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Chain-Length-Dependent Ligand Effects on the Direction of Fe^+-Mediated Activation and Cleavage of CC Bonds in Alkenyl Nitriles in the Gas Phase†

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Abstract: The study of mass-selected complexes of bare Fe^+ with unsaturated nitriles, $CH_3(CH_2)_nCH{=}CH(CH_2)_mCN$, in the gas phase permits a detailed understanding of the chain-length-dependent interaction of the two functional groups with the transition metal ion and its implications for the direction of allylic carbon–carbon bond cleavage processes. This fundamental reaction, which proceeds via a metal-containing cyclic intermediate, is operative only for systems with $m > 2$, and it involves, without exception in all cases studied, the "exocyclic" allylic CC bond (i.e., loss of alkenes from the $CH_3(CH_2)_n$ part of the nitrile). Double-bond migration constitutes a side reaction. In those cases in which this reaction is observed, the double bond preferentially migrates away from the CN group. The actual nature of bidentate complexation (and, in particular, the question of "side-on" versus "end-on" complexation of the nitrile group) is dependent upon the chain length $(CH_2)_m$. For $m = 2, 3$ the data suggest a bidentate complex in which both the CC double bond and the CN triple bond act as π donors (**21**); however, for larger chain lengths ($m \geq 4$) the bidentate complex may be described by an "end-on" complexation of the CN group to the metal ion which still interacts with the CC double bond (**23**). 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. The gas-phase chemistry of these systems ($m = 0, 1$) is practically identical with that of the previously described saturated alkyl nitriles for which "end-on" complexation (**22**) induces functionalization of remote CH bonds. The experimental findings are supported by the study of labeled isotopomers.

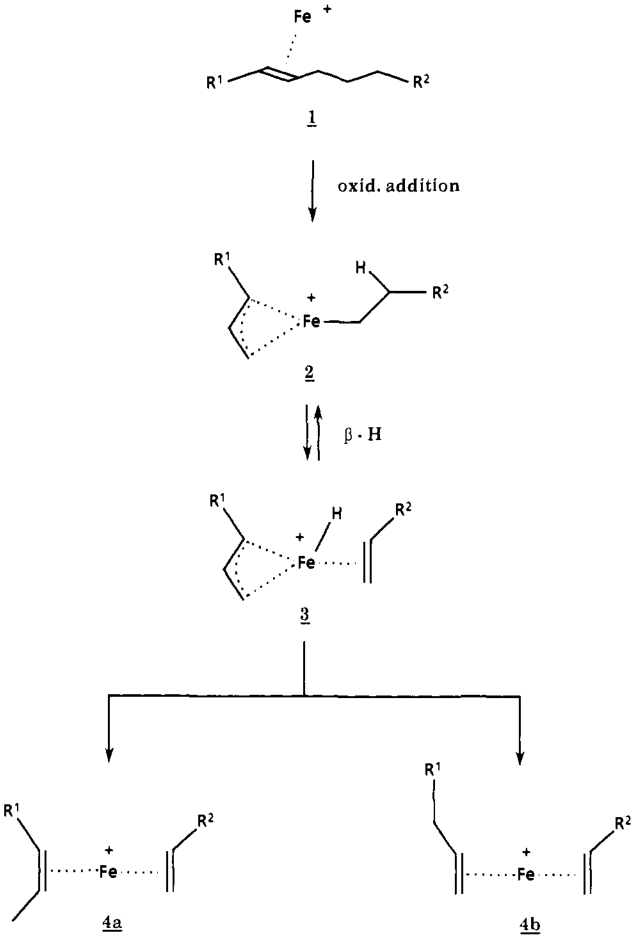
There exists ample experimental evidence for the highly site-specific reactions of bare transition metal ions, e.g., Fe(I) ions, with olefins.[1] These studies do not only provide a novel approach for the location of double (and even triple)[2] bonds, but, more interestingly, they also shed light on the intriguing problem of the activation of CH and CC bonds, a topic of considerable scientific and technological interest.[2,3] For the bare transition metal ion mediated activation and cleavage of CC bonds in olefins, it is now generally agreed upon that the most likely mechanism consists of the following steps (Scheme I). The initially formed complex **1**[4,5] rearranges by oxidative addition of the allylic CC bond to the metal ion (**1** → **2**). This step is followed by β-hydrogen transfer to generate, via the olefin/allyl complex **3**, the bis(olefin) complexes **4a** and/or **4b**. Upon collisional activation (CA),[6] the bis(olefin) complexes dissociate by loss of the ligand[7] having the smaller metal ion affinity. In practice, it turned out that it is the *smaller* olefin ligand which is eliminated from **4a,b**, and it has been suggested by Allison et al.[8] that a correlation may exist between the proton affinity (PA) of a ligand and its metal ion affinity.

