

Table VII. Exponents and Parameters for Uranium<sup>26c</sup>

orbital	$-H_{ii}/\text{eV}$	$\zeta_1$	$\zeta_2$	$C_1$	$C_2$
U 7s	5.5	1.914			
U 7p	5.5	1.914			
U 6p	30.03	4.033			
U 6d	9.19	2.581	1.207	0.7608	0.4126
U 5f	10.62	4.943	2.106	0.7844	0.3908

direction are presently being made.

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### Appendix

All the calculations were of the extended Hückel<sup>26</sup> type with modified  $H_{ij}$ 's.<sup>27</sup> The basis set for the metal atoms

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consisted of  $ns$ ,  $np$ ,  $(n-1)p$ ,  $(n-1)d$ , and  $(n-2)f$  orbitals. The  $s$  and  $p$  orbitals were described by single Slater type wave functions, and  $d$  and  $f$  orbitals were taken as contracted linear combinations of two Slater type wave functions.

The geometries of  $\text{U}(\text{C}_9\text{H}_7)_3$ ,  $\text{U}(\text{C}_9\text{H}_7)_3\text{I}$ ,  $\text{U}(\text{Cp}^*)_2(\text{Cl})\text{Me}$ , and  $\text{U}(\text{Cp}^*)_2(\text{Cl})$  were modeled as described above. The distances (pm) used were as follows:  $\text{U}-\text{Cp}^*$  or  $\text{U}-\text{C}_9\text{H}_7 = 253.4$ ,  $\text{U}-\text{I} = 304$ ,  $\text{U}-\text{Cl} = 265$ ,  $\text{U}-\text{Me} = 245$ ;  $\text{C}-\text{C}(\text{Cp}^*$  or  $\text{C}_9\text{H}_7) = 140$ ;  $\text{C}(\text{Cp}^*)-\text{Me}(\text{Cp}^*) = 150$ ;  $\text{C}-\text{H} = 108$ . The five- and six-membered rings were taken as regular pentagons and hexagons. All the other parameters were optimized.

Standard parameters were used for C, H, Cl, and I, while those for the uranium atom were obtained by using a semirelativistic approach (Table VII).<sup>26c</sup>

**Registry No.**  $[\text{HB}(3,5\text{-Me}_2\text{Pz})_3]\text{UCl}_2(\text{O}-t\text{-Bu})$ , 112812-84-7;  $[\text{HB}(3,5\text{-Me}_2\text{Pz})_3]\text{UCl}_2(\text{OCH}(\text{CH}_3)_2)$ , 112786-13-7;  $[\text{HB}(3,5\text{-Me}_2\text{Pz})_3]\text{UCl}_2(\text{N}(\text{SiMe}_3)_2)$ , 106354-63-6;  $[\text{HB}(3,5\text{-Me}_2\text{Pz})_3]\text{UCl}_2(\text{CH}(\text{SiMe}_3)_2)$ , 139461-22-6;  $[\text{HB}(3,5\text{-Me}_2\text{Pz})_3]\text{UCl}_2(\text{C}_5\text{H}_5)$ , 106354-62-5;  $[\text{HB}(3,5\text{-Me}_2\text{Pz})_3]\text{UCl}_3$ , 106354-68-1; U, 7440-61-1.

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## Gas-Phase Chemistry of Bare Transition-Metal Ions in Comparison. 2.<sup>1</sup> Reactions of $\text{Ti}^+$ to $\text{Zn}^+$ with 2-Ethylbutanenitrile

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The reactions of the first-row transition-metal ions from  $\text{Ti}^+$  to  $\text{Zn}^+$  with 2-ethylbutanenitrile (**23**) are studied using a Fourier transform ion cyclotron resonance (FTICR) spectrometer. The general behavior of the ions is compared and is found to be in line with previous studies. While the early-transition-metal ions  $\text{Ti}^+$  and  $\text{V}^+$  mainly give rise to C-H activation products,  $\text{Cr}^+$ ,  $\text{Mn}^+$ , and  $\text{Zn}^+$  are unreactive without collisional activation and form only adduct complexes. For  $\text{Fe}^+ - \text{Cu}^+$  three processes are operative whose relative importance varies: an ion/dipole mechanism which leads to  $\text{MHCN}^+$  ions and loss of HCN, remote functionalization forming  $\text{H}_2$  and  $\text{C}_2\text{H}_4$  from the chain termini, and an allylic mechanism which generates  $\text{CH}_4$  by initial C-CN insertion. The results are further compared with those of the lower homologue, 2-methylbutanenitrile, studied in part 1, and are found to be in very good agreement. Finally, an instrumental comparison is provided between ion/molecule reactions of  $\text{Fe}^+$  with **23** under FTICR conditions and metastable-ion decompositions of  $\text{Fe}(\text{23})^+$  adduct complexes in a sector mass spectrometer showing that the two approaches provide the same results within previously formulated restrictions.

### Introduction

Gas-phase organometallic chemistry<sup>2</sup> renders much of its current interest from the fact that intrinsic properties of bare ions may be studied without any interferences from solvents or counterions. These studies can be performed with either bare metal ions  $\text{M}^+$  or ligated metal ions  $\text{L}_n\text{M}^+$  so that the influence of the ligands may be exploited as well. Most of the studies have so far focused on reactions of  $\text{M}^+$  with various substrates. Despite the knowledge accumulated in recent years,<sup>2</sup> one important point is still not very well understood, the role of the substrate itself.

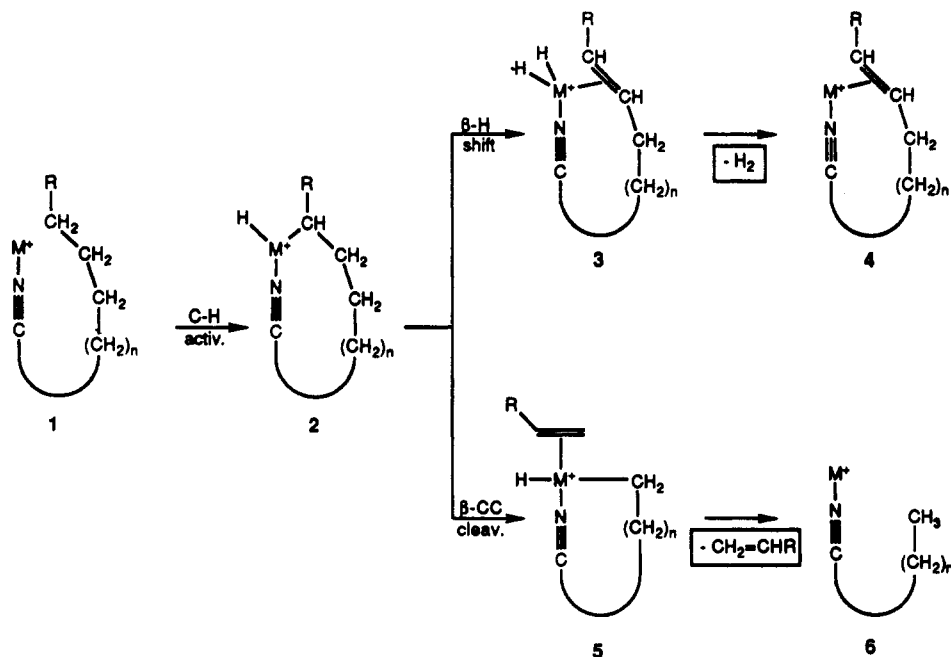
The general properties of the metal ions are reasonably well-known, but the products that are formed from a particular substrate are more or less unpredictable. For example, early-transition-metal ions like  $\text{Sc}^+$ ,  $\text{Ti}^+$ , or  $\text{V}^+$  often give rise to C-H activation with losses of up to three molecules of hydrogen or hydrogen together with other small neutrals being observed.  $\text{Cr}^+$ ,  $\text{Mn}^+$ ,  $\text{Cu}^+$ , and  $\text{Zn}^+$  are often unreactive and second- or third-row ions behave similar to the early-transition-metal ions. But especially for  $\text{Fe}^+$ ,  $\text{Co}^+$ , and  $\text{Ni}^+$ , a versatile chemistry is encountered which can vary significantly from substrate to substrate.

