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Iron(I)-Induced Demethanation of *tert*-Butyl-Substituted Nitriles in the Gas Phase. A Case of Remote Functionalization of Carbon–Carbon Bonds[†]

Tilmann Prüsse, Carlito B. Lebrilla, Thomas Drewello, and Helmut Schwarz*

Contribution from the Institut für Organische Chemie, Technische Universität Berlin, D-1000 Berlin 12, West Germany. *Received February 4, 1988*

Abstract: Experiments are described that indicate that the Fe^+-induced reductive demethanation of 8,8-dimethylnonanenitrile (**11**) follows a 1,2-elimination mode in which 90% of the CH_4 is generated from the *tert*-butyl group. The actual reaction sequence seems to commence with oxidative addition of a remote C–C bond to the complexed transition-metal ion, followed by a β-hydrogen migration. There is no experimental evidence for the operation of the long-sought-after β-methyl migration in the system studied. Other processes examined include the collision-induced losses of H_2, H_2/CH_4, CH_4/CH_4, C_4H_8, and H_2/C_4H_8 versus C_4H_{10}, C_5H_{12}, and C_6H_{12}, respectively, from the RCN/Fe^+ complex. Deuterium-labeling experiments are mandatory for an understanding of the reaction pathways.

The selective functionalization of C–H bonds remains one of the major focuses of catalytic and organic chemistry. High selectivity is often achieved by the presence of activating groups, which induce the reactivity of the neighboring C–H bonds. The functionalization of *remote* C–H bonds, i.e. several carbon atoms away from the activating group, represents a great challenge. While such reactions are common to enzymes, which corrdinate a functional group and *geometrically* select a specific site of the substrate, only a few cases in solution chemistry are reported[1] where a similar principle seems to be operative. Breslow[1d] has coined the term "remote functionalization" for this method of coordination of a functional group followed by selective reactions at sites away from the complexed functionality. We have recently demonstrated that a similar system exists in the gas phase.[2] The reaction of aliphatic, unbranched nitriles with bare transition-metal ions, e.g. Fe^+, is very unique, in that selective C–H activation occurs only at positions remote from the cyanide functionality. This unprecedented behavior contrasts with that of other unsaturated systems, such as alkenes[3] and alkynes,[4] where allylic and propargylic activations, respectively, of the C–C and/or C–H bonds are reported to be the major mode of reaction. The primary reason for the unique behavior of nitriles is due to the initial interaction of the cyanide group with the transition-metal ion Fe^+. The preferred coordination leads to an "end-on" complex **1** characterized by a "linear"[5] $-CH_2C{\equiv}NM^+$ entity (M = transition-metal atom). The linear fragment in turn constrains the remainder of the molecule such that Fe^+ activates C–H bonds while trying to minimize the strain. For nitriles containing four to seven 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**). This insertion is followed by either a β-hydrogen shift (**2** → **3**) to produce eventually H_2 in a site-specific 1,2-elimination mode or cleavage of the C–C bond (**2** → **4**). The latter intermediate may then undergo reductive elimination of C_2H_4 to generate RCN/Fe^+ complexes being shortened by the C_2H_4 unit, which originates exclusively from the ω and (ω – 1) positions of the alkyl chain.[6]

[†] Dedicated to Professor Rudolf Wiechert, Schering AG, Berlin, on the occasion of his 60th birthday.

(1) For selected reviews and examples, see: (a) Kerb, U.; Stahnke, M.; Schulze, P. E.; Wiechert, R. *Angew. Chem.* **1981**, *93*, 89. (b) Breslow, R. *Chem. Soc. Rev.* **1972**, *1*, 553. (c) Breslow, R.; Maresca, L. M. *Tetrahedron Lett.* **1977**, 623. (d) Breslow, R. *Acc. Chem. Res.* **1980**, *13*, 170.

(2) (a) Lebrilla, C. B.; Schulze, C.; Schwarz, H. *J. Am. Chem. Soc.* **1987**, *109*, 98. (b) Drewello, T.; Eckart, K.; Lebrilla, C. B.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1987**, *76*, R1. (c) Lebrilla, C. B.; Drewello, T.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1987**, *79*, 287. (d) Lebrilla, C. B.; Drewello, T.; Schwarz, H. *J. Am. Chem. Soc.* **1987**, *109*, 5639.

(3) (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.

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

(5) 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 nature of the transition-metal ion M^+ and on the internal energy of **1**, deviation from linearity of the $-CH_2C{\equiv}NM^+$ unit must occur (see ref 2c for a comparison of Fe^+, Co^+, and Ni^+, respectively), which may even result in the formation of a "side-on" complex for $M^+ = Cu^+$: Lebrilla, C. B.; Drewello, T.; Schwarz, H. *Organometallics* **1987**, *6*, 2450. Similarly, we have no information on the possible effects of electronically excited states of the metal ions on the reactivity with organic substrates. Though it has been reported that the reactions of larger organic molecules (in contrast to, for example, hydrogen) are relatively insensitive to the electronic state of, for example, Fe^+, there are also cases known that clearly demonstrate that the electronic state of the ion cannot, in general, be ignored. Unfortunately, our instrumentation does not permit us to perform state-selective reactions. For pertinent references, see: (a) Sonnenfroh, D. M.; Farrar, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 3521. (b) Armentrout, P. B. In *Structure/Reactivity and Thermochemistry of Ions*; Ausloos, P., Lias, S. G., Eds.; NATO ASI Series; Reidel: Dordrecht, The Netherlands, 1987; Vol. 193, p 97. (c) Ridge, D. P. Reference 56, 1987; Vol. 193, p 165. (d) Schulze, C.; Schwarz, H. *J. Am. Chem. Soc.* **1988** *110*, 67.

