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Gas-Phase Organometallic Chemistry: The Challenge and Prospect of Specifically Modelling the Course of a Reaction**

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Chemists are continuously facing questions and problems as follows: Is it possible to direct the course of a reaction according to one's intentions? Is the activation of specific bonds that are either remote or adjacent to a functional group feasible? What factors dictate the different behaviour of transition-metal ions in their reactions with organic substrates? Answers to these and other questions are provided by studying the gas-phase chemistry of «naked» first-row transition-metal ions with aliphatic nitriles. By systematically modifying both the nitriles and the metal ions, a quite detailed insight is achieved into the mechanisms that are operative, and knowledge is accumulated which permits to specify the conditions that are to be met in order to bring about specific processes. «Remote functionalization», the generation of ion/dipole intermediates, and the formation of multi-ligated metal-ion alkene complexes turn out to be the most important mechanisms in the reactions of aliphatic nitriles with transition-metal ions in the gas phase. The studies have been performed by using tandem mass spectrometry techniques in a sector-field mass spectrometer as well as ion/molecule reactions in a Fourier transform ion cyclotron resonance (FTICR) instrument.

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1. Introduction

Gas-phase experiments with bare transition-metal ions offer a valuable approach for a better understanding of the intrinsic properties of the metal ions in the absence of disturbing influences that arise from solvent, counter ion, and ligands which are present in the condensed phase and invariably mask the ions' behaviour. Especially the activation of C–H and C–C bonds in organic substrates is important for the control of catalytic processes[1], and a complete understanding of the mechanisms that are operative might help to design «tailored» catalysts in the future.

Although gas-phase organometallic chemistry, a rapidly developing branch of mass-spectroscopic studies, has been reviewed repeatedly[2] very recent results from our group[3] justify a further review which specifically addresses the questions raised in the Abstract.

2. Experimental

Most of the reactions described here have been studied with a triple-sector mass spectrometer (VG ZAB-HF-3F)[4]. The instrumental set-up has been described earlier and will therefore be mentioned only briefly (for details cf. [3] and references cited therein). 1:1 complexes of a transition-metal ion and the organic substrate are formed by different means in the ion source; they are subsequently mass and energy selected with the first two sectors (B_1E), and their metastable or collision-induced dissociations in the third field-free region are monitored by scanning of B_2 (B stands for magnetic and E for electric sector).

Another approach to investigate the systems of interest are ion/molecule reactions of the bare metal ions with the neutral organic substrate in a Fourier transform ion cyclotron resonance (FTICR) instrument (Spectrospin CMS 47X). The spectrometer and the general operating procedures have also been described earlier[5]. Briefly, metal ions are generated by e.g. laser desorption in the external ion source, transferred into the cell, and reacted with the organic substrate present there.

In general, reasonable agreement was found for the otherwise totally different approaches if several restrictions were kept in mind[5,6].

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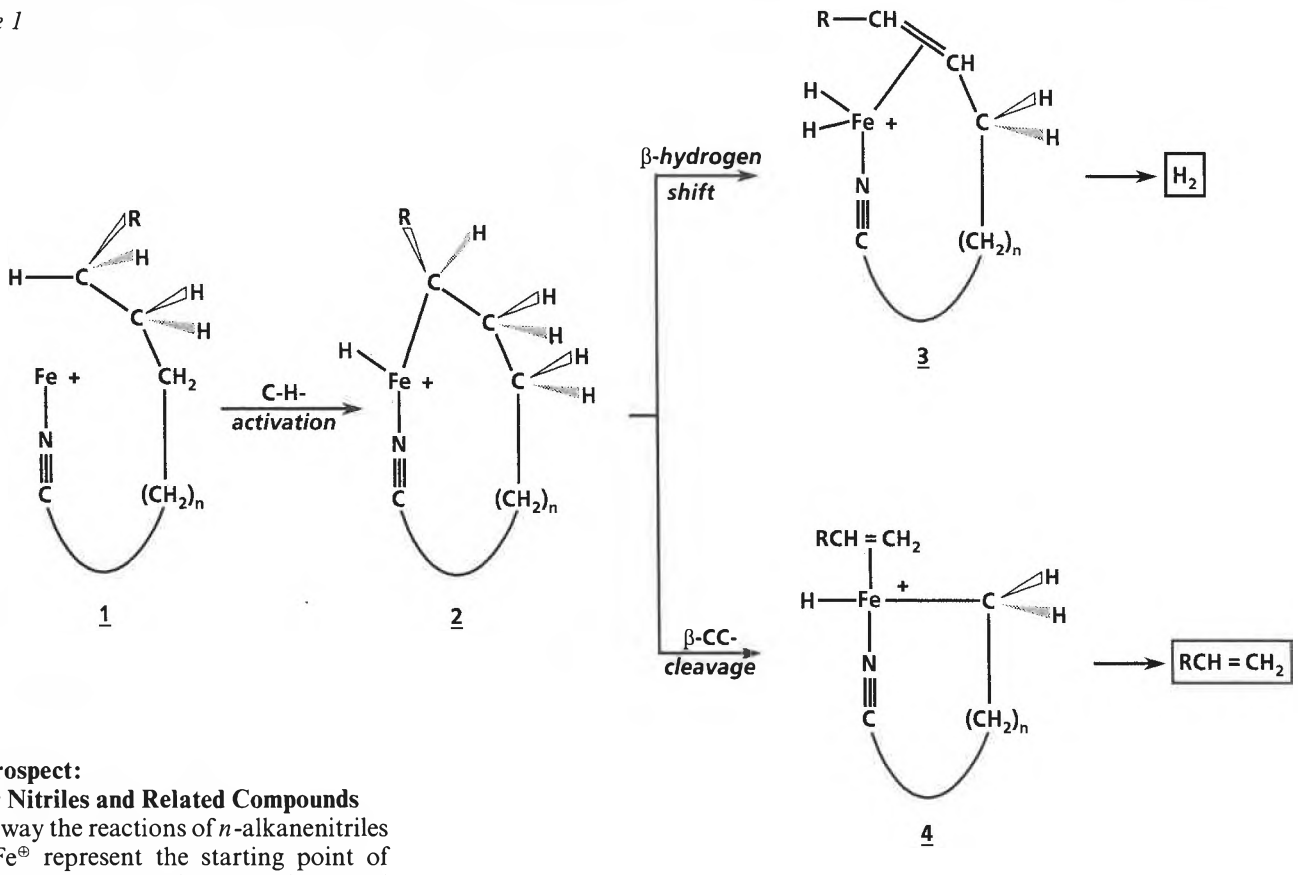
Scheme 1