Depending on the internal energy of **4a,b** gained in their formation, the olefin ligand detachment may even occur without collisional activation (metastable ion (MI) decomposition).

An obvious, yet unaddressed problem with regard to the *site specifity* of the oxidative addition is the following one. Let us assume that one can generate a bidentate[9] complex of type **5** in which the functional group X serves as an "anchor"[10] to which the metal ion M^+ is strongly bound (i.e., the metal ion affinity of M^+ to X is larger than that of M^+ to the CC double bond). Let us further assume that the reactivity of the ligated metal ion M^+ in **5** is still such that activation of CC bonds may occur. If so, the next question to address is whether, in dependence of the chain length separating the olefin unit from the functional group X, the "exocyclic" (Scheme II: process a) or the "endocyclic" allylic CC bond (process b) will be activated. Depending on the binding energies of the various ligands generated in the course of the oxidative addition of CC bonds to the (complexed) metal ion M^+ (and, of course, on the chain length "m"), the detachment of several neutral species[7] is conceivable, thus giving rise to the generation of the likely ionic species **6**, **7** and **8** (Scheme II).

The situation outlined in Scheme II is not as hypothetical as one might assume. On the contrary, in the course of a detailed study[11a-d] of the gas-phase chemistry of unbranched, saturated acyclic nitriles (RCN) with bare Fe^+, it was inter alia demon-

Scheme I. Fe^+-Induced Cleavage of Allylic CC Bonds According to Reference 1



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† Presented in part at the Annual Meeting of the German Mass Spectrometry Society, Würzburg (FRG), 25–27 May 1988.

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

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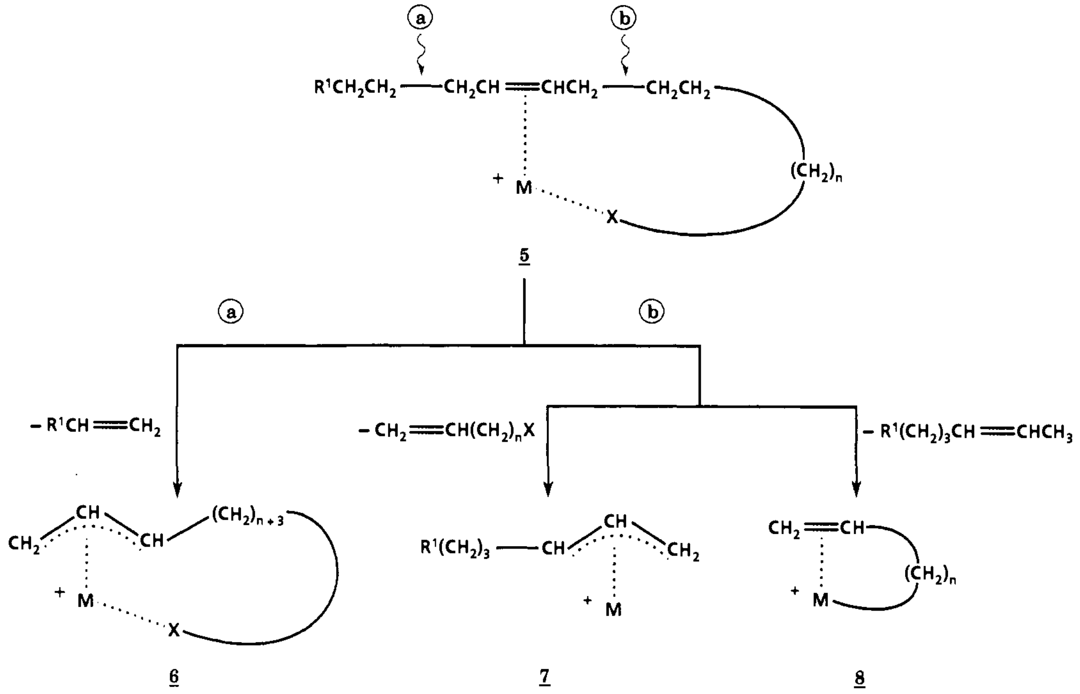
Scheme II. Possible Neutral Ligand Detachment and Ionic Products, Generated by the Activation of the "Exocyclic" (Path a) or "Endocyclic" (Path b) Allylic CC Bonds of **5**



