J. Am. Chem. Soc. **1987**, *109*, 5639-5644

Deceptive Similarities in the Reactions of Fe$^+$ and Co$^+$ with Linear Nitriles in the Gas Phase[†]

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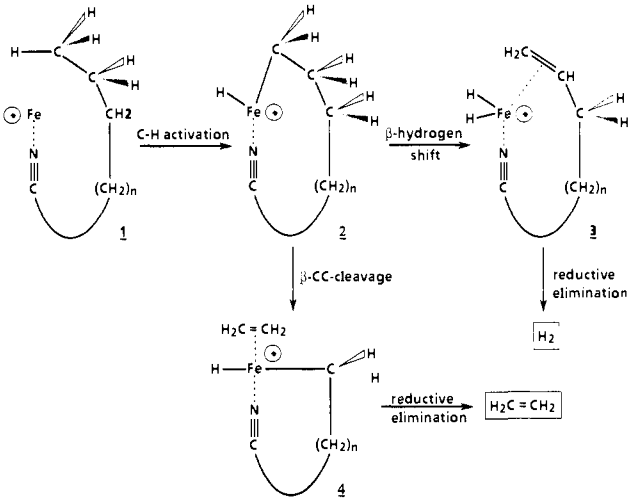
Abstract: The gas-phase reactions of the transition-metal ions Fe$^+$ and Co$^+$ with linear C(4)–C(12) nitriles are reported. In spite of an overall similar reactivity pattern, a more detailed analysis, based on the study of labeled nitriles, reveals distinct differences with regard to the mechanisms of elimination of alkenes and alkanes. For both metal ions, hydrogen and alkenes are generated from linear C(4)–C(12) nitriles, and the intermediates are formed via oxidative addition to terminal and internal C–H bonds. For the RCN/Fe$^+$ system insertion in an internal C–H bond commences at position C(8) of the nitrile; for the analogous RCN/Co$^+$ system, the oxidative addition to an internal C–H bond starts at position C(7) of the nitrile. Similarly, alkane formation is different for the two transition-metal ions. For RCN/Fe$^+$ the generation of alkanes is observed for nitriles having at least eight carbon atoms; in contrast, the elimination of alkanes from RCN/Co$^+$ is already observed for C(6) nitriles. Alkane elimination seems to follow the conventional mechanism (i.e., oxidative addition to a C–C bond, β-hydrogen transfer, and reductive elimination) for the RCN/Co$^+$ system, whereas for the RCN/Fe$^+$ complex there exists an additional mechanism. This mechanism corresponds to the loss of H$_2$ from an internal position of the alkyl chain followed by the elimination of an alkene. Some possible origins of the different behavior of Fe$^+$ vs. Co$^+$ are discussed.

The reaction of nitriles with transition-metal ions, e.g., Fe$^+$, in the gas phase is very unique, in that selective C–H activation occurs only at positions remote from the cyanide functionality.[1] This behavior contrasts with that of other unsaturated systems, such as alkenes[2] and alkynes[3] where allylic respective propargylic activations of the C–C and/or C–H bonds are reported to be the major mode of reaction. The primary reason is due to the initial interaction of the cyanide group with the metal. The preferred coordination leads to an "end-on" complex **1** characterized by a "linear"[4] Fe–N–C–CH$_2$ entity. The linear fragment in turn constraints the remainder of the molecule such that Fe$^+$ activates C–H bonds while trying to minimize the strain. For nitriles containing four to eight carbon atoms, this deformation results in the exclusive activation of the terminal methyl group by oxidative addition of the C–H bond to the (complexed) Fe$^+$ (Scheme I, **1** → **2**).

The structural rigidity of the resulting coordination may actually be advantageous in elucidating the mechanism of the C–H activating step. For example, if yet longer chain nitriles are used, does the metal eventually find a favored position on the chain? The size of the resulting metallacycle may, in principle, give some indication to the trajectory of the approach and may indicate whether a linear or trigonal structure is preferred as the transition structure for the C–H insertion.[5] A distinction between the two extremes of trajectories is all but easy to achieve. While it is trivial to state that the trajectory of interaction is governed by the ring size, it should be kept in mind that the size of the ring is a reflection of the back-bonding ability of the metal, since this governs the distortion of Fe–N–C–CH$_2$ unit from linearity.[6] It would, therefore, be of interest to compare the behavior of two different transition metals. To this end, we have performed further investigations with Co$^+$ since both Fe$^+$ and Co$^+$ are well-documented systems. (For exhaustive references see ref 3c.)

In the reaction of simple hydrocarbons with first-row transition metals such as Fe$^+$, Co$^+$, and Ni$^+$, C–C activation in addition to C–H activation has been commonly proposed as an initial reaction.[7a,b] However, the reaction of Fe$^+$ with the shorter chain length nitriles (<8 carbon atoms) is well explained by initial and exclusive C–H insertion. This insertion is followed by either β-hydrogen shift (**2** → **3**) to produce eventually hydrogen or cleavage of the C–C bond (**2** → **4**), which results in the formation of C$_2$H$_4$-containing complexes. Loss of C$_2$H$_4$ from complex **4** generates Fe$^+$/nitrile complexes being shortened by the C$_2$H$_4$ unit; the latter originates exclusively from the ω and (ω − 1) positions of the alkyl chain. With lengthening of the hydrocarbon chain, the geometric constraints should be relaxed, allowing initial C–C activation or other competing processes to take place.

Scheme I Proposed Mechanism for the C–H Activation of Linear Nitriles with Fe$^+$



[†] Dedicated to Professor Gerhard Quinkert, University of Frankfurt, on the occasion of his 60th birthday

(1) (a) Lebrilla, C. B.; Schulze, C.; Schwarz, H. *J. Am. Chem. Soc.* **1987**, *109*, 98. (b) Evidence for the insertion of transition-metal fragments like Cp*RhL (Cp* = η^5-Me$_5$C$_5$; L = PMe$_3$) in *primary* C–H bonds of alkanes in solution has been reported recently: Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332.