3. Retrospect: Linear Nitriles and Related Compounds

In a way the reactions of *n*-alkanenitriles with $Fe^{\oplus}$ represent the starting point of this work as a mechanism was discovered that had an enormous impact on the following studies. It was found that $Fe^{\oplus}$ is complexed «end-on» to the functional group and specifically activates a C–H bond of the terminal methyl group[7]. This interaction (Scheme 1) results in the formation of an intermediate metallacycle (**2**, R = H) that rearranges further either by β-hydrogen transfer (**2** → **3**) or by β-CC-cleavage (**2** → **4**). Reductive elimination of molecular hydrogen or ethylene detachment terminates the reaction sequence.

The specific activation of C–H or C–C bonds that are remote from a functional group still represents a challenge for condensed-phase studies; only a few examples are known where this could be achieved for *rigid* molecules. *Breslow* has coined the term «remote functionalization» for this kind of behaviour[8]. Varying the conditions by e.g. extending the chain length of the nitriles and using different metal ions, revealed the following results[9]:

- For longer-chain nitriles the activation of internal C–H bonds is also observed. This leads to the production of higher alkenes and molecular hydrogen from internal methylene groups (Scheme 1, $R = C_nH_{2n+1}$).
- The preferred ring size of the metallacycle **2** differs slightly for $Fe^{\oplus}$ versus $Co^{\oplus}$ and $Ni^{\oplus}$ while many other properties of these three metal ions are quite similar. $Cu^{\oplus}$ on the other hand shows a distinctly different behaviour that has been discussed in terms of a «side-on» coordination[10].

Transition-metal ion mediated reactions that are due to «remote functionalization» are by no means unique to nitriles[3,11]; it was recently shown that this mechanism is also operative for other substrates as well, including isocyanides[12], amines[13], alcohols[14], ketones[15], alkynes[16], and allenes[17].

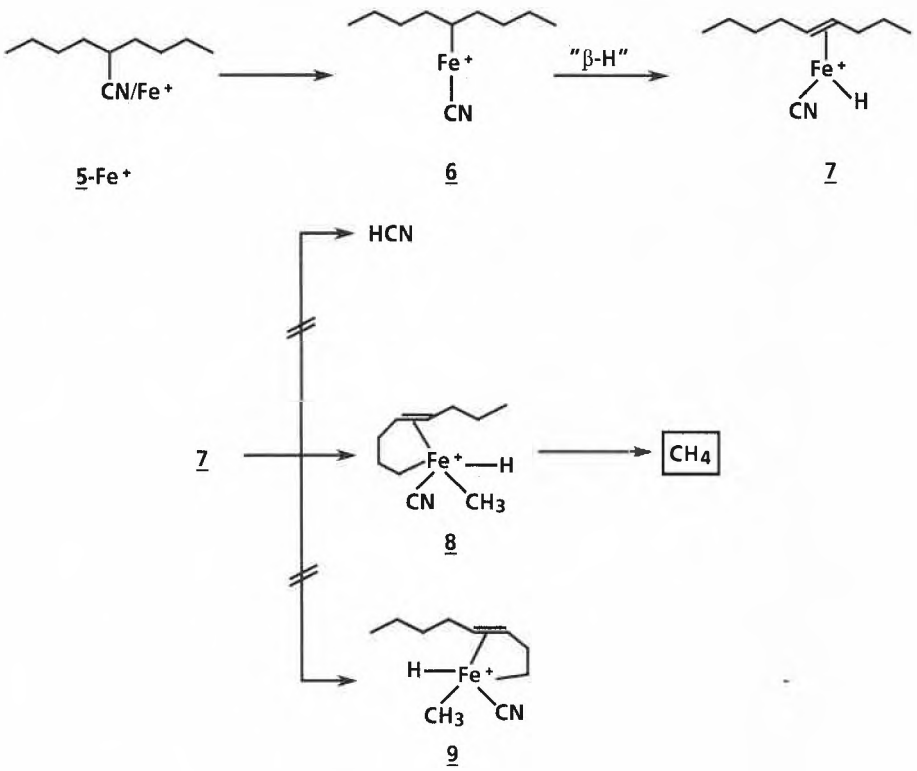
Replacement of the cyanide for the isocyanide function did not result in, as one might have anticipated, a similar behaviour of the molecules; rather, quite large differences were noted in the comparison[12]. The introduction of additional functionalities in the nitriles also leads to a change in the product distribution. For example, in going over to unsaturated nitriles the chemistry observed with $Fe^{\oplus}$ is dominated by an interplay of the double bond and the cyanide group; while the latter serves as an «anchor» for the transition-metal ion, the actual activation occurs at bonds in the vicinity of the double bond, provided the chain length separating the two functional groups is long enough to permit the formation of bidentate complexes. Similar to ordinary alkenes[18], mainly cleavage of the allylic C–C bond is observed[19]. The substitution of the terminal methyl- for a *tert*-butyl group results in a direction of the site of insertion. Initial insertion of the metal ion in a C–C bond of the *tert*-butyl group is followed by β-hydrogen shift for this system[20].