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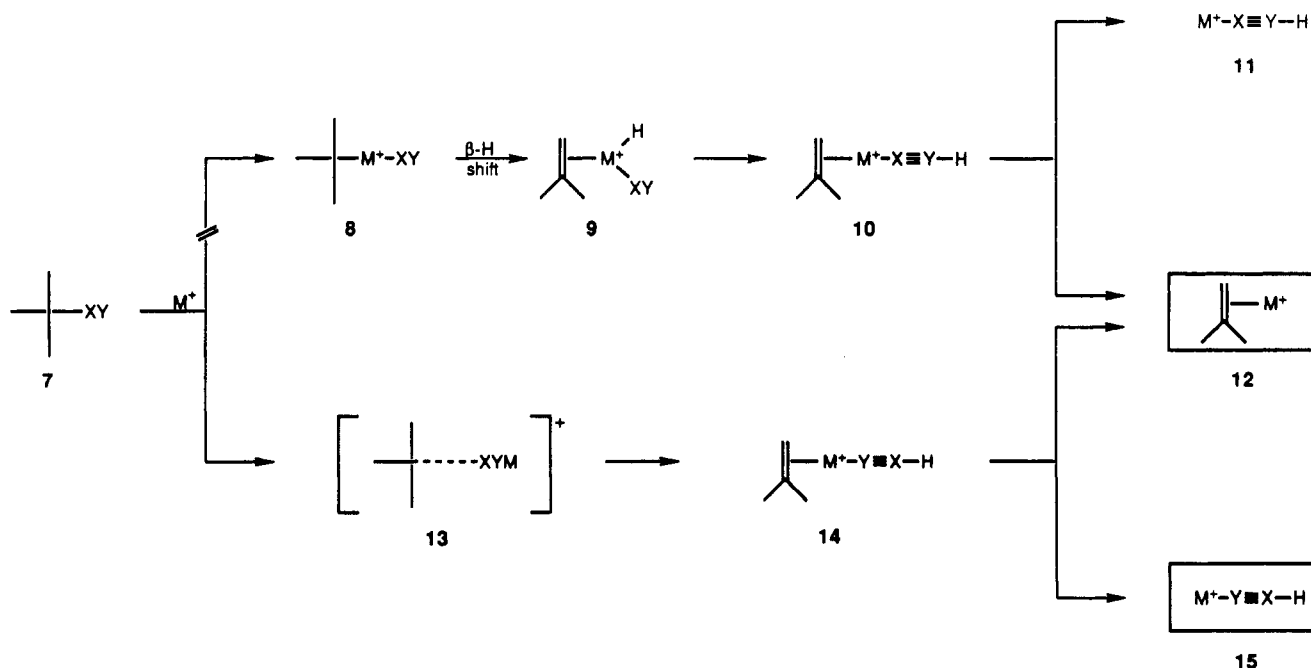
(1) Part 1: Eller, K.; Zummack, W.; Schwarz, H. *J. Am. Chem. Soc.* **1990**, *112*, 621.

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Scheme I



Scheme II



Even more difficult are predictions with regard to the mechanisms that will be operative to generate these products.

An approach to this problem is the study of related compounds, i.e., examination of homologous rows and comparison of isomeric or differently substituted compounds. The most thoroughly studied model system is undoubtedly the chemistry of nitriles.<sup>3</sup> Beginning with linear nitriles it was found that  $Fe^+$ ,  $Co^+$ , and  $Ni^+$  coordinated to the nitrile group and were thus unable to reach bonds in the vicinity of the functional group.<sup>4,5</sup> Instead,

they reacted by remote functionalization<sup>6</sup> of nonactivated C-H bonds, and it turned out that for a medium chain length exclusively the terminal  $CH_3$  group was oxidatively added to the metal center (Scheme I,  $R = H$ ). The resulting intermediate 2 undergoes competitive  $\beta$ -hydrogen shift or  $\beta$ -CC cleavage to generate hydrogen and a  $\omega$ -unsaturated nitrile or an alkene and a shortened nitrile, re-

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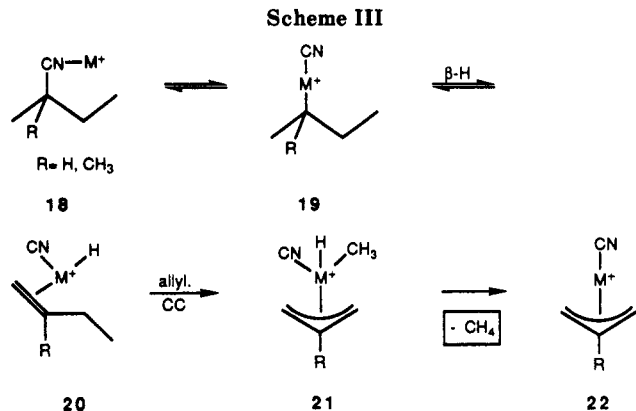
(4) (a) Lebrilla, C. B.; Schulze, C.; Schwarz, H. *J. Am. Chem. Soc.* 1987, 109, 98. (b) Lebrilla, C. B.; Drewello, T.; Schwarz, H. *J. Am. Chem. Soc.* 1987, 109, 5639. (c) Lebrilla, C. B.; Drewello, T.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* 1987, 79, 287. (d) Drewello, T.; Eckart, K.; Lebrilla, C. B.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* 1987, 76, R1. (e) See also: Stepnowski, R. M.; Allison, J. *Organometallics* 1988, 7, 2097.

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(6) This term was introduced to point out the analogy to Breslow's biomimetic studies: (a) Breslow, R. *Chem. Soc. Rev.* 1972, 1, 553. (b) Breslow, R. *Acc. Chem. Res.* 1980, 13, 170.

spectively. For longer nitriles the activation of internal methylene groups was observed, too, and led to the production of higher alkenes ( $R = C_nH_{2n+1}$ ). For nitriles with a short chain, naturally, deviations from the remote functionalization mechanism occurred since the strain induced particularly in **5** becomes prohibitively high for small values of  $n$ .<sup>7</sup> Ethane- and propanenitrile are completely unreactive or react only upon collisional activation.<sup>4,5,8</sup>  $Mn^+$  is reported to exclusively dehydrogenate heptanenitrile<sup>4e</sup> and is also unreactive with ethane- and propanenitrile.<sup>8</sup>  $Cr^{+4e}$  and  $Cu^{+7b,9-11}$  only form adduct complexes with linear nitriles, but upon collisional activation of the latter some products are formed.

The predominance of the remote functionalization mechanism for linear nitriles contrasts quite markedly with the results obtained for tertiary nitriles.<sup>3b,c,5,9,12</sup>  $Fe^+$  reacts with 2,2-dimethylpropanenitrile according to Scheme II ( $XY = CN$ ) via an ion/dipole mechanism.<sup>13</sup>  $Fe(HCN)^+$  is formed and, correspondingly,  $FeC_4H_9^+$  by loss of HCN. By comparison with the reactions of  $Fe^+$  with 2-isocyanato-2-methylpropane ( $XY = NC$ ), which affords  $Fe(HNC)^+$  and  $FeC_4H_9^+$  by loss of HNC, an insertion/ $\beta$ -hydrogen shift mechanism<sup>14</sup> could be excluded. High-energy collision-induced dissociation<sup>15</sup> in a sector mass spectrometer revealed that products **15** were formed in lieu of **11**, i.e.,  $Fe(HCN)^+$  from  $t-C_4H_9CN$  and  $Fe(HNC)^+$  from  $t-C_4H_9NC$ . Complexation of the metal ion to the functional group  $XY$  ( $XY = CN, NC$ ) induces cleavage of the C-X bond and gives rise to the ion/dipole complex **13**. The incipient carbenium ion therein now protonates the  $XYM$  dipole at the "unblocked" X site and generates **14**, which dissociates reflecting the relative binding energies of its two ligands. If **14** is formed from  $t-C_4H_9CN$ , it preferentially loses HCN whereas when formed from  $t-C_4H_9NC$ , it preferentially retains HNC as the stronger bound ligand; this indirectly reveals the identity of the neutral (H, CN) molecules that are formed. Ion/dipole complexes are known to be quite long-lived,<sup>13,16</sup> being trapped on the reaction coordinate by a potential-energy barrier on one side and an entropic bottleneck on the other side; on the contrary, hydrogen rearrangements in carbenium ions are fast processes,<sup>17</sup> so that H/D scrambling in **13** could be expected, although it cannot be observed for **7** owing to the equivalency of all hydrogen atoms. 2,2-



Dimethylbutanenitrile (**16**) with  $Fe^+$  and the secondary 2-methylbutanenitrile (**17**) with  $Co^+$ ,  $Ni^+$ , and  $Cu^+$ , however, also afford  $M(HCN)^+$  ions and loss of HCN. Since in these substrates the hydrogens are no longer equivalent,  $^2H$  labeling indeed proves that not only the  $\beta$ -hydrogen atoms but also, in fact, all other positions contribute to the hydrogen-transfer step.

