Formation and Fragmentation of Gas-Phase Ion-Molecule Complexes of Transition-Metal Ions with Organic Molecules Containing Two Functional Groups

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A mass spectrometer fast atom bombardment source has been used to synthesize, in the gas phase, the ion-molecule complexes of transition-metal ions (Ni^+ , Co^+ , Fe^+ , and Mn^+) with α - or β -unsaturated alkenenitriles, $\text{RCH}=\text{CHCN}$ ($\text{R}=\text{H}$, CH_3 , and C_2H_5) and $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CN}$, and 2-methyl glutaronitrile. The metastable ion fragmentations of the complexes are monitored in the first field-free region by B/E linked scans. Surprisingly, an intense HCN loss via an intermediate $(\text{C}_n\text{H}_{2n-2})-\text{M}^+(\text{HCN})$ is observed for the complexes of the alkenenitriles. The metal ions significantly affect the fragmentation processes. The coexistence of both end-on and side-on coordination modes is suggested to explain the fragmentations. (*J Am Soc Mass Spectrom* 1992, 3, 451-459)

Gas-phase ion-molecule reactions of transition-metal ions (both positive and negative, including cluster ions) with organic molecules in the gas phase have been an active research area for the last decade [1]. The gas phase is an ideal environment for the study of the intrinsic properties of metal ions in the absence of any complicating solvent effects. Mass spectrometry, such as ion cyclotron resonance (ICR) [2], especially the more recently developed Fourier transform ICR [3], ion beam experiments [4], quadrupole [5], and sector tandem mass spectrometry [6], has been applied to the gas-phase metal-ion chemistry [7].

Recently, Schwarz and co-workers [8] using a tandem sector mass spectrometer, have investigated the ion-molecule reactions of Fe^+ with unbranched alkenenitriles and found a selective functionalization of remote C—H and/or C—C bonds by Fe^+ in an "end-on" coordination mode I. The remote functionalization has since been extended to other systems like isonitrile [9], amines [10], alcohols [10b, 11], alkynes [12], allenes [13], and ketones [14]. Basically, this involves selective activation of a C—H (or C—C) bond at a position remote from the CN functional group, followed by β -H transfer or β -cleavage of a C—C bond which generates H_2 , alkenes, or alkanes. However, our studies of the transition-metal ions with alkenenitriles [15, 16] and phenyl-containing nitriles [17] suggested a coexistence of both "end-on" and "side-on" II coordination modes. When the nitrile

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chain is long enough, the end-on complexed metal-ion reaction will dominate. For short-chain nitriles (carbon number in the chain of less than 5), the side-on products are formed. Furthermore, end-on versus side-on complexation of the nitrile group is found in the alkenenitrile/metal-ion complexes [18]. For alkenenitriles in which the double bond and nitrile group are separated by four or more methylene groups, the metal ion is complexed in an end-on mode by the nitrile group with the C=C double bond as a π donor. The alkenenitriles, with less than four methylene groups between both the functional groups, complexes in end-on mode to the metal ion.

In this article we will show the coexistence of both side-on and end-on complexation of the metal ions (Ni^+ , Co^+ , Fe^+ , and Mn^+) with short-chain alken-

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enitriles (1-4) and 2-methylglutaronitrile 5 that contain two functional groups. To set the stage for the discussion of the reaction involving the short-chain alkenenitriles, we summarize the long-chain alkenenitrile reactions reported by Schwarz and co-workers [18]. (1) For systems with $m > 2$, the fundamental reaction proceeds via a metal-containing cyclic intermediate 6 and involves the exocyclic allylic CC bond cleavage to eliminate $\text{RCH}=\text{CH}_2$ (Scheme 1). (2) Partial migration of the double bond occurs preferentially away from the CN group. (3) If $m < 2$ ($\text{R} = \text{propyl}$ or butyl), the exocyclic allylic CC bond cleavage does not dominate any longer. In contrast, the product distribution is typical of that for a saturated nitrile [8], i.e., the chemistry is governed by the functionalization of remote C-H bonds by the end-on complexed Fe^+ .