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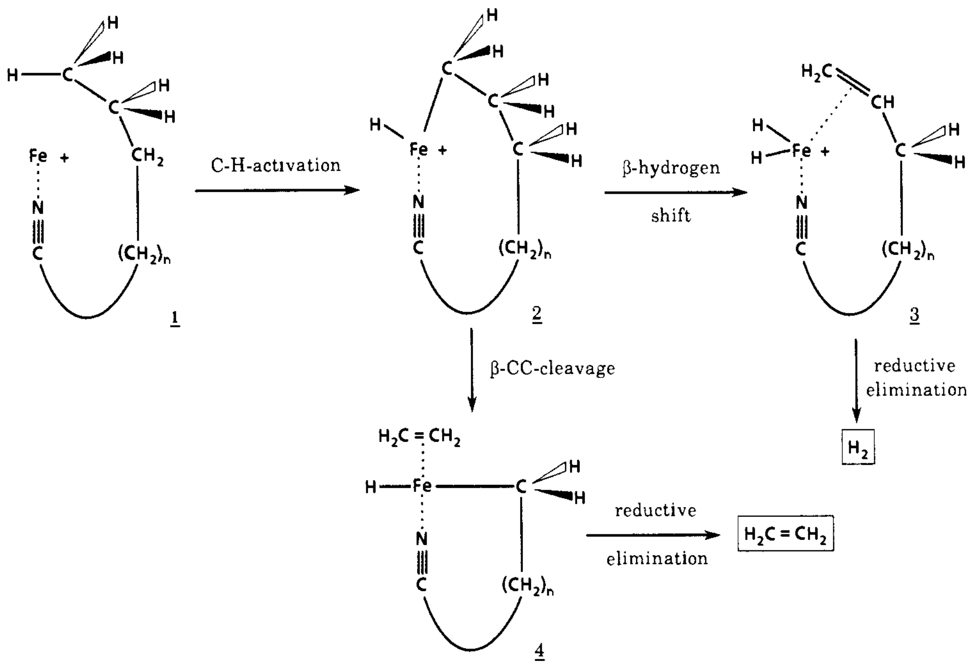
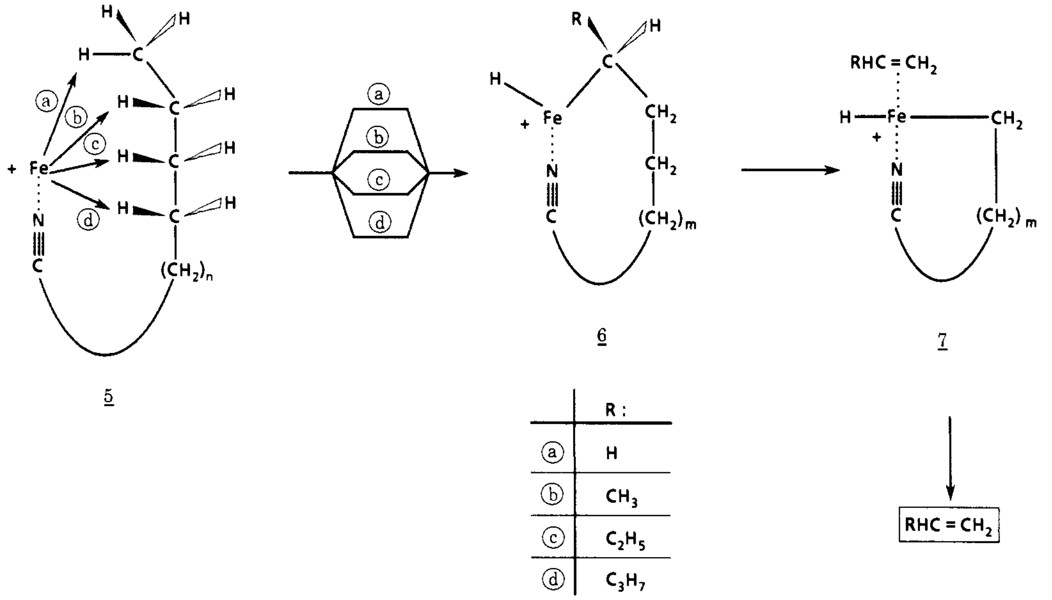
Scheme I. Proposed Mechanism for the C–H Activation of Linear Aliphatic Nitriles with Fe^+



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



	R:
ⓐ	H
ⓑ	CH_3
ⓒ	C_2H_5
ⓓ	C_3H_7

However, as the carbon chain is lengthened,[2a,d] activation of the internal CH groups starts to dominate. This is obvious from the following experimental findings:

(1) Hydrogen is no longer exclusively provided by the ω and (ω − 1) positions; it also originates from internal methylene groups.

(2) The fact that internal C–H bonds (Scheme II, **5** → **6**) are oxidatively added to the (complexed) metal ion has the consequence that, in addition to C_2H_4, higher alkenes $RCH{=}CH_2$ (R = alkyl) are also eliminated (Scheme II). Interestingly, Fe^+ shows a behavior deviating from that of Co^+ and Ni^+ ions, in that for the RCN/Fe^+ system insertion in an internal bond commences at position C(8) of the nitrile while the analogous RCN/M^+ (M = Co^+, Ni^+) complexes react at position C(7).[2c] 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 itself is a reflection of the back-bonding ability of the metal ion, since this controls the distortion of the $-CH_2C{\equiv}NM^+$ unit from linearity.[5,7] Moreover, the question of whether a linear or trigonal alignment[8] acts as the transition structure for the CH insertion will have a profound effect and may well differ for various transition-metal ions M^+.

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[6] Although labeling experiments clearly reveal the origin of the atoms that are involved in the oxidative addition/reduction elimination processes, there is no doubt that proposed structures are very often fictitious in mass spectrometric studies. In most cases, they are based on plausible considerations using as much direct and indirect evidence as available from experiments and model considerations. Strictly speaking, without detailed spectroscopic studies and state of the art high-level ab initio MO calculations, both of which cannot be applied in the present case due to the size of the molecules, none of the structures are proven. Nevertheless, their heuristic merits are undeniable in chemistry as long as speculations remain within acceptable limits. In that respect, it is not possible to unambiguously decide whether for example an equilibrium exists between **1** and **2** (Scheme I) and what the thermodynamics and kinetics of such an equilibrium would look like.

[7] For a theroetical analysis of the bond properties of $[M{-}CO]^+$ complexes, see: Schilling, J. B.; Goddard, W. A., III; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 582. No theoretical studies have yet been performed on the RCN/M^+ system. The interaction of HCN with transition metals has been studied by qualitative MO theory: Howell, J. A. S.; Saillard, J.-Y.; Le Benze, A.; Jaouen, G. *J. Chem. Soc., Dalton Trans.* **1982**, 2533.

[8] For example, see: (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) Muetterties, E. L. *Chem. Soc. Rev.* **1982**, *11*, 283. (d) Crabtree, R. M. *Chem. Rev.* **1985**, *85*, 245.

