Is the Fe^+-Induced C–H/C–C Bond Activation of α,ω-Alkanedinitriles Affected by Bifunctional Interactions?

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The metastable-ion mass spectra of Fe^+ complexes of alkanedinitriles $NC(CH_2)_nCN$ (n = 1–10) exhibit six types of reactions: (1) Loss of the intact ligand to regenerate bare Fe^+ as the exclusive (n = 1) or major reaction (n = 2) for the lower homologues; (2) generation of nitriles $H(CH_2)_mCN$ with m = 0–6; (3) formation of unsaturated nitriles $CH_2=CH(CH_2)_mCN$ with m = 0–4; (4) production of C_2H_4; (5) dehydrogenation, and (6) expulsion of the radicals $C_2H_5^{\bullet}$ and $CH_2CN^{\bullet}$. The branching ratios of these competing processes are governed by the chain length $(CH_2)_n$ separating the two CN groups. Mechanistic insight is provided by the study of isotopomers. A comparison of the present data with the previously described behaviour of RCN/Fe^+ complexes (R = alkyl) leaves no doubt that for the α,ω-alkanedinitriles it is the Fe^+-mediated interaction of the two functional groups which controls the gas-phase chemistry of these organometallic systems. For example, results are presented demonstrating inter alia that losses of H_2 and C_2H_4 proceed by completely different pathways when dinitriles serve as precursors, and either reaction is affected by neighbouring group participation. In distinct contrast, for RCN/Fe^+ complexes (R = alkyl) the existing data point to common intermediates.

The activation of C–H and C–C bonds of hydrocarbons by transition-metal complexes is of fundamental importance in catalysis and has attracted considerable attention[2]. Of particular interest are gas-phase experiments with completely "naked" and/or partially ligated transition-metal ions M^+ as they offer a unique opportunity to probe, in the absence of any solvation, ion pairing, and/or ligand effects, the intrinsic properties of reactive organometallic species and the potential role these remarkable transients play in the initial steps of the activation of C–H and C–C bonds. While the last decade has witnessed an ever increasing number of studies of reactions of *bare* transition-metal ions M^+ with alkanes and mono-functional organic substrates in the gas phase[3], analogous investigations of *multifunctional* molecules are comparatively scarce. This neglect is quite surprising in view of the fact that already in one of the earlier papers[4] published on the subject of gas-phase organometallic chemistry highly interesting directional effects were reported. It was observed, inter alia, that Co^+ induces an unusual combined loss of C_2H_5X/H_2 (X = F, Cl, Br) from 4-halo-1-butanols in the gas phase. This reaction, which is absent for the monofunctional compounds, was explained in terms of a substituent-directed insertion of the bis-complexed metal ion into the central C–C bond; from the intermediate $XCH_2CH_2-Co^+-CH_2CH_2OH$ formed, C_2H_5X is generated by β-hydrogen transfer followed by reductive elimination.

Directional effects were also invoked to explain the Fe^+-mediated, site-specific elimination of C_2H_4 from the intact internal C-4/C-5 positions of 1,7-octadiene[5], and the mechanism of the metal-ion dependent propene loss from the same precursor is, to some extent, also caused by the interaction of the two carbon-carbon double bonds[6].

A unique reactivity was also recently reported[7] for the gas-phase chemistry of Fe^+ complexes of ω-silyl-substituted alkanenitriles. In contrast to the Fe^+ chemistry of the monofunctional carbon analogues[8], due to a metal-ion-mediated cooperation of the $SiCH_3$ *and* the CN group a *regiospecific* activation of C–H bonds takes place.

Cooperative effects were also found to play a key role in the chain-length-dependent ligand effects on the direction of Fe^+-mediated activation and cleavage of C–C bonds in alkenenitriles of the general structure $CH_3(CH_2)_nCH=CH(CH_2)_mCN$[9]. For m = 2, 3 the data suggest a bidentate complex in which both the carbon-carbon double bond and the nitrile triple bond act as π donors; however, for larger chain lenghts ($m \geqslant 4$) the bidentate Fe^+ complex is better explained by an "end-on" complexation of the CN group to the metal ion which still interacts with the CC double bond. Obviously, the actual nature of bidentate complexation, i.e. the question of "side-on" versus "end-on" complexation of the nitrile group, is dependent upon the chain lenght $(CH_2)_m$. However, for either type of coordination it is always the "exocyclic" allylic CC bonds of the metallacycles which is eventually cleaved. Only for systems in which the two functional groups are separated by one or no CH_2 unit, the Fe^+ does not "feel" the presence of the double bond. For these systems (m = 0, 1) the gas-phase chemistry is practically identical with that of the previously described saturated alkanenitriles[10] for which "end-on" complexation induces functionalization of remote C–H and C–C bonds (Scheme 1).

