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Gas-Phase Chemistry of Bare Transition-Metal Ions in Comparison

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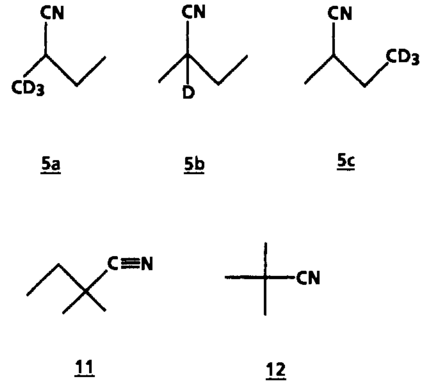
Abstract: Some basic principles of gas-phase organometallic chemistry are demonstrated, exemplified for the model compound 2-methylbutanenitrile (**5**). The reactions of first-row transition-metal ions with **5** and its deuterated isotopomers **5a–5c** reveal a distinct influence of the individual metal ion on the chemistry in these systems. While "early" transition-metal ions (Ti^+, V^+) mainly give rise to dehydrogenations, the activation of C–C bonds dominates for Fe^+. Closed d-shell ions (Cu^+, Zn^+) react under intermediate formation of ion/dipole complexes, and Co^+ and Ni^+ show inasmuch a "mixed" behavior, as many similarities to Fe^+ are noticed. However, part of the products are already formed via ion/dipole complexes. A clear trend is observed, going from Fe^+ to Cu^+ in that respect. Cr^+ is found to be unreactive as reported before in many other cases. The results were obtained by the combined use of ion/molecule reactions performed in a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer and metastable ion decompositions of adduct complexes, generated in the ion source of a triple-sector instrument.

Gas-phase organometallic chemistry renders its interest from the fact that, by the very nature of the physical isolation, the inherent properties of a specific metal ion (or complex) can be probed in the absence of other disturbing influences. These include ligand and solvent effects as well as ion pairing, which prevail in the condensed phase. In mass spectroscopic studies, these complications can be elegantly avoided with the corollary that is possible to study these otherwise highly reactive species and gain insight into their behavior. With regard to the understanding of many catalytic processes, a fundamental problem is concerned with the mechanism of activation of C–H and C–C bonds, which constitutes a crucial step in catalytic cycles[1] and which is also observed in the reactions of bare transition-metal ions with organic substrates in the gas phase.[2]

Especially the activation of specific bonds, *separated spatially from the site of complexation*, represents a great challenge for heterogeneous and homogeneous catalysis. This, however, is characteristic for enzymatic processes in that the enzymes specifically "anchor" a functional group and *geometrically* select remote sections of the flexible substrate. Breslow has coined the term "*remote functionalization*" for this kind of interaction.[3]

Chart I



5a **5b** **5c**

11 **12**

Recently, we were able to demonstrate that the mechanism of remote functionalization is also operative in gas-phase organometallic chemistry for a great variety of organic substrates,[2l,n] especially nitriles.[4] In general, the transition-metal ion is "anchored" at the functional group of the substrate (Scheme I), and it is observed to activate C–H and C–C bonds at positions *remote* from this functional group (Scheme I: **1** → **2**, for the nitrile case). Insertion of the metal ion into the terminal C–H bond is followed by competitive β-hydrogen shift (**2** → **3**) or β-CC cleavage (**2** → **4**). Reductive elimination of hydrogen or loss of ethylene terminates the reaction sequence.

More recently, a novel mechanism was established for α-branched nitriles,[5] which concerns the generation of methane. Based on extensive labeling experiments, it was demonstrated that insertion of Fe^+ into the C–CN bond has to be assumed as the first step in a multistep sequence which, via β-hydrogen shift and allylic C–C bond cleavage, eventually leads to the formation of methane. For the Fe^+ complex of the model compound 2-methylbutanenitrile (**5**), it was observed that CH_4 contains one

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(2) For reviews, see: (a) Müller, J. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 653. (b) Müller, J. *The Organic Chemistry of Iron*; Academic Press: New York, 1978; Vol. 1, p 145. (c) Beauchamp, J. L.; Stevens, A. E.; Corderman, R. R. *Pure Appl. Chem.* **1979**, *51*, 967. (d) Freiser, B. S. *Talanta* **1985**, *32*, 697. (e) Allison, J. *Prog. Inorg. Chem.* **1986**, *34*, 627. (f) Armentrout, P. B. In *Structure/Reactivity and Thermochemistry of Ions*; Ausloos, P., Lias, S. G., Eds.; D. Reidel: Dordrecht, 1987; No. 193, p 97. (g) Ridge, D. P. *Ibid.* 1987; No. 193, p 165. (h) Armentrout, P. B. In *Gas Phase Inorganic Chemistry*; Russell, D. H., Ed.; Plenum: New York, 1989. (i) Squires, R. R. *Chem. Rev.* **1987**, *87*, 623. (j) Beauchamp, J. L. In *High Energy Processes in Organometallic Chemistry*; Suslick, R. E., Ed.; ACS Symposium Series 333; American Chemical Society: Washington, DC, 1987. (k) Buckner, S. W.; Freiser, B. S. *Polyhedron*, **1988**, *7*, 1583. (l) 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; Vol. 2, p 203. (m) Schwarz, H. *Acc. Chem. Res.* **1989**, *22*, 282. (n) Eller, K.; Schwarz, H. *Chimia*, in press. (o) Armentrout, P. B.; Beauchamp, J. L. *Acc. Chem. Res.* **1989**, *22*, 315.