Secondary nitriles turned out to be very interesting as they not only provided a transition between the remote functionalization and the ion/dipole mechanism but also reacted by a third mechanism as well.<sup>1,5,9,18,19</sup> The symmetric 2-butylhexanenitrile formed hydrogen and ethene by remote functionalization upon reacting with  $Fe^+$ ; together they accounted for 97% of the products, and this allowed determination of intramolecular isotope effects using  $^2H$  labeling. For secondary nitriles with two long chains, even a successive, double remote functionalization of both alkyl chains was observed; alkene loss from one end of the molecule was followed by dehydrogenation of the other terminus.<sup>5,19</sup>

For small secondary nitriles, however, in addition to the products formed by remote functionalization, methane was an important product with  $Fe^+$ , too.<sup>1,5,9</sup> Scheme III depicts the mechanism for 2-methylbutanenitrile (**17**,  $R = H$ ). As  $^2H$  labeling revealed, one hydrogen of the  $CH_4$  product originates from the methyl group  $\beta$  to the nitrile function while the other three were provided by the terminal methyl group. This can be rationalized by initial C-CN insertion followed by a  $\beta$ -hydrogen shift to afford **20**. Reductive elimination of HCN from this intermediate must be kinetically hindered, though, since it is not observed. Instead, allylic C-C activation followed by methane loss generates the cyano-allyl complex **22**. This mechanism, called the allylic mechanism in the following, is also observed for 2,2-dimethylbutanenitrile (**16**,  $R = CH_3$ ,  $M = Fe$ ), but here it is slightly less important than for **17** due to competition with the ion/dipole mechanism.

Comparison of several secondary nitriles  $R^1R^2CHCN$  upon their reactivity with  $Fe^+$  revealed that the allylic mechanism was most prominent in cases where  $R^1$  and  $R^2$  were both small so that remote functionalization could not effectively compete.<sup>5</sup> As soon as one chain was, however, long enough to permit the operation of the latter mechanism, it was dominant. On the other hand, for  $R^1 = R^2 = CH_3$ , only ligand detachment, i.e., loss of the intact nitrile to regenerate  $Fe^+$ , was observed, indicating "unreactivity"<sup>20</sup> due to the fact that neither Scheme I nor III is a viable decomposition pathway.  $Co^+$ , however, is reported to form

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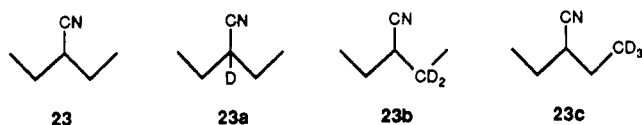
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(20) Cf.: Eller, K.; Schwarz, H. *Chem. Ber.* **1990**, *123*, 201.

Chart I



CoHCN<sup>+</sup> and HCN with (CH<sub>3</sub>)<sub>2</sub>CHCN;<sup>4e</sup> although this was interpreted as an insertion/ $\beta$ -H shift process, with regard to the findings for 17, it is much more likely that the ion/dipole mechanism applies.

Comparison of a particular secondary nitrile, viz. 2-methylbutanenitrile (17) in part 1, with various first-row transition-metal ions revealed that the allylic mechanism was most important not only for Fe<sup>+</sup> but also for Co<sup>+</sup>.<sup>1</sup> The allylic mechanism was found to be in competition with remote functionalization and the ion/dipole mechanism for M<sup>+</sup> = Fe<sup>+</sup>-Cu<sup>+</sup>. While remote functionalization had an intermediate maximum for Co<sup>+</sup> and Ni<sup>+</sup> and was absent for Cu<sup>+</sup>, the ion/dipole mechanism showed a steady increase from Fe<sup>+</sup>, where it was completely missing with 17, to Cu<sup>+</sup>, where it was the exclusive mechanism operative. This illustrates the inability of the d<sup>10</sup> Cu<sup>+</sup> ion to undergo oxidative additions. In contrast to the other two, the ion/dipole mechanism avoids any insertion steps and is therefore the only alternative left; in other words, *the extent by which it is operative depends on the need for it*. This conclusion is also supported by results for other substrates such as isonitriles,<sup>20</sup> isothiocyanates,<sup>21</sup> isocyanates,<sup>22</sup> and amines.<sup>23</sup> In line with the general expectations, Ti<sup>+</sup> and V<sup>+</sup> reacted with 17 mainly by C-H activation while Cr<sup>+</sup> and Zn<sup>+</sup> were unreactive, except for charge-transfer processes in the case of Zn<sup>+</sup>. Cr<sup>+</sup> does, however, react with tertiary nitriles via the ion/dipole mechanism.<sup>3b,c,24</sup>

We were interested to see how much of the results for 17 could be extrapolated to 2-ethylbutanenitrile (23) or if a completely new chemistry would be encountered. With regard to the unusual allylic mechanism and the difficulties in predicting mechanisms mentioned above, this seemed a very promising task. Choosing 23 had two advantages; firstly, it had shown the highest amount of methane loss with Fe<sup>+</sup>,<sup>5</sup> thus reflecting the greater facility of a  $\beta$ -H shift from a methylene over a methyl group as in 17,<sup>25</sup> and secondly, it is symmetric so that intramolecular isotope effects may be determined in order to obtain a better understanding of the individual steps in the mechanisms. We therefore studied 23 and its <sup>2</sup>H-labeled isotopomers 23a-c (Chart I) with all the first-row transition-metal ions from Ti<sup>+</sup> to Zn<sup>+</sup>. The results are compared with regard to the different behavior of the metal ions as well as with those of the lower homologue 17.

### Results and Discussion

The reaction products formed from the different transition-metal ions with 2-ethylbutanenitrile (23) are given in Table I. The ions can be grouped in three categories.

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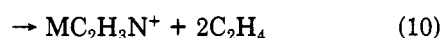
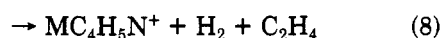
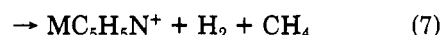
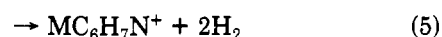
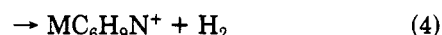
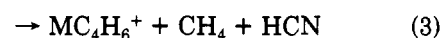
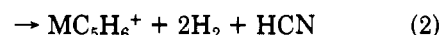
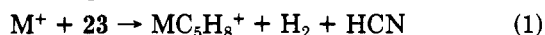
Table I. Amount of Products Generated (in Percent) in the Reactions of M<sup>+</sup> with 2-Ethylbutanenitrile (23)<sup>a</sup>

	Ti <sup>+</sup>	V <sup>+</sup>	Cr <sup>+</sup>	Mn <sup>+</sup>	Fe <sup>+</sup>	Co <sup>+</sup>	Ni <sup>+</sup>	Cu <sup>+</sup>	Zn <sup>+</sup>
MHCN <sup>+</sup>						20	13	49	
HCN								13	
HCN, H <sub>2</sub>	34	54							
HCN, 2H <sub>2</sub>	3								
HCN, CH <sub>4</sub>	7				21	3	1		
HCN, C <sub>2</sub> H <sub>4</sub>						3			
H <sub>2</sub>	2	24			2				
2H <sub>2</sub>	40	16							
3H <sub>2</sub>	3								
H <sub>2</sub> , CH <sub>4</sub>	1								
H <sub>2</sub> , C <sub>2</sub> H <sub>4</sub>	4	2					1		
CH <sub>4</sub>					41	2			
C <sub>2</sub> H <sub>4</sub>					28	56	71		
CH <sub>4</sub> , C <sub>2</sub> H <sub>4</sub>	5								
2C <sub>2</sub> H <sub>4</sub>	1				<1	4			
M(C <sub>6</sub> H <sub>11</sub> N) <sup>+</sup>		4	100	100	7	13	15	38	100

<sup>a</sup> Intensities are expressed in  $\sum$  products = 100%.

The first is formed by the early transition-metal ions Ti<sup>+</sup> and V<sup>+</sup> which give rise to intense dehydrogenations or losses of hydrogen in combination with other small neutrals. Group two contains Fe<sup>+</sup>-Cu<sup>+</sup>, and three mechanisms are operative that vary in their relative importance in sweeping through this group. The last group consists of "unreactive" metal ions, viz. Cr<sup>+</sup>, Mn<sup>+</sup>, and Zn<sup>+</sup>, which only form adduct complexes M(23)<sup>+</sup>. We will discuss the three groups in turn and compare the metal ions as well as 23 with 17 and FTICR with sector mass spectrometer data for Fe<sup>+</sup>/23 subsequently.