These few examples may suffice to illustrate the potentially rich chemistry of difunctional molecules when they react with bare transition-metal ions in the gas phase. In the present publication we focus on the chemistry of metastable Fe^+ complexes of α,ω-alkanedinitriles, $NC(CH_2)_nCN$ (n = 1-10). In addition to some familiar reactions, results are presented which point to specific processes brought about by the presence of the two CN groups. The interpretation is significantly aided by studying a set of selected isotopomers of the dinitriles.

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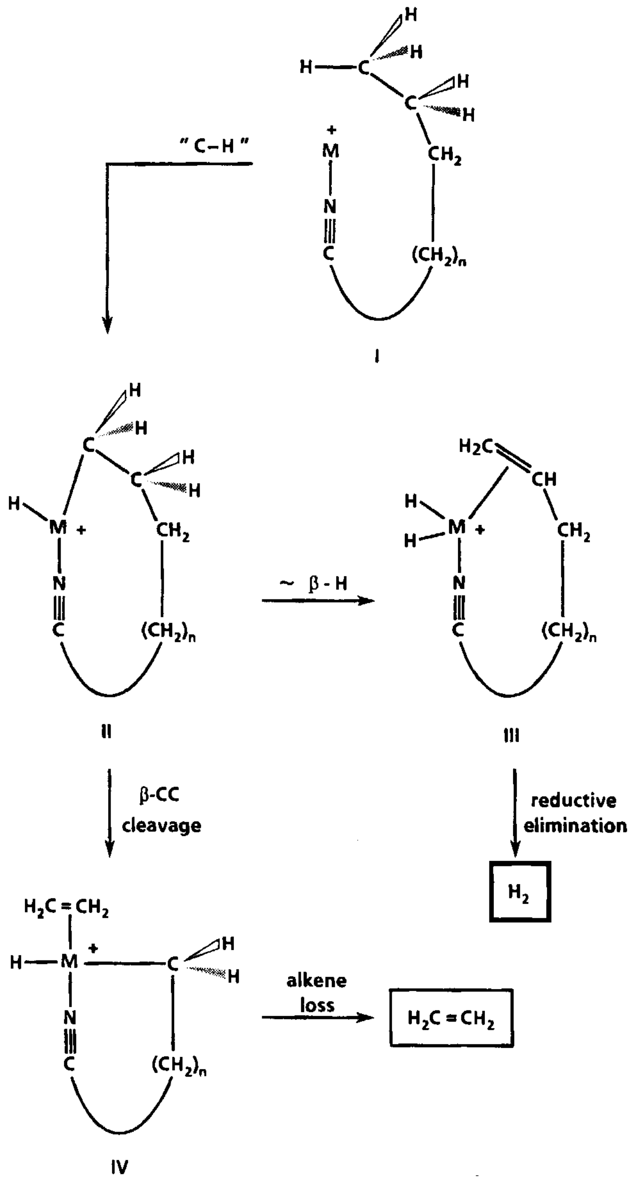
Scheme 1



Results and Discussion

In Table 1 the data for the MI mass spectra of the $NC(CH_2)_nCN/Fe^+$ complexes (n = 1–10) are given. The analysis of these data, together with the results of the labeling experiments (see below), is relatively straightforward.

We note six major types of reactions, which will be discussed separately. As is obvious from Table 1, the relative importance of these competing processes is extremely dependent on the chain length separating the two CN functions:

(1) Loss of the complete dinitrile ligand L to regenerate bare Fe^+;

(2) Generation of nitriles $H(CH_2)_mCN$, m = 0–6 (Δm = 27, 41, etc.);

(3) Formation of unsaturated nitriles $CH_2=CH(CH_2)_mCN$, m = 0–4 (Δm = 53, 67, etc.);

(4) Production of C_2H_4 (Δm = 28);

(5) Dehydrogenation (Δm = 2);

(6) Expulsion of the radicals $C_2H_5^{\bullet}$ (Δm = 29) and $^{\bullet}CH_2CN$ (Δm = 40).