4. Secondary Nitriles

In order to get further information about the kinetics of the individual steps in Scheme 1, symmetric secondary nitriles of the type $R_2CH–CN$ were studied. It could indeed be shown that except for a small signal due to loss of CH_4, which will be discussed in more detail below, the same products are formed for $R_2CH–CN$ and $RCH_2–CN$ ($R = C_4H_9$)[21]. This finding, of course, represents a necessary prerequisite for the determination of *intra*molecular kinetic isotope effects; the latter indicate which of the steps are rate-determining. Using an appropriate set of labeled nitriles it was possible to demonstrate that the first step, i.e. the C–H insertion, is not rate limiting; isotope effects were determined for ethylene detachment ($k_H/k_D = 1.25$ per deuterium atom), β-H-shift ($k_H/k_D = 1.59$), and reductive elimination of H_2 ($k_{H_2}/k_{D_2} = 1.7$ and $k_{HD}/k_{D_2} = 1.44$)[21].

The unimolecular formation of CH_4 is mechanistically particularly intriguing. Loss of methane is observed for linear nitriles $C_nH_{2n+1}CN$ in their reactions with $Fe^{\oplus}$, but only for $n \geq 6$ and provided the complexes are collisionally activated. The collision-free production of CH_4 in the system $(C_4H_9)_2CHCN$ (**5**) therefore points to a special process, possibly due to the secondary nature of the nitrile. Earlier labeling studies had revealed[9a] that for unbranched nitriles CH_4 originates from the ω and $(\omega - 2)$ positions, thus insertion into the $C–CH_3$ bond is followed by β-hydrogen transfer. For secondary nitriles, the fourth hydrogen is *not* supplied by the $(\omega - 2)$ position; rather, it originates from a position *β to the cyanide group!*[22] This is an indication that primarily an insertion of the metal ion into the C–CN bond must have occured (Scheme 2, **5** → **6**), which is

Scheme 2



followed by β-hydrogen transfer (**6** → **7**). The intermediate **7** now activates a *remote* C–CH_3 bond to form the metallacycle **8** from which CH_4 is lost via reductive elimination. Only intermediate **8** is formed, most likely because of the higher ring strain associated with the generation of **9**. Reductive elimination of HCN, which in principle might be feasible from **7** and/or **8** is not observed. This could be due to an unusually large activation barrier for this process; results discussed further below will substantiate this conjecture.

