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Registry No. 1, 82044-79-9; 2, 84879-23-2; 3, 97732-43-9; 4, 122214-24-8; 4*, 122214-26-0; 5, 97749-40-1; 6, 118084-23-4; 7, 122214-25-9; 8, 104413-70-9; 8*, 122214-27-1; 9, 118199-35-2; 10, 118084-28-9; CO_2, 124-38-9; $^{13}CO_2$, 1111-72-4; *trans,mer*-W(C_2H_4)$_2$(CO)(PMe_3)$_3$, 98720-85-5; LiOOCCH=CH_2, 13270-28-5; LiOOCCH_2CH_3, 6531-45-9; $WH_2Cl_2(PMe_3)_4$, 87738-93-0; $MoCl_4(PMe_3)_3$, 95797-64-1; $WCl_4(PMe_3)_3$, 73133-10-5; Mo(CO_3)(CO)(PMe_3)$_4$, 85405-73-8; W(CO_3)(CO)(PMe_3)$_4$, 122214-28-2; *trans*-Mo(CO)$_2$(PMe_3)$_4$, 122292-34-6; [Mo(CO_3)(CO)(PMe_3)$_3$]$_2$, 85405-74-9; $MoH_4(PMe_3)_4$, 82456-14-2; *cis*-Mo(CO)$_2$(PMe_3)$_4$, 30513-06-5; *fac*-Mo(CO)$_3$(PMe_3)$_3$, 19195-94-9; *mer*-Mo(CO)$_3$(PMe_3)$_3$, 30513-05-4.

Supplementary Material Available: Tables of more bond distances and angles for 3, 4 (X-ray), and 4 (neutron) and tables of atomic fractional coordinates and anisotropic thermal parameters for 3, 4 (X-ray and neutron), and 6 (18 pages); listings of structure factors for 3, 4 (X-ray), 4 (neutron), and 6 (104 pages). Ordering information is given on any current masthead page.

Origin of the Distinctly Different Gas-Phase Chemistry of Linear and α-Branched Aliphatic Nitriles with Bare Iron(I) Ions. Evidence for Oxidative Addition of the C–CN Bond to Fe^+, New Mechanisms for the Reductive Eliminations of Alkanes, and a Demonstration of Consecutive CH/CC Bond Activations of Different Sites of Flexible Molecules[†]

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For the first time unequivocal evidence is presented demonstrating that α-branched nitriles, in addition to the well-established remote functionalization of C–H bonds, are susceptible to oxidative addition of the C–CN bond to bare Fe^+. The so-formed intermediates give rise to several remarkable processes, the most prominent among which corresponds to the generation of methane. The study of many model systems including a large set of labeled compounds provides detailed insight which permits (i) the suggestion of a new mechanism of Fe^+-mediated methane formation and (ii) the definition of the structural requirements and limitations that dictate whether in RCN/Fe^+ complexes the Fe^+ is inserted in the R–CN bond or remote functionalization of C–H bonds occurs. Evidence is also presented showing that Fe^+-induced loss of "C_nH_{2n+2}" (n = 2, 3) from (n-C_6H_{13})$_2$CHCN consists of the consecutive eliminations of C_nH_{2n} and H_2 involving both alkyl chains. While the olefin is generated from the ω- and (ω − 1)-positions of one alkyl chain, the hydrogen molecule originates from the ω′- and (ω′ − 1)-positions of the *other* alkyl chain ("double remote functionalization").

Introduction

Gas-phase experiments with "bare" transition-metal ions offer an unique possibility to probe, in the absence of any solvation and ion-pairing effects, the intrinsic properties of reactive organometallic species and to evaluate the potential role these remarkable transients may play in the initial steps of the activation of C–H and C–C bonds. This topic is, not surprisingly, of fundamental interest in catalysis and has attracted considerable attention in the last decade.[1,2]

Table I. Metastable Ion (MI) Mass Spectra of RCN/Fe^+ Complexes[a]

	loss of					
R-CN	H_2	C_2H_4	RCH=CH_2	CH_4	RH	Fe^+
C_2H_5						100
C_3H_7	4	41				55
C_4H_9	75	21				4
C_5H_{11}	92	8				
C_6H_{13}	72	21	2[b]	5		
C_7H_{15}	59	32	6[b]	3		
C_9H_{19}	29	30	35[c]	5	1[d]	
$C_{10}H_{21}$	29	16	46[e]	6	3[f]	

[a] Intensities are expressed in the ∑fragment ions = 100%. The alkyl group is always unbranched. [b] R = CH_3. [c] R = CH_3 and R = C_2H_5 contribute in a ratio of 5.8:1 to the overall formation of RCH=CH_2. [d] R = C_2H_5. [e] R = CH_3, C_2H_5, and C_3H_7 contribute in ratios of 20:12:1 to the overall formation of RCH=CH_2. [f] C_2H_6, C_3H_8, and C_4H_{10} are formed in a roughly 1:1:1 ratio.

Many reactions of transition-metal ions, M^+, with organic substrates can be described by a mechanism (Scheme I) suggested or the first time by Allison and Ridge.[3] Oxidative addition of the C–X bond of the organic substrate 1 to M^+ generates 2 from which, via β-hydrogen transfer, the olefin hydrido complex 3 is generated; depending on the binding energies, 3 then undergoes either

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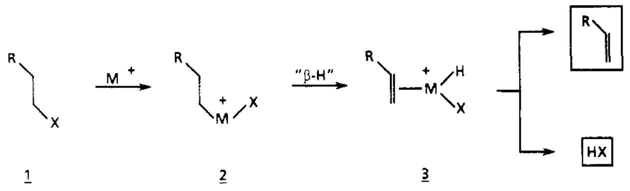
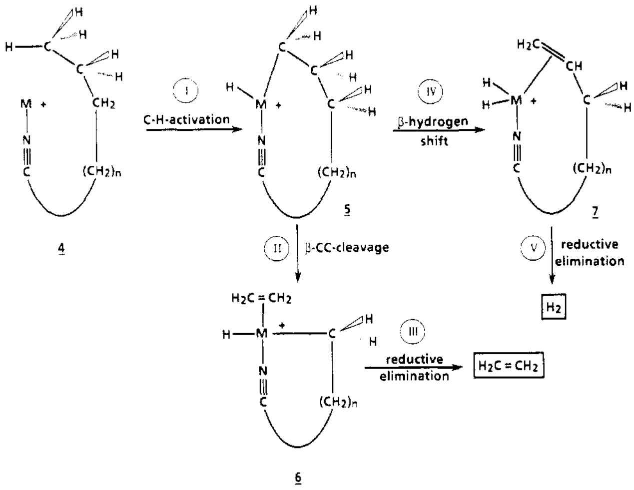
[†] Dedicated to Professor Rolf Huisgen, Universität München, in honor of his pioneering work and fundamental contributions to physical organic chemistry.