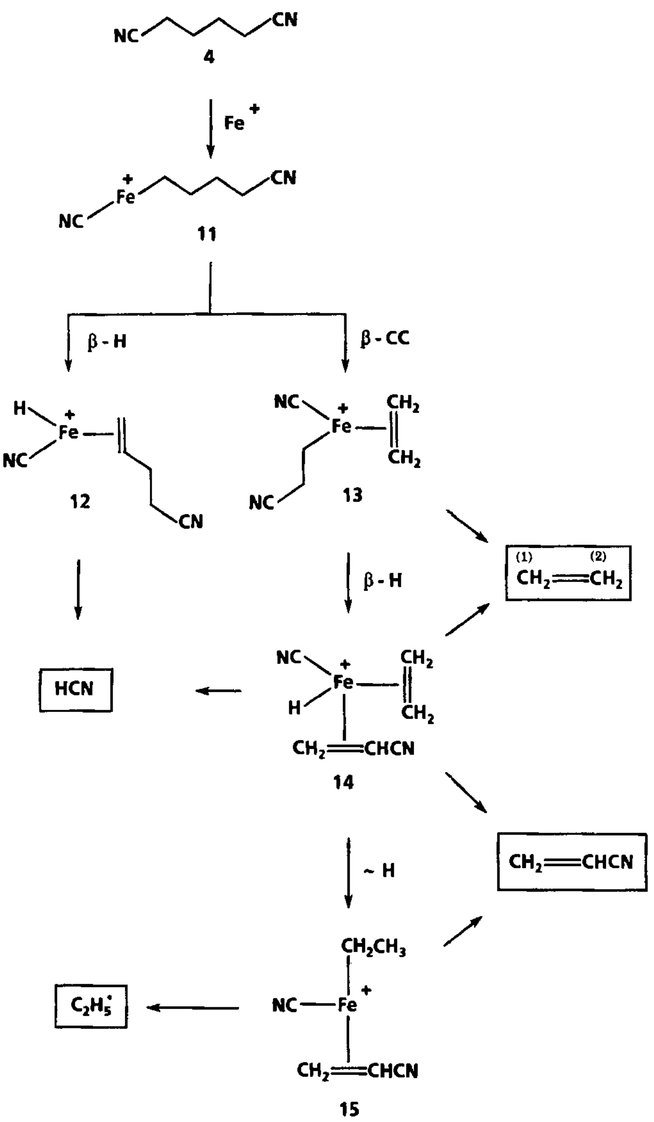
Ligand Loss, Generation of $H(CH_2)_mCN$ *and of* $CH_2=CH(CH_2)_mCN$: The elimination of the complete dinitrile ligand forms the major reaction channel for the lower dinitrile homologues **1** and **2**; in fact, for the complex $NCCH_2CN-Fe^+$ it constitutes the exclusive reaction. Possibly, the "anchored" Fe^+ is not capable (perhaps on geometric grounds) to insert into C–H/C–C bonds. Alternatively, one may argue that an insertion intermediate $NCCH_2-Fe^+-CN$ is, for whatever reasons, unable of further reaction. For the next higher homologue $NC(CH_2)_2CN$ (**2**) ligand loss from its complex **2**–Fe^+ is still the major reaction (92%); however, we also note loss of HCN (Δm = 27), which requests activation of the C–CN bond. This result is quite surprising in view of earlier studies[10l] which provided evidence that alkanenitriles do not undergo this reaction except for those substrates bearing alkyl substituents at the α-position[13]. HCN loss is also observed, with chain-lenght dependent abundancies, for the higher homologues, and the study of several labeled isotopomers reveals some interesting mechanistic details reflecting the effects exerted by both the chain length $(CH_2)_n$ and the presence of the second CN group. Basically, HCN loss may be described in terms of the sequence depicted in Scheme 2 for n = 4, i.e. insertion of the Fe^+ into the C–CN bond (**4** → **11**)[14] is followed by β-hydrogen transfer (**11** → **12**) and terminated by reductive elinination. This suggestion is, for example,

Table 1. Metastable-ion mass spectra of the Fe^+ complexes of α,ω-alkanedinitriles **1**–**10**[a)]

$NC(CH_2)_nCN/Fe^+$ n		Δm of "neutrals" 2	27	28	29	40	41	43	53	55	67	69	81	83	95	97	109	111	Ligand
1	**1**																		100
2	**2**		8																92
3	**3**		4	71			13		7										5
4	**4**		16	45	11	8	13		2	1	3								1
5	**5**		21	1		7	70		1										
6	**6**	9	16	22		16	36		1										
7	**7**	17	13	21		12	28	b)		1	1	6							
8	**8**	51	6	9	<1	2	9	2	c)	1	1	6	4	5					
9	**9**	47	8	8			7	3				8	3	13	1	2			
10	**10**	41	5	1			3					9		27	1	9	2	2	

a) Intensities are given in Σ fragment = 100%. — b) Δm = 45 with 1%. — c) Δm = 42 (1%), 59 (2%).