**Ti<sup>+</sup> and V<sup>+</sup>.** As can be seen from Table I, the majority of the products for Ti<sup>+</sup> and V<sup>+</sup> is due to loss of hydrogen. For both metal ions multiple dehydrogenation is observed and loss of H<sub>2</sub> together with other small neutrals (eqs 1-11). V<sup>+</sup>, except for the adduct complex in eq 11, forms



exclusively products due to C-H activation, and Ti<sup>+</sup> forms these products to 87%, the remainder being combined losses of HCN, CH<sub>4</sub>, and C<sub>2</sub>H<sub>4</sub>. In the case of V<sup>+</sup> it was possible to determine the sequence of the neutral losses for the main products; double resonance<sup>26</sup> showed that single dehydrogenation precedes loss of the second H<sub>2</sub> and also loss of HCN in eq 1. For Ti<sup>+</sup>, the rates of the reactions were too fast to be influenced by double-resonance pulses.

The results for the <sup>2</sup>H-labeled isotopomers 23a-c are given in Table II and provide some more insight into the

(26) (a) Comisarow, M. B.; Grassi, V.; Parisod, G. *Chem. Phys. Lett.* 1978, 57, 413. (b) McIver, R. T., Jr.; Bowers, W. D. In *Tandem Mass Spectrometry*; McLafferty, F. W., Ed.; Wiley-Interscience: New York, 1983; p 287.

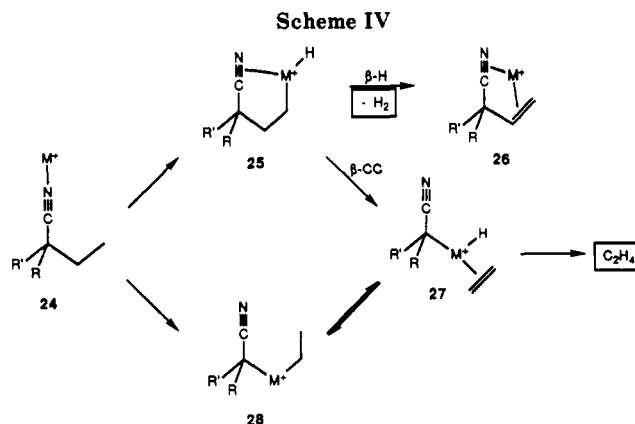
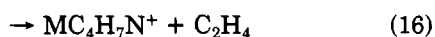
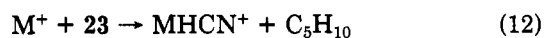
**Table II. Amount of Products Generated (in Percent) in the Reactions of  $Ti^+$  and  $V^+$  with  $^2H$ -Labeled 2-Ethylbutanenitriles 23a-c<sup>a,b</sup>**

	23a		23b		23c	
	$Ti^+$	$V^+$	$Ti^+$	$V^+$	$Ti^+$	$V^+$
HCN, $H_2$	95	100	54	43	46	50
[HCN, HD]	5	-	43	53	45	45
[DCN, HD]	-	-	3	3	8	5
HCN, $2H_2$	~100	-	28	-	-	-
[HCN, HD, $H_2$ ]	- <sup>c</sup>	-	58	67	-	-
[HCN, $2HD$ ]	-	-	24	33	-	-
HCN, $CH_4$	100	-	44	20	-	-
[DCN, $CH_4$ ]	-	-	37	43	-	-
[DCN, $CH_3D$ ]	-	-	19	-	-	-
[HCN, $CD_3H$ ]	-	-	-	37	-	-
$H_2$	23	76	56	55	<i>d</i>	83
HD	77	24	44	45	<i>e</i>	17
$2H_2$	26	85	56	44	54	35
$H_2$ , HD	74	15	43	56	34	52
[ $2HD$ ]	-	-	2	-	12	13
$3H_2$	73	-	37	-	-	-
$2H_2$ , HD	27	-	52	47	-	-
[ $H_2$ , $2HD$ ]	-	-	11	53	-	-
$H_2$ , $CH_4$	57	-	56	19	-	-
[HD, $CH_4$ ]	43	-	44	20	-	-
[HD, $CH_3D$ ]	-	-	-	13	-	-
[ $H_2$ , $CD_3H$ ]	-	-	-	48	-	-
$H_2$ , $C_2H_4$	75	100	-	-	-	-
[HD, $C_2H_4$ ]	25	-	53	30	31	-
[ $H_2$ , $C_2H_2D_2$ ]	-	-	47	70	49	100
[HD, $C_2H_2D_2$ ]	-	-	-	-	20	-
$CH_4$ , $C_2H_4$	37	-	26	-	-	-
[ $CH_3D$ , $C_2H_4$ ]	63	-	26	-	-	-
[ $CH_4$ , $C_2H_2D_2$ ]	-	-	48	26	-	-
[ $CD_3H$ , $C_2H_4$ ]	-	-	-	74	-	-

<sup>a</sup> Intensities are normalized to 100% for each neutral loss. Square brackets indicate uncertain labeling distributions among the neutrals. <sup>b</sup> The intensity of the  $[M - 2C_2H_4]^+$  products was too low for an exact determination. <sup>c</sup> Signal-to-noise ratio not sufficient for exact determination. <sup>d</sup> Present in the spectrum. <sup>e</sup> Resolution not sufficient, overlap with  $^{13}C$  isotope of  $[M - 2H_2]^+$ .

versatile chemistry encountered for the two early-transition-metal ions. There are clearly differences in the labeling distributions of  $Ti^+$  and  $V^+$ ; thus, in spite of the overall similarity, different mechanisms apply for the formation of the individual reaction products. For example, the single and double dehydrogenation of 23a for  $V^+$  involves mainly the primary and secondary C-H bonds while  $Ti^+$  predominantly activates the tertiary C-D bond. With the exception of eq 4, only multiple losses are observed; therefore it was impossible to derive mechanisms for the different products that were formed. Furthermore, it is likely that scrambling processes are active too.

**$Fe^+$ ,  $Co^+$ ,  $Ni^+$ , and  $Cu^+$ .** For the late-transition-metal ions  $Fe^+$ - $Cu^+$  the processes in eqs 3, 4, 8, and 10-16 are noted (Table I). The labeling distribution for 23a-c is given in Table III and can be interpreted as follows.






Loss of hydrogen and ethene clearly involves only the  $\beta$  and  $\gamma$  positions and could thus be explained by remote functionalization (Scheme IV, 24  $\rightarrow$  25  $\rightarrow$  26, 27). The presence of  $C_2H_3D$  loss for 23b and  $C_2HD_3$  loss for 23c is in line with previous studies on butanenitrile,<sup>1</sup> 2-methylbutanenitrile,<sup>1,5</sup> and 2,2-dimethylbutanenitrile,<sup>5</sup> which showed that for  $C_4$  nitriles an equilibrium between the hydrido-ethene structure 27 and the ethyl structure 28 is present. The absence of scrambling for the dehydrogenation reveals that this does not extend to 25. In fact, in view of the chain length involved, it is even feasible that 28 is formed directly from 24, and not by remote functionalization. The fact that from 23b and 23c the same amount of unlabeled ethene is produced shows that if 25 is an intermediate, its formation is at least not rate determining; otherwise one would expect a primary kinetic isotope effect (KIE) for the insertion into the C-D bond of 23c. On the other hand, it is also difficult to rationalize the overall KIE of  $k_{C_2H_4}/k_{C_2H_3D} = 1.25 \pm 0.05$  observed for both 23b and 23c. If the C-C insertion 24  $\rightarrow$  28 were rate determining, one would not expect a KIE in the case of 23c; as evidenced by the scrambling, the C-H breaking step 28  $\rightarrow$  27 also cannot be rate determining, so that one is left with the ethene detachment. One would, however, then expect differences between  $C_2H_4$  vs  $C_2H_3D/C_2H_2D_2$  (23b) and  $C_2H_4$  vs  $C_2H_2D_2/C_2HD_3$  (23c); yet, a constant 55 or 56%  $C_2H_4$  is observed. Correcting for statistical factors (3H and 2D for 23b and 2H and 3D for 23c), one obtains an approximate 11:22:33 ratio of  $C_2H_3D:C_2H_2D_2:C_2HD_3$  for all three ions; so the increase is clearly consistent. Only doubly labeled compounds might provide an explanation for the isotope effects observed and clarify the actual mechanism.

For  $Fe^+$  there is a small difference between the amount of  $H_2$  and of  $C_2H_4$  formed from 23b, while for 23c the same relative percentages are observed. This might, however, result from experimental uncertainties in the determination of the label distribution for the hydrogen loss; after all,  $H_2$  accounts for only 2% of the products formed. Loss of  $H_2/C_2H_4$  in the case of  $Co^+$  and loss of  $2C_2H_4$  for  $Fe^+$  and  $Co^+$  are probably secondary decompositions of the  $C_2H_4$  and/or  $H_2$  loss products. While for  $Co^+$  extensive scrambling is noted for eq 10, for  $Fe^+$  this process seems to be specific and even lacks the distribution of the ethyl hydrogens as in the case of the single ethene loss.