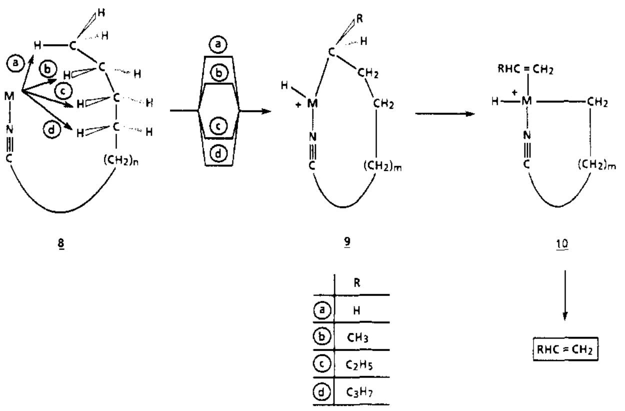
Scheme I



Scheme II

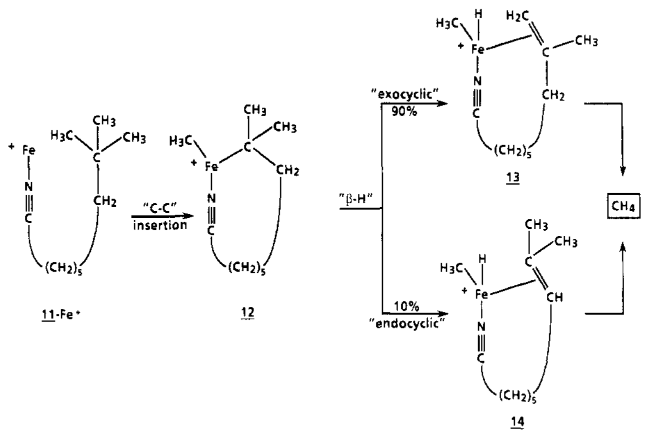


Scheme III



	R
ⓐ	H
ⓑ	CH_3
ⓒ	C_2H_5
ⓓ	C_3H_7

Scheme IV



olefin detachment (**3** → RCH=CH$_2$) or reductive elimination of HX (Scheme I).

The direct functionalization of *remote* C–H or C–C bonds, i.e. several carbon atoms away from the activating group, represents a great challenge. While such processes are common to enzymes, which anchor a functional group and *geometrically* select a specific segment of the substrate, only a few cases in solution chemistry are reported[4] where a similar principle seems to be operative. Breslow[4b] has coined the term "remote functionalization" for this method of coordination of a functional group followed by selective reactions at sites away from the complexed functionality. We[1v,w,5] and later others[6] have recently demonstrated that a similar principle holds true in the gas phase for quite a variety of organic aliphatic substrates including nitriles,[1v,5,6] isonitriles,[1v,7] amines,[3c,d,e] alcohols,[8] alkynes,[1v,2,9] and allenes,[10] respectively. For example, the chemistry of the Fe$^+$ complexes of aliphatic, unbranched nitriles, e.g., **4** (Scheme II, M = Fe), is unique, in that *selective C–H activation occurs only at positions remote from the CN group.* This unprecedented behavior contrasts sharply with that depicted in Scheme I. The primary reason for the behavior of nitriles is due to the initial interaction of the cyanide group with Fe$^+$. The preferred coordination leads to an "end-on" complex, **4**, characterized

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(1) Selected references: (a) Müller, J. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 653. (b) Parshall, G. W. *Catalysis* **1977**, *1*, 335. (c) Müller, J. *The Organic Chemistry of Iron*; Academic Press: New York, 1978; Vol. 1, p 145. (d) Beauchamp, J. L.; Stevens, A. E.; Corderman, R. R. *Pure Appl. Chem.* **1979**, *51*, 967. (e) Haggin, J. *Chem. Eng. News* **1982**, *60*, 13. (f) Gregor, I. K.; Guilhaus, M. *Mass Spectrom. Rev.* **1984**, *3*, 39. (g) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Reidel: Dordrecht, 1984. (h) Bergman, R. G. *Science (Washington, D.C.)* **1984**, *223*, 902. (i) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (j) Freiser, B. S. *Talanta* **1985**, *32*, 697. (k) Silvestre, J.; Hoffmann, R. *Helv. Chim. Acta* **1985**, *68*, 1461. (l) Green, M. L.; O'Hare, D. *Pure Appl. Chem.* **1985**, *57*, 1897. (m) Baudry, D.; Ephritikine, M.; Felkin, H.; Fillebeen-Khan, T.; Gault, Y.; Holmes-Smith, R.; Yingrus, L.; Zakrzewski, J. In *Organic Synthesis*; Streith, J., Prinzbach, H., Schill, G., Eds.; Blackwell Scientific Publications: Oxford, 1985; p 25. (n) Ephritikine, M. *Nouv. J. Chim.* **1986**, *10*, 9. (o) Allison, J. *Prog. Inorg. Chem.* **1986**, *34*, 627. (p) Armentrout, P. B. In *Structure/Reactivity and Thermochemistry of Ions*; Ausloos, P., Lias, S. G., Eds.; D. Reidel: Dordrecht, 1987; No. 193, p 97. (q) Ridge, D. P. *Ibid.* 1987; No. 193, p 165. (r) Squires, R. R. *Chem. Rev.* **1987**, *87*, 623. (s) Armentrout, P. B. In *Gas Phase Inorganic Chemistry*; Russell, D.H., Ed.; Plenum: New York, 1989. (t) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (u) Dahlenburg, L. *Nachr. Chem., Tech. Lab.* **1988**, *36*, 899. (v) Czekay, G.; Drewello, T.; Eller, K.; Lebrilla, C. B.; Prüsse, T.; Schulze, C.; Steinrück, N.; Sülzle, D.; Weiske, T.; Schwarz, H. In *Organometallics in Organic Synthesis*; Werner, H., Erker, G., Eds.; Springer-Verlag: Heidelberg, 1989; p 203. (w) Schwarz, H. *Acc. Chem. Res.*, in press. (x) Eller, K.; Schwarz, H. *Chimia*, in press.

(2) More than 100 references on the reactions of bare transition-metal ions with organic substrates, together with a detailed discussion of the reactions of gaseous octyne isomers with Fe$^+$, may be found in: Schulze, C.; Schwarz, H.; Peake, D. A.; Gross, M. L. *J. Am. Chem. Soc.* **1987**, *109*, 2368.

(3) (a) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 4998. (b) Babinec, S. J.; Allison, J. *Ibid.* **1984**, *106*, 7718. (c) For a revision and modification of this, otherwise quite general mechanism in the reactions of primary amines and alkanols with Fe$^+$ and Co$^+$, see: Karrass, S.; Eller, K.; Schulze, C.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 607. (d) Karrass, S.; Prüsse, T.; Eller, K.; Schwarz, H. *J. Am. Chem. Soc.*, in press. (e) Karrass, S. Diploma Thesis, Technical University Berlin, 1988.

(4) (a) Breslow, R. *Chem. Soc. Rev.* **1972**, *1*, 553. (b) Breslow, R. *Acc. Chem. Res.* **1980**, *13*, 170. (c) Kerb, U.; Stahnke, M.; Schulze, P. E.; Wiechert, R. *Angew. Chem.* **1981**, *93*, 89.

(5) (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 Proc.* **1987**, *76*, R1. (c) Lebrilla, C. B.; Drewello, T.; Schwarz, H. *Ibid.* **1987**, *79*, 287. (d) Lebrilla, C. B.; Drewello, T.; Schwarz, H. *J. Am. Chem. Soc.* **1987**, *109*, 5639. (e) Prüsse, T.; Lebrilla, C. B.; Drewello, T.; Schwarz, H. *Ibid.* **1988**, *110*, 5986. (f) Prüsse, T.; Drewello, T.; Lebrilla, C. B.; Schwarz, H. *Ibid.* **1989**, *111*, 2857. (g) Czekay, G.; Drewello, T.; Schwarz, H. *Ibid.* **1989**, *111*, 4561.

(6) Stepnowski, R. M.; Allison, J. *Organometallics* **1988**, *7*, 2097.

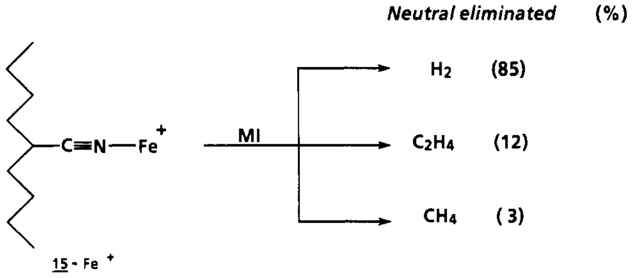
(7) Eller, K.; Lebrilla, C. B.; Drewello, T.; Schwarz, H. *J. Am. Chem. Soc.* **1988**, *110*, 3068.