Scheme 2



substantiated by the loss of HCN from the Fe$^+$ complexes of NCCD$_2$CH$_2$CD$_2$CN (**3a**-Fe$^+$) and of NCCD$_2$CH$_2$-CH$_2$CD$_2$CN (**4a**-Fe$^+$), respectively, and of DCN from NCCH$_2$CD$_2$CD$_2$CH$_2$CN (**4b**-Fe$^+$). However, loss of HCN from **4b**-Fe$^+$ and of DCN from **4a**-Fe$^+$ point to the operation of a mechanistic variant for the higher homologues. This alternative owes its existence to the fact that β-hydrogen transfer **11** → **12** competes with β-cleavage of a C–C bond **11** → **13**. The intermediate **13**, again, has an option for β-hydrogen transfer **13** → **14** with the consequence that the hydrogen atom of HCN is now provided by the C-2 and C-4 methylene groups of **4**. If one neglects the possible operation of kinetic isotope effects, the labeling data (Table 2) suggest that the direct route **11** → **12** → HCN and the multistep sequence via **14** contributes each to ca. 50% to the product.

Oxidative addition of the NC–C bond is not the only mode of C–C bond activation. The product distribution as well as the labeling results leave no doubt that insertion into the NCCH$_2$–CH$_2$ bond (Scheme 3: **4** → **16**) also takes place.

Table 2. Isotope distributions of neutrals "Δ*m*" in the MI mass spectra of Fe$^+$ complexes of isotopomers **4a**–**4d**[a]: NCCD$_2$(CH$_2$)$_2$CD$_2$CN (**4a**), NCCH$_2$(CD$_2$)$_2$CH$_2$CN (**4b**), N^{13}C(CH$_2$)$_4$^{13}CN (**4c**), and N^{13}CCH$_2$(CD$_2$)$_2$CH$_2$^{13}CN (**4d**)

	Δ*m*	**4a**	**4b**	**4c**	**4d**
"HCN, C_2H_4, $C_2H_5^{\bullet}$"	27	18	8		
	28	57	9	83	9
	29			17	9
	30	15	15		16
	31		21		19
	32	10	47		47
"$CH_2CN^{\bullet}$"	40		100		
	41			100	100
	42	100			
"CH_3CN"	42		100	100	
	43	100			100
"$H_2C=CHCN$"	54	100		100	
	55		100		
	56				100
"CH_3CH_2CN"	56			100	
	57		100		
	58	100			100
"$H_2C=CHCH_2CN$"	68			100	
	69	100			
	70		100		
	71				100

[a] Intensities are expressed in Σ fragments = 100% for each class of neutrals, except for "HCN, C_2H_4, C_2H_5". For **4a** and **4c** the isobaric nature of the multiplet at Δ*m* = 28 cannot be resolved.

Complex **16** serves, as indicated in Scheme 3, as a branching point for several processes. In the present context, the β-hydrogen (**16** → **17**) and β-C–C cleavage (**16** → **18**) are of interest. The former gives rise to reductive elimination of CH$_3$CN (Δ*m* = 41); the latter represents a pathway to eliminate C$_2$H$_4$ from *internal* positions. This reaction will be discussed together with C$_2$H$_4$ loss from **13** (or **14**) in an extra section further below.