Scheme III. Proposed Mechanism for the Elimination of Alkanes from RCN/Fe^+ via Insertion in C–C Bonds Followed by β-Hydrogen Transfer

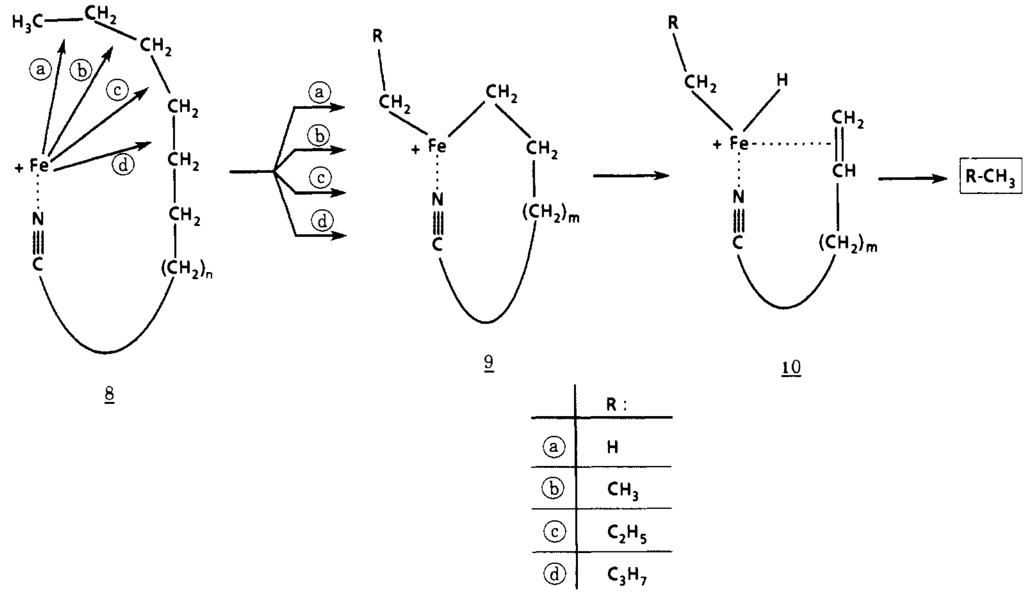


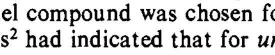
Table I. Neutral Products Formed upon Collisional Activation of RCN/Fe^+ Complexes, Generated from **11**, **11a**, and **11b** in the Gas Phase[a,b]

11–Fe^+			**11a**–Fe^+			**11b**–Fe^+		
neutral mass	assgnt	% base peak	neutral mass	assgnt	% base peak	neutral mass	assgnt	% base peak
2	H_2	12	2	H_2	5	2	H_2	19
			3	HD	8	3	HD	4
16	CH_4	100	16	CH_4	100	19	CD_3H	13
			17	CH_3D	5	20	CD_4	100
18	H_2/CH_4	10	18	H_2/CH_4	3	22	H_2/CD_4	6
			19	HD/CH_4	5	23	HD/CD_4	2
32	CH_4/CH_4	6	32	CH_4/CH_4	4	39	CD_3H/CD_4	3
			33	CH_4/CH_3D	2			
56	C_4H_8	21	56	C_4H_8	26	63	C_4HD_7	3
			57	C_4H_7D	3	64	C_4D_8	25
58	H_2/C_4H_8	17	58	H_2/C_4H_8	9	66	H_2/C_4D_8	15
			59	HD/C_4H_8	6	67	HD/C_4D_8	5
72	C_5H_{12}	10	73	$C_5H_{11}D$	11	81	$C_5H_3D_9$	8
84	C_6H_{12}	5	85	$C_6H_{11}D$	3	92	$C_6H_4D_8$	2
			86	$C_6H_{10}D_2$	6	93	$C_6H_3D_9$	7

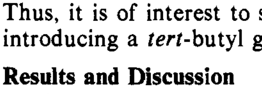
[a] Relative intensities are given in percent base peak. [b] For some product combinations other possibilities are conceivable; for example, the neutral 19 from **11a**–Fe^+ can in principle also correspond to H_2/CH_3D, etc. (for discussion see text).

(3) The reductive elimination of alkanes, which is practically absent for RCN/Fe^+ with up to seven carbon atoms and RCN/Co^+ with up to six carbon atoms, respectively, occurs from the higher, homologous complexes. Extensive labeling data[2d] reveal that the two metal ions exhibit a distinctly different behavior. Briefly, common to both metals is the reaction depicted in Scheme III. In addition, from the RCN/Fe^+ complexes, the higher alkanes RH (R ≥ C_2H_5) are also generated in a two-step sequence; in the first step, H_2 is eliminated from internal positions followed by the loss of alkenes.

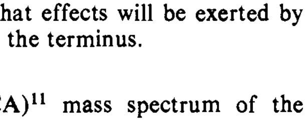
With regard to Scheme III and in particular to the loss of CH_4 (R = H), it should be mentioned that, strictly speaking, the same deuterium distribution would result for a reaction that commences with insertion of the metal ion in an internal C–H bond, followed by β-methyl migration to generate intermediate **10**. While β-alkyl migrations are reported to exist in a few organometallic systems in solution,[9] they are extremely rare in the gas phase.[10] It is this particular aspect that constitutes, among other topics, the main theme of the present paper. To this end, we have studied the gas-phase behavior of the *tert*-butyl-substituted nitrile **11** and its



11



11 a



11 b

isotopomers **11a** and **11b** with Fe^+ (for experimental details see below). This model compound was chosen for the reason that earlier experiments[2] had indicated that for *unbranched* nitriles of chain length comparable with **11** the chemistry of the (complexes) Fe^+ mainly occurs at the terminal part of the alkyl chain. Thus, it is of interest to study what effects will be exerted by introducing a *tert*-butyl group at the terminus.

Results and Discussion

The collisional activation (CA)[11] mass spectrum of the RCN/Fe^+ complex of 8,8-dimethylnonanenitrile (**11**) is given in

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[9] For example, see: Watson, P. L.; Roe, D. C. *J. Am. Chem Soc.* **1982**, *104*, 6471.

[10] (a) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 784. (b) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1982**, *1*, 963. (c) Houriet, R.; Halle, L. F.; Beauchamp, J. L. *Organometallics* **1983**, *2*, 1818. (d) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 5197. (e) Tolbert, M. A. Beauchamp, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 8117. (f) Tonkyn, R.; Ronan, M.; Weisshaar, J. C. *J. Phys. Chem.* **1988**, *92*, 92.

[11] (a) Levsen, K.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 509. (b) Cooks, R. G., Ed. *Collision Spectroscopy*; Plenum: New York, 1978. (c) Levsen, K.; Schwarz, H. *Mass Spectrom. Rev.* **1983**, *2*, 77.

