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Association Reactions and Remote C–H Bond Activation of Aliphatic Nitriles with $Fe(CH_3)^+$[†]

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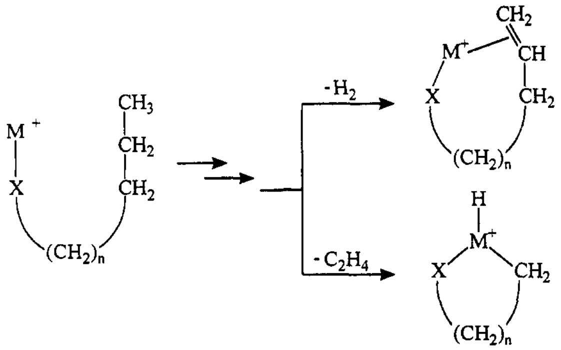
Unbranched aliphatic nitriles RCN (R = CH_3 through C_7H_{15}) are reacted in the gas phase with thermalized $Fe(CH_3)^+$ using Fourier-transform ion cyclotron resonance (FTICR) mass spectrometry. The reactions occur with collision rate for R $\geq C_3H_7$; CH_3CN and C_2H_5CN exhibit a much smaller reaction efficiency, i.e. 7 and 51%, respectively. While for all nitriles ligand association is observed, for R = C_6H_{13} and C_7H_{15}, in addition loss of CH_4 and H_2 takes place. Extensive labeling experiments reveal that the methyl group of $Fe(CH_3)^+$ remains intact in the course of C–H bond activation of the alkyl chain, which involves exlusively the ω-, $(\omega - 1)$-, and $(\omega - 2)$-positions of the two nitriles. These observations suggest that $Fe(CH_3)^+$ is end-on coordinated to the nitrogen atom of the nitrile group.

Hallmark of the gas-phase reactions of many monofunctional, unbranched alkanes with "bare" transition-metal ions M^+ is the unprecedented activation of C–H and C–C bonds *remote* to the functional group X.[1] Here, complexation of the metal ion with the functional group will effectively prevent (on geometric grounds) oxidative insertion into bonds within the proximity of X. Consequently, only remote bonds can be reached, e.g. by folding back of the alkyl chain. Depending on M and X for substrates with not a too long alkyl chain it is exclusively a C–H bond of the terminal CH_3 group that is activated, and the intermediate metallacycle will undergo competitively either β-hydrogen shift or β-C–C cleavage. Reductive elimination of H_2 furnishes an ω-unsaturated product, while loss of C_2H_4 yields a metallacycle shortened by two methylene groups originating from the $\omega/\omega - 1$ units of the alkyl chain (Scheme 1).[1]

In spite of an increasing number of publications, in comparison with *bare* metal ions much less is known about (and even much more less understood are) the reactions of *ligated* metal ions with organic substrates in the gas phase.[2] The chemistry of $Fe(CH_3)^+$ and $Co(CH_3)^+$ has been studied quite thoroughly with alkanes,[3] cycloalkanes and -alkenes,[4] simple alkenes and alkynes,[5] and some nitrogen[6] and oxygen bases.[7] As compared with the "bare" metal ions Fe^+ and Co^+, $M(CH_3)^+$ (M = Fe, Co) has generally been found to be much less reactive. The reaction of $M(CH_3)^+$ ions with alkenes is particularly important with regard to the mechanism of the Ziegler–Natta polymerization, where migratory insertion of alkenes into metal–alkyl bonds is regarded as a key step of the traditional Cossee–Arlman mechanism.[8] $Fe(CH_3)^+$, however, is unreactive toward ethene[5] [in contrast to $Fe(NH_2)CH_3^{+9}$], and although insertion is observed for $Co(CH_3)^+$, the product decomposes by loss of H_2 to the stable $Co(C_3H_5)^+$.[5] Metal–allyl complexes are also formed by $Fe(CH_3)^+$ and $Co(CH_3)^+$ from lower homologues of alkenes by loss of CH_4, and it is suggested that activation of an allylic C–H group takes place. Recently, evidence was presented that the gas-phase reaction of $M(CH_3)^+$ with 1-octyne is preceded by *interligand* C–C bond coupling as well as extensive hydrogen exchange.[10] In contrast, in the reaction of $M(CH_3)^+$ with 1-octene, the metal–methyl group retains its identity while the alkene ligand is subject to metal-mediated extensive hydrogen atom scrambling.[10] Obviously, ligation of the metal ion with a simple ligand, *viz.* a CH_3 group, profoundly affects the gas-phase chemistry. We have wondered if the intriguing reactions of aliphatic nitriles with "bare" transition-metal ions (Scheme 1: X = CN)[11] is also subject to a ligand effect. Recent results[12] on the reactions of Fe(alkene)$^+$ complexes with *n*-pentanenitrile support this conjecture.