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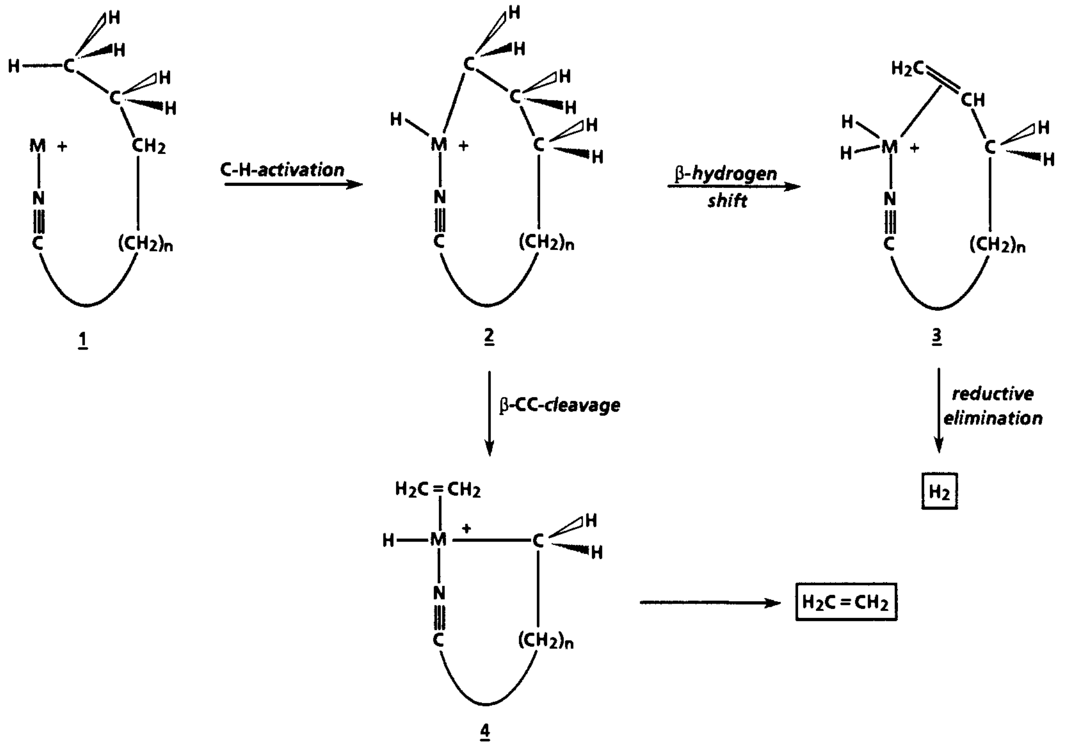
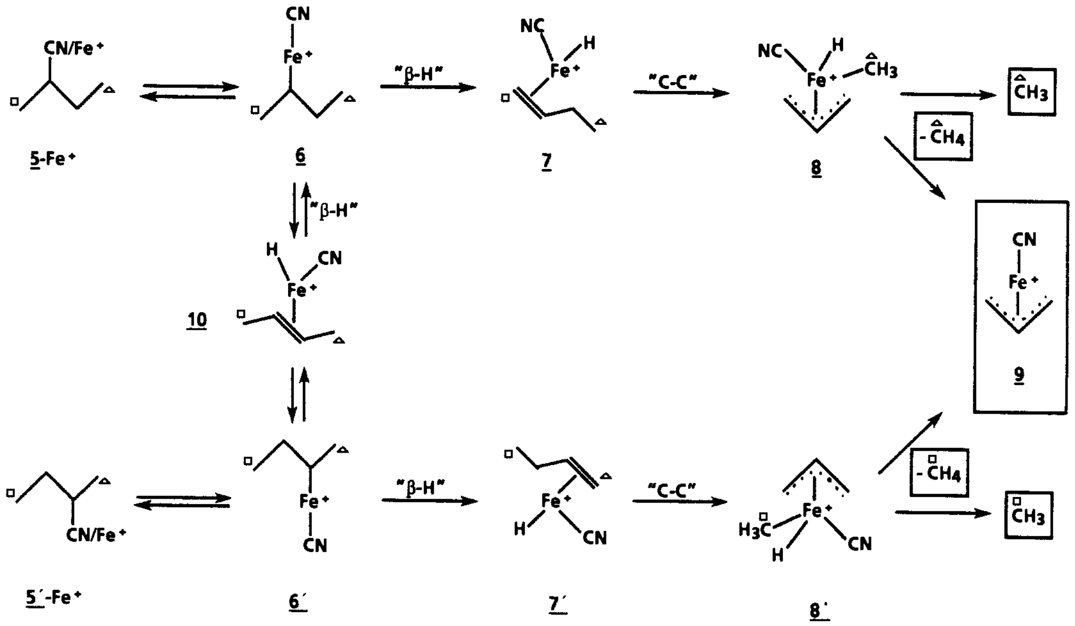
Scheme I



Scheme II



hydrogen from the methyl substituent (marked with a square in Scheme II), and the remaining three hydrogen atoms originate from the end of the chain (marked with a triangle). Reductive elimination of methane from intermediate **8** leads to the cyano–allyl complex **9**, whose structure has been probed via collisional activation in an MS/MS/MS experiment.[5] Furthermore, by use of the deuterated nitriles **5a**–**5c** (Chart I), not only was the proposed mechanism substantiated but evidence was presented for the operation of a degenerate isomerization (**5**–Fe$^+$ $\rightleftarrows$ **5′**–Fe$^+$).[5]

In support of the "allylic mechanism" (Scheme II) is the unimolecular loss of a methyl radical, which is also observed in ion/molecule reactions of Fe$^+$ with **5** under the conditions of Fourier transform ion cyclotron resonance (FTICR) mass spectrometry.[6] The labeling data clearly prove that both methyl groups are lost, with a preference, however, for the one originally located in the more remote position from the cyano group.[5] The production of methyl radicals is also suggested to proceed via intermediates **8** and **8′**, respectively.