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

(3) (a) Peake, D. A.; Gross, M. L. *Organometallics* **1986**, *5*, 1236. (b) Schulze, C.; Weiske, T.; Schwarz, H. *Chimia* **1986**, *40*, 362. (c) Schulze, C.; Schwarz, H.; Peake, D. A.; Gross, M. L. *J. Am. Chem. Soc.* **1987**, *109*, 2368. (d) Schulze, C.; Schwarz, H. *Chimia* **1987**, *41*, 29.

(4) In the present context we use the term "linear" very loosely, as we know little about the energetics and electronics of this coordination. No doubt, that depending on the internal energy of **1**, deviation from linearity of the CH$_2$—C≡N—Fe unit, must occur. Similarly we have no information on the possible effects of electronically excited states of the metal ions on the reactivity with organic substrates. It should, however, be mentioned that the reactions of larger molecules are relatively insensitive to the electronic state of, for example, Fe$^+$. For leading references see: (a) Sonnenfroh, D. M.; Farrar, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 3521 and ref 12 cited therein. (b) Armentrout, P. B. In *Structure/Reactivity and Thermochemistry of Ions*, Ausloos, P.; Lias, S. G., eds.; D. Reidel Publishing Co.: Dordrecht, **1987**; NATO ASI Series, Vol. 193, p 97. (c) Ridge, D. P. *Ibid.*, 1987, Vol. 193, p 165.

(5) See, for example: (a) Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006. (b) Lebrilla, C. B.; Maier, W. F. *Chem. Phys. Lett.* **1984**, *105*, 183. (c) For a review see: Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (d) Muetterties, E. L. *J. Chem. Soc. Rev.* **1983**, *11*, 283.

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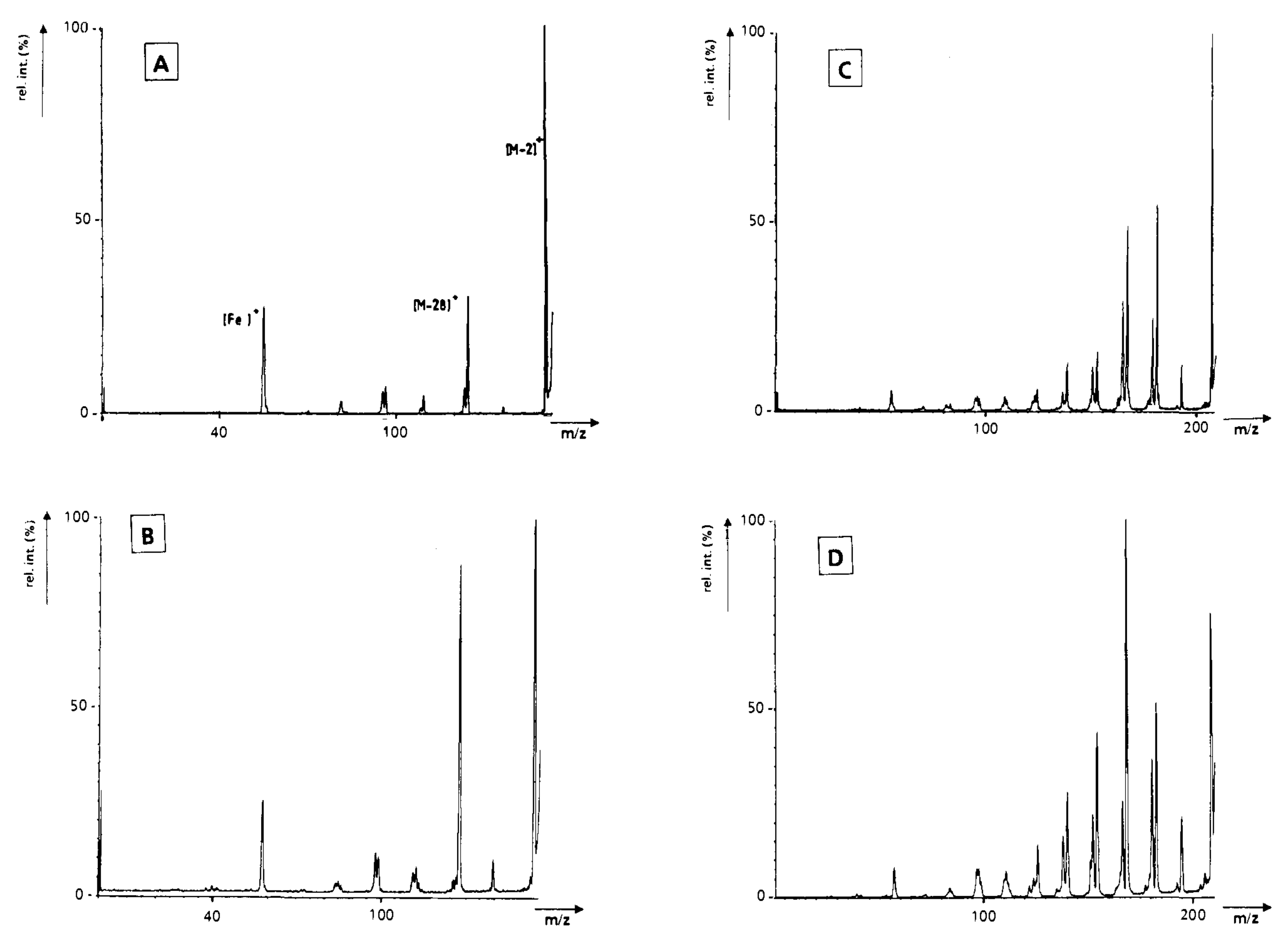

Figure 1. CA mass spectra of (A) $CH_3(CH_2)_4CN/Fe^+$, (B) $CH_3(CH_2)_4CN/Co^+$, (C) $CH_3(CH_2)_8CN/Fe^+$, and (D) $CH_3(CH_2)_8CN/Co^+$.