Scheme 1



[†] Dedicated to Professor Dietmar Seyferth on the Occasion of his 65th birthday.

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1994.

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In the present paper we wish to report the results of a detailed FTICR study of $Fe(CH_3)^+$ with unbranched, aliphatic nitriles RCN (R = CH_3 through C_7H_{15}), and we will focus on two aspects: (i) Is the activation of CH/CC bonds of the alkyl chain of RCN affected by the presence of the methyl ligand? To this end, extensive labeling experiments are employed in order to unravel the origin of the products formed in the ion–molecule reactions. (ii) Rate constants for the process $Fe(CH_3)^+ + RCN \rightarrow$ products are measured and compared with various theoretical models.

Experimental Section

The labeled compounds were synthesized according to well-established procedures and characterized by spectroscopic means. The gas-phase experiments were performed by using a Spectrospin CMS 47X Fourier-transform ion-cyclotron resonance mass spectrometer (FTICR), which was equipped with an external ion source;[13] the instrument and further details of its operation were previously described.[14] Briefly, metal ions were generated by laser desorption/ionization[15] by focusing the beam of an Nd:YAG laser (Spectron System; $\lambda = 1064$ nm) onto a stainless-steel target which was affixed in the external ion source. The metal ions were extracted from the source and transferred to the analyzer cell by a system of electrostatic potentials and lenses. The ion source, transfer system, and ICR cell were differentially pumped by three turbo-molecular pumps. After deceleration, the ions were trapped in the field of a superconducting magnet (Oxford Instruments, maximum field strength of 7.05 T). The most abundant isotope of the metal was isolated by using FERETS.[16] For collisional cooling of any excited states possibly formed and removal of kinetic energy remaining from the transfer, argon was present as a buffer gas with a constant "background" pressure of ca. 5×10^{-7} mbar, as measured with an uncalibrated ion gauge (Balzers IMG 070). For collision-induced dissociation (CID) experiments,[17] argon was also employed. For the generation of Fe(methyl)$^+$, Fe^+ was reacted with pulsed-in methyl iodides (CH_3I, CD_3I, or $^{13}CH_3I$), diluted with 90% argon to generate $Fe(CX_3)^+$ (X = H, D).[5]

The Fe(methyl)$^+$ species was isolated by double-resonance ejection, and great care was applied to avoid any off-resonance excitation of the ion of interest.[18] For the reaction of Fe(methyl)$^+$ with RCN, the nitriles were admitted to the ICR cell by a second leak value with a constant pressure of about $p \approx 6 \times 10^{-9}$ mbar. The elementary composition of the ions were determined by applying high-resolution FTICR as described earlier.[14a,c] All functions of the instrument were controlled by a Bruker Aspect-3000 minicomputer.

Results and Discussion

All nitriles RCN investigated give rise to the formation of adduct complexes (eq 1). For R = CH_3 through C_5H_{11} this is the sole process taking place. For R = C_6H_{13} and C_7H_{15}, in addition to the adduct formation (74 and 52%, respectively) we observe products due to the combined losses of CH_4/H_2 (eq 2) (26 and 48%, respectively). There is no indication whatsoever for C–C or C–N bond activation, as is observed for the reactions of "bare" Fe^+ with RCN.[11]

$$Fe(CH_3)^+ + RCN \rightarrow Fe(CH_3)(RCN)^+ \quad (1)$$

$$R = CH_3 \text{ through } n\text{-}C_7H_{15}$$

$$Fe(CH_3)^+ + RCN \rightarrow Fe(R'CN) + CH_4 + H_2 \quad (2)$$

$$R = n\text{-}C_6H_{13},\ n\text{-}C_7H_{15}$$

Although the actual structures of the product ions are unknown, the investigation of deuterium-labeled isotopomers of RCN and $Fe(CH_3)^+$ together with low-energy CID experiments provide some mechanistic insight as well as useful information on the gross structural features of the ionic products.