By introducing a further substituent in the α-position, e.g., studying 2,2-dimethylbutanenitrile (**11**, Chart I), a noticeable difference is observed. In addition to the products generated from the system **5**–Fe$^+$, i.e., CH_4, C_2H_4, and H_2, two new signals appear; one is due to the loss of HCN (or HNC) and the other corresponds to a complex of Fe$^+$ with [H, C, N].[5,6] These two products are clearly linked with each other and could, in principle, be produced by the traditional insertion/β-hydrogen shift mechanism, first proposed by Allison and Ridge.[7] It is helpful, however, before commenting on this interpretation, to mention briefly the results

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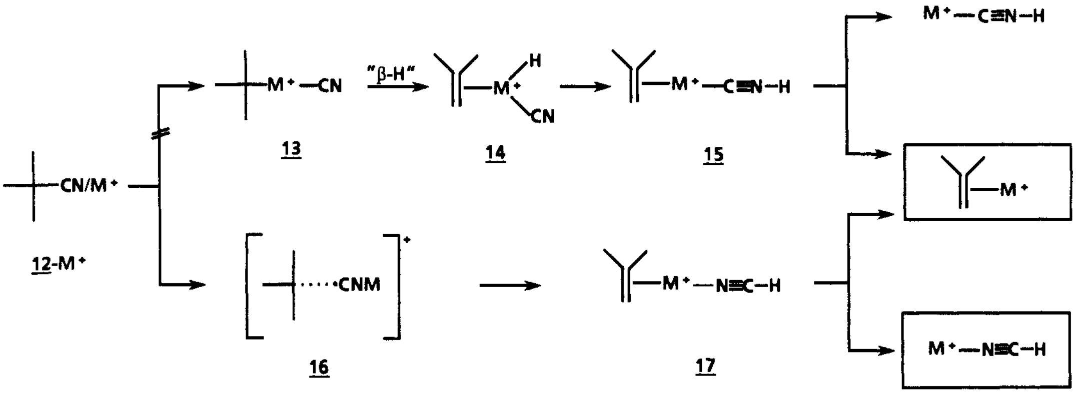
Scheme III



obtained for another structurally related nitrile, i.e., 2,2-dimethylpropanenitrile (**12**). Except for a weak signal in the MI spectrum of **12**-Fe^+ for the generation of methane (3%), only the two above-mentioned products, namely $Fe[H,C,N]^+$ and loss of [H,C,N], are observed.[6,8] If one assumes their formation according to the insertion/β-hydrogen shift mechanism (Scheme III, **12**-$M^+ \rightarrow$ **15** with M = Fe), one would except the transition-metal ion to be bound to the carbon part of the nitrile function. However, this is not born out by the experimental data; rather, they are consistent with the interpretation that the transition metal is attached to the nitrogen atom of an intact hydrogen cyanide ligand.[8,9] This result can be explained by the intermediate formation of an ion/dipole complex **16**, the carbenium-ion part of which serves, in a second step, as a protonating reagent for the FeNC dipole (**16** → **17**).[10]

For the $Fe[H,C,N]^+$ ion generated from **11**, the same result was found, thus pointing to a similar mechanism. In addition, the origin of the hydrogen atoms in the neutral products CH_4 and C_2H_4 from **11**-Fe^+ was elucidated by deuterium labeling.[5] The data leave no doubt that, while C_2H_4 is formed by the mechanism outlined in Scheme I ("remote functionalization"), CH_4 is produced analogous to Scheme II, i.e., via the "allylic mechanism".

Obviously, the course of the reaction of the nitriles with Fe^+ is determined by the degree of substitution at the α-carbon atom. For tertiary nitriles, a major part of the reaction products is formed via ion/dipole complexes, while for secondary nitriles insertion into the C–CN bond prevails. For nitriles having no substituents at the α-position, the Fe^+-mediated reactions involve only segments of the alkyl chain remote from the functional group. It remains open to speculation whether this reactivity pattern, as a function of the degree of α-substitution, is due to the different bond strengths of the C–CN bond[11] or whether it reflects the stability of the resulting intermediates.

The goal of the present study is 2-fold. The first purpose is to see what is the detailed influence of the transition-metal ion on the reactions of a given nitrile substrate. This is accomplished by the investigation of a larger set of metal ions encompassing "early" as well as "late" first-row transition metals, i.e., Ti^+, V^+, Cr^+, Fe^+, Co^+, Ni^+, Cu^+, and Zn^+. The second purpose is to further the comparison between FTICR and sector-field studies. It has already been shown[6] that these seemingly quite different approaches lead to the same results, as long as a few points are taken into account in the interpretation of the data. In fact, the earlier comparison[6] included structurally different substrates as nitriles and unsaturated hydrocarbons (the latter including both linear and branched ones), and the reactions of these substrates with several transition-metal ions which are already known to behave quite differently, like Cr^+, Fe^+ or Cu^+, were studied. The following results are worth recalling with regard to the present study:

(i) In the FTICR experiments, in which ion/molecule reactions of *bare* transition-metal ions with organic substrates are monitored, *multiple* losses of neutral molecules are favored to a much greater extent in comparison with metastable ion decompositions of adduct complexes studied in sector-field instruments.

(ii) The decomposition of biligated complexes of the type MAB^+ (M = transition metal) seems to depend very much on kinetic and thermodynamic factors which are, of course, different for both instruments. Not surprisingly, in the two experimental approaches used, differences in product distribution (MA^+ vs MB^+) can be noticed, which can even lead to a complete discrimination of one of the two conceivable products.