Experimental Section

The experimental setup has been described in an earlier paper.[1a] Briefly, Fe^+ is generated from $Fe(CO)_5$ and Co^+ from $Co(CO)_3NO$ by electron-impact ionization (70 eV).[8] A ZAB-HF-3F triple-sector mass spectrometer with B(1)EB(2) configuration was used for analysis. The apparatus has been described in detail elsewhere.[9] In a typical experiment 15 μL of nitrile and 3 μL of $Fe(CO)_5$, respective $Co(CO)_3NO$, are injected into a reservoir and permitted to flow into the ion source. For higher nitriles ($>C_{10}$) the direct insertion probe was used. The ions corresponding to RCN/Fe^+ respective to RCN/Co^+ having 8 keV kinetic energy are mass selected and focused with B(1)E. Collision gas (He, pressure ca. 2.0×10^{-5} mbar) is introduced in the collision chamber located in the 3rd field-free region, and fragments are analyzed by scanning B(2). In the collision experiment the intensity of the primary ion beam is attenuated to ca. 85%; this corresponds on average to 1.1 collisions.[10a] All unlabeled nitriles are commercially available (>98% purity) and were used without further purification. Labeled nitriles were prepared with use of known procedures and were purified by gas chromatography. The deuterium content was determined by mass spectrometry.

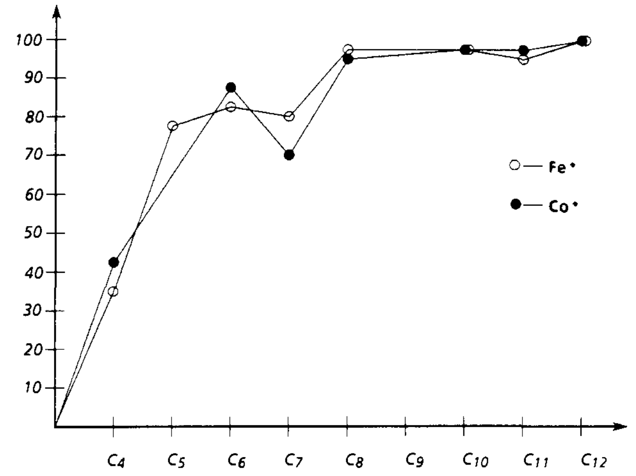

Figure 2. Relative reactivities (in arbitrary units) of Fe^+ and Co^+ as a function of the chain length of linear nitriles.

Results and Discussion

The types of products observed from the reaction of nitriles with Fe^+ and Co^+, followed by collisional activation (CA),[10] are practically identical for both metal ions. Only the relative abundances of the products are different. Figure 1 shows the CA mass spectra of both metal ions with C(6) nitrile (pentyl cyanide) and C(10) nitrile (nonyl cyanide).[11] We observe as *major*

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[6] (a) Bach, S. B. H.; Taylor, C. A.; Van Zee, R. J.; Vala, M. T.; Weltner, W., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 7104. (b) Schilling, J. B.; Goddard, W. A., III; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 582.

[7] See, for example: (a) Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1980**, *102*, 7129. (b) Houriet, R.; Halle, L. F.; Beauchamp, J. L. *Organometallics* **1983**, *2*, 1818. (c) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 5197. (d) Halle, L. F.; Houriet, R.; Kappes, M. M.; Staley, R. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 6293. (e) Beauchamp, J. L. *High energy processes in Organometallic Chemistry*; A.C.S. Symposium Series, 1986, in press. (f) Allison, J. *Prog. Inorg. Chem.* **1986**, *34*, 627.

[8] Recent FTICR results (ref 2c) have shown that in the reaction of alkynes and iron carbonyl, the alkyne/Fe^+ complex is formed from the reaction of the neutral alkynes with $Fe(CO)_x^+$ ($x = 1, 2$). Recent FTICR studies (Drewello, T.; Lebrilla, C. B.; Nibbering, N. M. M.; Schwarz, H., in preparation) demonstrate that the RCN/Fe^+ complexes are formed in a similar fashion.

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

[10] For leading references, see: (a) Holmes, J. L. *Org. Mass Spectrom.* **1985**, *20*, 169. (b) Levsen K., Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 509. (c) Levsen, K.; Schwarz, H. *Mass Spectrom. Rev.* **1983**, *2*, 77. (d) Cooks, R. G. *Collision Spectroscopy*; Plenum: New York, 1978.

[11] For brevity, the nitriles will be refered to with respect to the number of carbon atoms, including the nitrile carbon atom, and not according to IUPAC names.

Table I. Relative Percentage of Neutral Products Formed from RCN/Fe$^+$ and RCN/Co$^+$ upon Collisional Activation

	RCN/Fe$^+$			RCN/Fe$^+$		
nitrile	H_2	alkene	alkane	H_2	alkene	alkane
C(2)	0	0	0	0	0	0
C(3)	0	0	0	0	0	0
C(4)	17	83	0	19	81	0
C(5)	58	42	0			
C(6)	77	23	0	50	44	5
C(7)	57	43	0	32	54	14
C(8)	50	42	8	26	52	21
C(10)	34	44	22	18	53	29
C(11)	20	50	30	15	49	36
C(12)	21	43	36	17	46	37

[a] Data for the reactions of C(5) nitrile with Co$^+$ and C(9) nitrile with Fe$^+$ and Co$^+$, respectively, are not included. For reasons unknown to us, we obtained M$^+$/RCN complexes the intensity of which was not high enough for a CA analysis. Moreover, the signal intensity of the M$^+$/RCN species showed considerable fluctuations. For the remaining systems the data reported were obtained with an error of ±3%.

products for both metal ions only H_2 and C_2H_4 elimination for the shorter nitriles (Figure 1A,B and also ref 1a) and ionic products due to the losses of higher olefins and alkanes at longer chain length.