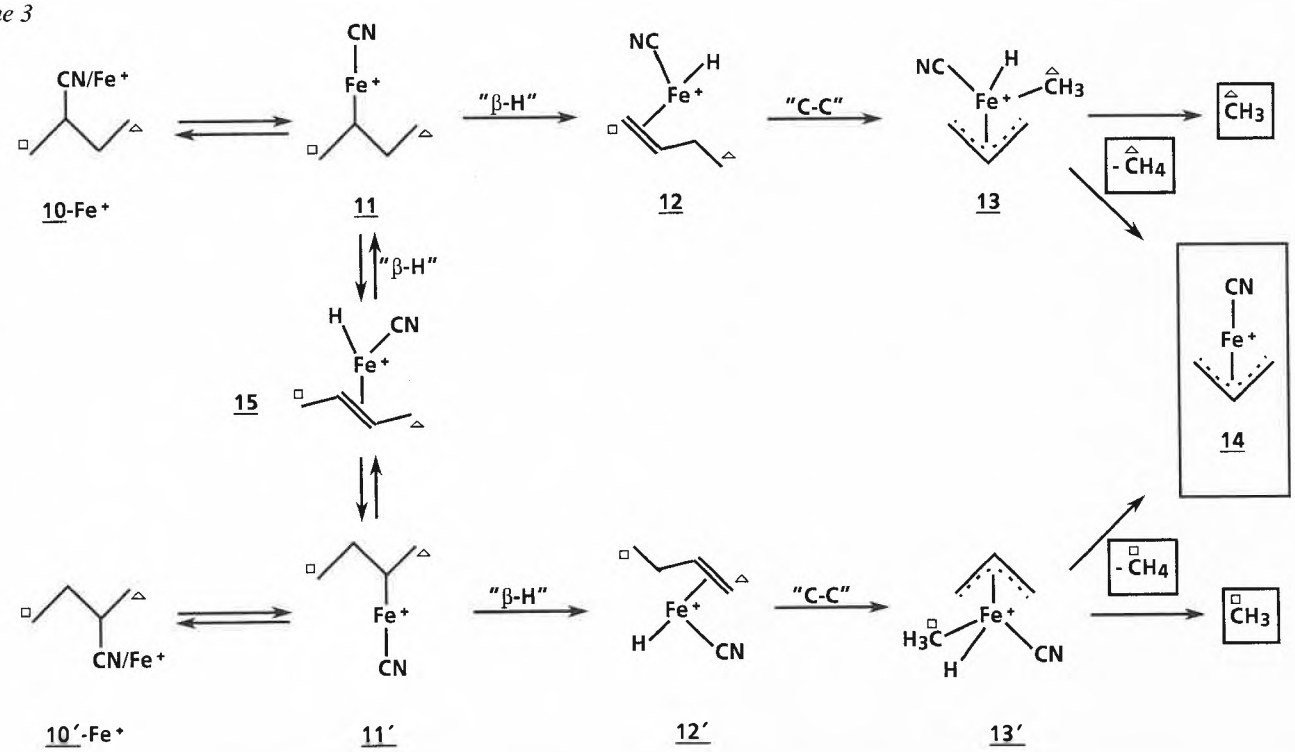
Can the mechanism for the methane loss, described in Scheme 2, be generalized or is it a unique feature of compound **5**? To answer this question, a series of symmetric and unsymmetric secondary nitriles RR′CHCN was examined in their behaviour towards $Fe^{\oplus}$ [22]. It was indeed shown for several systems that generation of CH_4 according to Scheme 2 is observed. While the reaction was absent for $R = R' = CH_3$ and for nitriles with at least one $R > C_5H_{11}$, methane loss was particularly pronounced for $R = C_2H_5$ and $R' = CH_3$, C_2H_5; the reason for this becomes obvious when we inspect Scheme 3 for the particular case of $CH_3CH(CN)C_2H_5$ (**10**). One immediately recognizes that the C–C insertion step now involves the activation of a relatively weak *allylic* C–C bond (**12** → **13**). The labeling experiments revealed also the existence of a degenerate isomerization **10**-$Fe^{\oplus}$ ⇄ **10′**-$Fe^{\oplus}$ in this particular system, which presumably proceeds via **15**. Collisional activation of the cyano-allyl complex **14** as well as the observation of $CH_3^{\odot}$ losses from **13** and **13′** further substantiate the outlined mechanism.

The simplest secondary nitrile, $(CH_3)_2CHCN$, does not give rise to loss of methane as the chain length does not permit the operation of the «allylic mechanism» according to Scheme 3. The only process that is observed in the metastable ion dissociations of $(CH_3)_2CHCN/Fe^{\oplus}$ complexes is ligand detachment, i.e. the loss of the complete ligand under reformation of the bare $Fe^{\oplus}$ ion. Ligand detachment is also present for the higher homologues but significantly reduced in intensity. In combining the data for the three different processes that are observed for RR′CHCN/$Fe^{\oplus}$ complexes, viz. ligand detachment, remote functionalization, and loss of CH_4 through initial insertion of $Fe^{\oplus}$ into the C–CN bond, one obtains the relationship expressed in Fig. 1.

The interplay between the three «mechanisms» and its striking chain-length dependence can be nicely deduced from Fig. 1:

- Remote functionalization is impossible on structural grounds for very small nitriles and gradually gains importance with increasing chain length. For the higher homologues it is in fact the only mechanism that is operative.

Scheme 3



- Ligand detachment, a process that can be viewed as an indication for the *inability* of a metal ion to react via a different pathway, i.e. to activate bonds of the organic substrate[12b], is most pronounced for the smaller nitriles where both, remote functionalization and methane generation, are unfavoured.
- The production of CH_4 reaches an intermediate maximum for those nitriles where the C–C activation step involves an allylic C–C bond; the process decreases in importance when the more favoured remote functionalization becomes possible.

In the metastable ion spectra of $R_2CHCN/Fe^{\oplus}$ complexes with sufficiently long alkyl residues ($R \geq C_5H_{11}$), in addition to the loss of H_2 and alkenes («remote functionalization»), one observes low-intensity signals which are formally due to loss of an alkane. Loss of C_nH_{2n+2} has also been observed for the longer linear aliphatic nitriles, but only upon collisional activation[9a]. A closer inspection revealed, however, that these products only seemingly correspond to the loss of authentic alkane molecules; actually, they correspond to the loss of H_2 followed by elimination of C_nH_{2n}[9a]. This process is observed for sufficiently long chains where loss of H_2 from internal methylene groups results in the formation of an unsaturated nitrile that reacts further via allylic insertion by loss of an alkene. Is the *unimolecular* generation of C_nH_{2n+2} from secondary nitrile/$Fe^{\oplus}$ complexes also due to an identical mechanism? To give the answer in advance, it is not! Labeling experiments and MS/MS/MS studies enabled us to show[15a,22] that:

(*i*) while loss of «C_nH_{2n+2}» for secondary nitriles also corresponds to a combined loss of C_nH_{2n} and H_2, the hydrogen molecule and the alkene originate from *different* alkyl chains!

(*ii*) Loss of the alkene precedes the loss of H_2 in these systems, and not *vice versa*.