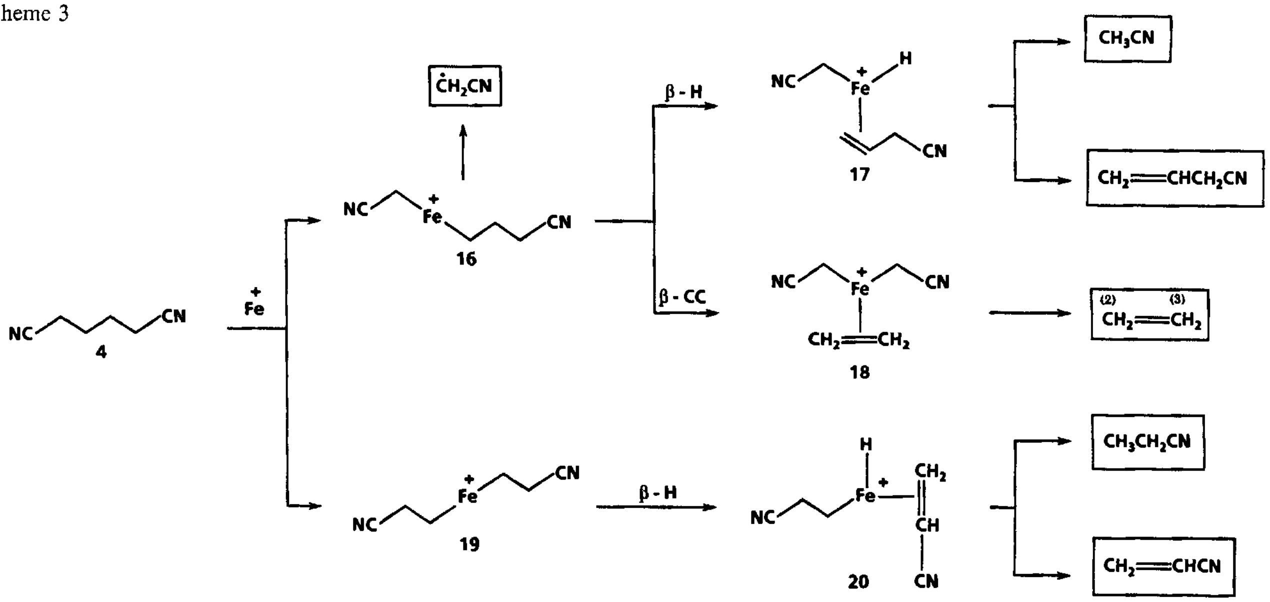
The formation of CH$_3$CH$_2$CN (Δ*m* = 55) from **4** and the isotope distribution request a further mode of C–C insertion, which commences with oxidative addition of the central C–C bond (**14** → **19**) followed by β-hydrogen transfer (**19** → **20**) and reductive elimination of CH$_3$CH$_2$CN.

For the generation of both HCN and CH$_3$CN we note a striking dependence on the chain length (CH$_2$)*n* such that either reaction passes through a maximum (*n* = 5 for loss of HCN and CH$_3$CN). This may well point to a chelation of the metal ion by the second CN group, the feasibility of which is, of course, affected by the chain length. As a consequence, competing processes which do not profit from this anchimeric assistance, like the C$_2$H$_4$ loss, will be diminished in importance.

Conversely, for the short-chain analogues like **3** C$_2$H$_4$ loss is favoured in comparison to the generation of HCN, CH$_3$CN, and CH$_2$=CHCN. We note, however, the extraordinary high specificity with which all neutrals are formed from **3** as far as the origin of the hydrogen atoms is concerned.

From Schemes 2 and 3 it is apparent that the unsaturated nitriles CH$_2$=CH(CH$_2$)$_m$CN (Δ*m* = 53, 67, ...) may be formed from several intermediates. Although the labeling

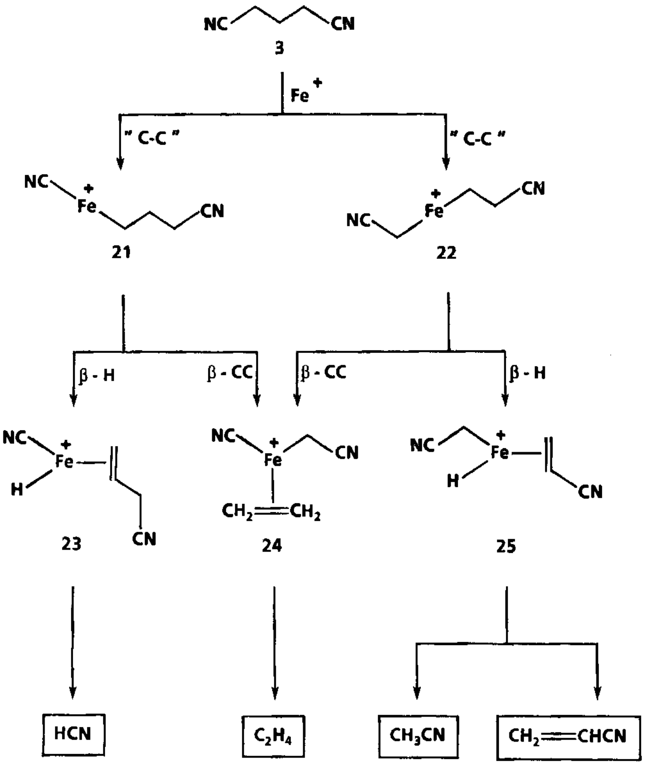
Scheme 3



data (Table 2) clearly establish the high selectivity of this multi-step sequence, we cannot rule out the existence of further mechanistic variants.