Experimental

A Kratos Concept IS double-focusing mass spectrometer of E/B configuration (Kratos Analytical, Urmost, Manchester, UK) controlled by a Kratos DS 90 Data General Eclipse based computer system was used. A Kratos Mach 3 data system running on a SUN SPARC station was used for further data workup. The normal fast atom bombardment (FAB) source has been modified so that it could accept a reservoir probe as the source of gaseous molecules for studying ion-molecule reactions. Detailed descriptions of the modified instrument and operating conditions are given elsewhere [15]. Briefly, the instrument was fitted with an Ion Tech (Middlesex, UK) saddle field atom gun. Xenon was used as the fast atom source. The fast atom-beam energy was 8 keV with a density corresponding to an emission current of about 1 mA. The source was operated at a temperature of 25 °C, a pressure of about 10^{-5} torr (measured in the source housing, not in the reaction region), and an accelerating voltage of 6 kV. Normal mass spectra were

Scheme 1. Loss of RCHCH_2 from alkenenitrile/ Fe^+ complex ($\text{X} = \text{CN}$).

recorded at a resolving power of ~ 1000 . Metastable ion (MI) or collision-induced dissociations (CID) in the first field-free region were monitored by B/E linked scans. The pressure of the helium collision gas in the collision chamber was maintained so as to reduce the main beam by 20% (approximately corresponding to 1.1 collisions [19]). Because there was some diffusion from the source into the collision chamber region, metastable ions for recording the MI spectra might have been partially activated. For other systems, however, we observed identical transitions of metastable ions in both the first and the second field-free region.

"Naked" metal ions were generated from $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, which had been dissolved in water and deposited by evaporation onto the FAB probe tip. The nitriles were introduced into the source by using the reservoir probe. A 3- μL sample of the liquid reagent was injected into the reservoir probe whose highest temperature was 150 °C. All samples were commercially available and used without further purification.

Results and Discussion

Reactions with Alkenenitriles 1-4

The ion-molecule reactions of the transition-metal ions (Ni^+ , Co^+ , and Fe^+) with the alkenenitriles 1-4 in the FAB source give monoadduct ions, RCN-M^+ , with an intensity (relative to corresponding metal ion) of 15-30% for RCN-Ni^+ , 5-13% for RCN-Co^+ , and 1-5% for RCN-Fe^+ . We also observed some fragment ions from the monoadducts. In addition, the dimer ions, $(\text{RCN})_2\text{M}^+$, form in lower intensities. In contrast, Mn^+ , under our experimental conditions, gives a less intense monoadduct ion ($\leq 1\%$) and no dimer. These relative monoadduct and dimer ion intensities may reflect the binding strength between the metal ions and alkenenitriles [20]. The fragmentation of the monoadduct ions was investigated by means of metastable ion techniques. The following discussion will focus on the MI studies.

The MI spectra of the monoadducts of Ni^+ , Co^+ , and Fe^+ have an intense peak corresponding to 27 μ loss (Table 1), except for 1- M^+ , which shows only detachment of the ligand. This process dominates the MI spectra of 3- M^+ and 4- M^+ . Ligand detachment alone is observed for RCN-Mn^+ except for 3- Mn^+ , which also shows the loss of H_2 . The loss of 27 μ is likely linked with the formation of $[\text{M} + 27 \mu]^+$ ion, i.e., both are produced from the same intermediate. High resolution mass measurement of the $[\text{Ni} + 27 \mu]^+$ ion demonstrates that its elemental composition is $[\text{Ni}, \text{H}, \text{C}, \text{N}]^+$. Therefore, the 27 μ unit is HCN and the elimination of HCN should involve a hydrogen transfer to the metal center. HCN loss has been observed for the metal-ion complexes of phenyl-containing nitriles [17] and α -branched nitriles [21, 22].