Figure 2 shows the relative reactivity of Fe$^+$ and Co$^+$ as a function of chain length. The relative reactivity is defined as previously,[1a] i.e., it expresses the formation of product ions from M$^+$/RCN (M$^+$ = Fe, Co) relative to the ligand loss process (re-generation of bare M$^+$). The data in Figure 2 demonstrate that for all practical purposes no major differences seem to exist for the two metal ions. This was also observed[7] for the reactions of Fe$^+$ and Co$^+$ with simple alkanes, which were only slightly dependent upon the nature of the two transition-metal ions.[7c]

The many reported similarities between Fe$^+$ and Co$^+$ have led earlier investigators to conclude that the mechanisms underlying the C–H/C–C activation steps are similar for the two metals.[7,12a–c] However, at least in the nitrile system, we will demonstrate that the similarities are deceptive; the actual chemistry of the RCN/Fe$^+$ vs. RCN/Co$^+$ system is quite distinct with regard to some essential steps.

To aid in the elucidation of the mechanisms, two deuterium-labeled C(10) nitriles were included in our investigation: nonyl-*10,10,10-d_3* cyanide (I) and nonyl-*8,8-d_2* cyanide (II).

The organization of the paper is such that we will describe first the RCN/Fe$^+$ system, followed by a discussion of the gas-phase chemistry of RCN/Co$^+$.

RCN/Fe$^+$. Three major classes of neutral products are generated in the gas-phase reaction of Fe$^+$ with nitriles, corresponding to the losses of hydrogen, alkenes, and alkanes. Eliminations of H_2 and C_nH_{2n} are observed for all nitriles studied provided they contain four and more carbon atoms. Starting with C(8) nitriles, in addition to these reactions, the elimination of alkanes becomes significant (Table I). We will first discuss the formation of H_2, C_2H_4, and higher alkenes and then turn to the mechanistic details of alkane formation.

Figure 3 shows the relative abundance of neutral olefin losses as a function of chain length. Ethylene loss is the major product of nitriles with chain length of up to C(8). At C(10), on the other hand, propene starts to dominate followed by butene for the C(11) nitrile.

In our earlier paper,[1a] we have shown that the elimination of both ethylene and hydrogen proceedes through the same intermediate **2**, and the mechanism is outlined in Scheme I. Initial C–H insertion (**1** → **2**) is followed by β-hydrogen shift to produce **3**, from which H_2 is eliminated. β-Carbon–carbon bond cleavage rearranges **2** to **4**; from **4** the C_2H_4 unit is eliminated. For alkyl nitriles with longer alkyl chains, for example, the C(10) nitrile, C_2H_4 and H_2 are still produced via the same mechanism, at least to some extent. Reaction of Fe$^+$ with I yields exclusively CD_2CH_2, while the complex Fe$^+$/II upon collisional activation splits off C_2H_4 without any deuterium incorporated in the neutral. Thus, ethylene originates exclusively from the ω and (ω – 1) positions, as was also demonstrated earlier for smaller alkyl nitriles. With regard to the generation of hydrogen which is coupled with the olefin formation,[1a] we observe a distinct behavior for the longer alkyl nitriles. For example, hydrogen is no longer formed from the ω and (ω – 1) positions, as is the case for C(4)–C(6) nitriles.[1a] Instead, from the complex Fe$^+$/I hydrogen is formed as HD and H_2 with 30 and 70% relative abundances, respectively, and from Fe$^+$/II the two neutrals are generated with the relative intensities of 45 and 55%. Thus, insertion of the (complexed) metal ion in the terminal positions is no longer the only reaction path for the C(10) nitrile; rather, insertion in *internal* C–H bonds competes. As will be discussed below, this competition may begin with the C(8) nitrile.

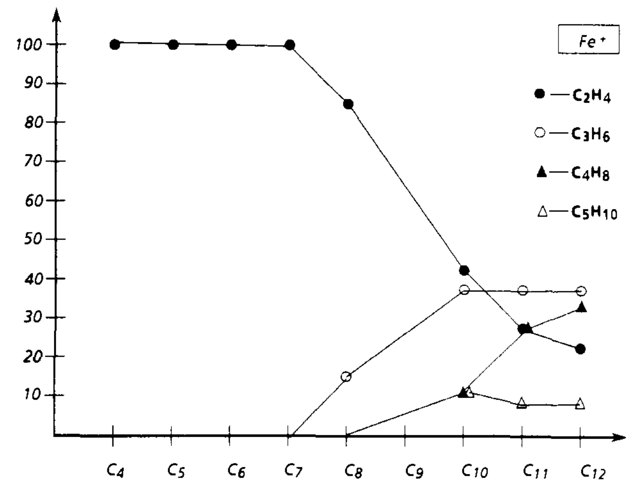

Figure 3. Relative formation (expressed as % $\sum C_nH_{2n}$ = 100) of olefins C_nH_{2n} (n = 2–5) from RCN/Fe$^+$ as a function of chain length.

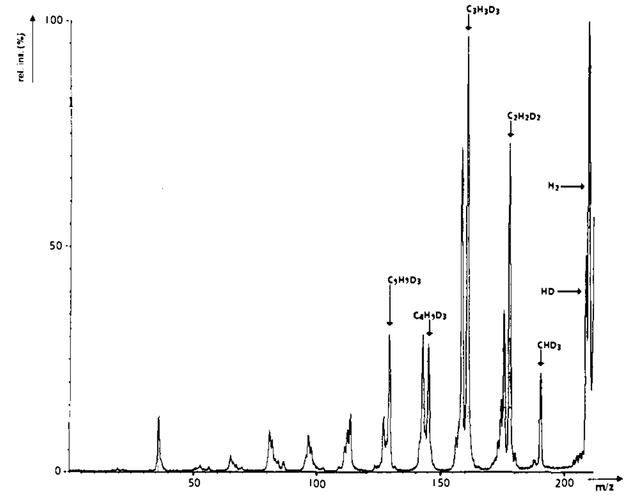

Figure 4. CA mass spectrum of $CD_3(CH_2)_8CN$/Fe$^+$.

The observed losses of higher olefins (n > 3) from alkyl nitriles containing seven and more carbon atoms are also consistent with insertion of Fe$^+$ in nonterminal C–H bonds. We note from Figure 4 that all olefinic neutrals eliminated contain the terminal CD_3 group.