The present work will significantly extend the comparison between FTICR and sector-field instruments by studying the reactions of **5** with different transition-metal ions under both instrumental conditions, thus filling a gap repeatedly noticed in the literature. Furthermore, the question of isotopic distribution is addressed; in particular, we would like to know if the different time scale of both instruments exerts a discernible influence on the extent of reversible steps and on the operation of kinetic isotope effects as well. The model compound **5** seems to be an ideal candidate for probing either topic, as the system is already known to exhibit reversible processes, e.g., the partial, degenerate isomerization (Scheme II).

Experimental Section

FTICR experiments were performed by using a Spectrospin CMS 47X instrument, which is equipped with an external ion source. The machine and its operation have been described in detail in an earlier communication.[6] Briefly, transition-metal ions are formed via laser desorption/ionization[2d,12] in the external ion source[13] by focusing the beam of a Nd:YAG laser (Spectron Systems, 1064 nm) onto a high-purity rod of the desired transition metal. The ions are extracted from the source and transferred into the analyzer cell by a system of electric potentials and lenses. The ion source, transfer system, and ICR cell are differentially pumped by three turbomolecular pumps (Balzers TPU 330 for source and cell, respectively, and Balzers TPU 50 in the middle of the transfer system). After deceleration, the ions are trapped in the field of the superconducting magnet (Oxford Instruments), which has a maximum field strength of 7.05 T. The metal's most abundant isotope is isolated via double-resonance ejection pulses and allowed to react for a variable amount of time (typically 50–500 ms) with the organic substrate, which is present in the cell with a constant pressure of the order of 10^{-8} mbar. For collisional cooling of eventually formed excited states, as well as for CID experiments,[14] argon was present as a buffer gas with a

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Table I. Reaction Products Generated from M^+ and 2-Methylbutanenitrile (**5**)[a]

	Fe^+		Co^+		Ni^+		Cu^+		
product	MI[b]	FTICR[c]	MI	FTICR	MI	FTICR	MI	FTICR	CID[d]
H_2	7	3	2	<1	3	<1			
$CH_3^•$	6	3	1	<1					
CH_4	42	41	4	2					
[HCN]			5		12		31	5	14
C_2H_4	23	15	67	49	58	55			
H_2/HCN			<1	2		6			
C_3H_6	2	3	2	1					
$M[HCN]^+$			7	6	20	23	46	15	21
M^+	20	*e*	11	*e*	7	*e*	23	*e*	65
$M(s\text{-}C_4H_9CN)^+$	*e*	35	*e*	39	*e*	16	*e*	80	*e*

[a] Intensities are expressed in $\sum$fragments = 100%. [b] Data taken from ref 5. [c] Data taken from ref 6. [d] Low-energy CID with the FTICR instrument. [e] See text for discussion.

constant pressure of (1–5) × 10^{-7} mbar, as measured with an uncalibrated ionization gauge (Balzers IMG 070). All functions of the instrument were controlled by a Bruker Aspect 3000 minicomputer; broad-band spectra were recorded with a fast ADC and digitized as 64K or 128K data points and subjected to one zero fill before Fourier transformation.

The experimental conditions of the studies with the sector-field instrument have already been described in detail previously.[2l,4–6,8,9] Briefly, the mass spectrometer used is a Vacuum Generators ZAB-HF-3F triple-sector machine with BEB configuration[15] (B magnetic, E electric sector). Complexes were generated by two different ionization methods; the first involves electron impact on a 1:5 mixture of $Fe(CO)_5$ (or another appropriate volatile organometallic compound) and the organic substrate in a high-pressure chemical ionization source (100 eV of ionizing energy, 0.5 mA of emission current, 0 V of repeller voltage, 200 °C source temperature, 10^{-6}-mbar source housing pressure). Here, complex formation is believed to happen via ion/molecule reactions of, e.g., $Fe(CO)_x^+$ ($x = 1, 2$) with the organic substrate or direct adduct formation with stronger bound ligands. The other technique employed in this study is the "FAB method",[16] which consists of bombarding a target of an inorganic salt (e.g., $NiCl_2$ or $CuSO_4$) with fast xenon atoms (Xe gas, 7–9 keV of kinetic energy, 0.1 mA of emission current in the FAB gun, 25 °C source temperature, 10^{-4}–10^{-5}-mbar source pressure). The sputtered metal ion forms adduct complexes with the organic substrate by an as yet not fully understood mechanism. Complexes that are 1:1, generated by either ionization method, are mass and energy selected (8 kV of acceleration voltage, 3000–5000 mass resolution in the 10% valley definition) with the first two sectors (B(1)E), and metastable or collision-induced dissociations occurring in the third field-free region between the electrostatic sector and the second magnet are monitored by scanning of B(2). The background pressure for recording metastable ion (MI) spectra is 10^{-8} mbar; for the high-energy collisional activation mass spectra, helium is introduced into the collision chamber (80% transmission, corresponding to ca. 1.1 collisions[17]). Spectra were processed on-line with the VG 11/250 data system, and 10–50 scans were averaged to improve the signal-to-noise ratio.

All substances were synthesized using established procedures and purified by preparative gas chromatography. The deuterium content was determined by NMR and GC/MS. For the FTICR experiments, the compounds were carefully degased by multiple freeze–pump–thaw cycles.