Scheme III. Ethane Loss from Saturated RCN/Fe$^+$ as a Combination of Reductive Elimination of H_2 and Ethylene

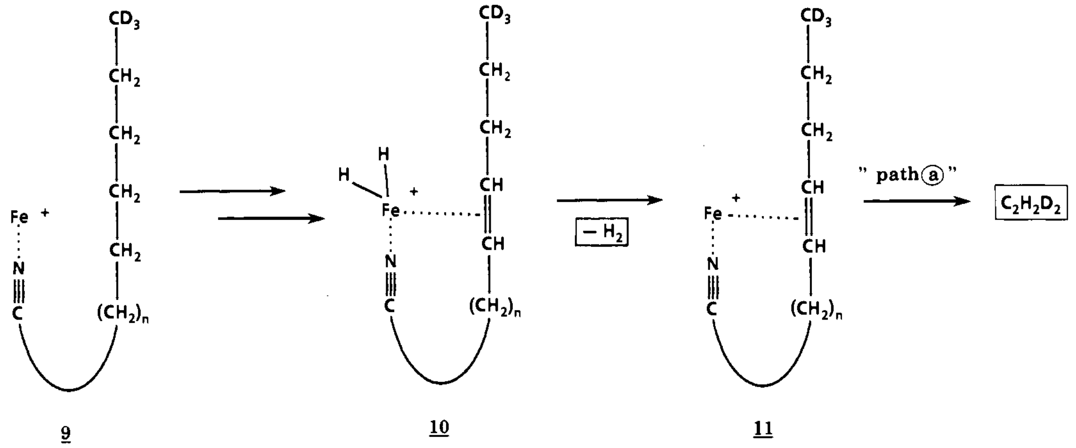


Table I. Metastable Ion (MI) Mass Spectra of RCN/Fe$^+$ Complexes

	neutral precursor $CH_3(CH_2)_nCH{=}CH(CH_2)_mCN$[b]		ligand detachment[a]						
	n	m	H_2	CH_4	C_2H_4	C_3H_6	C_4H_8	C_5H_{10}	C_6H_{12}
12	2	4	13	2	$\boxed{100}$	24	22	3	
13	3	4	12	1	28	$\boxed{100}$	8	3	
14	4	4	8	<1	5	22	$\boxed{100}$	4	
15	5	4	5	<1	2	4	15	$\boxed{100}$	2
16	3	3	4	<1	13	$\boxed{100}$	3		
17	4	3	5	<1	3	11	$\boxed{100}$	<1	
18	5	2	6	<1	2	3	4	$\boxed{100}$	
19	5	1	$\boxed{100}$	13	48	25	5	28	<1
20	6	0	$\boxed{100}$	12	32	23	3	<1	<1

[a] Intensities are expressed in % base peak. Signals due to the formation of other neutrals are, in total, less then 1%. [b] Except for **12** and **20**, the double bond is always of *Z* configuration.

strated that the generation of alkanes (C_nH_{2n+2}) from long-chain RCN/Fe$^+$ complexes is, to a significant extent, due to the combined losses of H_2 and an olefin (C_nH_{2n}). The mechanism, formulated in Scheme III, is in keeping with the experimental findings. The "end-on" ligated Fe^+ complex **9** interacts with both the terminal CD_3 group (not shown in Scheme III) and, provided the $(CH_2)_n$ is long enough, with the internal CH bonds. H_2 is liberated from **10** which is formed in the course of oxidative addition/β-hydrogen transfer. Preliminary studies showed that the so-formed product **11**, if subjected to collisional activation, undergoes loss of $C_2H_2D_2$. Alkene loss was also observed for other $[RCN/Fe^+ - H_2]^+$ species. Ionic products which would formally correspond to **7** or **8** (Scheme II) were, however, not detected. These observations suggest that process a (Scheme II: $\mathbf{5} \rightarrow R^1CH{=}CH_2 + \mathbf{6}$) is indeed operative, while path b does not seem to play a role in the chemistry of **5**.

In the present contribution a detailed report will be given which not only substantiates the earlier assumption[11b] but will also address specifically the role the "internal" chain length $(CH_2)_n$ plays on (i) the site specifity of CC activation (path a versus b), (ii) the structural nature of the "productive"[12] interaction of M^+ with X (for X = CN the major problem is concerned with the question of "end-on" versus "side-on" complexation[13]), and (iii) the tendency of double-bond migration preceding the ligand detachment process.