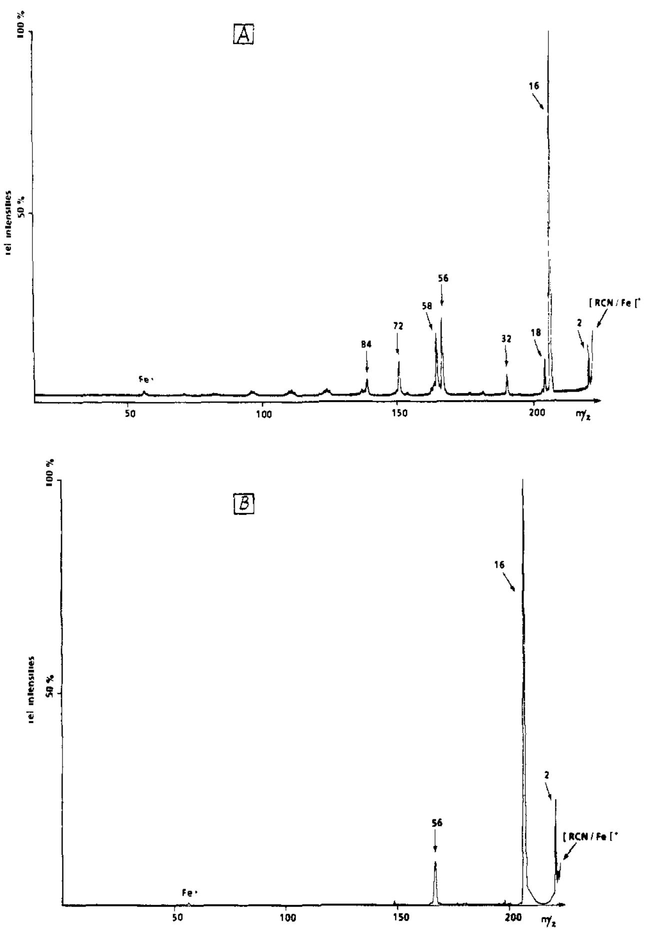


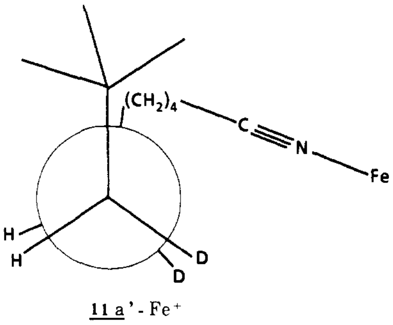
Figure 1. (A) CA mass spectrum of $(CH_3)_3C(CH_2)_6CN/Fe^+$. Numbers given at the signals correspond to the losses of neutral masses (amu) from the $RCN-Fe^+$ complex upon collisional activation. While for some numbers there cannot possibly exist any doubt concerning the corresponding neutrals formed, e.g. H_2 or CH_4, for others both the sequence of events as well as the neutral species formed are uncertain (see text for details). (B) Metastable ion mass spectrum of **11**–Fe^+.

Figure 1. The spectrum is dominated by the loss of CH_4.[12] Further interesting collision-induced reactions to which we will later refer correspond to the reductive eliminations of H_2 (loss of 2 amu), H_2/CH_4 (18 amu), CH_4/CH_4 (32 amu), C_4H_8 (56 amu), H_2/C_4H_8 and/or C_4H_{10} (58 amu), C_5H_{12} (72 amu), and C_6H_{12} (84 amu), respectively.

While the *actual* structures of both the ionic species and the neutrals[13] are unknown, the study of the labeled model compounds **11a** and **11b** (for data see Table I; note that the label distribution for both the unimolecular and the collision-induced losses of H_2, CH_4, and C_4H_8 are practically the same) nevertheless provides us with a wealth of useful information from which mechanistically important conclusions can be drawn.

(A) Loss of Hydrogen. As already mentioned, upon collisional activation, Fe^+ complexes of unbranched alkane nitriles eliminate H_2 mainly from the terminal part of the alkyl chain. In contrast to pure alkane/Fe^+ complexes for which both 1,2- and 1,4-elimination modes are operative,[14] for the RCN/Fe^+ systems so far only 1,2-elimination has been observed.[2] From the data shown in Table I, it is obvious that the introduction of a *tert*-butyl group brings about some pronounced changes. A comparison of the data for **11a** and **11b** reveals that most of the hydrogen eliminated does *not* involve the *tert*-butyl group but rather originates from those methylene groups that are remote from the functional group [i.e. C(6)/C(7)]. There are two more interesting points to note:

(1) From the complex **11a**–Fe^+ there is no D_2 eliminated upon collisional activation. This may indicate that the reductive elimination of D_2 would be associated with a significant kinetic isotope effect, which would suppress efficiently loss of D_2 in comparison with HD and H_2. Alternatively, one may argue that, due to the stereochemistry of **11a**, loss of D_2 would require an *eclipsed* (or nearly eclipsed) conformation (**11a′**–Fe^+) of the two large groups, i.e. t-C_4H_9 and $(CH_2)_4CN/Fe^+$, in order to bring about a syn orientations of the two deuterium atoms. For the time being we are in no position to sort out which of the two factors may dominate.



11a′-Fe^+

(2) In the Fe^+ complex of the *tert*-butyl fully deuteriated isotopomer **11b**, we observe mainly loss of H_2 (which must originate from the methylene groups of the alkyl chain); the absence of D_2 loss rules out a 1,3-elimination involving the *tert*-butyl group exclusively. Loss of HD is either due to some (for the time being unknown) exchange processes between the *tert*-butyl and the methylene hydrogens or, more likely, to a 1,4-elimination. Beauchamp, Bowers, and their co-workers have presented evidence[15] that metal ion induced 1,2- versus 1,4-eliminations may be distinguishable by the analysis of the kinetic energy release distributions associated with the reductive eliminations. Unfortunately, this otherwise powerful method is not applicable in the present case due to sensitivity problems.

(B) Loss of Methane. The Fe^+-induced demethanation constitutes the most favored reaction of **11**-Fe^+, for both the unimolecular and the collision-induced dissociation. The data in Table I reveal that the reaction is remarkably selective in that the neutral methane contains an intact methyl group of the *tert*-butyl group; if one ignores the (unlikely) operation of a significant kinetic isotope effect, the fourth hydrogen is provided to ca. 10% from a CH_2 unit of the methylene chain, presumably from C(7), and to 90% from a second methyl group of the *tert*-butyl substituent. With regard to the mechanisms, the experimental findings are in keeping with the processes depicted in Scheme IV. There exist two principal routes to generate intermediate(s) from which, via reductive elimination, CH_4 will be generated. One involves in the initial stage oxidative addition of a C–H bond to the (complexed) metal ion (**11**–Fe^+ → **12**; **11**–Fe^+ → **16**), followed by β-methyl transfers (**12** → **13**; **16** → **15**). In the alternative pathway, the reaction commences with insertion of a C–C bond to the metal ion (**11**–Fe^+ → **14**), followed by β-hydrogen transfer (**14** → **13**; **14** → **15**). Although we cannot settle this important question in an unambiguous way, we shall see below that the processes involving β-methyl migration (i.e. **12** → **13** and **16** → **15**) are less likely to occur. What is, however, obvious from the data in Table I is that intermediate **13** contributes to roughly 90% to the overall CH_4 formed, while **15** may provide the remaining 10%.