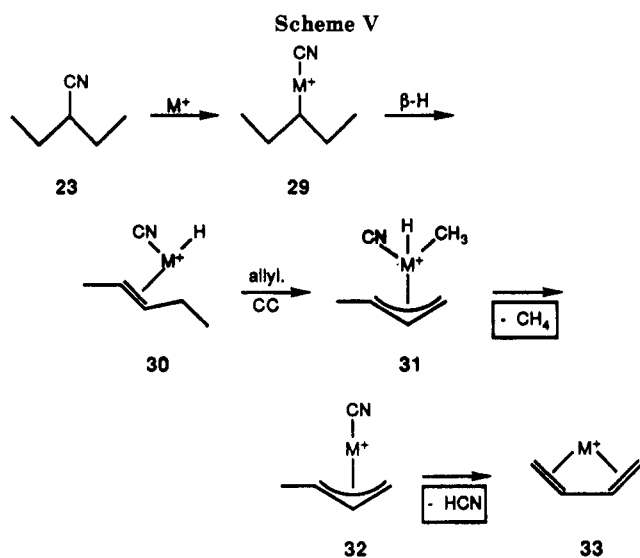
Methane loss is the dominant reaction for  $Fe^+$  and is also observed for  $Co^+$ , albeit as a minor process. Table III reveals that its formation can be described similar to Scheme III, since for both metal ions one hydrogen is provided by the  $\beta$ -methylene groups while the other three originate from the chain termini. Thus, the generation of  $CH_4$  proceeds completely analogous to 2-methylbutanenitrile<sup>1,5</sup> and 2,2-dimethylbutanenitrile<sup>5</sup> and hence proves

**Table III. Amount of Products Generated (in Percent) in the Reactions of Fe<sup>+</sup>-Cu<sup>+</sup> with <sup>2</sup>H-Labeled 2-Ethylbutanenitriles 23a-c<sup>a,b</sup>**

	 23a				 23b				 23c			
	Fe <sup>+</sup>	Co <sup>+</sup>	Ni <sup>+</sup>	Cu <sup>+</sup>	Fe <sup>+</sup>	Co <sup>+</sup>	Ni <sup>+</sup>	Cu <sup>+</sup>	Fe <sup>+</sup>	Co <sup>+</sup>	Ni <sup>+</sup>	Cu <sup>+</sup>
MHCN <sup>+</sup>		94	95	95	72	72	64		81	92	100	
MDCN <sup>+</sup>		6	5	5	28	28	36		19	8	-	
HCN				~100			64				100	
DCN				- <sup>c</sup>			36				-	
HCN, CH <sub>4</sub>	93	75	57		57	63	62	20	67	-		
[DCN, CH <sub>4</sub> ]	7	25	43		43	37	38	37	-	43		
[HCN, CD <sub>3</sub> H]	-	-	-		-	-	-	43	33	57		
HCN, C <sub>2</sub> H <sub>4</sub>		72								32		
[DCN, C <sub>2</sub> H <sub>4</sub> ]		28				44				25		
[HCN, C <sub>2</sub> H <sub>2</sub> D <sub>2</sub> ]		-				56				43		
H <sub>2</sub>	100				60			57				
HD	-				40			43				
CH <sub>4</sub>	100	100			51	57		53	44			
CH <sub>3</sub> D	-	-			49	43		-	-			
CD <sub>3</sub> H	-	-			-	-		47	56			
C <sub>2</sub> H <sub>4</sub>	100	100	100		55	55	55	56	56	56		
C <sub>2</sub> H <sub>3</sub> D	-	-	-		13	11	13	-	-	-		
C <sub>2</sub> H <sub>2</sub> D <sub>2</sub>	-	-	-		32	34	32	22	24	22		
C <sub>2</sub> HD <sub>3</sub>	-	-	-		-	-	-	22	20	22		
2C <sub>2</sub> H <sub>4</sub>	100	51			-	21		-	-	-		
C <sub>2</sub> H <sub>4</sub> , C <sub>2</sub> H <sub>3</sub> D	-	49			-	20		-	-	-		
[C <sub>2</sub> H <sub>4</sub> , C <sub>2</sub> H <sub>2</sub> D <sub>2</sub> ]	-	-			100	59		100	41			
[C <sub>2</sub> H <sub>4</sub> , C <sub>2</sub> HD <sub>3</sub> ]	-	-			-	-		-	59			

<sup>a</sup> Intensities are normalized to 100% for each neutral loss. Square brackets indicate uncertain labeling distributions among the neutrals.

<sup>b</sup> The intensity of the [M - H<sub>2</sub> - C<sub>2</sub>H<sub>4</sub>]<sup>+</sup> products was too low for an exact determination. <sup>c</sup> Possibly too weak to be detected.



that this mechanism is not restricted to the formation of 2-substituted allyl systems but may also yield 1-substituted cyano-allyl complexes (Scheme V).

In the latter case, however, part of the 32 ions may decompose further by loss of HCN to generate the butadiene complex 33. As the labeling data for Fe<sup>+</sup> reveals, there are reversible steps involved, either before or during the HCN loss. As the CH<sub>4</sub>/HCN loss is also observed for Ni<sup>+</sup>, which did not form CH<sub>4</sub>, it is more likely that for this ion an HCN loss product decomposes by further loss of CH<sub>4</sub> (see below). For Co<sup>+</sup> both possibilities have to be considered.

Exactly paralleling 2-methylbutanenitrile,<sup>1,5</sup> for Co<sup>+</sup>-Cu<sup>+</sup>, but not for Fe<sup>+</sup>, formation of MHCN<sup>+</sup> ions and loss of HCN is observed for 23, thus an ion/dipole mechanism

analogous to Scheme II applies here as well. As already mentioned in the Introduction, scrambling of the hydrogen atoms in the intermediate carbenium ion/dipole complex is expected and, as Table III reveals, is indeed observed. The only exception seems to be Cu<sup>+</sup>/23c where no CuDCN<sup>+</sup> or DCN loss is found. For 23c there is a steadily increasing ratio of MHCN<sup>+</sup> to MDCN<sup>+</sup> in the order Co<sup>+</sup> < Ni<sup>+</sup> < Cu<sup>+</sup>, so that it is likely that CuDCN<sup>+</sup> escapes detection due to its low intensity. There are two possible explanations for this behavior: either an increased or a decreased exothermicity of the CN abstraction. If the exothermicity of the cyanide abstraction increased in the row from Co<sup>+</sup> to Cu<sup>+</sup>, the lifetime of the intermediate ion/dipole complexes would decrease so that scrambling would concomitantly be reduced. Alternatively, decreasing exothermicity would render the primary C<sub>5</sub>H<sub>11</sub><sup>+</sup> ions in the course of the carbenium ion rearrangements inaccessible and hence would exclude the CH<sub>3</sub> protons from scrambling but not the internal ones. In fact, as the methyne proton participates in the exchange, this latter possibility seems more likely. The complete absence of HCN loss for Co<sup>+</sup> and Ni<sup>+</sup> is unusual but may be related to the observation of the combined losses of HCN and CH<sub>4</sub> or C<sub>2</sub>H<sub>4</sub>. If sufficient energy is still available in the M(C<sub>5</sub>H<sub>10</sub>)<sup>+</sup> complexes, they may decompose by further loss of CH<sub>4</sub> or C<sub>2</sub>H<sub>4</sub>.

The last products that are observed for Fe<sup>+</sup>-Cu<sup>+</sup> are adduct complexes M(C<sub>6</sub>H<sub>11</sub>N)<sup>+</sup> (eq 11). The intensity of M(23)<sup>+</sup> increases in the row from 7% for Fe<sup>+</sup> to 38% for Cu<sup>+</sup>, which is completely supported by previous studies that showed that increasing amounts of adduct complexes go in line with growing unreactivity.<sup>1,2,7b,9</sup>

**Cr<sup>+</sup>, Mn<sup>+</sup>, and Zn<sup>+</sup>.** These three ions are unreactive with 2-ethylbutanenitrile in the sense that exclusively adduct complexes are formed. We have studied the decompositions of these adducts by means of collision-in-

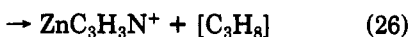
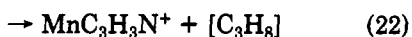
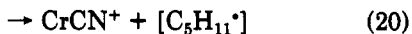
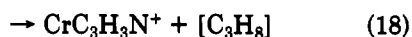
**Table IV. Amount of Products Generated (in Percent) upon CID of  $Cr^+$ ,  $Mn^+$ , and  $Zn^+$  Adduct Complexes with  $^2H$ -Labeled 2-Ethylbutanenitriles 23a-c<sup>a,b</sup>**

	23a			23b			23c		
	$Cr^+$	$Mn^+$	$Zn^+$	$Cr^+$	$Mn^+$	$Zn^+$	$Cr^+$	$Mn^+$	$Zn^+$
$MC_3H_3N^+$	-	-	-	50	~45	50	100	100	100
$MC_3H_2DN^+$	100	100	100	-	-	-	-	-	-
$MC_3HD_2N^+$	-	-	-	50	~55	50	-	-	-
$MHCN^+$	100	90	100	70	100	90			
$MDCN^+$	-	10	-	30	-	10			
$HCN$		~86		70		100			
$DCN$		~14		30		b			

<sup>a</sup> Intensities are normalized to 100% for each neutral loss.