(8) Prüsse, T.; Schwarz, H. *Organometallics*, in press.

(9) (a) Schulze, C.; Schwarz, H. *Chimia* **1987**, *41*, 29. (b) Schulze, C.; Schwarz, *J. Am. Chem. Soc.* **1988**, *110*, 67. (c) Schulze, C.; Weiske, T.; Schwarz, H. *Organometallics* **1988**, *7*, 898.

(10) Steinrück, N.; Schwarz, H. *Organometallics* **1989**, *8*, 759.

Scheme V



by a "linear"[11] $-CH_2C{\equiv}NM^+$ entity (M = transition-metal ion). The linear fragment in turn constrains the remainder of the molecule such that the transition-metal ion M^+ activates C–H bonds while trying to minimize the strain of the intermediate metallacycles. For nitriles containing four to seven carbon atoms, this deformation results in the exclusive activation of a C–H bond of the methyl group by oxidative addition of this bond to the (complexed) metal ion (Scheme II, **4** → **5**).[12] The insertion is followed by competitive β-cleavage of the C–C bond (**5** → **6**) or β-hydrogen shift (**5** → **7**) to generate the intermediates **6** and **7** from which eventually the neutral molecules C_2H_4 and H_2, respectively, are eliminated. From the study[5g] of labeled nitriles intramolecular kinetic isotope effects were determined that shed further light on the mechanism: (i) Step I, i.e. the oxidative addition of a C–H bond, is not rate-limiting. (ii) For the generation of ethylene, it is the ligand detachment (step III) that is associated with a kinetic isotope effect. (iii) Hydrogen formation is affected by two isotope effects that are operative for both the β-hydrogen migration **5** → **7** as well as the reductive elimination (step V).

Table II. Fe⁺-Mediated $CH_{4-x}D_x$ Formation from Isotopomers of 2-(*n*-Butyl)hexanenitrile 15[a]

precursor	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4
$C_4H_9CH(CN)(CH_2)_3CD_3$ (**15a**)	57			43	
$C_4H_9CH(CN)(CH_2)_2CD_2CH_3$ (**15b**)	100				
$C_4H_9CH(CN)CH_2CD_2C_2H_5$ (**15c**)	100				
$C_4H_9CH(CN)CD_2C_3H_7$ (**15d**)	55	45			
$C_4H_9CD(CN)C_4H_9$ (**15e**)	100				
$C_4H_9CH(CN)(CH_2)_2C_2D_5$ (**15f**)	57			43	
$CD_3(CH_2)_3CH(CN)CD_2C_3H_7$ (**15g**)	62				38

[a] Data are expressed in $\sum CH_{4-x}D_x = 100\%$. Uncertainties are better than ±1%.

However, as the carbon chain is lengthened,[5d] activation of the internal C–H bonds starts to dominate. This was evident by the following experimental findings: (i) Hydrogen is no longer exclusively provided by the ω- and (ω – 1)-positions; it also originates from internal methylene groups. (ii) The fact that internal C–H bonds (Scheme III, **8** → **9**) are oxidatively added to the (complexed) metal ion has the consequence that, in addition to C_2H_4, higher alkenes, $RCH{=}CH_2$ (R = alkyl), are also eliminated (Scheme III). Interestingly and not yet fully understood is the finding that the trajectory of the interaction for step **8** → **9** differs for Fe^+, Co^+, and Ni^+.[5c,d]

Unequivocal evidence for the direct oxidative addition of remote C–C bonds[13] was provided by the study of *tert*-butyl-substituted nitriles.[5e] Fe^+-mediated demethanation of 8,8-dimethylnonanenitrile **11** follows the sequence depicted in Scheme IV, commencing with insertion of Fe^+ into a terminal H_3C–C bond, followed by β-hydrogen transfer from either an "exocyclic" (ca. 90%) or an "endocyclic" (ca. 10%) C–H bond (Scheme IV).[14] There was no experimental support for the operation of the long sought after β-methyl migration[15] in the system studied.

As indicated in Table I, the Fe^+-mediated reductive elimination of higher alkanes is either absent or of negligible importance in the metastable ion (MI) spectra of *unbranched* aliphatic nitrile complexes RCN/Fe^+. Only upon collisional activation does this reaction gain some importance with the restriction, however, that for RCN/Fe^+ the higher "alkanes" are formed in a two-step sequence (combined losses of H_2/olefin).[5d]

Most interestingly and unexpectedly, Fe^+-mediated alkane losses and in particular the generation of methane were also observed to occur *without* collisional activation for *α-branched* aliphatic nitriles of the general structure R^1R^2CHCN (R^1, R^2 = alkyl). For example, from the Fe^+

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(11) 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 **4**, deviation from linearity of the $-CH_2C{\equiv}NM^+$ unit must occur (see ref 5c for a comparison of $M^+ = Fe^+$, 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[5f] for *unsaturated* aliphatic nitriles of the general structure $CH_3(CH_2)_nCH{=}CH(CH_2)_mCN$. Data were reported which demonstrate that, depending on the separation of the CC double bond and the CN group, *bidentate* Fe^+ complexes can be formed which may contain an "end-on" ($m \geq 4$) or a "side-on" complexed CN group (m = 2, 3).

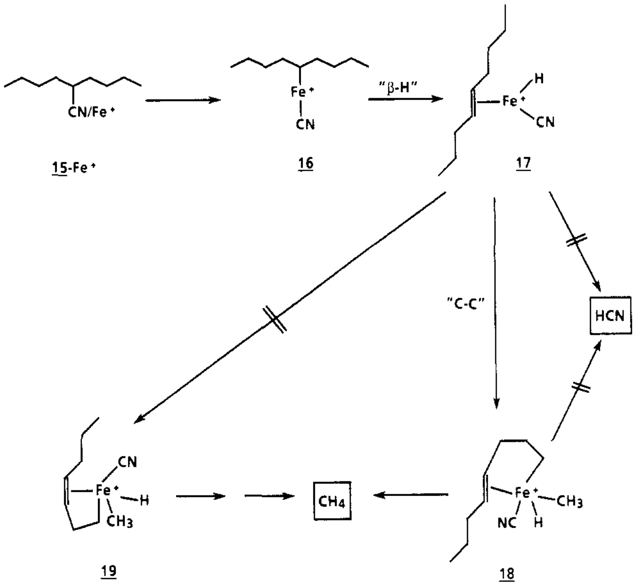
(12) Although labeling experiments clearly reveal the origin of the atoms that are involved in the multistep sequence, there is no doubt that as stated earlier by Müller,[1a] "proposed structures are very often hypothetical in mass spectrometric studies. In most cases they are based on plausibility arguments using as much direct and indirect evidence as available from experiments and model considerations. Their heuristic values are nevertheless unquestionable as long as speculations remain in acceptable limits." Moreover with regard to the detailed mechanism of the generation of RCN/Fe^+ it should be mentioned that according to FTICR studies ((a) ref 6; (b) Nibbering, N. M. M.; Schwarz, H.; de Koning, L. J.; Fokkens, R. H.; Lebrilla, C. B.; Drewello, T., unpublished results) $Fe(CO)_x^+$ ions (x = 1, 2) serve as major precursor species. However, it has to 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. One should also keep in mind that 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, for example, an CH_3CH isomer would be too costly energetically. In most cases studied, intensity problems preclude the characterization of the neutrals, cogenerated in the dissociation of metastable organometallic precursor ions, by using the otherwise powerful technique of collisionally induced dissociative ionization (CIDI). For pertinent reviews, see: (a) Wesdemiotis, C.; McLafferty, F. W. *Chem. Rev.* **1987**, *87*, 485. (b) Terlouw, J. K.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 805. (c) Holmes, J. L. *Mass Spectrom. Rev.*, in press. (d) Terlouw, J. K. *Adv. Mass Spectrom.* **1989**, *11*, 984. (e) Schwarz, H. *Pure Appl. Chem.* **1989**, *61*, 685.