Table II. Reaction Products Generated from Fe^+ and Labeled 2-Methylbutanenitriles[a]

	5a		**5b**		**5c**	
product	MI[b]	FTICR	MI[b]	FTICR	MI[b]	FTICR
H_2	65	69	>90	80	49	33
HD	35	31	<10	20	51	67
$CH_3^•$	70	67	100	100	10	33
$CD_3^•$	30	33			90	67
CH_4			100	100		1
CH_3D	75	95			6	3
CD_3H	25	5			94	96
C_2H_4	78	100	>95	96	6	3
C_2H_3D			<5	4		
$C_2H_2D_2$	13				55	48
C_2HD_3	9				39	49
C_3H_6			*c*			
C_3H_5D			*c*	100		
$C_3H_4D_2$	27	29			47	29
$C_3H_3D_3$	73	71			53	71

[a] Intensities are expressed in $\sum$fragments = 100% for each neutral loss, respectively. [b] Data taken from ref 5. [c] Signal-to-noise ratio not sufficient for exact determination.

Results and Discussion

For didactic purposes, the discussion of the individual metal ions will not follow their ordering in the periodic table of the elements. Rather, as most of the data have already been collected for the Fe^+ system, we will describe these results first.

The metastable ion dissociations of **5**–Fe^+ have been compared, from an instrumental point of view, with the reactions of bare Fe^+ with **5**.[6] These data are given in Table I and show a good correlation not only with regard to product distribution but also with intensities. Slight differences arise from the fact that the bare metal ion is the starting point in the FTICR experiment, and therefore, ligand detachment, i.e., loss of the complete ligand from already formed complexes **5**–Fe^+, cannot be monitored. On the other hand, metastable ion decays of **5**–Fe^+ in the tandem-MS studies exclude the quantitative analysis of adduct ion formation as an experimental parameter. Thus, part of the differences simply reflect the normalization procedure of the data. Table II gives the results from the measurements with the labeled isotopomers **5a**–**5c**. The complete set of labeling data for the losses of H_2, CH_3, CH_4, and C_2H_4 can be explained in a straightforward manner by the mechanism outlined in Schemes I and II, respectively. It is quite obvious that dehydrogenation proceeds via "remote functionalization". The at first glance unexpected isotopomer distributions for the individual systems are due to the fact that the degenerate isomerization (Scheme II) has already taken place to some extent.

The label distribution for the losses of methane and the methyl radical is well explained by Scheme II, and loss of C_2H_4 is once again due to remote functionalization. To explain the partial "scrambling" which is observed for the ethylene detachment, one has to conclude that the hydrido–ethylene complex **4** is in equilibrium with an ethyl structure. Reversible processes of the type **1** $\rightleftharpoons$ **2** $\rightleftharpoons$ **4** can be excluded, as no loss of D_2 is observed. This

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(16) This method was originally introduced by: (a) Freas, R. B.; Campana, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 6202. (b) Freas, R. B.; Dunlap, B. L.; Waite, B. A.; Campana, G. E. *J. Chem. Phys.* **1987**, *86*, 1276. It turned out to be a very useful approach that has been repeatedly applied in several studies from our laboratory: (c) ref 4c,d, 9. (d) Lebrilla, C. B.; Drewello, T.; Schwarz, H. *Organometallics* **1987**, *6*, 2450. (e) Eller, K.; Lebrilla, C. B.; Drewello, T.; Schwarz, H. *J. Am. Chem. Soc.* **1988**, *110*, 3068. (f) Karrass, S.; Eller, K.; Schulze, C.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 607. (g) Karrass, S.; Prüsse, T.; Eller, K.; Schwarz, H. *J. Am. Chem. Soc.*, in press. (h) Prüsse, T.; Schwarz, H. *Organometallics*, in press. (i) Eller, K.; Schwarz, H. *Chem. Ber.*, in press.

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Table III. Reaction Products Generated from Cu^+ and Labeled 2-Methylbutanenitriles[a]

	5a		**5b**		**5c**	
product	MI	FTICR	MI	FTICR	MI	FTICR
[HCN]	82	87	94	94	96	100
[DCN]	18	13	6	6	4	
$Cu[HCN]^+$	78	81	93	95	93	95
$Cu[DCN]^+$	22	19	7	5	7	5

[a] Intensities are expressed in $\sum$fragments = 100% for each neutral loss, respectively.

feature is not unique to **5** but is also observed for butanenitrile.[5] The minor production of propene (2%) remains a mystery for the time being, as we are unable to propose a mechanism that would account for *all* experimental findings. Further labeling studies could possibly provide a solution to this puzzle.

Agreement between FTICR and MI spectra is always good or excellent for all isotopomers of the system **5**–Fe^+, thus indicating that the gas-phase organometallic chemistry probed by these otherwise quite different methodologies is, at least for this particular system, (i) not fundamentally different and (ii) not instrument dependent.

The next transition-metal ion to be discussed is Cu^+. Due to its filled d^{10} configuration (^1S ground state), this ion is already known to exhibit unusual behavior. It is unreactive toward alkanes,[18] but products due to activation of CH/CC bonds were observed for esters and ketones,[19] alcohols,[20] alkyl chlorides,[12a,21] alkenes,[22] amines,[23] and methyl nitrite.[24] For linear nitriles, it was found[16d] that upon high-energy collisional activation the Cu^+ complexes give rise to several products, inter alia $Cu[H,C,N]^+$, while metastably only ligand detachment is observed.[6] Under FTICR conditions, *linear* nitriles only form adduct complexes of the type $Cu(RCN)_x^+$ ($x = 1, 2$).[6]

In those cases, where reactivity has been observed, this has often been explained[12a,19–21] in terms of a "dissociative attachment" mechanism or Lewis acid chemistry. Recently,[8] this rather ill-defined concept has been treated in more detail in conjunction with the reactions of Fe^+ with 2,2-dimethylpropanenitrile (**12**). Interestingly, the reaction of **12** with Fe^+,[8] which is believed to react normally via the insertion/β-hydrogen shift mechanism, as well as with Cu^+,[9] where dissociative attachment should prevail, results in the production of HCN–M^+ (M = Fe, Cu). This important observation implies that the *initial coordination site is conserved* in the course of the reaction. This is best explained, as already mentioned in the introduction, with the intermediate formation of ion/dipole complexes (Scheme III) and not the operation of a insertion/β-hydrogen shift mechanism.