For the conjugated alkenenitrile complexes, 2- M^+ and 3- M^+ , HCN formation seems to involve a simi-

Table 1. MI spectra of ion-molecule adduct $\text{RCN}-\text{M}^+$ ($\text{M}=\text{Ni}, \text{Co}, \text{Fe}, \text{Mn}$)

	$2-\text{M}^+$			$3-\text{M}^+$				$4-\text{M}^+$		
	Ni	Co	Fe	Ni	Co	Fe	Mn	Ni	Co	Fe
$-2\ \mu$				47	45	60	22			
$-26\ \mu$									< 1	2
$-27\ \mu$	17	15	10	100	100	100		34	100	100
$[\text{M} + 27\ \mu]^+$				47	39			100	54	4
$[\text{M} + 41\ \mu]^+$								41	6	
M^+	100	100	100	32	42	44	100		20	20

The abundances of the product ions are normalized to the corresponding base peak.

lar mechanism. One may assume complex formation by an ion/dipole mechanism, which is suggested for the formation of $\text{HCN}-\text{Fe}^+$ from *t*-butyronitrile/ Fe^+ complex [22] and expect that the transition-metal ions are attached to the nitrogen atom of the CN functional group in end-on form. According to this mechanism, the linked product $\text{M}^+[\text{HCN}]$ should have an $\text{HCN}-\text{M}^+$ structure and give $[\text{M} + \text{N}]^+$ ion after collisional activation (CA) [22]. For comparison, under the same experimental conditions we have recorded the CA spectrum of $\text{Fe}^+[\text{HCN}]$ ion generated by the reactions of Fe^+ with *t*-butyronitrile. Ligand detachment is the only process observed. In contrast, the CA spectra of the $[\text{M}, \text{H}, \text{C}, \text{N}]^+$ ions¹ formed by the reactions of M^+ ($\text{M} = \text{Ni}, \text{Co}, \text{ and Fe}$) with **3** show $[\text{M} + \text{H}]^+$, $[\text{M} + \text{CN}]^+$, and $[\text{M} + \text{C}]^+$ peaks in addition to the simple detachment product ion (Table 2). This result is consistent with a structure of $\text{H}-\text{M}^+-\text{CN}$. It is thus not unreasonable to suggest that the elimination of HCN involves an initial insertion of the metal ion into the $\alpha\text{-C}-\text{CN}$ bond to form an intermediate **9**, $\text{RCH}_2\text{CH}=\text{CH}-\text{M}^+-\text{CN}$ ($\text{R} = \text{H}$ or CH_3), followed by a hydrogen transfer (see Scheme II). Note that based on a consideration of their stability we assume that the eliminating $[\text{H}, \text{C}, \text{N}]$ species is HCN from the intermediate **10b** rather than $[\text{H}\cdot + \cdot\text{CN}]$. In fact, the CA spectra of the $\text{M}^+[\text{HCN}]$ ions are dominated by the loss of HCN (see Table 2). For **3** $-\text{M}^+$ ($\text{R} = \text{CH}_3$, $\text{M} = \text{Ni}$, and Co), the HCN loss is in competition with the formation of $\text{H}-\text{M}^+-\text{CN}$ via the loss of C_4H_6 . Unfortunately, there is not sufficient evidence to identify the origin of the migrating hydrogen and thus the structure of C_4H_6 . The intermediate **10a** is probably a cyclopropene **11**, allene **12**, or alkyne

complex **13**. In addition, a butadiene complex ($\text{R} = \text{CH}_3$), as well as a metallacycle are two other alternatives. Among these, the cyclopropene complex is not stable and easily undergoes a ring-opening reaction [23]. Therefore, the structure **11** can be excluded. Because β -hydrogen transfer is very common in these types of reactions, intermediate **13** formed via a β -hydrogen transfer after the metal-ion insertion is more energetically favorable [7c, 24].

It is of interest that the elimination of HCN has not

Scheme II. HCN loss from alkenenitrile/metal-ion complex.**Table 2.** CA spectra of $\text{M}^+[\text{HCN}]$ ions

Product ions	$\text{Ni}^+[\text{HCN}]$	$\text{Co}^+[\text{HCN}]$	$\text{Fe}^+[\text{HCN}]$
MH^+	2	9	17
MCN^+	12	6	8
MC^+	2	2	3

The product ion abundances are relative to those of M^+ ions corresponding to the base peaks.