Experimental Section

The experimental setup has been described in detail in earlier papers.[11,14] 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 B(1)EB(2) configuration was employed. The machine and its operation have been described elsewhere.[15] In a typical experiment, $Fe(CO)_5$ and the nitrile of interest in an approximate 1:2 ratio were introduced in the ion source and were bombarded with an electron beam of 100 eV kinetic energy. Organometallic ions corresponding to RCN/Fe^+ having 8-keV kinetic energy are mass slected and focused with B(1)E. Unimolecular reactions occurring in the field-free region between E and B(2) were recorded by scanning B(2). We have also performed CA experiments by introducing He in the collisional cell (located in the third field-free region) at a pressure which attenuates the primary ion beam intensity to ca. 85% relative intensity; this corresponds to an average of 1.1–1.2 collisions.[16] The results obtained in the collision experiments are very similar to those observed under collision-free conditions (metastable ion (MI) decompositions). Only the latter will be reported in this contribution. CA data are available from the authors upon request. All nitriles studied were synthesized by standard laboratory procedures; the compounds were purified by chromatographic means and fully characterized by spectroscopic methods.

Results and Discussion

In Table I the data for the MI mass spectra of the RCN/Fe^+ complexes, generated from compounds **12–20**, are given. The analysis of these data is straightforward. We note the following.

(i) For systems in which the two functional groups are separated by two, three, or four (CH_2) units, the preferred pathway corresponds to cleavage of the "exocyclic" allylic CC bond (Scheme II: path a). There are, in fact *no* signals present in the MI and CA mass spectra for processes which were indicative for an activation of the "endocyclic" CC bonds (Scheme II: path b).

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(2) Many leading references together with a detailed discussion of mechanistic aspects for the reactions of gaseous alkynes with Fe^+ may be found in: (a) Schulze, C.; Schwarz, H.; Peake, D. A.; Gross, M. L. *J. Am. Chem. Soc.* **1987**, *109*, 2368. (b) Schulze, C.; Weiske, T.; Schwarz, H. *Organometallics* **1988**, *7*, 898. (c) Schulze, C.; Schwarz, H. *J. Am. Chem. Soc.* **1988**, *110*, 67.

(3) Selected references: (a) Müller, J. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 653. (b) Parshall, G. W. *Catalysis* **1977**, *1*, 335. (c) Beauchamp, J. L.; Stevens, A. E.; Corderman, R. R. *Pure Appl. Chem.* **1979**, *51*, 967. (d) Collman, J. P.; Hegedus, L. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980. (e) Haggin, J. *Chem. Eng. News* **1982**, *60*, 13. (f) Gregor, I. K.; Guilhaus, M. *Mass Spectrom. Rev.* **1984**, *3*, 39. (g) Allison, J. *Prog. Inorg. Chem.* **1986**, *34*, 627. (h) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Reidel: Dordrecht, 1984. (i) Green, M. L.; O'Hare, D. *Pure Appl. Chem.* **1985**, *57*, 1897. (j) Bandry, D.; Ephritikine, M.; Felkin, H.; Fillebeen-Khan, T.; Gault, Y.; Holmes-Smith, R.; Yingrui, L.; Zakrzewski, J. In *Organic Synthesis*: Streith, J., Prinzbach, H., Schill, G., Eds.; Blackwell Scientific Publications: Oxford, 1985; p 25: (k) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332. (l) Armentrout, P. B. In *Structure/Reactivity and Thermochemistry of Ions*; Ausloos, P., Lias, S. G., Eds.; D. *Reidel*: Dordrecht, 1987; No. 193, p 97. (m) Ridge, D. P. *Ibid.* 1987; No. 193, p 165. (n) Simoes, J. A.; Beauchamp, J. L. *Chem. Rev.*, in preparation. (o) Beauchamp, J. L. *ACS Symp. Ser.* **1987**, 333. (p) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (q) Freiser, B. S. *Talanta*, **1985**, *32*, 697. (r) Janowicz, A. H.; Periana, R. A.; Buchanan, J. M.; Kovac, C. A.; Stryker, J. M.; Wax, M. J.; Bergman, R. G. *Pure Appl. Chem.* **1984**, *56*, 13. (s) Halpern, J. *Inorg. Chim. Acta.* **1985**, *100*, 41. (t) Rothwell, I. P. *Polyhedron* **1985**, *4*, 77. (u) Graham, W. A. G. *J. Organomet. Chem.* **1986**, *300*, 81.