(C) Combined Elimination of Hydrogen/Methane. As already indicated in the footnote to Table I, the assignments for the peaks

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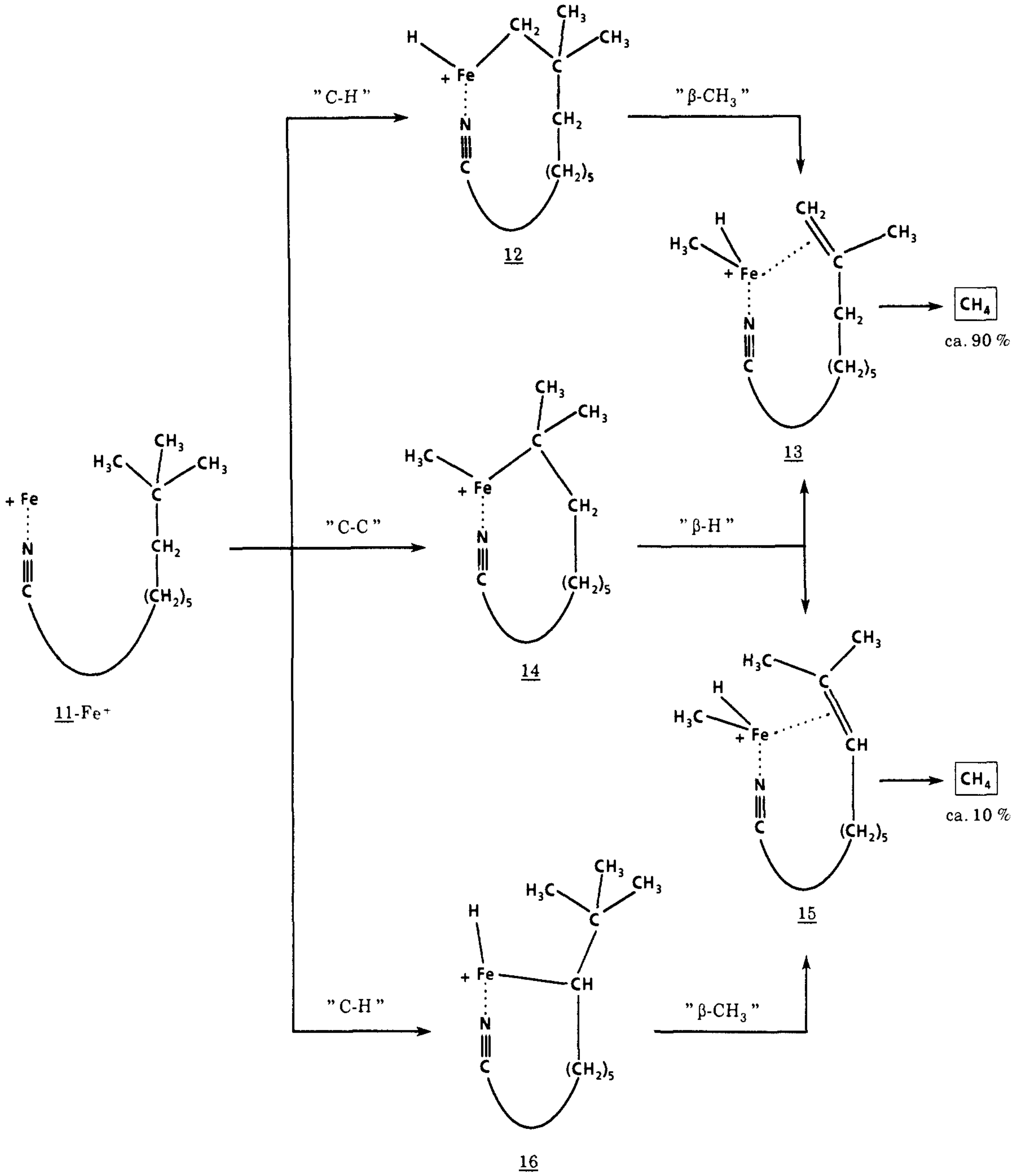
(12) In the absence of collision gas, the major product formed corresponds to loss of CH_4 from **11**-Fe^+, thus indicating that this reaction should be favored energetically (see Figure 1B).

(13) Due to sensitivity problems, we are unable to apply the otherwise powerful method of collisionally induced dissociative ionization (CIDI) for the characterization of the neutrals. For pertinent reviews, see: (a) Wesdemiotis, C.; McLafferty, F. W. *Chem. Rev.* **1987**, *87*, 485. (b) Terlouw, J. K.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 805. (c) Burgers, P. C.; Holmes, J. L.; Mommers, A. A.; Terlouw, J. K. *Chem. Phys. Lett.* **1983**, *102*, 1.

(14) Tolbert, M. A.; Mandich, M. L.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 5675, and references cited therein.

(15) Hanratty, M. A.; Beauchamp, J. L.; Illies, A. J.; van Koppen, P.; Bowers, M. T. *J. Am. Chem. Soc.* **1988**, *110*, 1.

Scheme IV. Proposed Mechanism for the Fe^+-Induced Demethanation of $(CH_3)_3C(CH_2)_6CN$ (See Text for Details)