The reaction products of Cu^+ with **5** (Table I) represent still another example, where formally "dissociative attachment" is operative, as only $Cu[H,C,N]^+$ and loss of [H,C,N] are observed. The structure of the former ion has been probed using high-energy collisional activation in the sector-field instrument; the resulting spectrum is identical with the hydrogen cyanide complex of Cu^+, obtained from **12**–Cu^+,[9] thus indicating the operation of a mechanism analogous to Scheme III. As the adduct complex **5**–Cu^+ is formed in high intensity under FTICR conditions, low-energy CID experiments have been conducted with this ion; however, no additional products showed up. A representative example is included in Table I; it can be seen that the ratio of $Cu[HCN]^+$ to HCN loss is exactly the same as in the MI spectrum. The results from the study of the labeled isotopomers of **5** are given in Table III, and they further support the postulated mechanism. Ion/dipole complexes are known to be quite stable and therefore long-lived, and as hydrogen scrambling in carbenium ions is a facile process,[25] all hydrogen atoms are expected to be involved in the protonation step. This is precisely born out experimentally. A slight preference for the internal methylene group can be noticed, and this is what one would also expect from the stabilities of the resulting alkene. Similarly, participation of the more remote methyl group is less important, but nevertheless clearly noticeable.

Table IV. Reaction Products Generated from Co^+ and Labeled 2-Methylbutanenitriles[a]

	5a		**5b**		**5c**	
product	MI	FTICR	MI	FTICR	MI	FTICR
H_2	64	*b*	>75	*b*	36	*b*
HD	36	*b*	<25	*b*	64	*b*
$CH_3^\bullet$	70	>90	100	100	15	<10
$CD_3^\bullet$	30	<10			85	>90
CH_4			100	100		
CH_3D	76	80			19	<10
CD_3H	24	20			81	>90
[HCN]	*c*		*c*		78	
[DCN]	*d*		*d*		22[e]	
C_2H_4	98	98	99	>97	*f*	<1
C_2H_3D			1	*g*		
$C_2H_2D_2$	1	1[h]			50	51[h]
C_2HD_3	1	1[i]			50	49[i]
C_3H_6						
C_3H_5D			100	100		
$C_3H_4D_2$	34	23			40	40
$C_3H_3D_3$	66	77			60	60
$Co[HCN]^+$	79	77	94	93	92	92
$Co[DCN]^+$	21	23	6	7	8	8

[a] Intensities are expressed in $\sum$fragments = 100% for each neutral loss, respectively. [b] Signal-to-noise ratio not sufficient for exact determination. [c] Present in the spectrum. [d] Isobaric with C_2H_4. [e] Contributions from C_2H_4 possible. [f] Isobaric with DCN. [g] Isobaric with H_2 + HCN. [h] Contributions from [HD + HCN] possible. [i] Contributions from [HD + DCN] possible.

In comparing MI and FTICR data, it can be seen that, although the ratio of the two reaction products differs, the individual labeling distributions show excellent agreement.

After having demonstrated the fundamentally different behavior of Fe^+ and Cu^+ in their reactions with the *secondary* nitrile **5** (with Fe^+ unable to break the C–CN bond by means of ion/dipole formation, while it is this very reaction by which products are formed with the stronger Lewis acid Cu^+), it is interesting to study whether a trend exists with regard to the behavior of the two transition-metal ions in-between. We will first describe the Co^+ system whose reaction products are listed in Table I. Except for the weak signal due to the combined losses of H_2 and HCN, which are likely to result in the formation of a Co^+–butadiene complex, all remaining products are already known from the reactions of **5** with Fe^+ and Cu^+. Most interestingly, *all* signals that were observed for these two systems are also present in the reactions of Co^+ with **5**. The agreement between tandem MS and FTICR is once again good; minor differences are observed for the dehydrogenation, which is less intense in the latter experiment, a phenomenon that has been referred to previously.[6] Loss of HCN is absent under FTICR conditions. As already mentioned in the introduction, the two dissociation pathways of a biligated complex are not necessarily observed in all cases.

Inspection of the labeling data in Table IV reveals that all processes show the expected behavior; obviously, no change in mechanism is operative. Losses of hydrogen and ethylene are due to remote functionalization combined with the degenerate isomerization process. The formation of C_2H_4 not only is the dominant pathway in this system, it also must be significantly faster than competing processes. This is indicated by the fact that the major portion of the detached isotopomers is generated *before* the de-

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Table V. Reaction Products Generated from Ni^+ and Labeled 2-Methylbutanenitriles[a]

product	**5a**, MI	**5b**, MI	**5c**, MI
H_2	67	>95	ca. 46[b]
HD	33	<5	ca. 54[b]
[HCN]	*c*	*c*	84
[DCN]	*d*	*d*	16[e]
C_2H_4	97[f]	>97[f]	*g*
C_2H_3D		<3	
$C_2H_2D_2$	2		45
C_2HD_3	1		55
$Ni[HCN]^+$	79	86	93
$Ni[DCN]^+$	21	14	7

[a] Intensities are expressed in $\sum$fragments = 100% for each neutral loss, respectively. [b] Signal-to-noise ratio not sufficient for exact determination. [c] Present in the spectrum. [d] Isobaric with C_2H_4. [e] Contributions from C_2H_4 possible. [f] Contributions from DCN possible. [g] Isobaric with DCN.