(4) For the generation of Fe(alkyne)$^+$ and Fe(nitrile)$^+$ complexes it has been shown by FTICR [(a) ref 2a. (b) Peake, D. A.; Gross, M. L. *Organometallics* **1986**, *5*, 1236. (c) Nibbering, N. M. M.; Schwarz, H. et al., unpublished results) that $Fe(CO)_x{}^+$ (x = 1, 2) serve as major precursor ions. It should, however, 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 condition. Similarly, the actual electronic state of the metal ion is not always known. However, while the reactions of Fe^+ with H_2 is dependent upon the electronic state of Fe^+, for reactions with larger organic molecules the reactivity was found to be insensitive to the state of Fe^+. See, for example: (a) ref 3e. (b) Schultz, R. H.; Armentrout, P. B. *J. Phys. Chem.* **1987**, *91*, 4433. (c) Schultz, R. H.; Elkind, J. L.; Armentrout, P. B. *J. Am. Chem. Soc.* **1988**, *110*, 44.

(5) As stated by Müller (ref 3a), suggested structures are hypothetical and speculative in nearly all cases studied in mass spectrometry. They are based on plausibility arguments using as much direct and indirect evidence available from experiments and model considerations. Nevertheless, the heuristic values of structural representation are undeniable as long as speculations remain within acceptable limits.

(6) (a) Cooks, R. G., Ed. *Collision Spectroscopy*; Plenum Press: New York, 1978. (b) Levsen, K.; Schwarz, H. *Mass Spectrom. Rev.* **1983**, *2*, 77.

(7) 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. While in many cases there cannot exist any possible doubt as to the actual structure of the neutral formed on energetic grounds, (for example, Δm = 2 corresponds to H_2, 16 = CH_4; 28 = C_2H_4, etc.), in other systems (for example, loss of 1- or 2-alkene from **4a**/**4b** in Scheme I) the structure is less obvious and one would like to further characterize the neutral fragments. However, for sensitivity reasons the otherwise powerful technique of neutralization–reionization mass spectrometry (NRMS) in its variant of collision-induced dissociative ionization (CIDI) cannot be applied. For leading references on NRMS and CIDI, see: (a) Wesdemotis, C.; McLafferty, F. W. *Chem. Rev.* **1987**, *87*, 485. (b) Terlouw, J. K.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 805. (c) Burgers, P. C.; Holmes, J. L.; Mommers, A. A.; Terlouw, J. K. *Chem. Phys. Lett.* **1983**, *102*, 1.

(8) For a discussion and references see: (a) Huang, S. K.; Allison, J. *Organometallics* **1983**, *2*, 883. (b) Lombarski, M.; Allison, J. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *49*, 281. (c) Tsarbopoulos, A.; Allison, J. *Organometallics* **1984**, *3*, 86. (d) Tsarbopoulos, A.; Allison, J. *J. Am. Chem. Soc.* **1985**, *107*, 5085.

(9) For early examples of multidentate ligand effects on organometallic systems in the gas phase, see ref 8.

(10) Breslow, R. *Acc. Chem. Res.* **1980**, *13*, 170.

(11) (a) Lebrilla, C. B.; Schulze, C.; Schwarz, H. *J. Am. Chem. Soc.* **1987**, *109*, 98. (b) Lebrilla, C. B.; Drewello, T.; Schwarz, H. *Ibid.* **1987**, *109*, 5639. (c) Drewello, T.; Eckart, K.; Lebrilla, C. B.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1987**, *76*, R1. (d) Lebrilla, C. B.; Drewello, T.; Schwarz, H. *Ibid.* **1987**, *79*, 287. (e) See also: Stepnowski, R. M.; Allison, J. *Organometallics* **1988**, *7*, 2097.

(12) "Productive" interaction implies in the present context only processes which eventually give rise to ligand detachment products.