(13) In solution, the direct addition of a C–C bond to a transition-metal center is only rarely observed for strained molecules.[1t] On both thermochemical and kinetic reasons, insertion of a metal center into C–C bonds cannot efficiently compete with the oxidative addition of C–H bonds.[1e,g,i,k,l,m,n,t,u] See also: Muetterties, E. L. *J. Chem. Soc. Rev.* **1983**, *11*, 283. For a clear-cut gas-phase example, demonstrating that C–C activation by M^+ can be brought about *without* C–H activation, see: Karrass, S.; Schwarz, H. *Helv. Chim. Acta* **1989**, *72*, 633.

(14) For the metal ion mediated alkane formation, in most cases reported it is not possible to distinguish between the two reaction sequences, i.e. (i) insertion of M^+ into a C–C bond followed by β-hydrogen transfer or (ii) oxidative addition of a C–H bond followed by β-alkyl migration to the metal center. Both variants generate the same intermediate from which eventually reductive elimination of RH occurs.

(15) While β-alkyl migrations are reported to exist in a few organometallic systems in solution (for example, see: Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471), they are extremely rare in the gas phase (Houriet, R.; Halle, L. F.; Beauchamp, J. L. *Organometallics* **1983**, *2*, 1818) if they exist at all: (a) ref 1v and 3c,d. (b) Eller, K.; Drewello, T.; Zummack, W.; Allspach, T.; Annen, U.; Regitz, M.; Schwarz, H. *J. Am. Chem. Soc.* **1989**, *111*, 4228.

Scheme VI



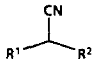
complex of **15**, in addition to H_2 and C_2H_4, CH_4 is generated under unimolecular conditions (Scheme V). Note, that in the metastable ion (MI) spectrum of the analogous *unbranched* $C_5H_{11}CN/Fe^+$ complex *no* signal is present for the loss of CH_4 (see Table I). While H_2 and C_2H_4 from **15**-Fe$^+$ are formed according to Scheme II (M = Fe), CH_4 is generated by an unprecedented reaction mechanism, which consists of the following steps: (i) insertion of Fe$^+$ into the C–CN bond;[16] (ii) β-hydrogen transfer to the metal center; (iii) oxidative addition of a remote H_3C–C bond; and (iv) reductive elimination of CH_4.

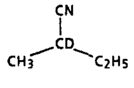
In the following, experimental results will be presented that provide evidence for this mechanistic proposal. In addition, several remarkable organometallic reactions will be described that are unique to α-branched nitriles.

Results and Discussion

The data for unimolecular methane generation from the Fe$^+$ complexes of several isotopomers of **15** are given in Table II. The analysis of this data is straightforward, and we note the following: (i) The reaction is not preceded by any hydrogen exchange processes (absence of "scrambled" $CH_{4-x}D_x$). (ii) Methane originates from an intact methyl group of one alkyl chain. The fourth hydrogen is provided by a methylene group from the *other* alkyl chain. (Specific losses of CH_4 and CD_4 from **15g** and of CH_4 and CH_3D from **15d**, respectively.) However, this corresponds only in a formal sense to a 1.5-elimination.[17] The possible operation of 1.*n*-eliminations (*n* = 1–4) of methane can be ruled out with certainty (no Fe$^+$-mediated losses of CD_4 from **15f** and of CH_3D from **15c**, **15g**, and **15e**, respectively). (iii) Kinetic isotope effects are observed. A *secondary* isotope effect of $k_H/k_D = 1.33$ is indicated by the losses of CH_4/CHD_3 from **15f**, pointing to a value of $k_H/k_D = 1.10$ per deuterium atom. From the ratio of formations of CH_4/CH_3D from **15d** one obtains a primary isotope effect of $k_H/k_D = 1.22$. Interestingly, the experimentally derived isotope effect for the generation of CH_4/CD_4 from **15g** is with $k_H/k_D = 1.63$ identical with the one predicted from the individual isotope effects associated with the Fe$^+$-mediated formations of $CH_{4-x}D_x$ from **15d** and **15f**, respectively.

Chart I





21c

	R^1	R^2
20	CH_3	CH_3
21	CH_3	C_2H_5
21a	CD_3	C_2H_5
21b	CH_3	CH_2CD_3
22	CH_3	*n*-C_4H_9
23	C_2H_5	C_2H_5
24	n-C_3H_7	n-C_3H_7
15	n-C_4H_9	n-C_4H_9
25	n-C_5H_{11}	n-C_5H_{11}
26	n-C_4H_9	n-C_6H_{13}
27	n-C_4H_9	n-$C_{10}H_{21}$
28	n-C_6H_{13}	n-C_6H_{13}
28a	n-$C_5H_{11}CD_2$	n-$C_5H_{11}CD_2$
28b	n-$CD_3C_5H_{10}$	n-$CD_3C_5H_{10}$

Table III. Metastable Ion Mass Spectra of RCN/Fe$^+$ Complexes[a]

precursor	CH_4	H_2	C_2H_4	RCH=CH_2	RH	Fe$^+$
20						100
21[b]	42	7	23	2[c]		20
22	16	73	11			
23	58	8	29			5
24	25	67	8			
15	3	85	12			
25	<1	63	28	5[c]	3[d]	
26	1	63	22	12[e]	2[f]	
27	16	22	11	43[g]	8[h]	
28	<1	47	30	18[i]	5[j]	

[a] See footnotes in Table I. [b] **21**-Fe$^+$ eliminates in addition to the neutrals given in Table III, a CH_3 radical (6%). [c] R = CH_3. [d] RH consists of R = C_2H_5 and C_3H_7 in a ratio of 5:1. [e] RCH=CH_2 consists of R = CH_3 and C_2H_5 in a ratio of 7.8:1. [f] RH consists of R = C_2H_5 and C_3H_7 in a ratio of 1.4:1. [g] RCH=CH_2 consists of R = CH_3, C_2H_5, and C_3H_7 in a ratio of 5.5:5.1:1. [h] RH consists of R = C_2H_5, C_3H_7, C_4H_9, and C_5H_{11} in a ratio of 1:1:3.6:1. [i] RCH=CH_2 consists of R = CH_3 and C_2H_5 in a ratio of 6.4:1. [j] RH consists of R = C_2H_5 and C_3H_7 in a ratio of 1.5:1.