A general mechanism for olefin losses from higher alkyl nitriles consistent with the experimental findings is suggested in Scheme II. We note that *the size of the olefin eliminated* is an indication of which C–H group(s) of the alkyl chain the initial C–H activation occurs. For example, the loss of ethylene indicates initial

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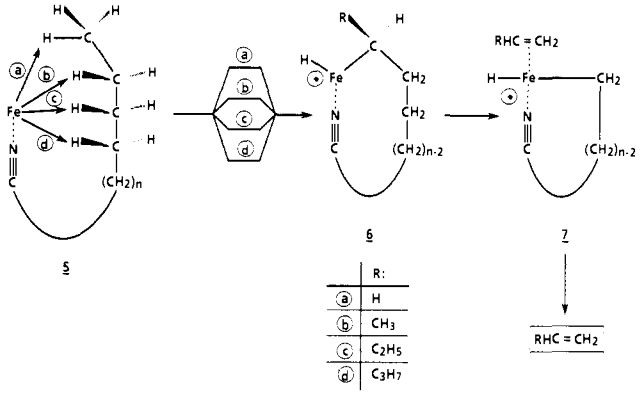
(12) (a) Tolbert, M. A.; Mandich, M. L.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 5675. (b) See, however, Hanratty, M. A.; Beauchamp, J. L.; Illies, A. J.; Bowers, M. T. *J. Am. Chem. Soc.* **1985**, *107*, 1788. (c) Also see: Hanratty, M. A.; Beauchamp, J. L., Illies, A. J.; van Koppen, P.; Bowers, M. T. *J. Am. Chem. Soc.*, submitted for publication. (d) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1977**, *99*, 35. (e) Byrd, D. G.; Burnier, R. C.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 3565.

Scheme II Proposed Mechanism for the Elimination of Alkenes from RCN/Fe^+ via Activation of Internal C–H Bonds



insertion in the terminal C–H bond. Similarly, propene formation starts with insertion in the ($\omega - 1$) C–H bond, and the generation of butene suggests activation of the ($\omega - 2$) C–H bond etc. Since the loss of propene is *not* observed for alkyl nitriles with less than eight carbon atoms (Figure 3) we conclude that insertion of Fe^+ in nonterminal C–H bonds must at least have this particular ring size.

The fact that C_2H_4 and C_3H_6 are formed in comparable amounts from the C(10) nitrile (Figure 3) implies that activation of the ω and ($\omega - 1$) C–H bonds occurs at approximately the same rate. With the methyl-labeled C(10) nitrile I one observes a slight preference for activation at the ($\omega - 1$) position (see Figure 4, which demonstrates that loss of $C_3H_3D_3$ is preferred over $C_2H_2D_2$ loss, while for the unlabeled system (Figure 3) C_3H_6 and C_2H_4 are eliminated with comparable intensities). The measured isotope effect (estimated from the $C_3H_3D_3$ vs. $C_2H_2D_2$ ratio in Figure 4) is, however, small (1.7), indicating that the transition structure for the metal ion insertion is likely to be asymmetric with regard to the development of the Fe–H–C bonds. However, a clear distinction whether we are dealing with an "early" or "late" transition structure is not possible, although the insertion step is likely to be exergonic thus favoring an "early" transition structure.[7e,12c] Similarly, as pointed out by Westheimer[13] small isotope effects can also result from nonlinear transition structures.

For the C(11) nitrile, propene formation becomes the major route for olefin loss, with the rate for butene formation equaling that of ethylene generation. Thus, a slight preference for the insertion of Fe^+ into the C(9) and C(10) positions of the chain seems to exist. That bond strength plays a role is perhaps not completely unexpected. The isotope effect, albeit small, does already indicate some dependence on the C–H/C–D bond strength. Similarly, the comparison of C(10) and C(12) nitriles reveals that propene loss is insensitive to the chain length while the increase in butene formation occurs at the expense of ethylene. This behavior indicates a strong preference of the attacking Fe^+ for any methylene *near the methyl group*, with only weak preferences for a particular one. Nonetheless, the fact that a point is reached where terminal C–H activation becomes no longer necessary indicates a certain stability perhaps in the size of the metallacycle formed. In reality, however, the actual behavior of the Fe–N–C–CH_2 portion of the chain, which governs the stability of any resulting metallacyclic ring, remains a mystery. This will become more evident as we discuss the results obtained for RCN/Co^+. Before doing this, we will try to understand the mechanism of alkane formation from the RCN/Fe^+ system.

With C(10) nitrile, losses corresponding to CH_4, C_2H_6, C_3H_8, etc., are already significant relative to the abundance of the corresponding olefin eliminations (Figure 1C). The most obvious and simple mechanisms would involve initial C–C cleavage (Scheme III, **8** → **9**) followed by β-hydrogen shift (**9** → **10**) and reductive elimination of CH_3R (R = H, CH_3, etc.).

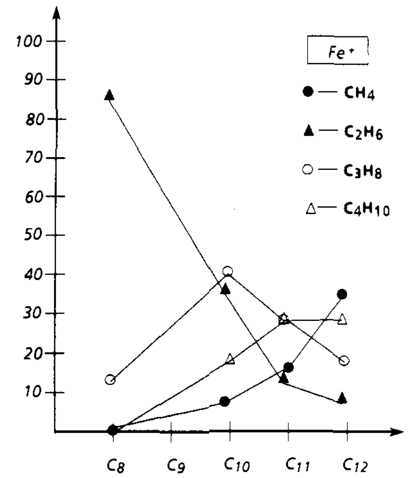
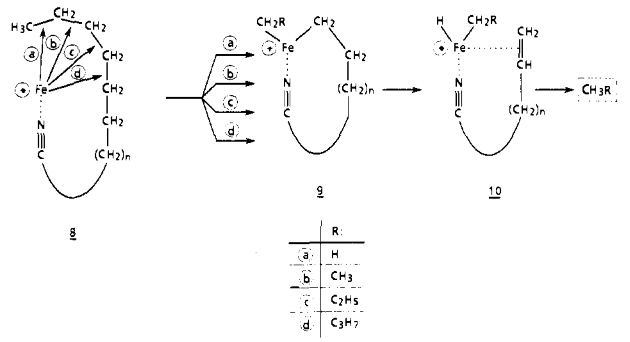


Figure 5. Relative formation (expressed as % $\sum C_nH_{2n+2} = 100$) of alkanes C_nH_{2n+2} (n = 1–4) from RCN/Fe^+ as a function of chain length.