(13) For the gas-phase studies of RCN with Fe^+, Co^+, and Ni^+ (ref 11), *all* results are in keeping with an initial "end-on" complexation of the nitrile by the bare transition metal ion. In contrast, the dissociation products of RCN/Cu^+ complexes point to a "side-on" complexation (Lebrilla, C. B.; Drewello, T.; Schwarz, H. *Organometallics* **1987**, *6*, 2450). In the condensed-phase examples for *both* types of coordination seem to exist. Except for X-ray structural data, the arguments presented, and conclusions drawn, are unfortunately not always unquestioned. This applies, in particular, for bidentate molecules. For a few examples, see: (a) Muetterties, E. L. *J. Chem. Soc. Rev.* **1983**, *11*, 283 and references cited therein. (b) Krogmann, K.; Mattes, R. *Angew. Chem.* **1966**, *78*, 1064. (c) Faroud, M. F.; Kraus, K. F. *Inorg. Chem.* **1970**, *9*, 1700. (d) Dunn, J. G.; Edwards, D. A. *J. Chem. Soc., Chem. Commun.* **1971**, 482. (e) Payne, D. H.; Frye, H. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 505. (f) Bland, W. J.; Kemmitt, D. W.; Moore, R. D. *J. Chem. Soc., Dalton Trans.* **1973**, 1292. (g) Zecchin, S.; Zotti, G.; Pilloni, G. *Inorg. Chim. Acta* **1979**, *33*, L 117. (h) Storhoff, B. N.; Lewis, H. C., Jr. *Coord. Chem. Rev.* **1977**, *23*, 1 and references cited therein. (i) Chebolu, V.; Whittle, R. R.; Sen., A. *Inorg. Chem.* **1985**, *24*, 3082. (j) Wright, T. C.; Wilkinson, G.; Moteralli, M.; Hurstkruse, M. B. *J. Chem. Soc., Dalton Trans.* **1986**, 2017. (k) Jones, P. G.; Roesky, H. W.; Schimkowiak, J. *J. Chem. Soc., Chem. Commun.* **1988**, 730. (l) Wexler, R. M.; Muetterties, E. L. *J. Phys. Chem.* **1984**, *88*, 4037. (m) Andrews, M. A.; Knotler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1979**, *101*, 7260. (n) For theoretical calculations see: Howell, J. A. S.; Saillard, J. Y.; Le Beuze, A.; Jaouen, G. *J. Chem. Soc., Dalton Trans.* **1982**, 2533.

(14) Prüsse, T.; Lebrilla, C. B.; Drewello, T.; Schwarz, H. *J. Am. Chem. Soc.* **1988**, *110*, 5986.

(15) (a) Weiske, T. Ph.D. Thesis, Technical University Berlin, D 83, 1985. (b) Terlouw, J. K.; Weiske, T.; Schwarz, H.; Holmes, J. L. *Org. Mass Spectrom.* **1986**, *21*, 665.

(16) Holmes, J. L. *Org. Mass Spectrom.* **1985**, *20*, 169.

(ii) Partial migration of the double bond is observed. For the systems in which the two functional groups are separated by two (**18**) or three (CH_2) groups (**16** and **17**), the double bond migrates toward the end of the alkyl chain. Products, which would reflect a double-bond migration toward the nitrile group, are either not observed or of very minor importance only (see, for example, the Fe^+ complex of **18** which does not undergo loss of C_6H_{12}). For systems which contain four (CH_2) units between the CC double bond and the CN group, some isomerizations in both directions occur; if possible for structural reason, the migration away from the CN group is, again, favored (see **13**, **14**, and **15**). In fact, signals due to losses of, for example, C_2H_4, C_3H_6, and C_4H_8 from **15**-Fe^+ are indicative for multiple double-bond shifts.

(iii) If the separation between the two functional groups contains *less* than two CH_2 units (in **19** and **20**), exocyclic allylic CC bond cleavage (Scheme II: path a) does not any longer dominate the spectra. In contrast, the product distribution is typical for that of a *saturated* nitrile; i.e., the chemistry is governed by functionalization of *remote* CH bonds. As shown earlier,[11] this reaction is the hallmark of "end-on" complexed RCN/Fe^+. In fact, the MI spectra of **20**-Fe^+, which is dominated by loss of H_2 and to a minor extent by the eliminations of C_2H_4 and C_3H_6, respectively, is very close to that for the saturated system $CH_3(CH_2)_8CN$.[11b] For the latter it has been shown that H_2, C_2H_4, and C_3H_6 are formed from the terminal part of the alkyl chain by mechanisms described in detail in ref 11b.

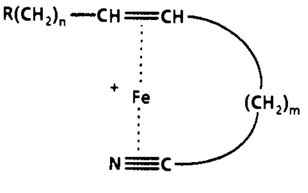
All these findings can be easily accounted for by the formation of an intermediate of the general structure **5** (Scheme II: X = CN). For alkenyl nitriles with a $(CH_2)_m$ chain too small (i.e., **19** and **20**) to permit the bidentate generation, the Fe^+-induced alkyl chain functionalization is exclusively dictated by the CN group. The presence of the double bond, reflected in allylic CC bond cleavage, is not "felt" at all by the transition metal ion. This is convincingly demonstrated by the spectrum of **20**. The allylic cleavage product (loss of C_6H_{12}) is negligible (<1%); rather, products are generated typical for the chemistry of *saturated* RCN/Fe^+ complexes. The clear preference of Fe^+ to complex the CN group rather than the CC double bond very likely reflects the higher binding energy of the former. Although no data seem to exist to make a quantitative comparison of the RCN/Fe^+ with an olefin/Fe^+ system, for the analogous RCN/Co^+ and olefin/Co^+ complexes, literature data[17] indicate that the binding energy of CH_3CN-Co^+ (60 kcal/mol) is significantly larger than that of $CH_3CH{=}CH_2/Co^+$ (~40 kcal/mol).