The importance of the latter aspect is highlighted by recalling that $M(RNCO)^+$ complexes (R = branched alkyl), formed in the reaction of RNCO and M^+, do not necessarily correspond to a simple adduct; rather, as shown recently[19] in the course of the ion–molecule reactions quite unexpected isomerizations took place which resulted in the formation of M(alkene)(HNCO)$^+$ clusters. Obviously, attachment of the ligand RNCO to the metal ion is accompanied by C–N and C–H bond activation. In order to clarify this aspect for the $Fe(CH_3)(RCN)^+$ systems, all ionic products mentioned in eqs 1 and 2 were subjected to low-energy CID-experiments (E_{lab} = 1–40 eV), and these results are presented first. For the products formed in eq 1 it was found that, depending on the collision energy, the complex first loses the intact RCN ligand, followed by the elimination of CH_3, and at higher CID energies both ligands are evaporated. No other neutrals are generated upon collisional activation. CID experiments on the products formed by employing labeled isotopomers provide evidence that no atom exchange of the metal–methyl group with the RCN ligand has taken place in the course of eq 1. These findings support the conjecture that the products formed in the ion–molecule reaction of $FE(CH_3)^+$ with RCN correspond to the association products $Fe(CH_3)(RCN)^+$, which are probably stabilized by collisional or radiative cooling.[20] As the bond dissociation energy (BDE) of $Fe^+–CH_3$ exceeds that of Fe^+–(RCN) (ca. 58[21] versus ca. 42 kcal/mol[22]), the observed sequence of ligand evaporation from $Fe(CH_3)(RCN)^+$ is self-explaining and lends also support to the structural assignment.[23]

The interpretation of the CID experiments on the products Fe(R′CN) formed according to eq 2 is also

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Table 1. Isotope Distributions Obtained in the Reactions of $Fe(CH_3)^+$ with Isotopomers of *n*-Heptanenitrile (1) and *n*-Octanenitrile (2)[a]

precursor	ligand association (eq 1)[b]	"products"[c] "CH_6"	"CH_5D"	"CH_4D_2"
$CD_3(CH_2)_5CN$ (**1a**)	85		9	6
$CH_3CD_2(CH_2)_4CN$ (**1b**)	84	8	8	
$CH_3CH_2CD_2(CH_2)_3CN$ (**1c**)	84	7	9	
$CD_3(CH_2)_6CN$ (**2a**)	59	21	20	
$CH_3CD_2(CH_2)_5CN$ (**2b**)	60	20	20	
$CH_3CH_2CD_2(CH_2)_4CN$ (**2c**)	62	18	20	

[a] Data are expressed in % of the products formed in eqs 1 and 2. [b] The branching ratios for eq 1 versus eq 2 amount to 74:26 for **1** and 52:48 for **2**, respectively. [c] See ref 24–26.

straightforward. Over the whole energy regime ($E_{lab} \leq 30$ eV), the only process observed corresponds to the loss of the entire R′CN ligand. This indicates that R′CN consists of *one* ligand attached to Fe^+. When $Fe(R'CN)^+$ is reacted further with RCN, the resulting adducts $Fe(R'CN)(RCN)^+$ upon CID exhibit also a clear-cut behavior. At collision energies smaller than 20 eV (uncalibrated) only RCN is evaporated while R′CN remains attached to the metal ion. At high energies ($E_{lab} \geq 20$ eV), loss of R′CN can be brought about. These findings indicate that in the complexes $Fe(R'CN)(RCN)^+$ (i) R′CN is bound more strongly to Fe^+ than RCN and (ii) in the formation of the adduct complexes the two ligands retain their identity. Interestingly, even at reaction times exceeding 60 s (which permit ca. 100 collisions), in contrast to $Fe(RCN)^+$ [12] and $Fe(CH_3)(RCN)^+$ [23] the adduct $Fe(R'CN)(RCN)^+$ is not able to form higher association products, e.g. $Fe(R'CN)(RCN)_x^+$ ($x \geq 2$), thus pointing to a higher degree of "saturation" of the metal center in the $Fe(R'CN)(RCN)^+$ system.