Loss of Ethylene: The next reaction to be discussed concerns the Fe^+-mediated generation of ethylene. As indicated in Scheme 1 for long-chain alkanenitriles, this neutral is formed in a straightforward reaction involving remote functionalization of the ω/ω − 1) positions of the alkyl chain[15]; for $CH_3(CH_2)_nCN-Fe^+$ complexes with $n = 0, 1$ loss of C_2H_4 is not observed. A different, more complex situation prevails for the dinitriles. For the complex $NC(CH_2)_3CN-Fe^+$ unimolecular loss of C_2H_4 corresponds to the major process (71%), and the study of $NCCD_2CH_2CD_2CN$ (**3a**) demonstrates the high specificity of the reaction involving C-1/C-2 exclusively. H/D exchange reactions are practically absent. The mechanism depicted in Scheme 4 may well account for this reaction as well as for the generation of the remaining products, i.e. HCN (4%), CH_3CN (13%), and $CH_2{=}CHCN$ (7%); except for HCN, all other neutrals are formed in a highly specific fashion.

Scheme 4



For the next higher homologue $NC(CH_2)_4CN$ (**4**), the labeling experiments (Table 2) uncover the existence of two reaction paths for the generation of C_2H_4 (Schemes 2, 3). One involves C-1/C-2 and proceeds via intermediates **13** and/or **14** (Scheme 2), and the second path accounts for the elimination of the internal positions C-2/C-3; the latter reaction may involve intermediate **18** (Scheme 3). If one ignores isotope effects, the labeling data indicate that the second path is favoured over the first one by a ratio of 3:1.

For the Fe^+ complex of dinitrile **6** $[NC(CH_2)_6CN]$, the study of the isotopomers **6a**−**c** (Table 3) points to the operation of at least two competing processes: The minor one involves C-1/C-2 and may take a course similar to that described in Scheme 2; major contributor to the genesis of C_2H_4 are positions C-2 and C-3 presumably in analogy to Scheme 3. The set of isotopomers studied and the isobaric nature of $\Delta m = 28$ (C_2H_4, DCN, $H^{13}CN$), however, do not permit us to unequivocally decide whether or not the internal positions C-3/C-4 also participate in the formation of ethylene (Table 3). However, the investigation of **8a** $[NC(CH_2)_3CD_2CD_2(CH_2)_3CN]$ indicates that the C-3/C-4 positions are only marginally involved in the formation of ethylene (<8%); the major share goes to C-1, C-2, and C-3 (see Table 4). As elimination of C_2D_4 from **8a**-Fe^+ is not observed we can safely conclude that the internal positions C-4 and C-5 are not activated as far as ethylene loss is concerned. However, as will be demonstrated in the next section, this does not apply to activation of C–H bonds.

Table 3. Isotope distributions of neutrals "Δ*m*" in the MI mass spectra of Fe$^+$ complexes of isotopomers **6a**–**c**[a]: $NCCD_2(CH_2)_4CD_2CN$ (**6a**), $NCCH_2CD_2(CH_2)_2CD_2CH_2CN$ (**6b**), and $N^{13}C(CH_2)_6{}^{13}CN$ (**6c**)

	Δ*m*	**6a**	**6b**	**6c**
"H_2"	2	100	50	100
	3		50	
"HCN, C_2H_4"	27	35	9	
	28	51	26	
	30	14	65	
"$CH_2CN^\bullet$"	40		100	
	41			100
	42	100		
"CH_3CN"	41		100	
	42			100
	43	100		

[a] See footnote[a] in Table 1.

Table 4. Isotope distribution of neutrals "Δ*m*" in the MI mass spectrum of the Fe$^+$ complex of **8a**

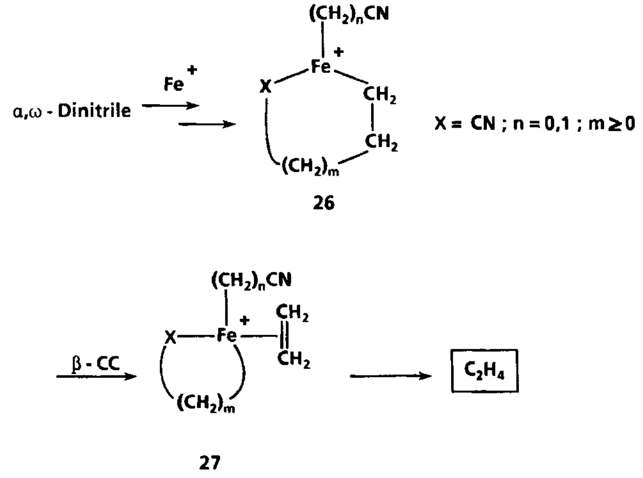
	Δ*m* "H_2" 2	3	4	"HCN" 27	"C_2H_4" 28	30	32
$NC(CH_2)_3CD_2CD_2(CH_2)_3CN$	29	48	23	100	92	8	–

[a] Intensities are expressed in Σ fragments = 100% for each class of neutrals.