The preferential complexation of the CN group does, however, not exclude interaction with the CC double bond. Provided the alkyl chain separating the two "ligands" is long enough to permit the generation of cyclic intermediates, a *site-specific* activation of CC bonds is observed. The data suggest that the methylene chain separating the CC double bond and the CN group must contain at least two (CH_2) units; this would point to the formation of five- or six-membered cyclic intermediates depending on the nature of coordination of the CN group ("side-on" versus "end-on"). While this structural feature, strictly speaking, remains unsettled, the data for the Fe^+ complexes of **16**, **17**, and **18** permit some meaningful speculation.[5] There cannot exist any doubt that even in these complexes, in which the two functional groups are separated by only two (**18**-Fe^+) or three (CH_2) units (**16**-Fe^+ and **17**-Fe^+), the chemistry reflects *the cooperation of both functional groups* as indicated by **5** (Scheme II: X = CN; *n* = 0, 1). While model considerations demonstrate that it is impossible to build up for **18**-Fe^+ a strain-free, bidentate complex of type **5** with an "end-on"-coordination of the CN group by Fe^+, it is tempting to suggest that for the Fe^+ complexes of **16**, **17**, and **18** the preferred arrangement may be close to that depicted in structure **21**. This is perhaps due to the fact that the combined effects of two π-bond complexations of Fe^+ (as in **21**) are energetically more favored than the only complexation by the nitrogen lone pair (as in **22**). The latter is typical for saturated RCN/Fe^+ systems[11] and, by analogy, also likely to exist for the unsaturated complexes **19**-Fe^+ and **20**-Fe^+. If the chain length separating the CN group and the CC double bond increases, it may well be that the nature of complexation changes again and may be best described by the structural representation **23**.

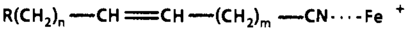
Table II. Olefin Losses (MI Spectra) from Fe^+ Complexes of the Isotopomers **12a**, **12b**, and **12c**[a]

	precursor		
	$CD_3(CH_2)_2CH{=}CH(CH_2)_4CN$	$CH_3CH_2CD_2CH{=}CH(CH_2)_4CN$	$C_3H_7CD{=}CD(CH_2)_4CN$
C_2H_4	<3	>99	>95
C_2H_3D	<2	<1	<4
$C_2H_2D_2$	>95	<1	<1
C_3H_6			82
C_3H_5D		30	18
$C_3H_4D_2$		70	
$C_3H_3D_3$	100		
C_4H_8		<1	
C_4H_7D		>99	>99
$C_4H_6D_2$			<1
$C_4H_5D_3$	100		

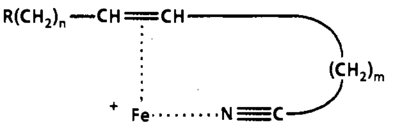
[a] Intensities are expressed in %Σolefin = 100% for each olefin separately. Data for the losses of C_5 isotopomers were not included because of the poor signal-to-noise ratios.



21 (m = 2, 3, 4 (?))



22 (m = 0,1)



23 (m ≧ 4)

Irrespective of the detailed structural nature of the interaction of the bare Fe^+ with the two functional groups of compounds **12**–**18**, it is *the interplay of the two ligands which eventually gives rise to a highly site-specific cleavage of the "exocyclic" allylic CC bond* (Scheme II: path a). This unexpected, remarkable result is not likely to reflect the thermochemistry of the possible products formed but rather points to a kinetic discrimination of the functionalization of "internal" CC bonds (Scheme II: pathway b). Similarly, recent results,[14] concerning β-hydrogen transfers from endo versus exocyclic CH bonds to (complexed) transitional metal ions, also indicate that "exocyclic" bonds are more prone to be oxidatively added to a metal ion than endocyclic ones. No doubt that a comprehensive understanding of these novel findings warrants further studies.[18]

Some insight into the specificity of the olefin eliminations from **12** is provided by the study of the labeled isotopomers **12a**–**c**. From the data given in Table II the following conclusions can be drawn.