The mechanism, depicted in Scheme VI, fully accounts for the experimental findings. Insertion of the metal ion in the C–CN bond[18] is followed by a nonreversible β-hydrogen migration (**16** → **17**). Complex **17** then activates a *remote* H_3C–C bond of the *n*-butyl chain to generate **18**.[19] The latter serves as immediate precursor for the reductive elimination of CH_4. Noteworthy are the following points: (i) Neither **17** nor **18** undergo reductive elimination of HCN. The origin for the absence of this process will be

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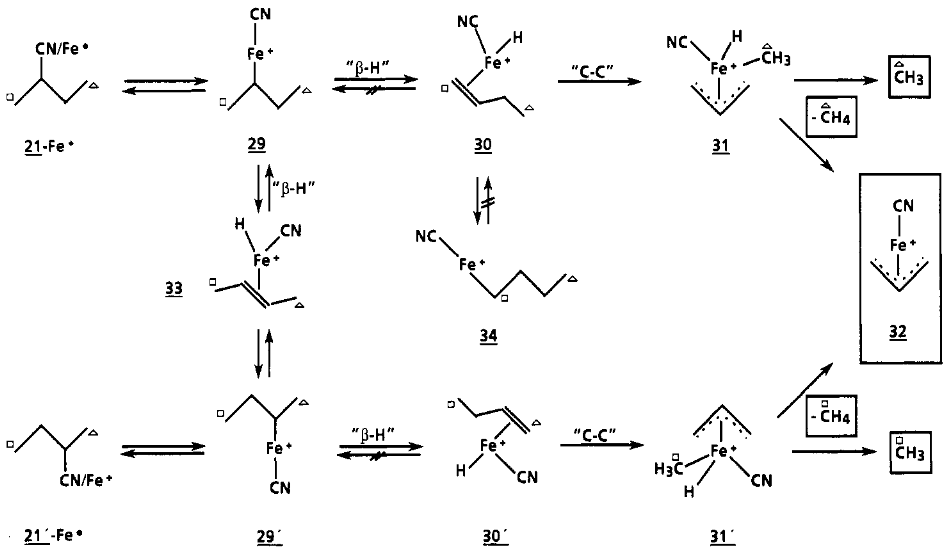
[16] Stepnowski and Allison reported recently[6] that Co$^+$, to some extent, inserts into the C–CN bond of $(CH_3)_2CHCN$. Due to the lack of appropriately labeled precursors and a limited set of model compounds investigated, no definitive mechanistic conclusions concerning the formation of alkanes could be drawn in this study.

[17] A genuine, unprecedented 1.6-demethanation across the triple bond of linear alkynes was recently described for the 4-octyne/Mn$^+$ complex.[9b,c] In contrast, Co$^+$-induced demethanation of *n*-hexane does not, as suggested in ref. 10, follow a 1.5-elimination mode resulting in the formation of a saturated cobalt metallacycle. Instead, in the original paper (Houriet, R.; Halle, L. F.; Beauchamp, J. L. *Organometallics* **1983**, *2*, 1818) the deuterium-labeling data are interpreted in terms of the conventional mechanism, i.e. a combination of C–C and C–H insertion reactions, thereby bypassing high oxidation states of Co$^+$.

[18] Note, however, that this reaction step does *not* account for the generation of C_2H_4 and H_2 from **15**-Fe$^+$. These neutrals are formed according to Scheme II (see Ref 5g).

[19] We agree with a reviewer's comment that structure **18**, with a formal oxidation state of +5 at the Fe center, is unusual. However, we do not see how the specific isotopomer distribution (Table II) can be explained otherwise. In particular, if methane loss would commence with direct insertion of Fe$^+$ into the terminal C–C bond, it is difficult, if not impossible, to explain the *specific* hydrogen transfer from the other alkyl chain. The same argument, developed here for **15**-Fe$^+$, holds true for the other branched nitriles discussed below.

Scheme VII



discussed further below. (ii) Oxidative addition of a C–CH_3 bond from the propyl chain (17 → 19) cannot compete with reaction 17 → 18. It is likely that this discrimination reflects kinetic preferences for the formation of the "metallacycle" 18 versus 19.

In order to obtain further insight into the structural limitations of the mechanism outlined in Scheme VI, the Fe^+ complexes of the branched nitriles, given in Chart I, were generated in the gas phase and their MI mass spectra recorded. Data for the unlabeled systems are given in Table III. The results obtained for **21** and its isotopomers **21a**, **21b**, and **21c** will be discussed separately.

The qualitative analysis of the data given in Table III is not too difficult. The observation that in the Fe^+ complex of $(CH_3)_2CHCN$ (**20**) no C–H and/or C–C bond activations occur (the only process observed corresponds to ligand detachment) is a direct consequence of the fact that, on structural grounds, neither of the mechanisms outlined in Schemes II, III, IV, and VI is possible for **20**.[20] In all other systems studied, C–H and C–C bond activation is observed, including the formation of CH_4. The latter is, however, formed in largely varying amounts reflecting the fact that several competing pathways are open for the various RCN/Fe^+ systems. Comparison of the data suggests that CH_4 formation is favored for $C_2H_5CH(CN)R$ (R = CH_3 (**21**) and R = C_2H_5 (**23**)). This is likely to reflect the fact that for these two systems, reactions analogous to Scheme II are slowed down on steric reasons. In contrast, when both alkyl chains are lengthened, the generations of H_2 and alkenes gain importance with the consequence that for **28** the generation of CH_4 drops to <1%. In addition, labeling experiments indicate that for the long-chain nitriles methane is formed in a formal 1.2-elimination mode ("remote functionalization") rather than according to Scheme VI. This is supported by the study of, for example, the complex **28a**-Fe^+ from which exclusively CH_4 is generated. As the initial stages of Scheme VI are still feasible for this particular system, it is conceivable that for **28**-Fe^+ the efficient formation of a metallacycle analogous to 17 → 18 (Scheme VI) is no longer favored. If one combines the labeling data for **28**-Fe^+ and **15**-Fe^+, and in particular the absence of process 17 → 19 (Scheme VI), it becomes obvious that transition-metal ion mediated demethanation of α-branched aliphatic nitriles is a process being extremely susceptible to relatively minor structural changes in the substrate.

Table IV. Metastable Ion Mass Spectra of the Fe^+ Complexes of Labeled 2-Methylbutanenitriles

	precursor		
neutral[a]	**21a**	**21b**	**21c**
H_2	65	49	>90
HD	35	51	<10
CH_3	70	10	100[b]
CD_3	30	90	...
CH_4			100
CH_3D	75	6	
CHD_3	25	94	
C_2H_4	78	6	>95
C_2H_3D			<5
$C_2H_2D_2$	13	55	
C_2HD_3	9	39	
C_3H_6		*b*	
C_3H_5D		*b*	
$C_3H_4D_2$	27		47
$C_3H_3D_3$	73		53

[a] The isotopomer distributions are normalized to each class of neutrals = 100%. [b] Signal-to-noise ratio not sufficient for exact determinations.

This will become even more evident in the analysis of the metastable ion spectra of **21**-Fe^+ and the complexes of the isotopomers **21a–c**.

The discussion of this system consists of three sections which aims at explaining how neutral methane, ethylene, hydrogen, and a methyl radical are formed from metastable **21**-Fe^+.

The minor production of propene (2%) remains a mystery for the time being as we are unable to propose a mechanism, which would account for *all* experimental findings. Further labeling studies could possibly provide a solution to this puzzle.

(i) Generation of Methane. As indicated by the labeling experiments (Table IV), the methane molecule

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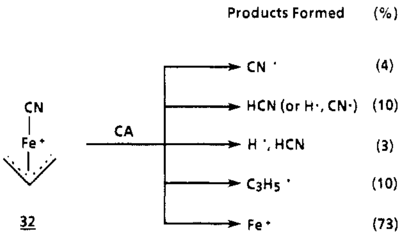
[20] As stated by a reviewer, the nonreactivity of $(CH_3)_2CHCN$ (**20**) with Fe^+ is surprising in view of the fact that CH/CC bond activation by Fe^+ is seen from propane. One possibility is that **20** is exclusively complexed at the lone pair of the nitrogen atom ("end-on"), thus generating a species which is unable, on geometric grounds, to permit the "anchored" Fe^+ to insert into CH/CC bonds; as a consequence, the complex can only revert to its components; i.e., ligand detachment occurs as observed experimentally. Alternatively, one may wonder whether in **20** Fe^+ inserts into the C–CN bond, and the so-formed intermediate is, for whatever reasons, not capable of further reacting, e.g. according to Scheme I. Unfortunately, no reliable data are available that would permit a useful thermochemical comparison for the probabilities of the competing insertion processes.