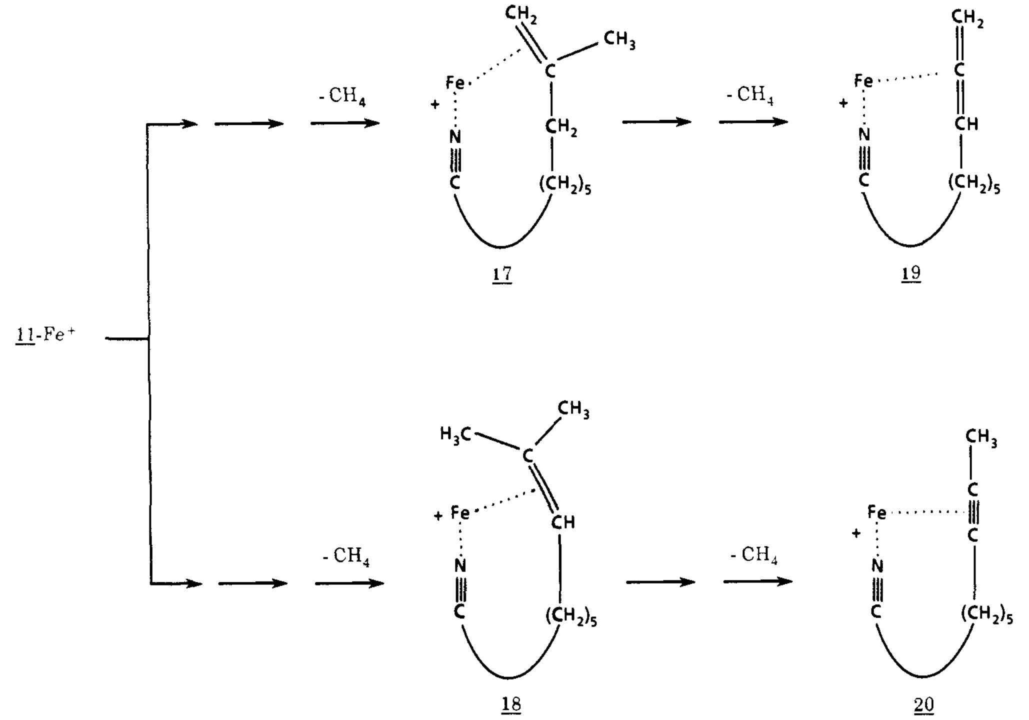


due to losses of 19 and 22 mass units from the complexes **11a**–Fe^+ and **11b**–Fe^+, respectively, are not unambiguous. They could either correspond to the combination HD/CH_4 versus H_2/CH_3D and H_2/CD_4 versus HD/CD_3H. Moreover, it is not possible to demonstrate convincingly the actual sequence of events, i.e. whether hydrogen loss precedes the elimination of methane or vice versa. From a qualitative point of view, however, the observed intensity distributions are, to a first approximation, quite similar to the one observed for the loss of hydrogen. This may indicate that, for example, the peak due to loss of 18 amu is indeed formed via sequential elimination of H_2 and CH_4 and not CH_4 loss followed by elimination of H_2.

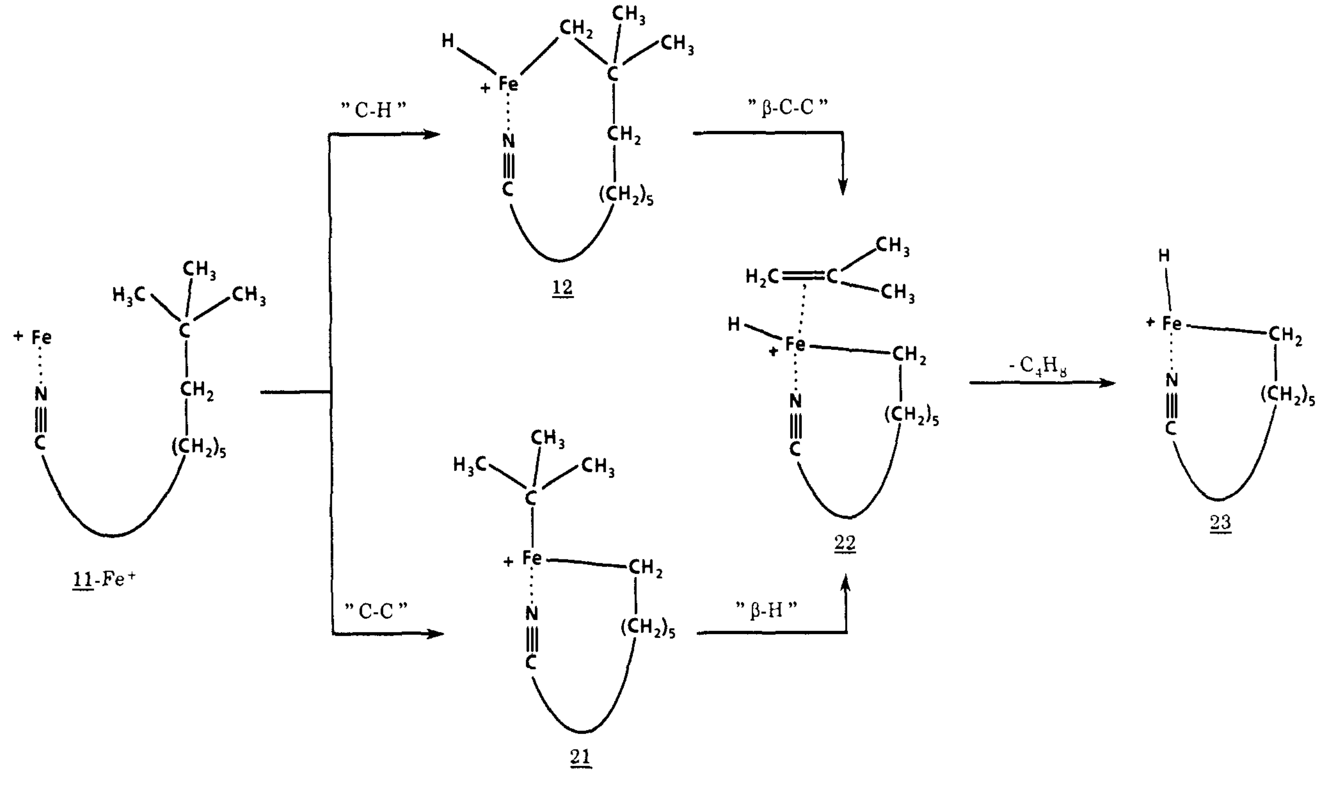
(D) Losses of Two Neutral Methane Molecules. Although this process is not a very pronounced one (7% relative intensity), from a mechanistic point of view, this reaction deserves some attention. The labeling results again rule out any significant scrambling processes but rather point to a quite specific process. A feasible mechanism is proposed in Scheme V. It is suggested that the demethanation products of **13** and **15** (i.e. **17** and **18**, formed according to Scheme IV) may undergo a further 1,2 methane elimination to eventually generate the allene and acetylene complexes **19** and **20**, respectively. Unfortunately, the weak signal intensities of the resulting products do not permit us to perform further experiments aimed at verifying this interesting possibility.