With regard to the combined losses of CH_4/H_2 (eq 2) from the encounter complexes $Fe(CH_3)(RCN)^+$ (R = n-C_6H_{13}, n-C_7H_{15}), further insight is obtained from the labeling experiments. In the reactions of $Fe(CD_3)^+$ and $Fe(^{13}CH_3)^+$ with the two nitriles, we observe exclusively the eliminations of "CD_3H_3" and "$^{13}CH_6$".[24] Obviously, the methyl ligand of Fe(methyl)$^+$ remains intact in the course of methane formation. From the study of deuterated *n*-heptanenitriles 1 and *n*-octanenitriles 2[25] the origin of the three hydrogen atoms can be inferred which together with the methyl group gives rise to CH_4/H_2. The results (Table 1) are quite revealing in that they demonstrate that all three hydrogen atoms originate from the ω, ($\omega - 1$) and ($\omega - 2$) positions of the alkyl chain. None of the other methylene groups of 1 and 2 is involved.

The labeling experiments suggest that the methane molecule formed contains the intact Fe^+–methyl group and a hydrogen atom from the terminal methyl group of the nitriles, and the mechanism depicted in Scheme 2 is in keeping with the experimental findings. The metallacycle **5** is obviously formed with internal energy high enough to induce a further C–H bond activation, most likely via a sequence of β-hydrogen transfer steps. The labeling data for the precursors **1b** and **2b** demonstrate that the ($\omega - 1$) positions deliver one and only one hydrogen atom to the combined formation of CH_4/H_2 (and its isotopomers); in addition, this position does not seem to be involved in the hydrogen exchange processes. The latter are confined to the original $\omega/\omega - 2$ positions of the alkyl chain, and it is conceivable that the step **6** ⇄ **7** ⇄ **8** is reversible. If this holds true, one has to conclude that the hydrogen atom transferred from the $\omega - 1$ position to the metal center (**5** → **6**) remains distinct[27] and is precluded, most likely on steric grounds from the exchange process via **6** ⇄ **7** ⇄ **8**. We also note from the branching ratio the operation of kinetic isotope effects favoring the associative reaction (eq 1) as compared with the C–H bond activation process (eq 2).

Table 2. Experimentally Determined Rate Constants, k_R, for the Reactions of $Fe(CH_3)^+$ with Linear Nitriles RCN, Calculated Rate Constants as Predicted by Langevin, ADO, CLD, and CAP Theories, and Dipole Locking Constant c[a]

nitrile	k_R	k_L	k_{ADO}[b]	k_{CLD}[c]	k_{CAP}[d]	k_R/k_{CAP}	c
CH_3CN	2.4	9.6	28.7	81.7	36.4	0.07	
C_2H_5CN	18	10.5	28.2	78.2	35.1	0.51	
C_3H_7CN	38	11.3	27.9	75.7	34.2	1.11	0.41
C_4H_9CN	39	11.9	27.9	74.3	33.2	1.15	0.43
$C_5H_{11}CN$	39	12.6	27.5	72.1	32.9	1.19	0.44
$C_6H_{13}CN$ (**1**)	37	13.2	27.5	71.1	32.6	1.13	0.41
1a	34	13.1	27.4	70.7	32.5	1.05	0.36
1b	33	13.1	27.4	70.8	32.5	1.02	0.34
1c	35	13.1	27.4	70.8	32.5	1.08	0.38
$C_7H_{15}CN$ (**2**)	35	13.7	27.6	70.4	32.4	1.08	0.38
2a	38	13.6	27.5	70.1	32.3	1.18	0.43
2b	35	13.7	27.5	70.2	32.3	1.08	0.38
2c	36	13.7	27.5	70.2	32.3	1.11	0.40

[a] All rate constants are given in units of 10^{-10} cm^3 s^{-1} molecule^{-1}. The estimated error of k_R is ±25;[22] the error is mostly due to different ion gauge sensitivities for different substances in comparison with rate constants taken as references from the literature.[31a,b] Ion gauge sensitivities were estimated according to ref 31c. [b] k_{ADO} calculated according to the revised method of Su et al.[30] [c] k_{CLD} (*C*ompletely *l*ocked-in *d*ipole) is calculated based on k_{ADO}; the dipole locking constant c (as defined in ref 30a) depends on the polarizability α and the dipole moment μ_D. α(RCN) was either taken from the literature (ref 32) or calculated by using the Miller–Savchik formula (ref 33). The following values (in Å^3) were used for RCN (R = CH_3 through n-C_7H_{15}): 4.42, 6.27, 8.11, 9.95, 11.80, 13.65, 15.49. The dipole moments μ_D(RCN) were taken from the literature for R ≤ C_4H_9 (ref 32) or estimated by an extrapolation procedure which was calibrated using μ_D(RCl) and μ_D(RBr). The following data (in D) were used for CH_3CN through n-$C_7H_{15}CN$: 3.92, 4.02, 4.07, 4.12, 4.07, 4.07, 4.07. [d] k_{CAP} (Capture rate constant) was calculated as described in ref 29.