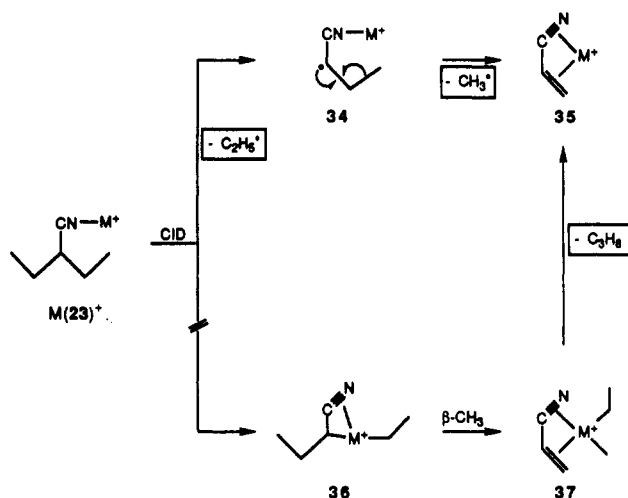
<sup>b</sup> Possibly too weak to be detected.

duced dissociation (CID).<sup>27</sup> The overall behavior upon CID is very similar for the three nitrile complexes. The main product is always the bare metal ion; i.e., ligand detachment is favored as is expected for a nondissociated adduct complex. Formation of  $MC_3H_3N^+$  ions is also observed for all three ions and either  $MHCN^+$  or  $MCN^+$  fragments are produced as well. The individual decomposition patterns are given in eqs 17-29 while data for the CID spectra of the labeled nitriles 23a-c is given in Table IV and is relatively straightforward in its interpretation.



The labeling distribution for the  $MC_3H_3N^+$  products proves that acrylonitrile complexes 35 (Scheme VI) are formed; two conceivable mechanisms for their generation will be discussed here. We believe that the  $C_3H_8$  loss is in fact a two-step process that proceeds via carbon-carbon cleavages in the course of the collision process. Formation of the radical ion 34 is supported by delocalization of the unpaired electron to the  $CN^{\cdot}$  moiety. It subsequently loses a methyl radical, a process fueled by the formation of the bidentate acrylonitrile ligand. Absence of  $H^{\cdot}$  loss

Scheme VI



from 34 can easily be rationalized on the basis of its heat of formation ( $\Delta H_f^{\circ}{}_{298}(H^{\cdot}) = 52.095 \text{ kcal mol}^{-1}$  while  $\Delta H_f^{\circ}{}_{298}(CH_3^{\cdot}) = 33.2 \text{ kcal mol}^{-1}$ <sup>28</sup>).

An alternative mechanism involves insertion of the metal ion into the  $C_2-C_3$  bond followed by a  $\beta$ -methyl shift and reductive elimination of propane. We will discuss this pathway since recently there has been some renewed discussion about metal ion insertions being a prerequisite for neutral losses. Collision-induced loss of  $CH_3^{\cdot}$  and  $C_2H_5^{\cdot}$  from propanenitrile/ $M^+$  and  $CH_3^{\cdot}$  from ethanenitrile/ $M^+$  ( $M = Mn, Fe, Co, Ni$ ) has been interpreted with the help of C-C insertions.<sup>8</sup> Quite similarly, formation of 35 upon CID of  $RCN-Cu^+$  complexes was also explained by C-H insertion/ $\beta$ -alkyl shifts.<sup>10</sup> In both cases it was assumed that reactive complexes possessed a side-on coordination. CID of  $Cu^+$ /isonitrile complexes also affords an isocyan-ethene complex, isomeric to 35, but no mechanism was proposed to explain its formation.<sup>20</sup> In the present system C-C insertions can be excluded for the  $[C_3H_8]$  loss, as it is highly unlikely that in 36 the  $\beta$ - $CH_3$  shift could compete with a  $\beta$ -H shift. 36 is identical to 28 in Scheme IV ( $R = H, R' = C_2H_5$ ) and thus one would expect  $C_2H_4$  loss instead of  $C_3H_8$  elimination. Similar arguments apply to the linear systems,<sup>8,10,20</sup> where the products can be explained by simple C-C and C-H cleavages as well.

The  $MHCN^+$  products as well as the  $HCN$  loss are undoubtedly due to the operation of the ion/dipole mechanism (Scheme II); the necessary activation energy is provided by the collision energy. The results for the labeled substrates are ambiguous in the case of  $Cr^+$  due to the low intensity of the  $CrHCN^+$  product, yet for  $Zn^+$  the expected scrambling is noted, and within the experimental uncertainty identical labeling distributions are found for  $ZnHCN^+/ZnDCN^+$  and  $HCN/DCN$  loss. The  $MCN^+$  products might in principle arise from separation of the ion/dipole intermediate 13; the absence of  $C_5H_{11}^+$ , however, makes this less likely. The simplest explanation is C-CN cleavage in the course of the collision process, and this applies for the  $C_2H_5^{\cdot}$  and  $CH_3^{\cdot}$  losses from  $C_2H_5CN-M^+$  and  $CH_3CN-M^+$  ( $M = Mn-Ni$ ), respectively,<sup>8</sup> as well.  $MnH^+$  probably arises from H abstraction by kinetically excited  $Mn^+$  fragment ions and the  $C_xH_y^+$  ions observed in the case of  $Zn^+$  could arise either by decomposition of  $C_5H_{11}^+$  fragments formed by separation of 13 or by direct C-C cleavages with subsequent decompositions.

(27) (a) Cody, R. B.; Freiser, B. S. *Int. J. Mass Spectrom. Ion Phys.* 1982, 41, 199. (b) Cody, R. B.; Burnier, R. C.; Freiser, B. S. *Anal. Chem.* 1982, 54, 96. (c) Cody, R. B.; Freiser, B. S. *Anal. Chem.* 1982, 54, 1431. (d) Cody, R. B.; Burnier, R. C.; Cassady, C. J.; Freiser, B. S. *Anal. Chem.* 1982, 54, 2225. (e) Burnier, R. C.; Cody, R. B.; Freiser, B. S. *J. Am. Chem. Soc.* 1982, 104, 7436. (f) Cody, R. B. *Analysis* 1988, 16 (6), XXX.

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**Comparisons.** In comparing the overall behavior of the different metal ions with **23** one encounters a chemistry that is very similar to what is found with many other substrates and what can be loosely characterized as their intrinsic reactivity. For the two early-transition-metal ions included in this study we observe predominantly C–H activation, with 87% (Ti<sup>+</sup>) and 96% (V<sup>+</sup>) of the products being produced by either dehydrogenation or dehydrogenation in combination with the loss of another small neutral molecule. The reaction mechanisms are difficult to derive, though, as the occurrence of multiple losses per se complicates the interpretation of the labeling data, and there are also reversible steps involved that worsen the case even further. Ti<sup>+</sup>, more extensively than V<sup>+</sup>, gives rise to multiple dehydrogenations with a much higher percentage of 2H<sub>2</sub> and even 3H<sub>2</sub> loss, for instance. All of these features, preferential C–H activation, multiple losses, scrambling, and Ti<sup>+</sup> being more reactive than V<sup>+</sup>, are also encountered with alkanes,<sup>29</sup> alkenes,<sup>29e,j,k,30</sup> nitriles,<sup>1</sup> isonitriles,<sup>20</sup> isocyanates,<sup>22</sup> isothiocyanates,<sup>21b</sup> amines,<sup>31</sup> and silanes.<sup>32</sup>