Scheme III Proposed Mechanism for the Elimination of Alkanes from RCN/Fe^+ via Insertion in C–C Bonds



In a recent paper,[14] a correlation between the site of insertion of bare metal ions (Fe^+, Co^+, Ni^+) into C–C bonds in alkanes was reported. It was suggested that the preference of insertion into a particular skeleton bond increases with decreasing ionization energies (IE) of the corresponding C_nH_{2n+1} radical. This qualitative model explains well why loss of CH_4 from alkane/transition metal ion complexes is a minor process. Insertion into a terminal C–C bond is not favored because of the high ionization energy of $CH_3\bullet$. Rather insertions in weaker C–C bonds are favored. Inspection of the data, given in Figure 5, is quite revealing in that alkane loss from the RCN/Fe^+ system must follow a mechanism that is fundamentally different from that of alkane/transition metal ion complexes.[7f,14]

However, a certain anomaly must exist for the RCN/Fe^+ system which is inconsistent with the traditional mechanism. When the losses of neutral alkanes are plotted as a function of increasing chain length, the production of CH_4 increases from zero at C(8) to become the major alkane product at C(12) (>30%, Figure 5). If we were to assume that the differences between the C(methyl)–C(methylene) and the C(methylene)–C(methylene) bond strengths are analogous to that of H–C(methyl) and H–C(methylene), then the plot of the relative abundances of the alkane losses should mirror the trend observed for that of olefin losses (Figure 3). In the olefin losses, ethene, which is produced via activation of the methyl C–H bond, is the major product early in the series and steadily decreases after a specific chain length. Similarly, the major alkane formed early in the series should be methane since the terminal C–C bond is initially the most available one. Methane loss should then eventually decrease as the chain length becomes longer, just as with the ethylene loss. Instead, an opposite trend is observed.

When we inspect the types of methanes produced from the labeled precursors, we find that only CD_3H is obtained from the

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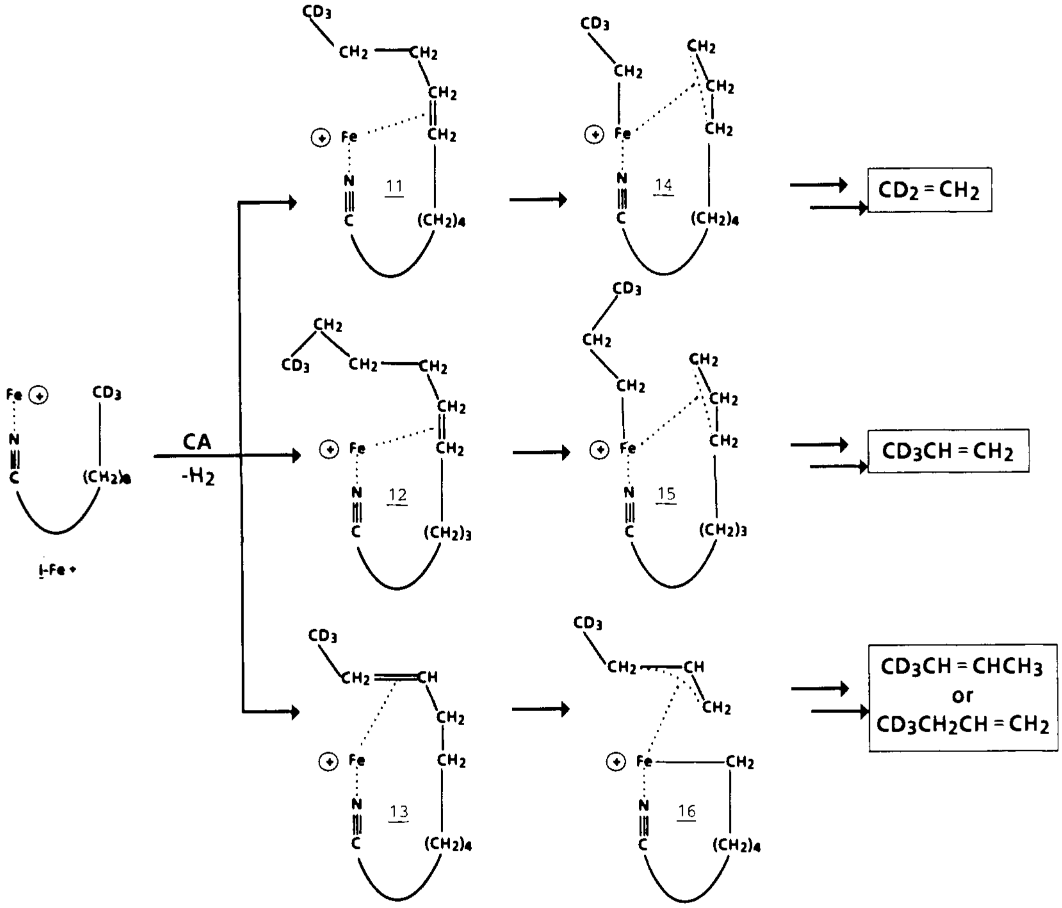
(13) Westheimer, F. H. *Chem. Rev.* **1961**, *61*, 265.

(14) Radecki, B. R.; Allison, J. *Organometallics* **1986**, *5*, 411.