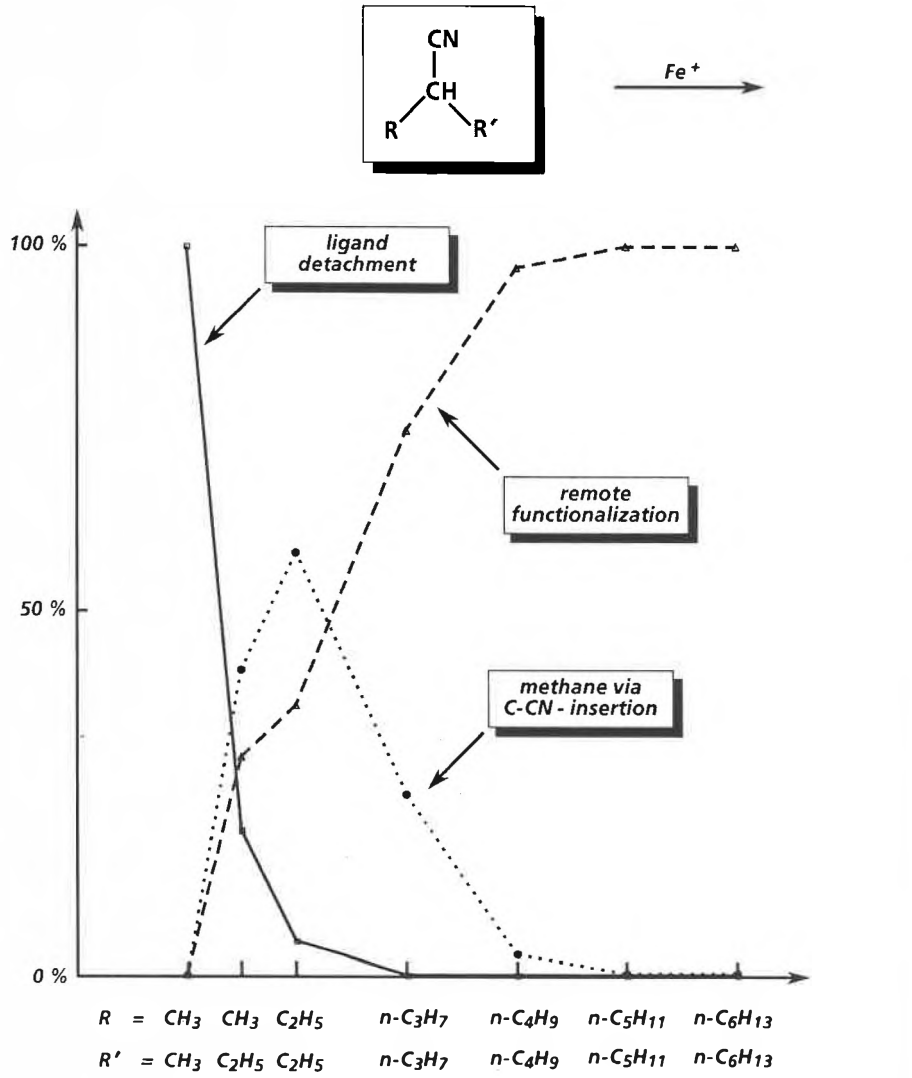
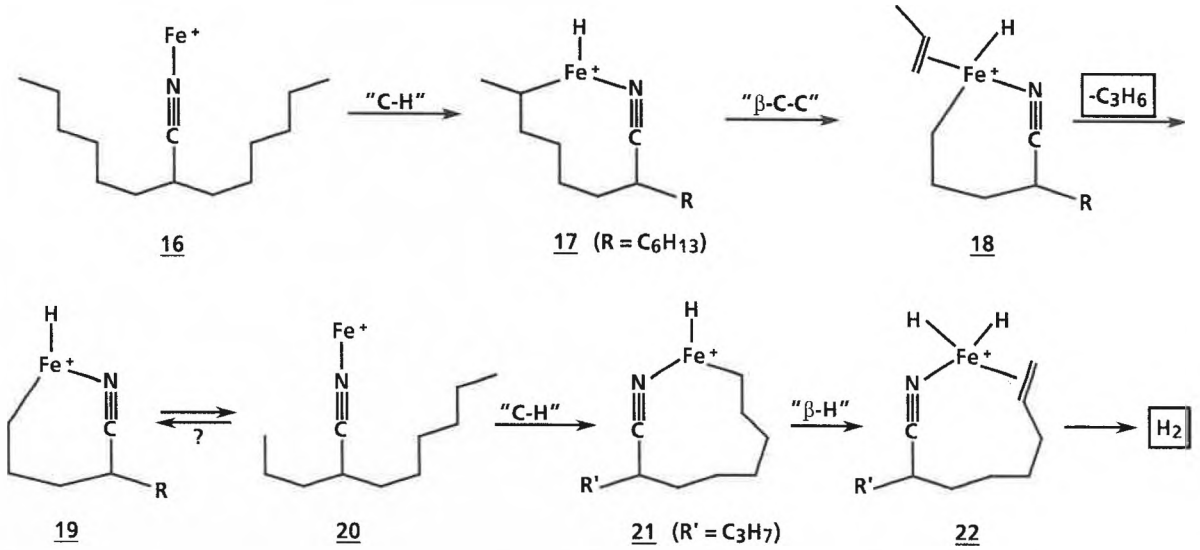


Fig. 1. Effects of alkyl chain-length variation on three types of reactions of secondary nitriles with bare $Fe^{\oplus}$ (cf. text).