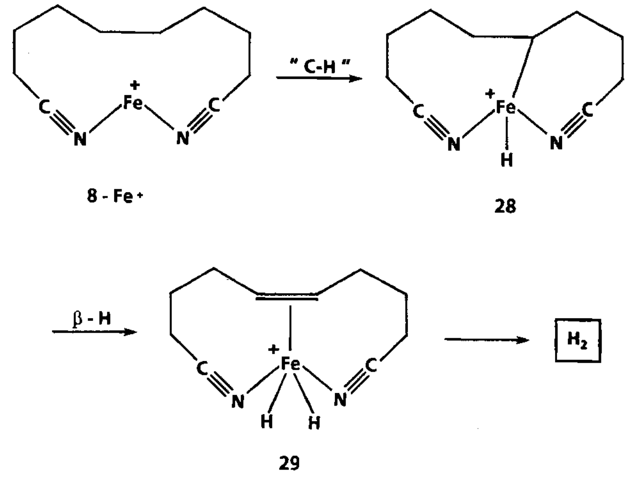
A comparison of the Fe$^+$-mediated C_2H_4 formation from alkanenitriles (Scheme 1) and α,ω-alkanedinitriles (Schemes 2–4) is quite revealing. The preference of the latter substrates to oxidatively add the NC–C or the $NCCH_2$–C bonds to the metal ion suggests (but by no means prove) that the actual mechanism of C–C bond activation in dinitriles may be more complex than indicated by the mechanism depicted in Schemes 2–4. It is tempting to speculate that in dinitriles the "anchored" metal ion first forms metallacycles of the general structure **26** (X = CN; the coordination "end-on" versus "side-on" depends, of course, on the ring size of the metallacycle[9]), from which C_2H_4 is liberated by β-C–C cleavage (Scheme 5). The subtle, in its details yet unknown interplay between the ring strain of the metallacycles formed and the ability of a given C–C bond to be oxidatively added to the metal ion centre may be responsible for the branching ratio observed for elimination of C-1/C-2 or C-2/C-3 as ethylene (Scheme 5).

Dehyrogenation: In the Fe$^+$-induced dehydrogenation of α,ω-alkanedinitriles the presence of the second CN group drastically alters the details of reaction when compared with RCN–Fe$^+$ complexes (R = alkyl). This becomes already obvious when one recalls that for the latter loss of alkene and H_2 show, to a first approximation, the same chain length dependence. A quick look at the data given in Table 1 reveals that this is not observed for the α,ω-alkanedinitriles. While C_2H_4 loss takes place already for $NC(CH_2)_3CN$, the Fe$^+$-mediated dehydrogenation is only observed for $NC(CH_2)_nCN$ with $n \geqslant 6$. In addition, a pronounced maximum is found for $n = 8$. More revealing is the study of the deuterated isotopomers (Tables 3, 4). For example, deuteration of the α-methylene groups does not result in any loss of HD or D_2; in contrast, for the centrally labeled D_4 isotopomer **8a** [$NC(CH_2)_2CD_2CD_2(CH_2)_2CN$] we find loss of H_2, HD, and D_2 in a ratio of 29:48:23 (Table 4). As the reductive elimination of molecular hydrogen from Fe$^+$ complexes of many substrates is found[16] to be subject to sizeable isotope effects, discriminating against elimination of HD and D_2, the present results clearly establish that for alkanedinitrile-Fe$^+$ complexes *the central part of the methylene chain separating the two functional groups is preferentially activated.* This finding is in distinct contrast to the results reported above for C_2H_4 loss. Obviously, for α,ω-dinitriles the two reactions, e.g. generation of H_2 and C_2H_4, are not coupled with each other. A common intermediate which is suggested[10] to control the chemistry of alkanemononitrile complexes does *not* exist for the dinitrile complexes. For the Fe$^+$-induced dehydrogenation of α,ω-dinitriles, the mecha-

Scheme 5



Scheme 6



nism depicted in Scheme 6 accounts for a substantial fraction of the overall loss of molecular hydrogen, and its key feature is the double-ligation of the metal-ion centre. Again, the detailed type of co-ordination of the CN group ("end-on" versus "side-on") remains open to speculation, and further studies are under way to probe the stereochemistry of the hydrogen transfer in the sequence **8**-Fe^+ → **28** → **29**.