Table VI. Reaction Products Generated from V^+ and 2-Methylbutanenitrile (**5**)[a]

product	MI	FTICR
H_2	88	39
$2H_2$	<1	8
H_2/HCN	2	39
V^+	10	*b*
$V(s\text{-}C_4H_9CN)^+$	*b*	15

[a] Intensities are expressed in $\sum$fragments = 100%. [b] See text for discussion.

Table VII. Reaction Products Generated from V^+ and Labeled 2-Methylbutanenitriles[a]

	5a		**5b**		**5c**	
product	MI	FTICR	MI	FTICR	MI	FTICR
H_2	93	93	82	68	36	44
HD	7	7	18	32	51	46
D_2	*b*	*b*			13[b]	10[b]
$2H_2$	ca. 57[c]	59[d]	*c*	22	*d*	*d*
H_2/HD	ca. 43[c]	41	*c*	78	56	43
[2HD]					44	57
H_2/HCN	<20	16	>90	98	<10	
$[H_2,D,CN]$	>80	84	<10	2	>90	93
$[H,D_2,CN]$					<10	7

[a] Intensities are expressed in $\sum$fragments = 100% for each neutral loss, respectively. [b] Isobaric with $2H_2$. [c] Signal-to-noise ratio not sufficient for exact determination. [d] Isobaric with D_2.

Table VIII. Reaction Products Generated from Ti^+ and 2-Methylbutanenitrile (**5**)[a]

product	FTICR	product	FTICR	product	FTICR
H_2	7	H_2/CH_4	5	C_3H_6	3
$2H_2$	35	H_2/HCN	35	CH_4/HCN	3
CH_4	5	$[C_2H_6]$	4	$Ti[HCN]^+$	2

[a] Intensities are expressed in $\sum$fragments = 100%.

generate isomerization could have taken place. Just as for Fe^+, a partial equilibration between the hydrogen atoms from the "ethyl chain" is observed. The losses of $CH_3^•$ and CH_4 strictly follow Scheme II, and the label distributions also resemble the Fe^+ system in all respects.

The weak signal due to loss of DCN is unfortunately obscured by the signal due to loss of the isobaric C_2H_4, but from the $Co[H,C,N]^+$ signal, it is evident that no differences to Cu^+ are present; therefore, this finding represents another example of the operation of an ion/dipole mechanism (Scheme III). High-energy collisional activation experiments reveal that the $Co[H,C,N]^+$ ion has the structure $HCN\text{-}Co^+$, completely in line with the above proposal. Both experimental methods give virtually identical data with respect to every individual process.

The data for Ni^+, given in Tables I and V, is in full accord with Fe^+, Co^+, and Cu^+; therefore, with the labeled nitriles, only MI experiments have been conducted. We note the following points:

(i) Losses of $CH_3^•$ and CH_4, already reduced in intensity for Co^+ as compared to Fe^+, are absent for Ni^+.

(ii) Processes due to the ion/dipole mechanism have gained importance relative to Co^+, but ethylene loss still represents the dominant pathway.

(iii) According to high-energy collisional activation, the $Ni[H,C,N]^+$ ion also possesses the structure $HCN\text{-}Ni^+$.

The next transition-metal ion to be discussed is V^+. From the data in Table VI, the strong tendency of V^+ for dehydrogenations is obvious. In the MI spectra, single dehydrogenation is the only process of importance, except for 10% ligand detachment. Under FTICR conditions, double dehydrogenation and the combined losses of H_2 and HCN are observed; the latter processes quite likely generate a V^+–butadiene complex, which is also observed in the MI data, though with much less intensity. These deviations between both methods are due to the increased tendency for occurrence of multiple losses in FTICR experiments (see above). Inspection of the data for the labeled compounds (Table VII) leads to the following conclusions:

(i) While all hydrogen atoms participate in the hydrogen loss, dehydrogenation across the central C–C bond is slightly preferred, as indicated in the higher amount of HD loss in the spectra of **5b**-V^+ compared to **5a**-V^+.

(ii) The losses of D_2 and $[H_2,D_2]$ in the spectra of **5c**-V^+ indicate that reversible steps are operative *only* for the dehydrogenation of the C(3)–C(4) bond. This could suggest, that we are dealing with the rare case of remote functionalization, where structures analogous to **2** and **3** are in an equilibrium. This is distinct from all previously studied nitrile-M^+ complexes (M = Fe, Co, Ni) for which the step **2** → **3** was found to be irreversible.[2l,m,4,5]

(iii) The production of the V^+–butadiene complex by combined losses of H_2 and HCN (or HNC) does not follow a highly specific pathway, as partial scrambling is observed for all three isotopomers. The most prominent peak in any case is due to simple 1,2-eliminations of H_2 and HCN, respectively.

(iv) Although the overall pattern of the three reaction channels differs substantially for the FTICR and MI data, the agreement for each individual neutral loss is nevertheless reasonably good, pointing to a common mechanism in every case.

The chemistry of Ti^+ with **5** was examined only with the FTICR instrument, because the occurrence of oxygen-containing species precluded reproducible measurements with the sector-field machine. The product spectrum of Ti^+ with **5** is a particular complicated one, as quite a variety of processes are operative (Table VIII). More than 80% of these include the production of hydrogen molecule(s) and combined losses of H_2 with CH_4, and HCN, respectively, thus indicating a preference of Ti^+ for C–H activations. The already complicated spectrum of unlabeled **5** got even worse for the deuterated nitriles **5a** and **5c** to the extent that no further conclusions could be drawn. From the spectrum of **5b**, it was obvious, however, that a large amount of either hydrogen scrambling or a multitude of reversible steps is operative.