Scheme IV. Proposed Mechanism for Collision-Induced Alkene Losses from H_2 Elimination Products, Generated upon Collisional Activation of $CD_3(CH_2)_8CN/Fe^+$



Fe^+/I complex. From the Fe^+/II complex only CH_3D loss is observed. Thus, methane loss can conveniently be described in terms of the mechanism outlined in Scheme III (insertion of Fe^+ in the terminal C–C bond, followed by irreversible β-hydrogen transfer, and terminated via reductive elimination). It should be mentioned that, strictly speaking, the same deuterium distribution for methane losses from I and II would be observed if the reactions commence with insertion of Fe^+ in the C–H bond of C(8), followed by β-methyl migration. However, β-alkyl migrations, while reported to exist,[7b] are extremely rare in the gas phase.[3c,d]

The formation of ethane, on the other hand, represents a different case. The ethane lost from Fe^+/I complex contains only 30% CD_3CH_3 (the expected C–C activation product). The remaining 70% corresponds to the masses for $C_2H_4D_2$. This totally unexpected result may be attributed to several factors, one of them being some type of H/D scrambling. However, H/D scrambling to such a large extent has never been observed.[15] We propose, instead, that the alkanes *larger* than methane are produced by a different mechanism. In fact, they may not even be alkanes at all! The observed molecular formula can also be obtained if we consider a sequential loss of H_2 from whithin the chain followed by the loss of $C_2H_2D_2$ from the terminal position. Indeed, when the H_2 eliminiation product generated from the methyl-labeled C(10) nitrile I is mass selected and subjected to collisional activation, one obtains a spectrum (Figure 6) that contains signals due to the losses of $C_2H_2D_2$, $C_3H_3D_3$, and $C_4H_5D_3$, respectively. The elimination of these species can be interpreted by the mechanism outlined in Scheme IV: H_2 elimination from internal positions (which accounts for 70% of the total hydrogen loss) is likely to involve the C(9)–C(5) positions (the HD loss from Fe^+/II, which contributes to 50% of the hydrogen lost, provides ample evidence that the C(8) carbon is involved). The resulting bidentate complexes **11–13** may then isomerize via a multitude of competing processes, among which the most prominent ones are of the allylic insertion and hydrogen migration type. Intermediates **14–16**, once formed, may then split off alkenes that contain the original methyl group of the nitrile. This unprecedented mechanism would thus not only explain the observed deuterium distribution but also explain the anomaly between the formation of methane on the one hand and the higher "alkanes" on the other hand in Figure 5; i.e., we are comparing two different processes: one involves alkane loss (methane) and the other some sequential elimination of H_2 and olefin. Both processes are independent of each other. We want to emphasize, however, that although Scheme IV may be the major process for alkane loss, it, by no means, is the only one. C–C bond cleavage is still a competing reaction, and some intramolecular scrambling may occur before the loss of the olefins.[15]

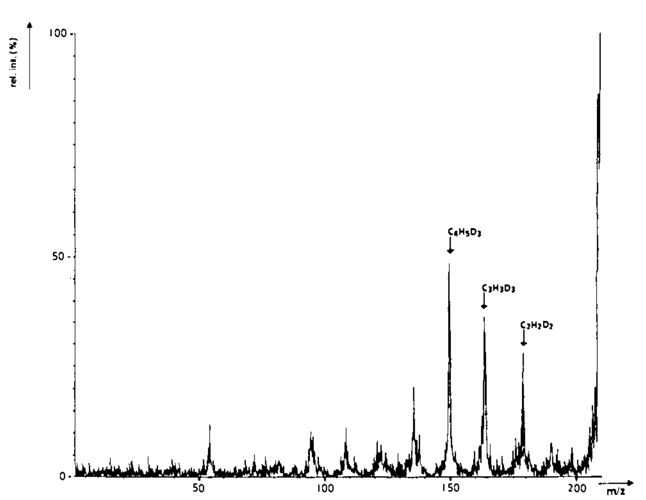


Figure 6. CA mass spectrum of H_2 loss product generated from $CD_3(CH_2)_8CN/Fe^+$.

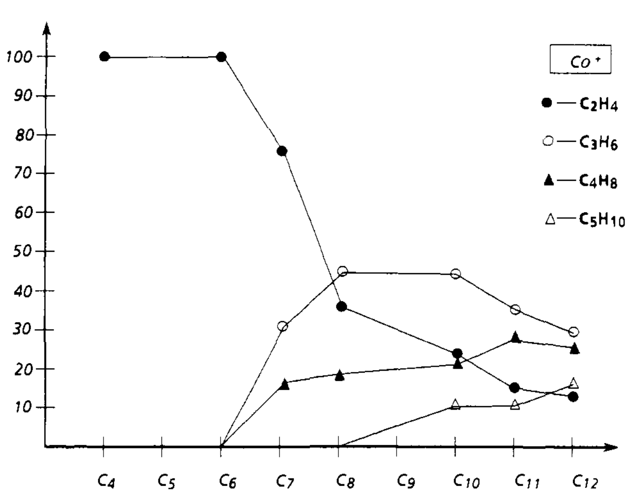


Figure 7. Relative formation (expressed in % $\sum C_nH_{2n} = 100$) of alkenes C_nH_{2n} (n = 2–5) from RCN/Co^+ as a function of chain length.

It has not escaped our notice that the CA mass spectrum of the H_2 loss product generated from I–Fe^+ (Figure 6) does not contain any major signals for H_2/HD eliminations. This result may not be unexpected as sequential hydrogen eliminations have so far not been reported for first-row transition-metal ions (except for Ti^+[12d,e]) but were observed for second-row metals, in particular Ru^+ and Rh^+.[12a]

RCN/Co^+. As mentioned earlier, all neutrals produced by the gas-phase reaction of Fe^+ with nitriles are similarly produced by Co^+ (Table I). Losses corresponding to H_2 and C_2H_4 are observed from C(4) to C(12) nitriles. The formation of alkanes from RCN/Co^+, however, begins earlier (with C(6) nitrile) in the series with Co^+. For unknown reasons, the formation of the C(5) nitrile/Co^+ complex could not be observed.