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(18) While not directly comparable to the present results, it should be mentioned that highly interesting directional effects were also reported by Tsarbopoulos and Allison (ref 8c) using ICR. 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 carbon–carbon bond; from the so-formed intermediate $XCH_2CH_2-Co^+-CH_2CH_2OH$, C_2H_5X is generated via β-hydrogen transfer followed by reductive elimination.

(i) With regard to ethylene loss, the reaction is highly specific, involving the terminal CH_3CH_2 unit with β-hydrogen transfer from the methyl group, analogous to Scheme III. Hydrogen scrambling amounts to less than 5%.

(ii) The generation of C_3H_6 (presumably propene) requires a double-bond isomerization, corresponding formally to a partial isomerization **12** → **16**. Not surprisingly, hydrogen atoms of the terminal methyl group are not involved in this process. In contrast, hydrogens of the CC double bond and the allylic methylene group of the propyl unit participate in the double-bond migration.

(iii) The elimination of C_4H_8 (presumably butene) requires in a formal sense a twofold double-bond isomerization prior to the neutral formation. The high specificity (all neutral isotopomers are formed with >99% isotopic purity) is worth mentioning.

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Gas-Phase Electron Photodetachment Spectroscopy of the Molecular Anions of Nitroaromatic Hydrocarbons at Atmospheric Pressure

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Abstract: Low-resolution, electron photodetachment (PD) spectra of the molecular radical anions of nitrobenzene and 30 other nitroaromatic hydrocarbons bearing methyl, fluoro, chloro, bromo, and cyano substituents are reported for the first time. A unique feature of these measurements is that they have been obtained at atmospheric pressure by use of a specialized electron capture detector (ECD) in which the molecular anions are formed by resonance electron capture at 200 °C. Absolute PD cross sections, σ_d, for these anions over the spectral range 300 to 1200 nm have been obtained by use of I^- as a calibration reference. It is shown that the nitroaromatic anions undergo photodetachment by two mechanisms, direct PD and resonance PD. Through measurements of direct PD in the spectral region of photodetachment onset, the minimum photon energy, E_{th}, necessary to cause PD has been determined for each nitroaromatic anion. These measurements have been compared with the adiabatic electron affinities (EA) of the corresponding molecules which had been determined previously from studies of gas-phase electron transfer equilibria. This comparison indicates a high level of agreement between these two data sets and is consistent with a simple model of the energetics and structural changes which are thought to accompany the negative ionization of the nitroaromatic hydrocarbons. The occurrence of resonance PD for these anions is supported by a comparison of several of the PD spectra with UV–vis absorption spectra of the corresponding anions previously measured in τ-irradiated frozen glassy solutions. By the resonance PD mechanism, peak maxima of high absolute cross section are observed for many of the nitroaromatic anions. The largest PD cross section observed here was that of the 9-nitroanthracene anion for which σ_d = 0.42 Å^2 at 600 nm. For several instances in which σ_d was not large relative to the absorption cross section at peak maxima, low quantum efficiency for resonance PD is thought to result from poor Frank–Condon overlap of the excited molecular anion and the neutral molecule.

Electron photodetachment from atomic and polyatomic anions has proven to be a useful means of studying thermochemical and spectroscopic properties of negative ions and their photoproducts.[1-5] In particular, PD has been extensively used for the measurement of gas-phase electron affinities (EA), an application of considerable importance to a wide variety of chemical disciplines.[6,7] The photodetachment spectra of polyatomic negative ions has also been shown to provide information concerning the excited states of the negative ions and the neutral products involved in the PD process. We have recently shown in our laboratory[8] that PD may also be of considerable use in the field of analytical chemistry when used in conjunction with an electron capture detector (ECD) for gas chromatographic detection.

While a number of experimental techniques have been used for observing PD in the gas phase, those using the ion cyclotron resonance mass spectrometer (ICR–MS) in conjunction with a light source have been most extensively applied to the study of relatively large polyatomic negative ions.[1,4] The ICR–MS is well-suited to the study of PD because of its ability to generate a variety of mass-identified negative ions and then to trap and study them for a relatively long period of time. Certain limitations, however, are also recognized in the use of the ICR–MS for PD measurements. One of these is that the internal energy of the negative ions which can be readily produced in an ICR cavity are generally not under tight experimental control, and this fact can complicate the interpretation of PD spectra.[1,4] The negative ions are typically formed by energetic chemical means, and the excess internal energy thereby imparted to the product ions is not efficiently removed by collisions in the 10^{-8} to 10^{-5} Torr low-pressure environment of the ICR cavity.[9-11] This problem is expected to be particularly severe when a negative ion is formed through resonance electron capture, as shown in reaction 1, from a molecule, M, of high electron affinity (EA).

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