H_7N^+$. We have already shown above that the dehydrogenation proceeds via remote functionalization; the mechanism would therefore require a γ,δ-unsaturated nitrile as the product. We performed CID experiments on the $FeC_5H_7N^+$ ion to get further information. The main product that is produced is unfortunately the nonstructure-indicative Fe^+, but, besides several weak fragments, the loss of HCN and the concomitant formation of $FeC_4H_6^+$ is also observed. This CID fragment seems to be in accordance with the expectations; a 1,2-elimination of HCN with the production of a conjugated double bond, viz butadiene, is probably a facile process for the assumed structure. To find further support for this interpretation and to clarify the locations of the remaining hydrogen atoms, once again CID experiments on *all* individual dehydrogenation products were conducted (Table IV). The result was somewhat surprising, but rather informative.

While the CID spectra of the ions generated from **1a** and **1c** are in line with the expectations, Scheme IV, parts a and b, the simultaneous production of HCN and DCN from **1b** and **1d** is at first glance puzzling. Both compounds give rise to an identical labeling distribution; thus we are facing still another degenerate isomerization in this system. A reasonable explanation for this finding is presented in parts c and d of Scheme IV. The production of an allylic system would easily explain the exchange of exclusively the $C_{(\beta)}/C_{(\delta)}$ hydrogens; it is well-known that the terminal positions of an allylic system exchange rapidly.[3i,26v,27a,30] The activation of the allylic C–H bond most likely *precedes* the actual CID process; otherwise the identical results for **1b** and **1d** would be hard to explain. A conclusion that can be derived then is that a kinetic isotope effect of $k_H/k_D = 2.3$ is operative for the hydrogen cyanide elimination. Note, however, that this does not apply if the CID process samples **12** instead of **14**; in this case different preferences for allylic versus vinylic positions will influence the measured ratio. It might also be conceivable that the allylic system is shifted into conjugation with the cyanide group; yet the exclusive formation of HCN from the dehydrogenation products of **1a** and **1c** rules out this possibility. The only reasonable explanation for the fixation of the allylic system is an additional complexation of the Fe^+ ion to the cyanide function, e.g., in a *side-on* fashion, which would be impossibe if both complexation sites were in direct proximity.[10c]

Conclusions

By analyzing the reactions of bare, gas-phase Fe^+ cations with a complete set of deuterium-labeled isotopomers of *n*-pentanenitrile (**1**), the following observations were made.

(1) The agreement between ion/molecule reactions of Fe^+ with **1** in two different FTICR mass spectrometers and metastable decompositions of adduct complexes **1**-Fe^+ in a sector-field instrument is once again good, showing that the results that are obtained do not depend on the instrumental approach that is chosen. Rather, they reflect intrinsic properties of the organometallic systems in question. Low-energy CID on **1**-Fe yields the same products observed in the ion/molecule reactions. However, products arising from multiple collisions can dominate the spectra.

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Scheme IV

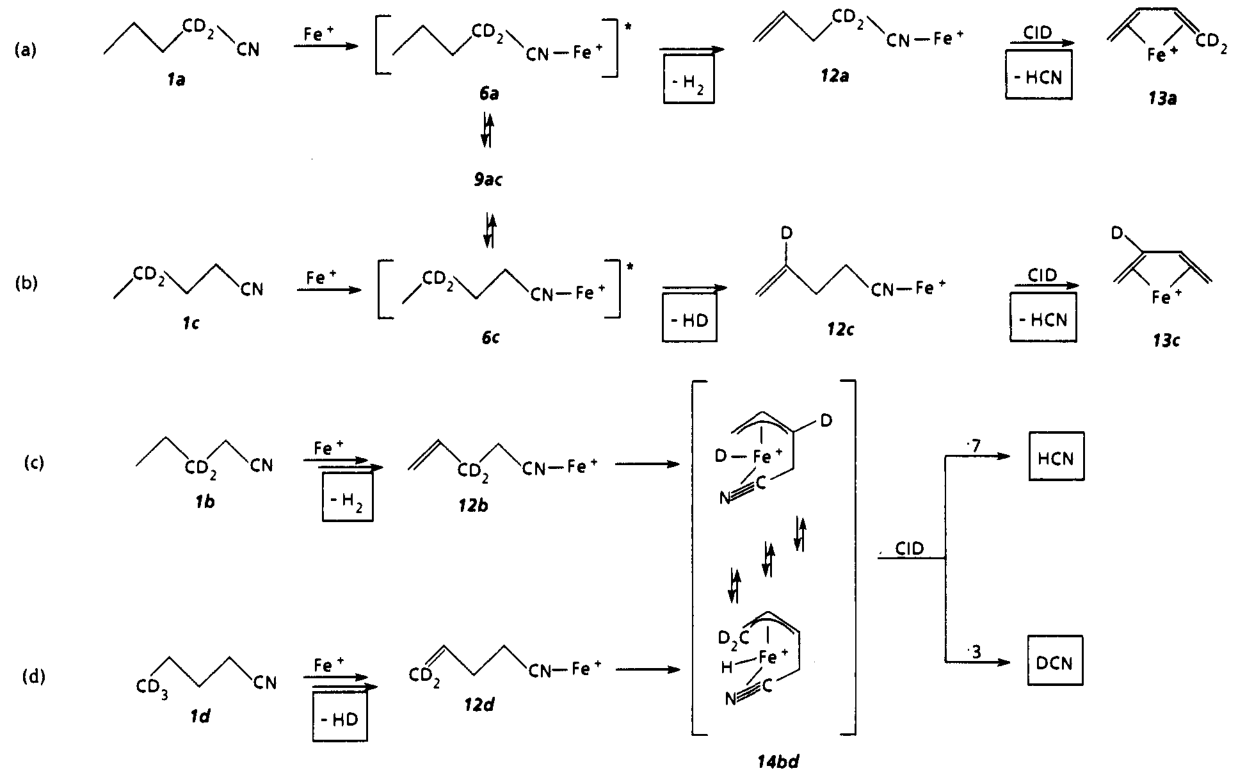

Table IV. CID Spectra of the Isotopomeric Dehydrogenation Products Generated from Fe⁺ and **1a–d**