Scheme VIII



originates from both methyl groups of the two alkyl chains of **21**. While hydrogen scrambling can be ruled out, the data leave no doubt that the direct route (Scheme VII) **21**-Fe$^+$ → **29** → **30** → **31** → **32** is, to some extent, accompanied and/or preceded by a degenerate isomerization of the initial insertion product, e.g. **29** ⇄ **33** ⇄ **29′** (triangles and squares are used in Scheme VII to "label" the original methyl groups of the starting nitrile). The absence of CH_2D_2 loss in the MI spectra of **21a**-Fe$^+$ and **21b**-Fe$^+$ rules out that the step **29** (**29′**) → **30** (**30′**) is reversible. Similarly, the exclusive generation of CH_4 from **21c**-Fe$^+$ requires that, if **34** is formed from **30** at all, the reverse reaction **34** → **30** is not operative on the time scale of the Fe$^+$-mediated methane formation from **21**.

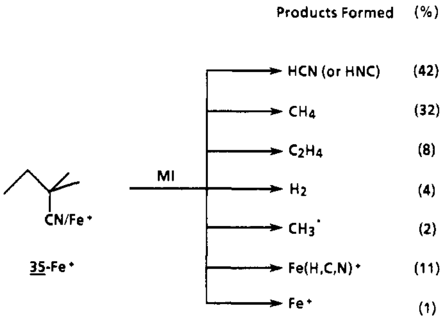
In order to further support the suggestion that methane loss from **21**-Fe$^+$ gives rise to a cyano allyl Fe$^+$ complex, **32**, a collisional activation (CA) experiment on this mass-selected ion (for details see Experimental Section) was conducted. If **32** is indeed generated from **21**-Fe$^+$, one would expect that this species, upon CA, would split off CN$^\bullet$ and $C_3H_5^\bullet$. As shown in Scheme VIII, these two structure-indicative reactions are indeed observed. In addition, loss of HCN (or a combination of H$^\bullet$ and CN$^\bullet$) as well as the combined losses of CN$^\bullet$/$C_3H_5^\bullet$ take place.

(ii) Generation of Ethylene and Molecular Hydrogen. The fact that both C_2H_4 and $C_2H_2D_2$ are formed from the Fe$^+$ complexes of **21a** and **21b** (Table IV) are, again, compatible with a partial (<20%) degenerate isomerization, **21** ⇄ **29** ⇄ **33** ⇄ **29′** ⇄ **21′**. The actual ethylene loss, we presume, proceeds via the mechanism outlined in Scheme II ("remote functionalization"). However, in addition, the production of C_2HD_3 from both isotopomers requires hydrogen exchange processes prior to the ligand detachment. From the ratio 1.4:1 for the losses of $C_2H_2D_2/C_2HD_3$ from **21a** and **21b** one can conclude that the hydrogen exchange is nearly complete. Ignoring isotope effects, one would predict for a "$C_2D_3H_2$" system a ratio of 1.5:1 for the competitive production of $C_2H_2D_2$ and C_2HD_3.[21]

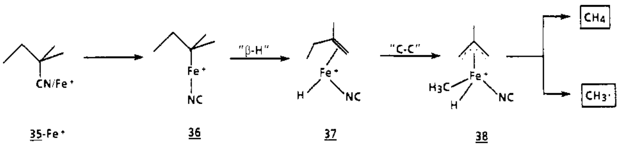
The degenerate isomerization **21** ⇄ **21′**, followed by "remote functionalization", is also indicated by the observation that the hydrogen molecule originates from both the methyl and ethyl side chains (Table IV).

(iii) Generation of a Methyl Radical. Transition-metal ions do only rarely mediate the formation of alkyl *radicals* from organometallic complexes in the gas phase.[1,2] This holds also true for the nitriles studied so far[5] with the exception of $CH_3CH(CN)C_2H_5$ (**21**). As shown in Table III, from the complex **21**-Fe$^+$ the radical $CH_3^\bullet$ is generated unimolecularly (6%), and the study of the isotopomers **21a**, **21b**, and **21c** reveals that the methyl radical originates from either alkyl chain. Hydrogen exchange processes are not preceding or accompanying the expulsion of the radical. Out of the many conceivable mechanistic variants, we prefer the process described in Scheme VII.[22]

Scheme IX



Scheme X



The next Fe$^+$ complex of α-branched nitriles to be discussed is **35**-Fe$^+$. Its major[23] unimolecular reactions are given in Scheme IX. In the present context we shall confine the discussion to the formations of CH_4, $CH_3^\bullet$, C_2H_4, HCN, and Fe(HCN)$^+$, respectively. The mechanistic proposals are based on the investigation of the isotopomers $C_2H_5C(CD_3)_2CN$ (**35a**) and $CH_3CD_2C(CH_3)_2CN$ (**35b**).

(iv) Generation of Methane and of a Methyl Radical. The fact that from **35a**-Fe$^+$ only CH_3D and from **35b**-Fe$^+$ only CH_4 are generated suggests that methane is formed in a highly specific fashion; the mechanism, suggested in Scheme X, is in full accord with the experimental findings. The methyl radical liberated from **35**-Fe$^+$ originates specifically from the ethyl group (exclusive loss of $CH_3^\bullet$) from either **35a**-Fe$^+$ and **35b**-Fe$^+$. Intermediate **38** (Scheme X) may well account for this finding.

(v) Loss of HCN and Formation of (HCN)Fe$^+$. In contrast to **15** and **21**, from **35**-Fe$^+$ the formation of these two products is observed. Obviously, the production of the two species is linked to each other as (HCN)Fe$^+$ is due to loss of C_5H_{10} from **35**-Fe$^+$ while elimination of HCN[24] gives rise to a Fe(C_5H_{10})$^+$ complex. A mechanism that involves a common intermediate of the type (HCN)-

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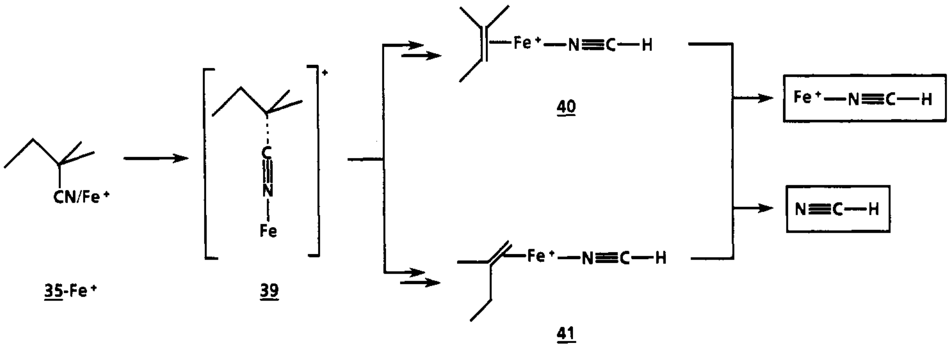
[21] The partial hydrogen scrambling, associated with loss of ethylene (but *not* of methane and hydrogen), is best explained by assuming that the hydrido ethylene complex (analogous to **6** in Scheme II) is in equilibrium with an ethyl structure. Reversible reactions of the type **4** ⇄ **5** ⇄ **6** can be excluded, as neither loss of D_2 nor "scrambled" $CH_{4-x}D_x$ products are observed. It should be noted that this phenomenon is not restricted to **21** as ethylene loss from the unbranched C_4-nitrile complex $CH_3CH_2CH_2CN$/Fe$^+$ shows practically the same behavior as **21**-Fe$^+$ with regard to the scrambling. For example, from $CD_3CH_2CH_2CN$/Fe$^+$ both $C_2H_2D_2$ and C_2HD_3 are eliminated in a ratio 1.5:1. Also, a similar result is obtained for $CH_3CH_2C(CH_3)_2CN$ (**35**) (see below).