with regard to the actual mode of coordination of the nitrile group, i.e. *end-on* versus *side-on*,[28] the absence of any C–H bond activation products (eq 2) for RCN (R ≤ C_5H_{11}) as well as the different branching ratios for associative (eq 1) versus C–H bond activation (eq 2) of 1 and 2 (Table 1) clearly point to the formation of *end-on* complexes **3**. For the smaller nitriles RCN (R ≤ C_5H_{11}), an *end-on* complex may also result in the reaction with $Fe(CH_3)^+$. However, steric strain associated with the formation of the metallacyclic intermediates will prevent

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(23) At longer reaction times, $Fe(CH_3)(RCN)^+$ undergoes clustering with RCN to form $Fe(CH_3)(RCN)_x^+$ (x = 2, 3). CID of these secondary products results in the stepwise losses of RCN, and at higher energies expulsion of CH• takes place.

(24) The notation "CD_3H_3" etc. simply implies that for several combinations the isotope distribution between the neutral products of eq 2, i.e. methane and molecular hydrogen, cannot be given.

(25) In addition to the isotopomers described in Table 1, we have labeled the nitriles 1 and 2 in *all* methylene groups. None of the positions α to ($\omega - 3$) of 1 and 2 serves as a hydrogen source to generate CH_4/H_2. In addition, for these isotopomers the branching ratios for association (eq 1) versus CH_4/H_2 loss (eq 2) is unchanged when compared with the unlabeled substrates. This holds true also for the reactions of $Fe(CD_3)^+$ and $Fe(^{13}CH_3)^+$ with 1 and 2.

(26) In the reactions of $Fe(CH_3)^+$ with **1a** and **2a** no neutral products of the composition "CD_3H_3" are observed.