precursor nitrile	hydrogen isotopomer lost	ion isolated for CID	CID product(s)
$CH_3CH_2CH_2CD_2CN$ (**1a**)	H_2 HD	$FeC_5H_5D_2N^+$ $FeC_5H_6DN^+$	HCN HCN
$CH_3CH_2CD_2CH_2CN$ (**1b**)	H_2	$FeC_5H_5D_2N^+$	HCN (70%) DCN (30%)
$CH_2CD_2CH_2CH_2CN$ (**1c**)	H_2 HD	$FeC_5H_5D_2N^+$ $FeC_5H_6DN^+$	HCN HCN
$CD_3CH_2CH_2CH_2CN$ (**1d**)	HD	$FeC_5H_5D_2N^+$	HCN (69%) DCN (31%)

(2) A hidden degenerate isomerization via a ferracyclobutane intermediate partly equilibrates the α and γ positions before *any* neutral products are lost.[31]

(3) Loss of H_2 proceeds by remote functionalization of the $\omega/(\omega - 1)$ positions. The resulting γ,δ-unsaturated nitrile reacts further by activating the allylic C–H bond from $C_{(\beta)}$, generating a hydrido-allyl structure. The outer hydrogens of this allylic system are rapidly equilibrated, but additional complexation of Fe⁺ to the cyanide function fixes the allyl system to the terminal carbon atoms.

(4) Loss of ethylene involves the β and γ positions and generates CH_3–Fe⁺–CH_2CN, a distinguishable isomer of $Fe(CH_3CH_2CN)^+$; propene stems from the terminal carbon atoms.

(5) Only CID experiments of isotopomeric reaction products, generated from the same precursor nitrile, allowed the structure determinations and the elucidation of the deuterium distribution *after* the degenerate isomerization had taken place and the neutral products were lost. A distinction between statistical behavior (scrambling) and specific processes is thus possible.

Experimental Section

The two mass spectrometers were operated under the usual conditions previously described by the respective groups.[3a–d,5,7] Briefly, the Purdue instrument is a Nicolet FTMS-2000 Fourier transform mass spectrometer modified to a single cell configuration, while a Spectrospin CMS-47X with an external ion source[32] is used at the TU Berlin. Metal-ion formation is accomplished in both cases by laser desorption from a stainless-steel target, employing the fundamental frequency (1064 nm) from a Quanta Ray (Purdue) or a Spectron Systems (TU Berlin) Nd:YAG laser. Reagents were introduced by leak valves with variable pressures in the 10^{-8}-mbar range. To quench excited states of the metal ion, and also for the collision-induced dissociation (CID) experiments,[28] argon is also present at a constant "background" pressure of $1–2 \times 10^{-7}$ mbar. Initially, the $^{56}Fe^+$ isotope is isolated from the other iron isotopes and minor steel constituents. For cooling a delay of 1–2 s was inserted in the pulse sequence, and the meanwhile formed reaction products were ejected afterwards to reisolate the Fe⁺. To be certain not to inadvertently excite the Fe⁺, ejection chirps sufficiently distinct in frequency from *m/z* 56 were used at this stage. Next, the Fe⁺ is allowed to react for a variable time, typically 1–10 s, with the nitrile. After a reaction time of ca. 4 s, around half of the original Fe⁺ ions have formed products, and a reaction product is isolated for CID. CID conditions were deliberately chosen to *resemble* single-collision conditions with the collision times quite short ($\leq$50 ms). Otherwise, multiple collisions and further decompositions of CID products complicate the interpretation.

The labeled nitriles were synthesized according to established techniques, purified by preparative gas chromatography, and characterized by NMR and GC/MS. The deuterium content was determined by the reagents employed ($LiAlD_4$, 98 atom % D, and CD_3I, 99.5 atom % D), and in only two cases corrections for incomplete labeling had to be made.

Acknowledgment. The Berlin group gratefully acknowledges the continuous support of their work by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie (FCI), the Graduiertenkolleg Chemie (Berlin), and the Volkswagen-Stiftung. K.E. especially thanks the Stiftung Stipendien Fonds of the FCI for a scholarschip support. The Purdue group wishes to acknowledge the Division of Chemical Sciences in the Office of Basic Energy Sciences, U.S. Department of Energy (Grant DE-FG02-87ER13766) for supporting this research and the National Science Foundation (Grant CHE-8612234) for continuing support of FTMS methodology. This group also wishes to thank Extrel for the loan of the single-cell system.

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(31) A related situation was recently encountered for the unimolecular ethylene loss for n-$C_7H_{15}Si(CH_3)_3/Fe^+$ complexes. A ferracyclopentane was invoked to explain equilibration of the α/β and γ/δ methylene groups: Hässelbarth, A.; Prüsse, T.; Schwarz, H. *Chem. Ber.* **1990**, *123*, 213.

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