¹ $\text{Fe}[\text{H}, \text{CN}]^+$ ion is not observed in the metastable fragmentation of **3** $-\text{Fe}^+$ adduct, although the ion is formed in the FAB source. In fact, by CA, **3** $-\text{Fe}^+$ gives the $\text{Fe}[\text{H}, \text{CN}]^+$ ion. These results suggest that the formation of the $\text{Fe}[\text{H}, \text{CN}]^+$ ion involves a higher energy channel.

been observed for long-chain alkenenitrile/metal-ion complexes ($R \geq$ butyl for **8** in Scheme II) [18]. The difference may be explained in terms of coordination mode. Schwarz and co-workers [18] suggested three possible structures for the alkenenitrile/ Fe^+ complexes. When the double bond and the CN group are separated by two or more methylenes, a bidentate complex **14** with a side-on coordination of the CN group by Fe^+ may be the most favorable. This is perhaps due to the fact that the combined effects of two π -bonds to Fe^+ are energetically more favored than σ complexation by the nitrogen lone pair (**15**). If the chain length separating the CN group and the double bond increases, the structure may be best described by the structure **16**. Based on these assumptions, the alkenenitriles **1-4** should coordinate to the metal ion with a structure such as **15**. However, the approximately linear combination of the atoms in **15** keeps the metal ion far from the chain as in alkenenitrile/metal-ion complexes. In this case, the end-on complexed metal ion can only attack the C—C or C—H bonds further out than the ω position [8]. Obviously, structure **15** cannot account for the α -C—CN insertion (See Scheme II). We thus suggest another coordination mode, side-on mode **17**, because the side-on complexed metal ion is close enough to the α -C—CN bond so as to be able to insert. Side-on coordination has been suggested for the complexation of transition-metal ions with phosphalkynes [25] and specially for Cu^+ reacting with nitriles [26].

14 ($m = 2, 3, 4$)

15 ($m = 0, 1$)

16 ($m \geq 4$)

17 ($m = 0, 1$)

It seems that there is coexistence of both end-on and side-on coordination modes for the α - or β -unsaturated alkenenitrile complexes. Due to the higher

stability of the end-on structure than the side-on, the main coordination mode is expected to be the end-on. When the alkenenitrile chains is long enough, for example, with a nitrile with $n = 6$ and $m = 0$ in **15**, the end-on complexed metal ion selectively attacks the terminal C—C and C—H bond to give the end-on products [18]. In fact, the end-on decomposition product, H_2 , is already observed for $3-M^+$ complexes. This reaction is described, by Schwarz and co-workers, in terms of ω -C—H insertion/ β -H transfer/elimination of H_2 . However, an α - or β -unsaturated linear alkenenitrile consisting of less than five carbon atoms produces only the side-on products such as HCN in addition to the detachment. This is similar to the metal-ion complexes of phenyl-containing nitriles [17]. The coexistence of both end-on and side-on modes has been suggested for the metal-ion complexes of alkenenitriles [15, 16] and alkaneisocyanides [9].

For the complexes of $4-M^+$, Ni^+ gives a different MI spectrum than Fe^+ . Co^+ shows characteristics of both (see Table 1). The base peak in the MI spectrum of $4-Ni^+$ corresponds to $[Ni + 27 \mu]^+$ ion. In addition, peaks corresponding to the loss of HCN and $[Ni + 41 \mu]^+$ ion are also present. No ligand detachment is observed. In contrast, for $4-Fe^+$, the HCN loss is the most important and the $[Fe + 27 \mu]^+$ peak becomes less abundant. The different behavior between complexed Ni^+ , Co^+ , and Fe^+ has been noted for the complexes of phenyl-containing nitriles [17].

The $[Ni + 27 \mu]^+$ ions formed by the reactions of Ni^+ with either of **3** or **4** give the same CA spectrum, suggesting that they have the same structure $H-M^+-CN^2$. These results indicate that the α -C—CN insertion is again involved in the formation of HCN and $H-M^+-CN$ (Scheme III). This is similar to the ion-molecule reactions of the metal ions with alkenes [27]. A hydrogen transfer then occurs to produce a butadiene cyano complex **20** from which either HCN or butadiene is eliminated. A β -H transfer in **18** may also occur to yield methylene complex, which accounts for retaining or losing HCN. The insertion of metal ions into C_{sp^3} -CN bond of nitriles has been recently reported [17, 21, 28].