An example for this «double remote functionalization» is given in Scheme 4 for the loss of «C_3H_8» from $(C_6H_{13})_2CHCN/Fe^{\oplus}$. The fact that an «anchored» transition-metal ion is capable of *successively activating different sites of a flexible molecule* has no precedent in either gas-phase or solution chemistry[23]. Quite recently[15] we came across a second example. In the reactions of aliphatic ketones RC(O)R, being

Scheme 4



structurally quite close to secondary nitriles RCH(CN)R, with bare $Fe^{\oplus}$ we also observed loss of first an alkene, followed by loss of a hydrogen molecule from the *other* alkyl chain.

5. Tertiary Nitriles

A markedly different chemistry is encountered if the reactions of *tert*-butyl cyanide (**23**), the first example of a tertiary nitrile, with $Fe^{\oplus}$ are studied. Except for a weak signal due to loss of methane that only appears in the metastable ion spectrum but not in FTICR experiments, two completely «new» products are formed[24]. These are a complex of $Fe^{\oplus}$ with {H,C,N} and $[FeC_4H_8]^{\oplus}$ by loss of {H,CN}; the two products are obviously related to each other in that they arise from a common intermediate of the general structure $[(H,CN)Fe^{\oplus}(C_4H_8)]$.

The two reaction products suggest almost automatically themselves to be explained by the insertion/β-hydrogen-shift mechanism, formulated more than 10 years ago by *Allison* and *Ridge* for substrates others than nitriles[25]. If one applies this mechanism to the reactions of **23**-$Fe^{\oplus}$ it would commence with an insertion of the metal ion into the C–CN bond (Scheme 5, **23**-$Fe^{\oplus}$ → **24**), followed by a β-hydrogen shift (**24** → **25**). Rearrangement then leads to the bi-ligated complex **26** which looses its two ligands according to their relative binding energies with respect to the metal ion. Although this mechanism could in principle explain the loss of {H,CN} and the formation of $[Fe\{H,C,N\}]^{\oplus}$, further experiments reveal that it does *not* apply in the present case.

High-energy collisional activation of the $[Fe\{H,C,N\}]^{\oplus}$ ions shows that these ions do *not* possess the structure **27**; rather, they are complexes of hydrogen cyanide with the metal ion, viz. **31**. Distinction between **27** and **31** is possible because both isomers can be independently generated in starting from either aliphatic isocyanides (→ **27**) or tertiary nitriles (→ **31**), respectively[26]. Furthermore, the reactions of $Cu^{\oplus}$ with 2-methylbutanenitrile (**10**)[6] and of $Fe^{\oplus}$ with 2,2-dimethylbutanenitrile[22] also give rise to HCN-$M^{\oplus}$ ions (M = Fe, Cu) and loss of {H,CN}. As in these two substrates the hydrogen atoms are no longer equivalent, labeling reveals that *not only* specifically the β-hydrogen atoms, but *all* positions of the alkyl part contribute to the hydrogen-transfer step, albeit in different amounts. These results were interpreted in terms of an ion/dipole mechanism. Complexation of the metal ion to the nitrogen atom of the cyanide function induces cleavage of the C–CN bond and gives rise to the intermediate ion/dipole complex **29**[27]. The incipient carbenium ion now serves as an intramolecular protonating reagent for the CNM-dipole; this leads to the bi-ligated complex **30** which eventually dissociates reflecting the binding energies of its ligands. As ion/dipole complexes in the gas phase are known to be quite long-lived[28], facile hydrogen rearrangements in the carbenium-ion-like part can take place which explains the observed partial H/D scrambling.