(E) Formation of the Neutral C_4H_8 (Loss of 56 amu). The label distribution indicates that this process is quite selective in that hydrogen exchange processes preceding the formation of C_4H_8 amount to less than 10%. The neutral product formed from **11**–Fe^+ seems to originate mainly from the intact *tert*-butyl group, and for the actual process there, again, exists two possible mechanistic variants (Scheme VI). As in the case of Fe^+-induced demethanation, the only distinction concerns the sequence of CH versus CC addition to the metal ion. It should, however, be mentioned that the product formed upon unimolecular loss of C_4H_8 from metastable **11**–Fe^+ does indeed correspond to **23**. The latter species, which is identical with the primary insertion product of Fe^+ into **1** (Scheme I, **1** → **2**, with $n = 3$), was found to give upon further collisional activation in the third field-free region a spectrum that is identical with that reported for $CH_3(CH_2)_5CN/Fe^+$ species generated in the ion source and subjected

Scheme V. Proposed Mechanism for the Combined Losses of Two Methane Molecules from **11**–Fe^+



Scheme VI. Proposed Mechanism for the Formation of C_4H_8 from **11**–Fe^+

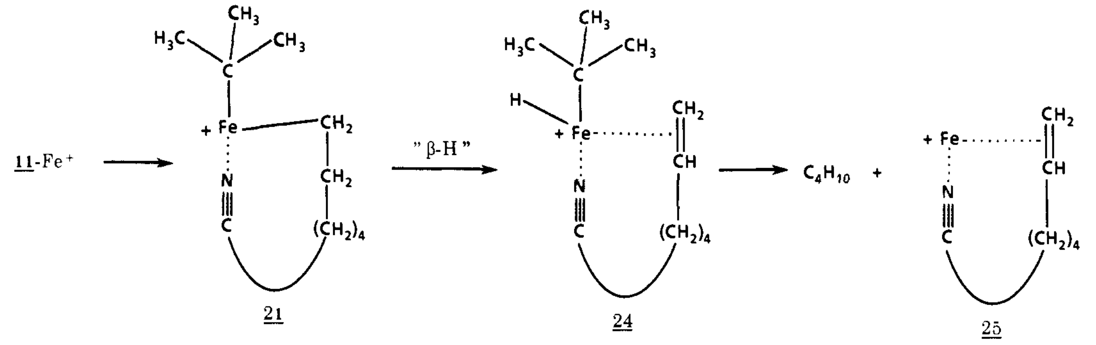


to CA in the second field-free region.

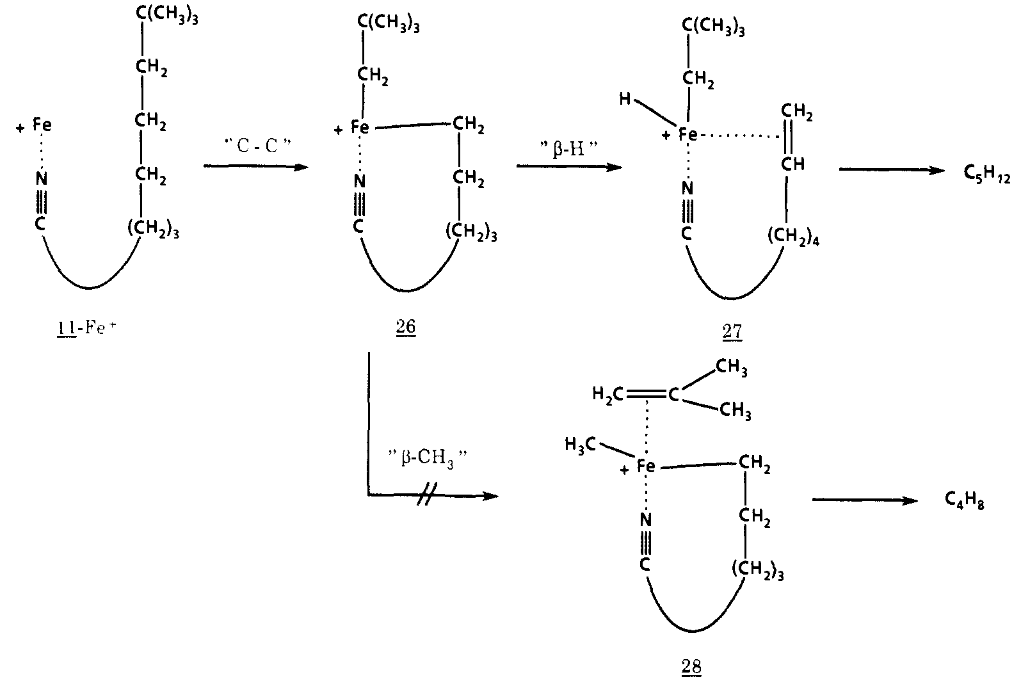
(F) Combined Elimination of Hydrogen/Isobutene (Loss of 58 amu). What has been mentioned for the loss of 18 amu (H_2/CH_4) also applies to some extent to the elimination of 58 amu. The label distribution may, again, be interpreted in forms of loss of H_2, followed by the elimination of C_4H_8 (presumably isobutene). However, it is also feasible that (at least to some extent) the neutral generated actually corresponds to the C_4H_{10} species. This hypothesis is supported by the presence of a signal corresponding to the loss of 67 amu (HD/C_4D_8 and/or C_4HD_9). In fact, the generation of a saturated C_4 hydrocarbon is quite conceivable from intermediate **21** (Scheme VII), which via *β*-hydrogen transfer from a methylene position (**21** → **24**) may undergo reductive elimination of isobutane (**24** → **25**). This sequence would also account for the loss of 59 amu from **11a**–Fe^+.

(G) Generation of Neutral C_5H_{12}. According to the labeling results, this reaction is not accompanied by hydrogen exchange processes involving the *tert*-butyl group and the methylene groups of C(6)/C(7): From **11a**–Fe^+ exclusively $C_5H_{11}D$ and from **11b**–Fe^+ only $C_5H_3D_9$ are generated. These findings are best explained by assuming that in the initial stage a C–C bond is oxidatively added to the metal ion (Scheme VIII, **11**–Fe^+ → **26**); the reaction is then followed by a hydrogen transfer (**26** → **27**) and terminated by the reductive elimination of C_5H_{12}. What is

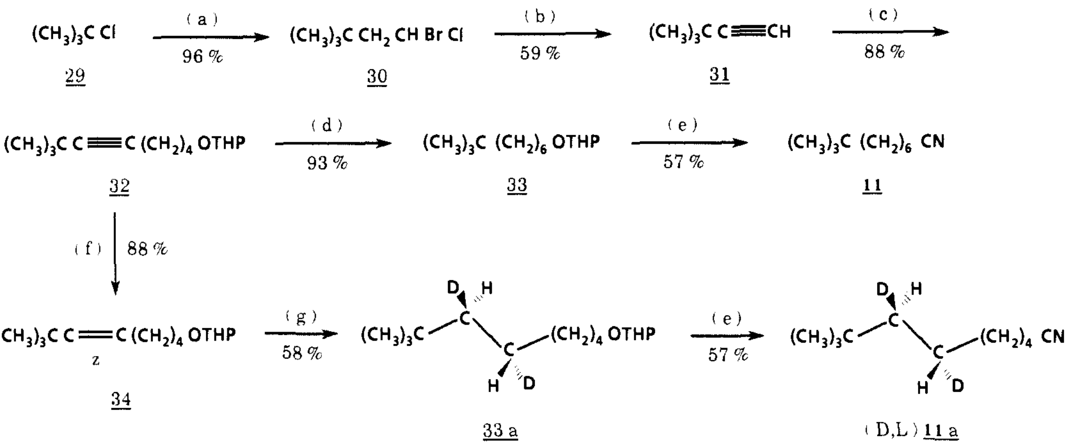
Scheme VII. Proposed Mechanism for the Generation of the 58 amu Neutral from **11**-Fe^+