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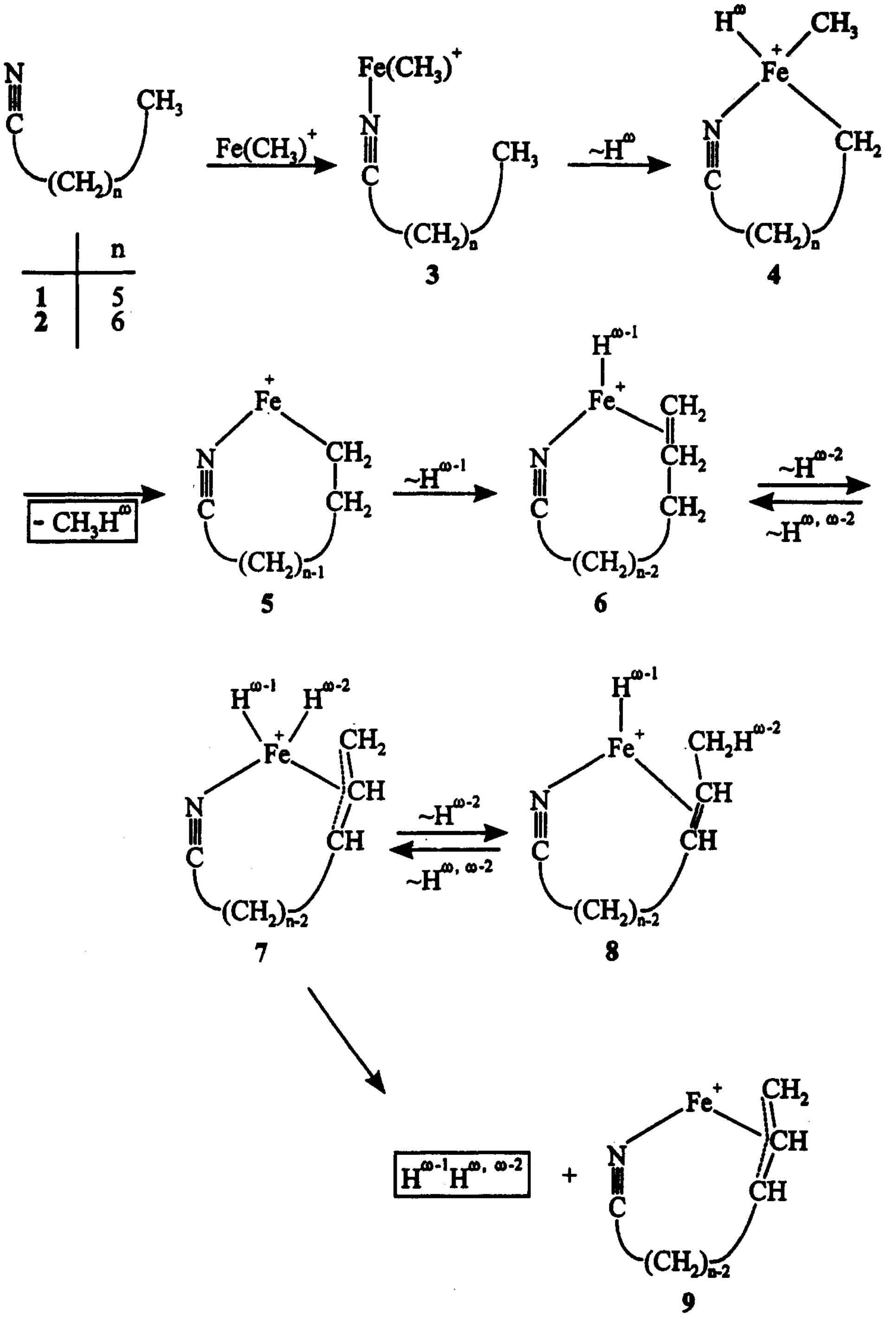
Scheme 2



the system to bring about remote functionalization analogous to Scheme 2.

In the following, we will briefly report the experimentally determined rate constants, k_R, for the reactions of Fe$(CH_3)^+$ with RCN (R = CH_3 through n-C_7H_{15}) and compare these with calculated rate constants as predicted by various theoretical approaches (Table 2). In a previous study of the reactions of n-C_4H_9CN with $Fe(L)^+$ (L = olefin),[12] it was found that k_R matches best with the capture rate constant, k_{CAP}.[29] In addition, the dipole locking constant c which, for nitriles, had caused in the past some difficulties in successfully applying the averaged dipole orientation (ADO) approach[30] was redetermined to $c = 0.47$ for n-C_4H_9-CN;[12] this number contrasts with the previously used number of $c = 0.255$.[30b]

As shown by the data in Table 2, best agreement of k_R is as previously[12] found with k_{CAP}; however, within the experimental error, k_{ADO} also matches k_R. For nitriles RCN with R ≥ n-C_3H_7, the reaction efficiency as defined

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by the ratio k_R/k_{CAP} is unity. In contrast, for the smaller system, i.e. CH_3CN and C_2H_5CN, the efficiency is much smaller (7 and 51%, respectively) which may point to a less-efficient stabilization of the association complex via infrared radiative or collisional cooling. The dipole locking constant c centers for all nitriles around $c \approx 0.4$, and this number compares well with the recently determined value for *n*-pentanenitrile ($c = 0.47$) using a different set of reactions.[12]

In conclusion, in the present study we have demonstrated that remote functionalization of RCN by $Fe(CH_3)^+$ is possible provided the alkyl chain is longer than $R \geq C_6H_{11}$. Labeling experiments reveal the existence of a highly specific activation of the terminal region of the alkyl chain resulting in the introduction of a terminal alkyl group (Scheme 2: →**9**). C–C bond activation is not observed in contrast to the reaction of bare Fe^+ with RCN. For the smaller nitriles ($R \leq C_5H_{11}$), the only product observed corresponds to an association process. Except for CH_3CN and C_2H_5CN, all nitriles react with $Fe(CH_3)^+$ at collision rate, and CID experiments on the resulting association complexes $Fe(CH_3)(RCN)^+$ as well as the products of C–H bond activation, i.e. $Fe(R'CN)^+$, provide some insight in the nature of the species formed.

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