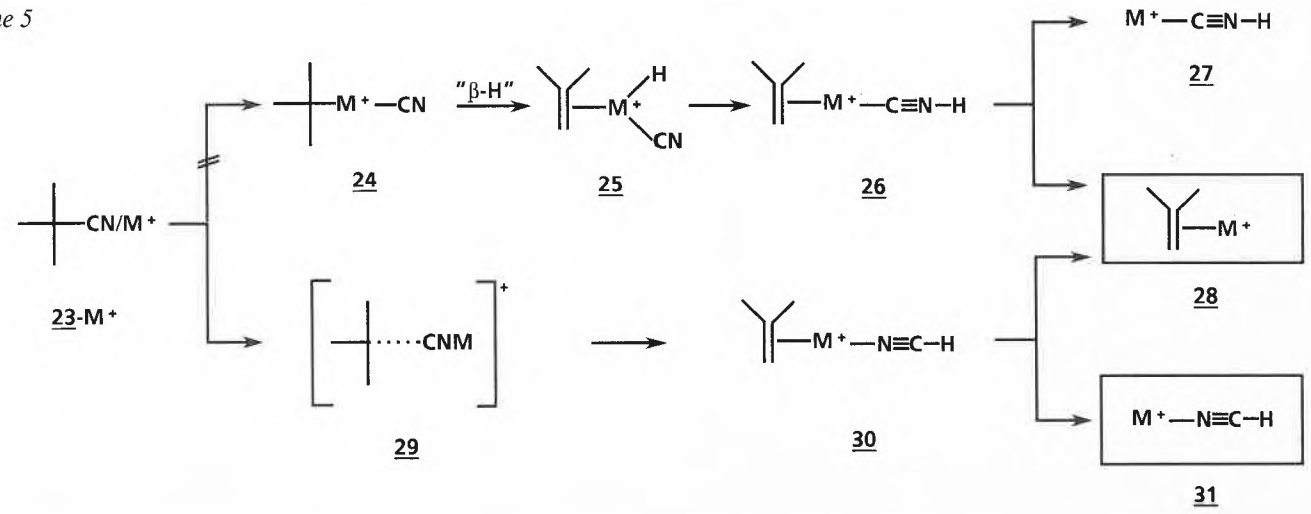
A comparison of the branching ratios for competitive losses of {H,CN} and alkenes from **26** versus **30**, generated from isocyanides and tertiary nitriles, respectively, also supports the ion/dipole mechanism[24]. Starting from *tert*-$C_4H_9CN/Fe^{\oplus}$ (**23**-$Fe^{\oplus}$), the branching ratio reflects the presence of a hydrogen cyanide ligand that is a relatively weaker bound ligand than is hydrogen isocyanide in **27**[29]; it is observed that the ratio for the ion abundance **[28]**/**[31]** is significantly larger for **30** compared with **[28]**/**[27]** from the independently generated **26**. Moreover, the result that it is the degree of substitution at the α-carbon atom, which determines whether $Fe^{\oplus}$ reacts with a given nitrile via the ion/dipole mechanism is a clear indication that the strength of the C–CN bond is a vital factor. With *secondary* nitriles, $Fe^{\oplus}$ is unable to react via this mechanism; a tertiary nitrile is required to induce the cleavage. On the other hand, $Cu^{\oplus}$, which is known to be a much stronger Lewis acid than $Fe^{\oplus}$, is able to react already with secondary nitriles under formation of HCN–$Cu^{\oplus}$ and {H,CN}.

6. How Do Different Transition-Metal Ions Affect the Reactions of Nitriles?

As alreadys mentioned above, different metal ions afforded slightly different products with linear nitriles; a much more dramatic effect is noted for secondary and tertiary nitriles. The totally different products that resulted from the rections of $Fe^{\oplus}$ and $Cu^{\oplus}$ with 2-methylbutanenitrile (**10**) caused us to use this compound as a model substance for a comparative study of most of the first d-row transition-metal ions. While for $Fe^{\oplus}$ the dominant reaction corresponds to the generation of methane according to Scheme 3 and a slightly smaller amount of remote functionalization (Scheme 1), for $Cu^{\oplus}$ only the two products of the ion/dipole mechanism (Scheme 5) were observed. It was gratifying to see that ions of the two elements in-between, i.e. $Co^{\oplus}$ and $Ni^{\oplus}$, nicely fit into the picture as a gradual *switching between the three mechanisms* could be noted[6]. For $Co^{\oplus}$, products due to all three mechanisms were present, and for $Ni^{\oplus}$ remote functionalization and ion/dipole mechanism applied. The relative amount by which each mechanism contributes to the formation of products can be seen for the four metal ions, $M^{\oplus} = Fe^{\oplus}$, $Co^{\oplus}$, $Ni^{\oplus}$, and $Cu^{\oplus}$, in Fig. 2. While for $Fe^{\oplus}$ the «allylic mechanism», i.e. loss of CH_4 and the CH_3 radical via insertion into the newly formed allylic bond, is the most prominent one, it sharply drops for $Co^{\oplus}$ and is already absent for $Ni^{\oplus}$. In contrast, the ion/dipole mechanism, that is not observed for $Fe^{\oplus}$ and secondary nitriles, continuously increases in importance in going over from $Fe^{\oplus}$ to $Cu^{\oplus}$, where it even represents the only mechanism operative. Remote functionalization, already second-most important for $Fe^{\oplus}$, reaches a maximum for $Co^{\oplus}$, slightly drops for $Ni^{\oplus}$, and disappears for $Cu^{\oplus}$.

For other first-row metal ions a different behaviour was noted[6]. «Early» transition-