Retaining versus losing HCN for both $3-M^+$ and $4-M^+$ depends on the metal ions. As shown in Table 2, one can see that the ability of the metal ions for retaining HCN follows the order: $Ni^+ > Co^+ > Fe^+$. This order implies that the relative bonding energies, $D(RNi^+-NCH)$ compared to $D(R-Ni^+NCH)$ are greater than $D(RFe^+-NCH)$ (R = unsaturated hydrocarbons, see Schemes II and III). Except for $4-Ni^+$, **3**

² It is well known that CA presents a probe with stable ions being investigated, because in a CA process the ion upon collision is a stable species of low internal energy. However, it should be noted that the possibility of rearrangement prior to fragmentation in a CA process can not be completely neglected, because the time spent by the ions to reach the collision zone is long enough for rearrangement.

—M⁺ and 4-M⁺ prefer to lose HCN. Although most of the energies of the HCN—M⁺ and R—M⁺ bonds have not been measured, it is believed that these bond energies correlate with corresponding proton affinities [29]. Molecules with greater proton affinities bond more strongly with the metal ions. In fact, the unsaturated hydrocarbons have greater proton affinities than HCN [30]. The intense loss of HCN from 3-M⁺ and 4-M⁺ is thus understandable.

Finally, the [Ni + 41 u]⁺ ion produced from 4—Ni⁺ deserves comment. Although high resolution mass measurement fails to provide its elemental composition due to low ion intensity, this ion is likely a complex CH₃CN—Ni⁺ or CH₃—Ni⁺—CN. The CA spectrum of this ion gives NiCN⁺ and Ni⁺ ions, similar to that of reference ion CH₃CN—Ni⁺ synthesized in the source by the reaction of Ni⁺ with CH₃CN [15]. This suggests that the [Ni + 41 u]⁺ ion is probably the complex CH₃CN—Ni⁺. Note the other candidate, CH₃—Ni⁺—CN, cannot be completely precluded because it may also produce NiCN⁺ ion after CA. Furthermore, although initial complexation of metal ions with molecules are, in most cases, not clear, metal-ion insertion into a polar bond is very common in the gas phase [31]. Formation of the CH₃CN—Ni⁺ complex may involve a β-C—C insertion of Ni⁺ followed by a hydrogen transfer to the metal center, similar to the mechanism suggested in Scheme II. No analogous CH₃CN—Fe⁺ ion is observed. These results reveal a preference of the insertion of complexed Fe⁺ into the α-C—C bond over the β-C—C bond.

It is interesting to compare the metastable fragmentation of the alkenenitrile-metal complexes with corresponding alkanenitrile-metal complexes. The α C—CN insertion that dominates the MI spectra of the alkenenitrile-metal ions is completely absent for butyronitrile and valeronitrile complexes [16]. The difference arises mainly from coordination mode and reaction thermodynamics. In both systems both the side-on and the end-on coordination coexist. For the alkenenitriles, however, when metal ions are connected to the cyano group in the side-on mode, interaction between the metal ions and the C=C bond stabilizes the coordination [32]. The side-on coordination that accounts for the α C—CN insertion is thus more favorable for the alkenenitriles than for the alkanenitriles. On the other hand, metal-ion insertion into an α C—CN bond of the alkenenitriles forms allylic intermediates and appears to be energetically more accessible [33].

Reactions with 2-Methylglutaronitrile

Table 3 gives the MI spectra of the 5—M⁺ complexes. If these data are compared with n-pentanenitrile/M⁺ where more than 96% of the fragmentation is due to the losses of H₂ (75%) and C₂H₄ (21%) [34], it is obvious that the presence of the second CN functional group dramatically induces additional fragmentation. Moreover, we do not observe the hydrogen loss that should be generated by the remote functionalization of end-on complexed metal ions. These results are similar to those obtained by Schwarz and co-workers [35] for the complexes of Fe⁺ glutaronitrile where the ethylene loss is the most important fragmentation process. It is thus not unreasonable to consider that among the possible coordination modes (a, a', b, c, c' or d) the two π-bond structure d is the preferred arrangement.