The strong tendency of Ti^+ and V^+ for dehydrogenations has also been noted by other groups. Freiser et al. observe in the reactions of Ti^+[26] and V^+[27] with alkanes mainly dehydrogenations and only a few products that arise from C–C cleavage. Allison, Ridge, and co-workers report exclusive loss of one or two H_2 molecules in the reactions of Ti^+ with alkanes[28] and alkenes;[29] for ethane, those are the only exothermic processes with V^+.[30] Using collisional activation mass spectrometry, Peake and Gross observe loss of H_2 and $2H_2$ as the main products for Ti^+ and V^+

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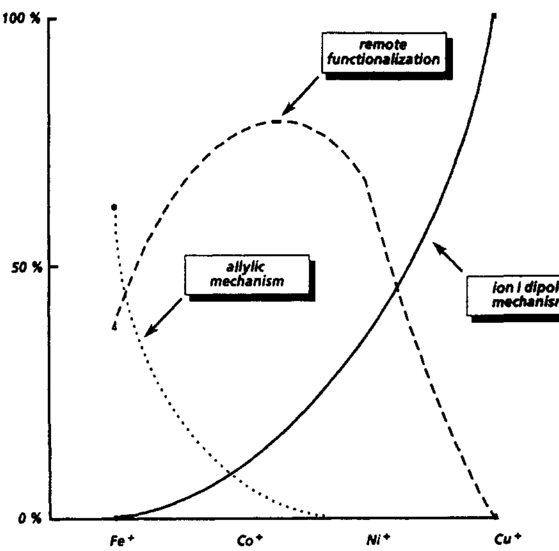

Figure 1. Contribution of the transition-metal ions Fe^+, Co^+, Ni^+, and Cu^+ to the activation of 2-methylbutenenitrile (**5**) via (i) allylic mechanism (···), (ii) remote functionalization (- - -), and (iii) ion/dipole mechanism (—). The distribution is based on the MI data of **5**–M^+.

complexes of 1-pentene.[22] Under multicollision conditions, the two ions also exclusively activate C-H but not C–C bonds in alkanes,[18a,c] and show the highest degree of dehydrogenation of all first-row ions in the reactions with isocyanides.[16i]

The versatile chemistry of Ti^+ is in strong contrast to the last two elements to be discussed here. Cr^+ was found to be totally unreactive toward **5**; the unimolecular decompositions of **5**–Cr^+ and **5a**–**c**–Cr^+ show only ligand detachment, while upon high-energy collisional activation some minor products in low intensity are observed. Under FTICR conditions, the only reactions observed, are the formations of adduct complexes $Cr(C_4H_9CN)_x^+$ ($x = 1, 2$). Low-energy CID on **5**–Cr^+ affords only Cr^+. The inability of Cr^+ toward CH/CC activation with a variety of different substrates has been observed very often[31] and is usually attributed to the half-filled d shell of this ion in its ground state (^6S). For Zn^+, adduct formation is the dominant pathway (94%) under FTICR conditions, besides 3% $Zn[H,C,N]^+$ and 3% protonated **5**. Formation of the latter is believed to occur either via loss of neutral ZnH[32] or via charge exchange from Zn^+ ions,[33] which is followed by subsequent "self-CI",[34] respectively. Low-energy CID on the adduct complex **5**–Zn^+ gives, depending on the energy deposited, 2–5% $Zn[H,C,N]^+$; the remaining part of the products is due to simple ligand detachment. The isotopic distribution for the $Zn[H,C,N]^+$ ions, generated from **5a**–**c** either via ion/molecule reactions or by CID, indicates that this product is formed by ion/dipole complexes, just as for Co^+, Ni^+, and Cu^+.

Conclusions

The chemistry of 2-methylbutanenitrile (**5**) with the first-row transition-metal ions Fe^+ through Cu^+ is dominated by three major processes. For Fe^+, the main reaction corresponds to the formation of methane via an "allylic mechanism" that involves initial insertion into the C–CN bond, followed by β-hydrogen transfer and allylic C–C cleavage; the reaction is terminated by reductive elimination of CH_4. Besides, H_2 and C_2H_4 are generated via "remote functionalization". "Superimposed" over both processes is a degenerate isomerization **5**–$Fe^+ \rightleftharpoons$ **5′**–Fe^+ that is closely linked with the formations of CH_4 and $CH_3^•$.

For the next metal ion, Co^+, remote functionalization strongly gains importance while production of methane decreases; consequently, the amount of the degenerate isomerization is also reduced. As new processes, formations of HCN and $Co[HCN]^+$ are observed; these products are due to an ion/dipole mechanism. For Ni^+, production of CH_4 is no longer observed, remote functionalization is still the major process, but the ion/dipole mechanism already accounts for more than 30% of the reaction products. Cu^+ finally does react exclusively under intermediate formation of the ion/dipole complexes. The observed "switching" between the three mechanisms in going over from Fe^+ to Cu^+ is illustrated in Figure 1.

For the "early" transition-metal ions Ti^+ and V^+, dehydrogenations are the main or exclusive processes, in line with their general behavior toward other substrates. Cr^+ is unreactive with **5**, and Zn^+ gives rise to only a very small amount of $Zn[HCN]^+$, hence a product of the ion/dipole mechanism.

It is also evident from this work that two contrary methods, ion/molecule reactions of bare transition-metal ions in an FTICR instrument and metastable ion decompositions of adduct complexes in a sector-field mass spectrometer, can be compared to a large extent. Differences that arise are mainly due to multiple losses under FTICR conditions. A very good agreement is found when individual processes are compared; i.e., the labeling distribution for each neutral product is by and large identical for FTICR and MI data.

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