Generation of $C_2H_5^{\bullet}$ and $CH_2CN^{\bullet}$: We will briefly comment on the loss of the radicals $C_2H_5^{\bullet}$ and $^{\bullet}CH_2CN$ from dinitrile-Fe^+ complexes. Fe^+-induced loss of alkyl radicals is indeed a quite rare process in organometallic systems, and in our extensive studies of nitriles $CH_3^{\bullet}$ loss is only observed from the α-branched nitrile $CH_3CH(CN)C_2H_5$[10l,m,17].

In the MI mass spectrum of the Fe^+ complexes of **1**–**10**, $C_2H_5^{\bullet}$ loss is limited to $NC(CH_2)_4CN$ (11%). From the study of the labeled analogues **4a**–**d** (Table 2) there is no doubt that the neutral compound owes its formation to a highly specific process, in the course of which the intact C-1/C-2 methylene groups are coupled with a hydrogen atom from the methylene group C-4. This result can be accounted for in terms of Scheme 2 (**4** → **11** → **13** → **14** → **15**). Quite remarkable, in our view, is the complete absence of any hydrogen exchange reactions which point to completely *irreversible* transformations. This holds true as well for the generation of $^{\bullet}CH_2CN$. As this radical, which is built up from the intact $\mathbf{NCCH_2}-(CH_2)_nCN$ unit (Tables 2–4) is only observed in the MI spectrum of the Fe^+ complexes of **4**–**8**, one is tempted to interpret this finding as further support of our conjecture that (hidden) bifunctional interaction affects the detailed course of seemingly one-bond cleavage reactions[18].

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Experimental

The experimental set up has been described in earlier papers[5–10]. Briefly, a 1:5-10 mixture of $Fe(CO)_5$ and the organic substrate is bombarded with 100-eV electrons in the chemical ionization source (repeller voltage 0 V) of a modified ZAB-mass spectrometer of BEBE geometry (B stands for magnetic and E for electric sector). Although the actual mechanism by which the complexes are formed is yet unknown, the pressure in the ion source is high enough to permit collisional cooling thus increasing the lifetime of the complexes FeL^+ (L = dinitrile) such that time-delayed decomposition reactions after ca. 1 μs take place [metastable ion (MI) dissociations]. Organometallic complexes corresponding to FeL^+ having 8-keV kinetic energy are mass selected and focussed with B(1)E(1) at a resolution sufficient to separate isobaric multiplets (usually 4000–5000, 10% valley definition). Unimolecular reactions occurring in the field-free region between E(1) and B(2) were recorded by scanning B(2). Spectra were recorded on-line and averaged by using signal-averaging techniques employing the VG 11/250 or the AMD Intectra data system[11]. It should be kept 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 most mass differences correspond to one isomer only. In addition, further support for the assignement of the neutrals is provided by the study of labeled isotopomers which turned out to be extremely valuable in the elucidation of mechanistic details. Direct characterization of the neutrals, cogenerated in the dissociation of metastable organic ions, by using the otherwise powerful technique of collisionally induced dissociative ionization (CIDI)[12] is precluded by sensitivity problems. — All compounds were synthesized by standard laboratory procedures, purified by chromatographic means and fully characterized by NMR and MS.

CAS Registry Numbers

1: 109-77-3 / **1**-Fe^+: 128328-51-8 / **2**: 110-61-2 / **2**-Fe^+: 128328-52-9 / **3**: 544-13-8 / **3**-Fe^+: 128328-53-0 / **4**: 111-69-3 / **4**-Fe^+: 128328-54-1 / **5**: 646-20-8 / **5**-Fe^+: 128328-55-2 / **6**: 629-40-3 / **6**-Fe^+: 128328-56-3 / **7**: 1675-69-0 / **7**-Fe^+: 128328-57-4 / **8**: 1871-96-1 / **8**-Fe^+: 128328-58-5 / **9**: 71172-36-6 / **9**-Fe^+: 128328-59-6 / **10**: 4543-66-2 / **10**-Fe^+: 128328-60-9 / Fe^+: 14067-02-8

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