Cr<sup>+</sup>, Mn<sup>+</sup>, and Zn<sup>+</sup> only form the nitrile adduct complex with **23**, and Cu<sup>+</sup> in addition reacts by the ion/dipole mechanism, i.e., avoiding oxidative addition steps. These d<sup>5</sup>, d<sup>5s</sup>, d<sup>10</sup>, and d<sup>10s</sup> ions with their half-filled or filled d shell are also the only first-row ions that do not react with alkanes,<sup>2,25d,29g,33</sup> Cr<sup>+</sup>, Mn<sup>+</sup>, and Zn<sup>+</sup>, in contrast to Cu<sup>+</sup>,<sup>30c</sup> are also inert toward alkenes.<sup>30c,33g,34</sup> While Mn<sup>+</sup> reacts with heptanenitrile,<sup>4e</sup> Cr<sup>+</sup> is unreactive with linear and secondary nitriles<sup>1,4e</sup> but reacts with tertiary nitriles via the ion/dipole mechanism.<sup>3b,c,24</sup> Cu<sup>+</sup>, similarly, is unreactive with linear nitriles<sup>7b,9–11</sup> but reacts with secondary and tertiary nitriles via the ion/dipole mechanism,<sup>1,11,35</sup> and finally, Zn<sup>+</sup> is more or less unreactive with secondary nitriles.<sup>1</sup> Mn<sup>+</sup> and Zn<sup>+</sup> are unable to activate propylamine while Cr<sup>+</sup> and Cu<sup>+</sup> presumably dehydrogenate this amine.<sup>36</sup> With aldehydes and ketones, Cr<sup>+</sup> and Mn<sup>+</sup> are unreactive,<sup>33h,37</sup> and while Cu<sup>+</sup> does form products in some cases, these are believed to arise by “dissociative attachment” and not by insertion steps.<sup>38</sup> All four of them are again the only first-row ions that are either completely unreactive with halobenzenes or only react by adduct complex formation, halide abstraction, or charge transfer.<sup>39</sup> Similar to other ions they also do not react with benzene or toluene.<sup>39a,40</sup>

The CID products observed for the chromium, manganese, and zinc adduct complexes also underline the unreactive nature of these metal ions. In contrast to adduct complexes of “reactive” metal ions, where similar products as in ion/molecule reactions are observed,<sup>1,2,9,11,33a,41</sup> radical losses prevail, and there is no indication for an active involvement of the metal ion. The findings compare favorably with the reinterpretation of other systems<sup>8,10,20</sup> given in this paper.

Finally Fe<sup>+</sup>, Co<sup>+</sup>, and Ni<sup>+</sup> demonstrate a versatile chemistry with 2-ethylbutanenitrile. As for many other systems,<sup>2</sup> they are the only ions that are able to afford C–C activation in a significant amount. Fe<sup>+</sup> is the most reactive ion in that sense, since for Co<sup>+</sup> and Ni<sup>+</sup> there is already a higher amount of simple condensation to M(**23**)<sup>+</sup> observed and both ions also react via the ion/dipole mechanism. The latter finding points to enhanced barriers for other processes like the allylic mechanism to yield CH<sub>4</sub> or the remote functionalization to yield C<sub>2</sub>H<sub>4</sub>; otherwise the ion/dipole mechanism would not be able to compete with them. As already mentioned in the Introduction, the extent by which this mechanism is operative depends on the need for it.

In comparing 2-methylbutanenitrile (**17**)<sup>1</sup> with 2-ethylbutanenitrile (**23**), one finds that excellent agreement is obtained. For Ti<sup>+</sup>, the two main products in both systems are identical, 2H<sub>2</sub> and H<sub>2</sub>/HCN, and both are produced in comparable amounts, respectively. The same applies for V<sup>+</sup>; again, the two main products, H<sub>2</sub> and H<sub>2</sub>/HCN, are identical for **17** and **23**, and the only other significant loss observed is 2H<sub>2</sub> in both cases. For both metal ions in both systems it was impossible to draw any mechanistic conclusions from the labeled compounds due to the occurrence of multiple losses and reversible steps that caused scrambling.

Cr<sup>+</sup> is unreactive with both secondary nitriles, and the same is true for Zn<sup>+</sup> which exclusively affords the adduct complex with **23** and does so with **17** to 94% as well. CID of Cr(**17**)<sup>+</sup> affords only ligand detachment, which is also the main product in the case of Cr(**23**)<sup>+</sup>, while Zn(**17**)<sup>+</sup> upon CID, besides the metal ion, yields weak signals for ZnHCN<sup>+</sup>, which is a product for Zn(**23**)<sup>+</sup> too. Absence of MC<sub>3</sub>H<sub>3</sub>N<sup>+</sup> formation (Scheme VI) might be due to the size of the system that would require the loss of smaller, and hence more unfavorable, radicals. Mn<sup>+</sup> has not been studied with **17**.

For Fe<sup>+</sup> the main product for both nitriles is CH<sub>4</sub>, produced by the allylic mechanism (Schemes III and V) and with coincidental 41% yield, respectively. C<sub>2</sub>H<sub>4</sub> is also

produced by the allylic mechanism (Schemes III and V) and with coincidental 41% yield, respectively. C<sub>2</sub>H<sub>4</sub> is also

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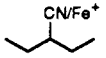
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**Table V. Amount of Products Generated (in Percent) in the Reaction of  $Fe^+$  with 2-Ethylbutanenitrile (23) under FTICR<sup>a</sup> and MI<sup>b</sup> Conditions<sup>c</sup>**

	FTICR	MI
CH <sub>4</sub>	41	58
C <sub>2</sub> H <sub>4</sub>	28	29
H <sub>2</sub>	2	8
CH <sub>4</sub> , HCN	21	—
2C <sub>2</sub> H <sub>4</sub>	<1	—
Fe <sup>+</sup>	<i>d</i>	5
Fe(23) <sup>+</sup>	7	<i>d</i>

<sup>a</sup> Present study. <sup>b</sup> Data taken from ref 5. <sup>c</sup> Intensities are expressed in  $\sum$  products = 100%. <sup>d</sup> See text for discussion.

produced in comparable amounts and by the same mechanism (Scheme IV), including the equilibration of the ethyl hydrogen atoms. A difference between the two systems is the subsequent decomposition of 32 in the case of 23, yielding CH<sub>4</sub>/HCN loss which, of course, is impossible for 17. For reasons not yet understood, 17 in MI and FTICR spectra affords loss of CH<sub>3</sub><sup>•</sup> radicals, and this process or homologous C<sub>2</sub>H<sub>5</sub><sup>•</sup> losses are absent for 23. The CH<sub>3</sub><sup>•</sup> loss is a minor process, though. For Co<sup>+</sup> and Ni<sup>+</sup> the two main products are once again identical, with a dominant C<sub>2</sub>H<sub>4</sub> loss and smaller amounts of MHCN<sup>+</sup> formation. The same mechanisms apply for the homologous substrates, viz. Scheme IV and the ion/dipole mechanism. Finally, for Cu<sup>+</sup> the three products formed are identical for both nitriles, i.e., MHCN<sup>+</sup> and HCN from the ion/dipole mechanism plus the adduct complex. As expected, the relative amount of the adduct complex is always higher (V<sup>+</sup>, Fe<sup>+</sup>, Co<sup>+</sup>, Ni<sup>+</sup>, and Cu<sup>+</sup>) for 17 than for 23. As has been pointed out elsewhere,<sup>1,2,7b,9</sup> the intensity of the adduct complex reflects the "unreactivity" of the system and for the longer nitrile 23 many intermediates are more favorable due to higher alkyl substitution.

Altogether, the chemistry encountered with 23 is a natural extension of the one with 17, and (fortunately) no new mechanisms are found. All metal ions give the same results with the two homologous compounds and thus support the mechanisms that were formulated for 17.<sup>1,5</sup> In particular, the unusual allylic mechanism is again observed as had to be predicted on the basis of the results for 17 and 2,2-dimethylbutanenitrile (16).

Completing this section we will briefly present a comparison of the FTICR results for 23 and Fe<sup>+</sup>, i.e., ion/molecule reaction products, with metastable ion (MI) decompositions of Fe(23)<sup>+</sup>.<sup>5</sup> The data are provided in Table V. As has been discussed in previous comparisons of this kind,<sup>1,9</sup> two points have to be considered to obtain a meaningful interpretation. A trivial point arises from the fact that Fe<sup>+</sup> is the starting ion in the FTICR and the adduct complex Fe(23)<sup>+</sup> in the MI experiment. Hence, ligand detachment in the former and adduct formation in the later approach cannot be monitored and the normalization of the product ions to 100% may distort the data. Fortunately, in the present system both processes are of similar importance and so the rest of the data can be directly compared. The more important restriction is due to the pronounced occurrence of multiple losses in FTICR experiments owing to the differences in energy and time scale. The combined CH<sub>4</sub>/HCN loss is an example of this point. As shown in Scheme V, HCN is lost from the CH<sub>4</sub> loss product and thus this intensity should be added to the CH<sub>4</sub> loss for the purpose of this comparison. In doing so, one finds a very good agreement between the two fundamentally different approaches, proving that indeed intrinsic properties of the system under study are probed.