As in the case of alkenenitrile/metal-ion system, complexation in mode d rather than a or a' is due to the fact that the combined effects of the two π-bonds to M⁺ are energetically more favored than the σ complexation by the nitrogen lone pair. Structures b, c, and c' must contain considerable ring strain because of the approximately linear —CN—M⁺ combination in an end-on mode, and are thus energetically unfavorable. Furthermore, we show below that the

Table 3. MI spectra of ion-molecule complexes $5-M^+$ ($M = Ni, Co, Fe$, and Mn)

Neutral loss	5-Ni ⁺	5-Co ⁺	5-Fe ⁺	5-Mn ⁺
CH ₃ ·	24	25	22	
CN·	3	3	7	
HCN	100	100	40	
C ₂ H ₄	69	44	59	
NCCH ₂ ·		4	25	
CH ₃ CN	24	35	100	
C ₃ H ₆		5	83	
C ₃ H ₃ N	50	28	33	
C ₃ H ₄ N·	16	3	14	7
C ₃ H ₅ N	36	19	13	
Detachment	3	17	39	100

Abundances are normalized to the base peaks.

structure **d** is consistent with the fragmentations observed for the $5-M^+$ complexes. However, because metastable ions contain significant amounts of internal energy, all of the possible structures may be present, although structure **d** is the most favorable.

The effects of the metal ions on the fragmentations are distinct. Fe^+ is more reactive than Ni^+ . Co^+ is intermediate. In contrast, $5-Mn^+$ mainly undergoes ligand detachment producing Mn^+ , revealing a much lower reactivity of Mn^+ . The relative reactivity has been explained by Babinec and Allison [36b] in terms of promotion energy. When a metal ion inserts into a single bond of an organic molecule to form two σ -bonds, the metal ion has to be in a configuration in which two electrons are not in *d* orbitals. The promotion energy required to achieve this configuration falls in the order, $Mn^+ > Ni^+ > Co^+ > Fe^+$. These promotion energies are believed to correlate with the metal ion reactivity. Among the four metal ions, Fe^+ has the lowest promotion energy and shows a high reactivity.

Based on the structures of the product ions elucidated by CA, we propose the following fragmentation mechanisms of $5-M^+$ in Scheme IV. Our discussion focuses on the identification of the major product ion structures and their formation mechanisms.

Loss of HCN. As shown in Table 3, the loss of HCN constitutes the base peaks of the MI spectra of $5-Ni^+$ and $5-Co^+$. Insertion of Fe^+ into the α C—CN bond followed by β -H transfer is suggested to explain the HCN loss from glutaronitrile- Fe^+ complex [35]. As in the case of alkenenitriles discussed above, the α C—CN insertion indicates that the initial complexation concerns a side-on coordination. Although both of the C—CN bonds in **5** may be involved in the insertion process, the C—CN bond containing the secondary CN group is more likely because it corresponds to a dicoordinated product ion **23** that is more stable than the ions generated via the other C—CN bond insertion (see Scheme IV).

In contrast with 2-methylbutyronitrile/ Fe^+ , where the C—CN bond insertion is followed by a β -H and a methyl transfer to the metal center to eliminate methane and methyl radical [21, 29], HCN is eliminated from $5-M^+$ after the β -H migration. Formally, the β -hydrogen may originate from the terminal methyl group or from the internal methylene group, respectively producing complex **23** or $CH_3CH=CHCH_2CN/M^+$ ($4-M^+$). However, the CA spectrum of the product ion formed via the loss of HCN from $5-Ni^+$ is quite different from that of $4-Ni^+$ (Scheme V). This is also due to the stability of the product ion **23** with the two π -bonds. Similarly, the HCN loss from $5-Fe^+$ produces ion **23** rather than $4-Fe^+$.