Scheme 5



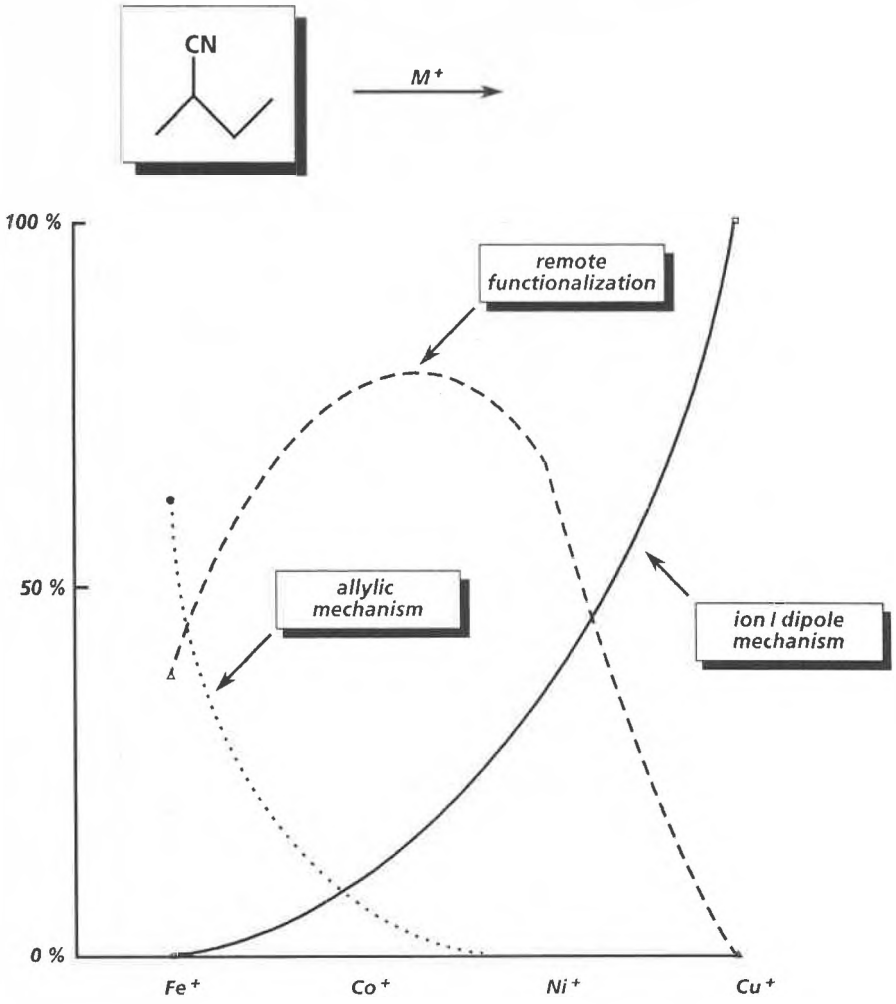


Fig. 2. Effects of different transition-metal ions on the relative contribution of different types of reactive mechanisms operative in $CH_3CH(CN)C_2H_5/M^{\oplus}$ complexes (M = Fe, Co, Ni, Cu).

metal ions like $Ti^{\oplus}$ and $V^{\oplus}$ do not activate C–C bonds; rather they almost exclusively react via C–H activation. For example, losses of H_2, $2H_2$, and H_2 together with other neutrals are observed in the reactions of **10**. Labeling studies reveal the operation of several competing processes that are in no obvious manner related to the ones already discussed[6]. The strong tendency for dehydrogenations induced by $Ti^{\oplus}$ and $V^{\oplus}$ is completely in line with results from other groups on different substrates[30].

$Cr^{\oplus}$ is totally unreactive with **10**; under FTICR conditions only adduct formation ($[Cr(C_4H_9CN)_x]^{\oplus}$; x = 1, 2) is observed[6]. Low-energy collisional activation of **10**-$Cr^{\oplus}$ in the FTICR as well as metastable ion dissociations of this complex only result in $Cr^{\oplus}$, i.e. ligand detachment. This inability of $Cr^{\oplus}$ towards CH/CC-activation[12b] with a variety of substrates has been observed quite often[30a,c,d,31] and is usually attributed to the half-filled d-shell of this ion in its ground state. One can, however, force $Cr^{\oplus}$ also to reactions by providing sufficient internal energy; encounter complexes of ligands with a high binding energy to the metal ion are able to react. The gas-phase chemistry of 4-octyne represents a case in point in that reactivity has been observed for $Cr^{\oplus}$[16b, 32]. *tert*-C_4H_9CN (**23**) also reacts with $Cr^{\oplus}$ and the two products of the ion/dipole mechanism are observed[33]; thus the energy gained by the complexation of $Cr^{\oplus}$ is sufficient to cleave the weak *t*-C–CN bond via Scheme 5, while, analogous to $Fe^{\oplus}$, secondary nitriles cannot react by this or other mechanisms.

For $Zn^{\oplus}$, adduct formation with **10** is the dominant pathway; in addition, only small amounts of products due to charge-transfer reactions[34] and the ion/dipole mechanism are observed[6].

7. Conclusions and Outlook

We have demonstrated that by systematically modifying a substrate, a variety of different gas-phase processes can be induced by bare transition-metal ions. By using linear nitriles and $Fe^{\oplus}$, specific activation of remote C–H and C–C bonds is observed; the usage of $Co^{\oplus}$ or $Ni^{\oplus}$ enables one to vary the ring size to a certain degree. Secondary nitriles can be activated by, depending on the chain lengths, various combinations of methane generation via initial insertion into the C–CN bond and remote functionalization of C–C bonds. Small tertiary nitriles react preferentially via the ion/dipole mechanism; however, increasing the chain length affords a combination of all three mechanisms (cf. 2,2-dimethylbutanenitrile/$Fe^{\oplus}$[22]), and, as new studies indicate, it is even possible to trade off ion/dipole against remote functionalization[33]. By changing the metal ion the chemistry can be influenced very strongly indeed. Using «early» transition-metal ions results in preferential activation of C–H bonds while with the group 8–11 metal ions a switching between all three mechanisms is possible (Fig. 2). Steric effects can make a nitrile more or less reactive (ligand detachment vs. activation, Fig. 1), and can in part influence the kind of mechanism that is operative.

It can be safely proposed that further controlled variation of the experimental conditions of the type described in this review will greatly enhance our understanding of inherent transition-metal properties. Thus, it seems feasible that in a not too distant future chemists will be in a position to reliably predict the course of gas-phase organometallic chemistry. No doubt that quite distinct areas will benefit from the progress made in this seemingly narrow field of chemistry.

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