## Conclusions

This study compares the reactions of the first-row transition-metal ions from Ti<sup>+</sup> to Zn<sup>+</sup> with 2-ethylbutanenitrile and three <sup>2</sup>H-labeled isotopomers thereof in an FTICR instrument. In line with the available knowledge about the intrinsic behavior of the metal ions under survey,<sup>2</sup> the early-transition-metal ions Ti<sup>+</sup> and V<sup>+</sup> almost exclusively activate C–H bonds in the substrate, and many combined losses are observed, mainly small neutrals like CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, or HCN in combination with preceding dehydrogenations. The ions with a filled or half-filled d shell, i.e., Cr<sup>+</sup>, Mn<sup>+</sup>, Cu<sup>+</sup>, and Zn<sup>+</sup>, are either completely unable to form any products except for M(23)<sup>+</sup> adduct complexes or react by an ion/dipole mechanism that avoids any insertion steps. Upon collisional activation of the adduct complexes, radical cleavages without involvement of the metal ion are observed. Fe<sup>+</sup>, Co<sup>+</sup>, and Ni<sup>+</sup> react by three mechanisms including C–C activation steps, and a decrease in reactivity can be noted in proceeding to the right side of the row. This decrease manifests itself in a higher amount of M(23)<sup>+</sup> and a larger percentage of products formed by the ion/dipole mechanism. Compared to the lower homologue of 23, 2-methylbutanenitrile (17), no differences in behavior are observed for the individual ions, and thus the present results give further strong support for the mechanisms formulated for 17 in part 1.<sup>1</sup> Furthermore, no significant differences exist between the chemistry obtained for Fe<sup>+</sup> in an FTICR and in a sector instrument where metastable ion decompositions are monitored.

## Experimental Part

The experiments were performed by using a Spectrospin CMS 47X Fourier transform ion cyclotron resonance (FTICR) mass spectrometer which is equipped with an external ion source;<sup>42</sup> the instrument and further details of its operation have been previously described.<sup>1,9,11</sup> To this end, metal ions were generated by laser desorption/ionization<sup>43</sup> by focusing the beam of a Nd:YAG laser (Spectron Systems, 1064 nm) onto a high-purity rod of the desired transition metal which was affixed in the external ion source. The ions are extracted from the source and transferred into the analyzer cell by a system of electrostatic 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 was isolated by using FERETS<sup>44</sup> and allowed to react with the substrate that was present with a constant pressure of (1–3) × 10<sup>-8</sup> mbar; reaction times are typically 1–10 s. For collisional cooling of any excited states possibly formed, for removal of kinetic energy remaining from the transfer, and for CID experiments,<sup>27</sup> argon was present as a buffer gas with a constant pressure of (1–5) × 10<sup>-7</sup> mbar, as measured with an uncalibrated ionization gauge (Balzers IMG 070). All functions of the instrument are controlled by a Bruker Aspect 3000 minicomputer; broad-band spectra are recorded with a fast ADC, digitized as 64K or 128K data points and zero-filled<sup>45</sup> to 256K before Fourier transformation. Reaction products were unam-

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biguously identified with high-resolution spectra and mass analysis and their formation pathways by double-resonance and MS/MS techniques.<sup>26</sup>

The nitriles were synthesized and fully characterized using established procedures, purified by preparative gas chromatography, and carefully degassed by multiple freeze-pump-thaw cycles immediately before the experiments. The label content was determined with NMR and mass spectrometry techniques.

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**Registry No.** 23, 617-80-1; Ti<sup>+</sup>, 14067-04-0; V<sup>+</sup>, 14782-33-3; Cr<sup>+</sup>, 14067-03-9; Mn<sup>+</sup>, 14127-69-6; Fe<sup>+</sup>, 14067-02-8; Co<sup>+</sup>, 16610-75-6; Ni<sup>+</sup>, 14903-34-5; Cu<sup>+</sup>, 17493-86-6; Zn<sup>+</sup>, 15176-26-8.

## Chalcogenometallacyclohexadienes by Thermally Induced Migratory Ring Enlargement of Furyl- and Thienylzirconocene Complexes

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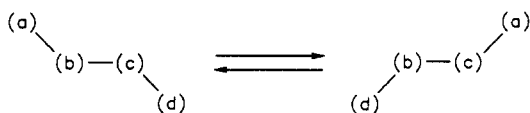
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Zirconocene dichloride reacts with 2 molar equiv of (2-furyl)lithium to give bis(2-furyl)zirconocene (1a). The ( $\sigma$ -furyl)zirconocene complexes Cp<sub>2</sub>ZrR(2-furyl) (R = CH<sub>3</sub>, Ph, SiMe<sub>3</sub>) were similarly prepared by treatment of the respective Cp<sub>2</sub>Zr(R)Cl complexes with (2-furyl)lithium. Cp<sub>2</sub>Zr(SiMe<sub>3</sub>)(2-thienyl) was obtained from the reaction of Cp<sub>2</sub>Zr(SiMe<sub>3</sub>)Cl with (2-thienyl)lithium. The Cp<sub>2</sub>ZrR(2-furyl) complexes with R = 2-furyl, methyl, or phenyl all undergo an intramolecular high-temperature ( $\geq 180$  °C)  $\sigma, \sigma$ -exchange reaction to give the oxazirconacyclohexadienes Cp<sub>2</sub>ZrOCH=CHCH=C(R) (2a-c). The 1a  $\rightarrow$  2a rearrangement follows first-order kinetics in the temperature range 140–180 °C and is characterized by the activation parameters  $\Delta H^\ddagger = 30.9 \pm 2.0$  kcal mol<sup>-1</sup> and  $\Delta S^\ddagger = -9 \pm 5$  cal mol<sup>-1</sup> K<sup>-1</sup>. The complexes Cp<sub>2</sub>Zr(SiMe<sub>3</sub>)(2-furyl) (1d) and Cp<sub>2</sub>Zr(SiMe<sub>3</sub>)(2-thienyl) (1e) undergo the analogous dyotropic rearrangements much faster. The 1d  $\rightarrow$  2d isomerization is fast at 0 °C and already takes place during the formation of 1d from Cp<sub>2</sub>Zr(SiMe<sub>3</sub>)Cl and (2-furyl)lithium. The activation parameters of the 1e  $\rightarrow$  2e ring enlargement reaction of the (2-thienyl)metallocene system are  $\Delta H^\ddagger = 20.4 \pm 2.0$  kcal mol<sup>-1</sup> and  $\Delta S^\ddagger = -12 \pm 5$  cal mol<sup>-1</sup> K<sup>-1</sup>. The oxa- and thiazirconacyclohexadienes Cp<sub>2</sub>Zr-X-CH=CHCH=C(SiMe<sub>3</sub>) (X = O, 2d; X = S, 2e) were characterized by X-ray diffraction. Complex 2d crystallizes in space group P1 with cell parameters  $a = 9.783$  (1) Å,  $b = 11.514$  (1) Å,  $c = 15.806$  (1) Å,  $\alpha = 96.27$  (1)°,  $\beta = 101.64$  (1)°,  $\gamma = 98.89$  (1)°,  $Z = 4$ ,  $R = 0.037$ , and  $R_w = 0.053$ . Complex 2e crystallizes in space group Cc with cell parameters  $a = 13.988$  (4) Å,  $b = 30.774$  (2) Å,  $c = 9.788$  (4) Å,  $\beta = 122.93$  (1)°,  $Z = 8$ ,  $R = 0.034$ , and  $R_w = 0.035$ . Both chalcogenazirconacyclohexadienes are monomeric in the solid state and exhibit nonplanar metallacyclic conformations with the metal-chalcogen vectors rotated significantly relative to the planes of the endocyclic conjugated diene moieties.

### Introduction

Dyotropic rearrangements<sup>1</sup> are thermally induced concerted rearrangement processes in which the two groups a and d exchange their positions relative to a pivotal system of groups or atoms (b, c). Most known examples



of compounds undergoing such coupled  $\sigma, \sigma$ -exchange have very electropositive main-group (Si)<sup>2</sup> or transition metals

(Zr, Hf) and at the same time electronegative elements (O, S) involved.<sup>3-6</sup> For a variety of examples stepwise (i.e. nonconcerted) reaction mechanisms have been proposed or proven.<sup>5-9</sup>

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