Losses of C_2H_4 and C_3H_3N . CA of the product ion **32**, formed via loss of C_2H_4 from $5-Fe^+$, produces $Fe^+(CH_2=CHCN)$ (100%), $Fe(CN)^+$ (6%), and Fe^+ (3%). This result is consistent with the proposed structure **32**. The formation mechanism is expected to involve consecutive insertion into the C(4)—CN and C(2)—C(3) bonds (or C(2)—C(3) and C(4)—CN) to form an intermediate **31**, as in the case of n-pentanenitrile/ Fe^+ . However, for the n-pentanenitrile/ Fe^+ complex, Fe^+ first inserts into the C—CH₃ bond and then further into the C—CN bond. In fact, the insertion into the C—CH₃ bond is also observed for $5-M^+$ ($5-M^+ \rightarrow 38$), but the subsequent fragmentation is only via the elimination of $\cdot CH_3$.

From the intermediate **31**, a β -H transfer takes place. A cyano ethylene complex **34** then forms after the loss of $CH_2=CHCN$. Supporting the proposed structure, the CA spectra of **34** ($M = Ni$ and Fe) show an $M(HCN)^+$ ion peak in addition to the metal ion peak.

Losses of CH_3CN and C_3H_6 . The loss of CH_3CN can be simply considered as the result of a direct C(3)—C(4) bond insertion of the metal ions followed by a β -H transfer (**26** $\rightarrow$ **27**), a traditional mechanism of complexed metal ions with organic molecules [7c]. This process produces α -methylpropenenitrile/ M^+ **28**. Except for ligand loss, no structure-characteristic products are given by the CA of **28**. We thus compare it with the $CH_2=CHCN/M^+$ complex. In fact, due to the unfavored oxidative addition of the vinyl C—H or C—C bonds to the metal ions, the CA spectrum of the reference complex also shows solely the ligand detachment.

The complexed metal ions in the intermediate **26** can also insert into the C(2)—CN bond, forming a cyano propene complex **24** that eliminates propene to generate ion **25**. The structure of **25** is identified by its CA spectrum, which shows $M^+(CN)$ ion peak (loss of $\cdot CH_2CN$). The reaction sequence for the formation of **25** may start with the first insertion of the metal ions into the C(2)—CN bond followed by insertion into the C(3)—C(4) bond.

Scheme V. Comparison between CA spectra of product ions from $5-M^+$ via HCN loss and $4-M^+$ ($M = \text{Ni}$ and Fe).

Conclusions

1. Both the end-on σ and side-on π coordination modes seem to coexist in the complexation of α or β unsaturated alkenenitriles with the transition-metal ions. As the chain gets longer (e.g., in the case of **3**), the end-on decomposition product ion H_2 becomes detectable. For the complexes of 2-methyl glutaronitrile **5**, bis(side-on) coordination is probably more stable than the other possible modes. Furthermore, the fragmentation of $5-M^+$ is consistent with the proposed biscoordination.

2. Some interesting fragmentations are observed for the complexes of the alkenenitriles. Competition between HCN elimination and $\text{H}-M^+-\text{CN}$ formation is the most important factor for the metastable fragmentations of the monoadducts of **3** and **4**. Ni^+ and Co^+ prefer to retain HCN compared to Fe^+ . The difference is explained by the relative bond energies. These reactions can be described in terms of $\alpha\text{-C}-\text{CN}$ insertion of a side-on complexed met ion, rather than ion-dipole mechanism.

3. Metastable fragmentations of the complexes of the bifunctional nitriles are significantly affected by the metal ions. Different characteristics between Ni^+ and Fe^+ are distinct. For example, $5-\text{Ni}^+$ prefer to eliminate HCN, whereas $5-\text{Fe}^+$ eliminates CH_3CN and C_3H_6 . Relative strengths of Fe^+ -alkyl versus Co^+ -alkyl and Ni^+ -alkyl bonds account for the different product distribution. It should be noted that Armentrout and Beauchamp [38] have reported that product distribution also depends on lifetimes of reaction intermediates. As the lifetime decreases, or the intermediate gets more energetic, thermodynamic decomposition becomes possible. Different fragmentation might be observed if the experimental conditions such as collision gas pressure and accelerating voltage are changed. In fact, we have investigated the decomposition under CA conditions. We observed some additional products, but the product ions observed already in metastable fragmentation remained the most important. We also considered measurements at

different voltages but sensitivity drops too fast at reduced accelerating potentials.

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