Although one might conclude from Figure 2 that the overall reactivity of Co^+ is similar to that of Fe^+, distinctly different features with respect to alkene and alkane formations are observed. Let us begin with the discussion of olefin losses. As with Fe^+, olefin formation is observed as the major product for shorter nitriles. However, already at C(7) nitrile, propene formation is significant (>30%) for the RCN/Co^+ system. For Fe^+, this analogous "point of reactivity" occurs at a much longer chain length, i.e., for the C(10) nitrile.

The mechanism for olefin loss from RCN/Co^+ may be similar if not identical to that of RCN/Fe^+ (Scheme II). In fact, reaction of Co^+ with $CD_3(CH_2)_3CN$ produces all the same products as Fe^+ does, i.e., $CD_2{=}CH_2$, $CD_3CH{=}CH_2$, $CD_3CH_2CH{=}CH_2$, etc. With regard to the dehydrogenation, formation of HD and H_2 occurs in the same proportion as with Fe^+.

The faster drop-off of C_2H_4 formation for Co^+ strongly implies a different in the actual coordination behavior between Fe^+ and Co^+. However, the ring size of the interactions of Co^+ ions with CH/CC bonds of the alkyl chain indicates that Co^+ too favors an end-on complexation with the nitrile, just as Fe^+. The difference may be as trivial as the differences in the lengths of the nitrogen–metal bond, which would increase or decrease the reacting range of the metal. Unfortunately, any reliable gas-phase bond lengths are unavailable for these systems. Alternatively one may argue that electronic factors play a role such as the difference in the back-bonding ability of the two metals. If back-bonding is large then electron density is donated to the π^* MO of the C–N triple bond, thereby modifying the hybridization of the carbon atom. This would effectively distort the N–C–C bond angle from the 180° alignment. The net result would be to bring the hydrogen atoms closer to the metal even at shorter carbon chain length. Although a few studies exist that address similar points none have really approached this particular subject in detail.[16] We, therefore, want to emphasize the role that theoretical chemistry can play in these types of studies and we strongly encourage these types of calculations.

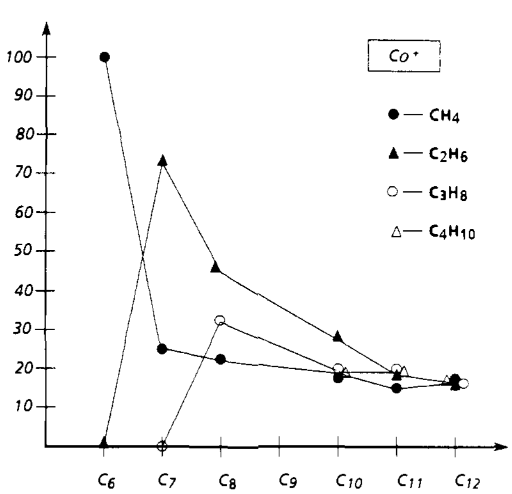


Figure 8. Relative formation (expressed as % $\sum C_nH_{2n+2} = 100$) of alkanes C_nH_{2n+2} (n = 1–4) from RCN/Co^+ as a function of chain length.

As already mentioned for the RCN/Co^+ system the shorter reach of Co^+, as observed in the olefin losses, is also found for the alkane elimination. Losses corresponding to alkane masses begin early in the series with C(6) nitrile compared to C(8) nitrile for Fe^+. Furthermore, the loss of alkanes with Co^+ is a true loss of an intact alkane unit. This is readily demonstrated by the reaction of $CD_3(CH_2)_8CN$ with Co^+. As with iron, loss of methane is exclusively CD_3H. The loss of ethane, on the other hand, is all $C_2H_3D_3$, unlike iron, suggesting a mechanism identical with that of methane loss (Scheme III).

That alkanes are readily produced is further confirmed by the behavior of the relative abundance of the alkane losses as a function of chain length (Figure 8). At C(6) nitrile the only alkane lost corresponds to CH_4. Methane loss is then quickly overtaken by loss of ethane at C(7) nitrile, which in turn is overtaken by propane at C(11), etc. (Figure 8). This type of behavior is expected for a true C–C bond cleavage. However, for a complexed metal ion C–C bond cleavage must also be governed by geometrical constraints as is C–H cleavage. Therefore, C–C cleavage must also begin at the position closer to the metal which, for the shorter length nitriles, is the terminal position. Again, the distinctly different reactivity pattern of Fe^+ vs. is quite remarkable.

Conclusion

Despite the many similarities in terms of overall reactivity (i.e., the type of neutrals lost) in the reactions of Fe^+ and Co^+ with linear nitriles, the two metals react via distinct mechanisms producing, in some cases, different products. It is therefore dangerous to compare reactivity on these criterion alone. The use of labeled compounds is crucial in these studies.

Acknowledgment. The continuing support of our work by the Deutsche Forschungsgemeinschaft (Projekt Schw 221/6-4), the Fonds der Chemischen Industrie, Stiflung Volkswagenwerk, and the Technische Universität Berlin is gratefully acknowledged. C.B.L. thanks the Alexander von Humboldt Foundation and the NATO-NSF for providing a post-doctoral fellowship. We are also indebted to Marileka Angelidou for her help in the synthesis of the labeled compounds and to Professor J. L. Beauchamp, Pasadena, for providing us with preprints of his work.

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(15) We do observe scrambling with Fe^+/II from which elimination of C_2H_6 amounts to only 60% of the total ethane production; the remaining 40% correspond to C_2H_5D. Neither the mechanism involving initial C–C insertion nor the one we will be describing below can explain the formation of this species. We are currently investigating the mechanism for these intramolecular H/D exchange reactions.

(16) There are a few experimental studies that deal with the coordination of nitriles to metals. For references see: (a) Wexler, R. M.; Muetterties, E. L. *J. Phys. Chem.* **1984**, *88*, 4037. (b) Andrews, M. A.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1979**, *101*, 7260. (c) Fewer yet are theoretical calculations dealing with this subject. One such investigation which, however, deals only with the nitrile ligand is the following: Howell, J. A. S.; Saillard, J. Y.; Le Beuze, A.; Jaouen, G. *J. Chem. Soc., Dalton Trans.* **1982**, 2533.