[22] A reviewer has suggested that Fe$^+$-induced loss of $CH_3^\bullet$, which is indeed a quite rare process in organometallic systems, reflects that complex **21**-Fe$^+$ is formed with a significant amount of internal energy. We doubt this on the following grounds: (i) The complexes are formed under multiple-collision conditions in a chemical ionization source. Thus, excess energy possibly gained in the complex formation is carried off by the "buffer" gas. (ii) Recently, we were able to demonstrate that exactly the same data are obtained if **21**-Fe$^+$ (and its isotopomers) is formed and studied under FTICR conditions. ((a) Eller, K.; Schwarz, H. *Int. J. Mass Spectrom. Ion Proc.* in press. (b) Eller, K.; Zummack, W.; Schwarz, H. *J. Am. Chem. Soc.*, submitted for publication.) Thus, we believe that $CH_3^\bullet$ loss from **21**-Fe$^+$ reflects the particular properties of the intermediate **31** (see also further below).

[23] Minor fragments (<1%) are due to the eliminations of 43 and 55 amu; on the basis of the labeling experiments, for the time being no meaningful structural assignments are possible.

[24] The alternative that Δ*m* = 27 corresponds to HNC rather than HCN cannot rigorously be ruled out; on thermochemical grounds, the generation of HCN is, however, more favored by >10 kcal/mol: Koch, W.; Frenking, G.; Schwarz, H. *Naturwissenschaften* **1984**, *71*, 473 and references therein.

Scheme XI



$Fe^+(C_5H_{10})$ is further supported by the results obtained from **35a** and **35b**. From both isotopomers HCN and DCN are generated as well as the corresponding complexes $(HCN)Fe^+$ and $(DCN)Fe^+$. While no exact data can be given for the loss of HCN/DCN,[25] we note a ratio for $(HCN)Fe^+$ vs $(DCN)Fe^+$ of 1.6:1 (**35a**) and 1.3:1 (**35b**) which is quite close to the estimated values for HCN vs DCN. While it is tempting to explain the formation of these two products with the common insertion/β-hydrogen-shift mechanism (Scheme I), the very similar case of the t-C_4H_9CN/Fe^+ complex provides evidence against this assumption. It was possible to demonstrate[26a] the operation of an ion/dipole mechanism[27] where initial "end-on" complexation of the metal ion to the nitrile function induces cleavage of the C–CN bond (Scheme XI, **35**-Fe^+ → **39**). The incipient C_5H_{11} unit then serves as a protonating reagent for the CNFe dipole. This mechanistic conclusion was gained by (i) comparison of RCN/Fe^+ with the corresponding RNC/Fe^+ complexes (the former give rise to $HCN{-}Fe^+$ and the latter to $HNC{-}Fe^+$ ions) and (ii) structural assignment of the last two ions using high-energy collisional activation mass spectrometry. It shall only be mentioned here that both complexes can be distinguished by a structure-indicative signal for FeN^+ that arises from $HCN{-}Fe^+$ and that is absent in the spectra for $HNC{-}Fe^+$.[26a] In fact, similar mechanisms and other $HCN{-}M^+$ complexes were recently obtained in the reactions of Cu^+,[26b] Co^+,[26c] and Ni^+,[26c] with other α-branched nitriles. High-energy collisional activation on the $Fe(H,C,N)^+$ ions generated from **35**-Fe^+ also indicates the $HCN{-}Fe^+$ structure. Further evidence for an ion/dipole mechanism is gained by the labeling distribution observed for **35a** and **35b**. If an intermediate C_5H_{11} "carbenium-like ion" takes part in the reaction, hydrogen exchange processes should be fast and contributions from several C–H positions are expected; i.e., **39** → **40** and **39** → **41**. Indeed, this is experimentally verified. From the so-formed diligated complexes, HCN and C_5H_{10} are formed in competition, presumably reflecting their different binding energies to the metal ion. Interestingly, for Fe^+ complexes of nitriles, the presently available data[26] require an α,α-disubstituted nitrile, while for transition-metal ions having higher Lewis acid character, viz. Co^+, Ni^+, and Cu^+, the ion/dipole mechanism is already operative with *α-monosubstituted* nitriles. This finding may well account for the absence of HCN and $HCN{-}Fe^+$ in the spectra of **15**-Fe^+ and **21**-Fe^+. In addition, this interpretation strongly suggests that reductive elimination of HCN from the general structure $LFe^+(H)CN$ is not a favored process (L = ligand).

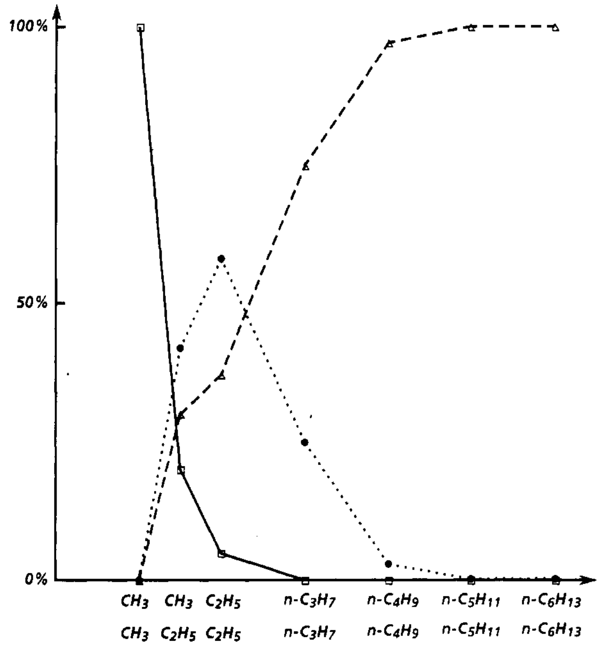


Figure 1. Neutrals generated from α-branched Fe^+ complexes. R^1R^2CHCN: —, ligand detachment; - - -, neutrals generated via remote functionalization; ···, Loss of CH_4 due to initial insertion of Fe^+ into the C–CN bond.

(vi) Generation of Ethylene. In the formation of ethylene the two α-methyl groups of **35** are not involved; this is clearly evident by the fact that in the MI spectrum of **35a**-Fe^+ no signals due to losses of 29 or 30 amu are present. However, in analogy to its lower homologue **21**-Fe^+, the ethyl group from which ethylene is eventually formed undergoes partial equilibration of the hydrogen atoms. This is evident by the fact that from **35b**-Fe^+ the neutrals $C_2H_2D_2$ and C_2H_3D are formed in competition (2:1). Note, however, that the degenerate isomerization that prevails to some extent in the gas-phase chemistry of $CH_3CH(CN)C_2H_5/Fe^+$ (**21**-Fe^+) is absent in the homologous $(CH_3)_2C(CN)C_2H_5/Fe^+$ (**35**-Fe^+) system.

In conclusion, the present results demonstrate for the first time that the C–CN bond of *α-branched* nitriles is

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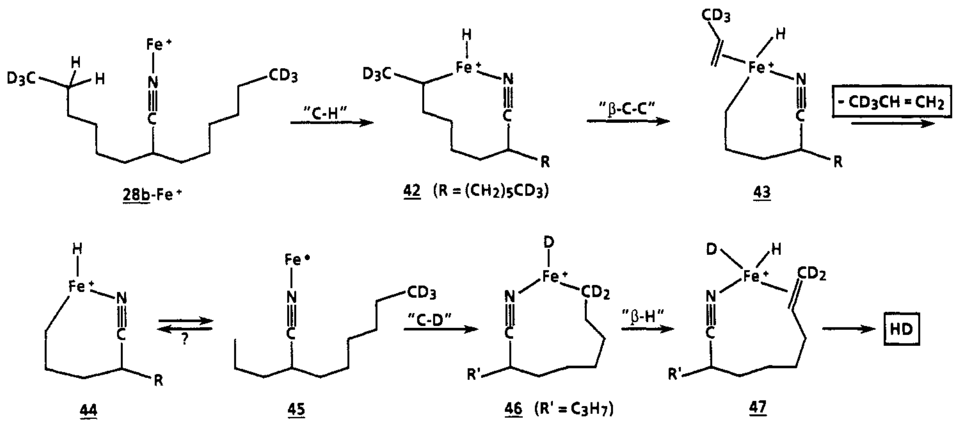
(25) Due to the presence of the isobaric "C_2H_4 loss" peak and the limited daughter ion resolution in the MI experiment, no quantitative analysis is possible to separate the C_2H_4/DCN doublet. However, a comparison of the "27/28 losses" for the unlabeled precursor **35**-Fe^+ with its isotopomer complexes **35a**-Fe^+ and **35b**-Fe^+ indicates that HCN/DCN is formed in approximate ratios 1.8:1 from **35a**-Fe^+ and 1.2:1 from **35b**-Fe^+, respectively.

(26) (a) Eller, K.; Schwarz, H. *Organometallics*, in press. (b) Eller, K.; Sülzle, D.; Schwarz, H. *Chem. Phys. Lett.* **1989**, *154*, 443. (c) Eller, K.; Zummack, W.; Schwarz, H. *J. Am. Chem. Soc.*, submitted for publication.

(27) There is considerable precedent for ion/(induced) dipole complexes as intermediates in unimolecular reactions of gaseous cations. For pertinent reviews, see: (a) Morton, T. H. *Tetrahedron* **1982**, *38*, 3195. (b) McAdoo, D. J. *Mass. Spectrom. Rev.* **1988**, *7*, 363. (c) Heinrich, N.; Schwarz, H. In *Ion and Cluster Ion Spectroscopy and Structure*: Maier, J. P., Ed.; Elsevier, Amsterdam, 1989; p 329. (d) Heinrich, N.; Louage, F.; Lifshitz, C.; Schwarz, H. *J. Am. Chem. Soc.* **1988**, *110*, 8183 and references cited therein. (e) Hammerum, S. *J. Chem. Soc., Chem. Commun.* **1988**, 858.

Scheme XII



indeed susceptible to "direct"[28] insertion of a transition-metal ion. The so-formed intermediate serves as a branching point for many remarkable processes, the mechanistic details of which can only be unravelled by the study of labeled model compounds. The data reported here further indicate that the probability of this direct activation of a C–C bond is strongly dependent upon structural features of the nitriles studied. If the alkyl chain is large enough to permit "remote functionalization" of C–H bonds (Schemes II and III),[5,6] these reactions control the fate of RCN/Fe^+. As a consequence, the metal ion mediated generation of, for example, CH_4, is greatly diminished. This is clearly exhibited by the data given in Figure 1.

In the concluding section we return to the concept of "remote functionalization" and we shall briefly describe that Fe^+ may even be capable of *activating both alkyl chains of α-branched nitriles in a consecutive manner.* As shown in Table III, the metastable ion of **28**-Fe^+ generates inter alia neutrals that can be ascribed to C_2H_6 and C_3H_8. There exist two pertinent questions related to the formation of these species: (i) Do the neutrals correspond to genuinely formed alkanes C_nH_{2n+2}, or are the mass differences due to the combined productions of C_nH_{2n}/H_2? (ii) If the latter applies, are both species formed from the same alkyl chain, as is the case for the collision-induced losses from unbranched RCN/Fe^+ complexes,[5d] or do the neutral fragments originate from both alkyl chains?

The experimental findings are unambiguous in favor of the second alternative. This is evidenced by the study of the Fe^+ complex of $(CD_3(CH_2)_5)_2CHCN$ (**28b**). If ethane and propane would be generated according to the established[5d,14] pathway, the metastable ion of **28b**-Fe^+ should undergo losses of CD_3CH_3 ($\Delta m = 33$) and $CD_3CH_2CH_3$ ($\Delta m = 47$). These two mass differences are not observed; rather one finds $\Delta m = 33$ and $\Delta m = 48$. Moreover, if one selects the $[M - 28]^+$ and $[M - 42]^+$ species unimolecularly generated from **28**-Fe^+ and studies their MI mass spectra, the *only* product formed corresponds to the production of H_2. While the latter experiment leaves no doubt that actually no alkanes but rather alkenes *and* hydrogen are formed,[29] the labeling experiment proves for the "C_3"-neutral (and, by analogy, the same is presumed for the "C_2"-neutral) that *both* alkyl chains are involved in the metal ion mediated C–H and C–C bond activation reactions. For the formation of "$C_3H_4D_4$" a likely mechanism is depicted in Scheme XII. To the best of our knowledge, this result demonstrates for the first time that an *"anchored" transition-metal ion is capable of consecutively activating different sites of a flexible molecule.*[31]

Experimental Section

The experimental setup has been described in earlier papers.[1v,2,5,7,9,10,15b,26] Briefly, Fe^+ is generated from $Fe(CO)_5$ by electron-impact ionization (100 eV). A VG Instruments ZAB-HF-3F triple-sector mass spectrometer with a B(1)EB(2) configuration was used for the analysis (B stands for magnetic and E for electrostatic sector). The machine and its operation have been described elsewhere.[30] In a typical experiment $Fe(CO)_5$ and the nitrile of interest were introduced in an approximate 1:3–5 ratio in a chemical ionization source (repeller 0 V) and bombarded with an electron beam of 100 eV. Organometallic ions corresponding to RCN/Fe^+ having 8-keV kinetic energy are mass selected and focused with B(1)E.[12] Unimolecular reactions occuring in the field-free region between E and B(2) were recorded by scanning B(2). The MS/MS/MS experiment, which forms the basis for Scheme VIII, was conducted in the following way: Complex **21**-Fe^+ was mass selected by means of B(1), the product due to metastable loss of CH_4 in the field-free region between B(1) and E was "isolated" by using E, and collisional activation (collision gas helium; primary beam attenuation ca. 20%) of this species was brought about in the next field-free region; fragment ions were recorded by scanning B(2). An analogous multistage experiment (however, without collision gas) was performed to probe the multistep decomposition of **28**-Fe^+. In all experiments described here, the signal-to-noise-ratio was significantly improved by using signal-averaging techniques employing the VG 11/250 data system.

All compounds were synthesized by established laboratory procedures; they were purified by chromatographic means and fully characterized by standard spectroscopic methods.

Acknowledgment. We appreciate the continuous financial support of our work by the Stiftung Volkswagenwerk, the Fonds der Chemischen Industrie, and the Gesellschaft von Freunden der Technischen Universität Berlin. We are indebted to Daniel Krüerke for his assistance in the synthesis of labeled precursors and to the reviewers for helpful comments.

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(28) The exact "timing" of this oxidative addition, including the possibility that a "side-on" complexed species precedes the actual insertion, remains open to speculation.

(29) The reverse sequence, i.e. loss of H_2 followed by elimination of $RCH{=}CH_2$, does *not* contribute to the formation of "alkanes". This is evidenced by studying the $[M - 2]^+$ species formed from **28**-Fe^+; no alkene signals are observed in this spectrum.

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

(31) Very recently, an analogous behavior was reported for Fe^+ complexes of ketones: Czekay, G.; Eller, K.; Schröder, O.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.*, in press.