Scheme VIII. Proposed Mechanism for the Generation of Neutral C_5H_{12} from **11**-Fe^+



Scheme IX. Schematic Description of the Synthesis of **11** and **11a**[a]



[a] $CH_2{=}CHBr/AlCl_3$;[20] (b) (1) $NaNH_2/NH_3(l)$, (2) NH_4Cl;[21] (c) (1) BuLi, (2) $THPO(CH_2)_4Cl$;[22] (d) $H_2/Pd/C/EtOH$;[23] (e) (1) MeOH/HCl, (2) PBr_3, (3) NaCN/DMSO (110 °C);[24] (f) H_2/Lindlar;[25] (g) $N_2D_2/MeOD/DOAc$.[26]

remarkable is that intermediate **26** is *not* able to undergo a β-methyl transfer to eventually form an isobutene-complexed species **28**. If the latter would be formed one should expect loss of C_4H_8 with a label distribution very different from that reported in Table I. *Thus, we conclude that in the present system β-methyl migration is a very unfavorable process not being able to compete with other intramolecular reactions.* If one applies this argument to the Fe^+-induced demethanation of **11** (Scheme IV), an immediate corollary is that intermediate **13** will *not* be formed via the sequence **11**-Fe^+ → **12** → **13** but rather via oxidative addition of a *remote* C–C bond to the (complexed) Fe^+, followed by β-hydrogen migration.

(H) Loss of Neutral C_6H_{12}. In view of the weak signal intensity of this reaction and the poor signal-to-noise ratio, we are reluctant to overinterpret the data reported in Table I. It is quite likely that some hydrogen exchange processes precede the acutal dissociation; the latter may proceed via the conventional scheme, i.e. addition of a C–C bond to the metal ion, followed by β-hydrogen

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transfer and terminated by reductive elimination.

Experimental Section

The experimental setup has been described in earlier papers.[2] Briefly, Fe$^+$ is generated from Fe(CO)$_5$ by electron impact ionization (100 eV). A VG Instruments ZAB-HF-3F triple-sector mass spectrometer with a B(1)EB(2) configuration was used for the analysis. The machine and its operation have been described elsewhere.[16] In a typical experiment Fe(CO)$_5$ and the nitrile **11** were mixed in a specially designed test tube[17] in an approximate ratio of 2:3. The ions corresponding to RCN/Fe$^+$ having 8-keV kinetic energy are mass selected and focused with B(1)E. Collision gas (He, pressure ca. 5×10^{-6} to 1×10^{-5} Torr) is introduced in the collision chamber located in the third field-free region, and fragment ions are recorded 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.[18] Due to the poor signal-to-noise ratio, signal-averaging techniques were used only in the case of the MI/CA experiment of structure **23** generated from **11**-Fe$^+$ (Scheme IV, and text under heading E); all other spectra were obtained by single scans only.

Compounds **11** and **11a** were synthesized according to Scheme IX by standard laboratory procedures as described in the references given in Scheme IX. For the synthesis of **11c**, the starting *tert*-butyl chloride **29** was replaced by its fully deuteriated isotopomer (CD$_3$)$_3$CCl, which was synthesized in 82% yield from **29** by either H/D exchange with DCl/D$_2$O (110° C for 24 h)[19] or reaction of isobutene with DCl/D$_2$O (room temperature for 24 h). All compounds were fully characterized by spectroscopic methods and purified by various chromatographic means. Full details are reported in ref 17.

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Do Supra–Antara Paths Really Exist for 2 + 2 Cycloaddition Reactions? Analytical Computation of the MC–SCF Hessians for Transition States of C_2H_4 with C_2H_4, Singlet O_2, and Ketene

Fernando Bernardi,[*,†] Andrea Bottoni,[†] Massimo Olivucci,[†] Michael A. Robb,[*,‡]
H. Bernard Schlegel,[§] and Glauco Tonachini[‖]

Contribution from the Dipartimento di Chimica "G. Ciamician", Universita di Bologna, Via Selmi 2, 40126 Bologna, Italy, Department of Chemistry, King's College London, Strand, London WC2R 2LS, England, Department of Chemistry, Wayne State University, Detroit, Michigan 48202, and Instituto di Chimica Organica, Universita di Torino, Via Bidone 36, Torino, Italy. *Received December 7, 1987*

Abstract: The "transition structures" for the $2_s + 2_a$ cycloaddition of ethylene with ethylene, with singlet O_2, and with ketene have been determined by MC–SCF gradient methods. The subsequent characterization of these critical points by analytical Hessian computation shows that in each case the critical point is a saddle point of index 2 (i.e., there are two imaginary vibrational frequencies). Thus, the results show that the supra–antara reaction path may not exist at all for 2 + 2 cycloadditions.

One of the novel features of the Woodward–Hoffmann treatment of 2 + 2 cycloadditions[1] was the hypothesis that there are two concerted pathways, a least motion pathway with suprafacial attack on both reactants (supra–supra attack denoted as $2_s + 2_s$) and a non least motion pathway with suprafacial attack on one reactant and antarafacial attack on the other (supra–antara attack denoted as $2_s + 2_a$). Furthermore, while the $2_s + 2_s$ process is supposed to be thermally forbidden, the $2_s + 2_a$ process should be thermally allowed.

In 2 + 2 cycloadditions of normal olefins the $2_s + 2_a$ process is expected to be energetically unfavorable because of steric hindrance and framework distortion. However, this reaction path may become the preferred one in the cycloadditions of olefins with cumulenes, since in the latter species orbitals belonging to two orthogonal planes can be involved, thereby reducing the effects associated with steric hindrance and framework distortion.

This important hypothesis can now be tested rigorously in terms of ab initio computations. In the present paper we present the results obtained on three different cycloaddition reactions for a supra–antara approach: (i) ethylene + ethylene, (ii) ethylene + singlet oxygen, and (iii) ethylene + ketene. The ethylene + ethylene reaction is the textbook example normally used in the discussion of the supra–antara approach. The ethylene + singlet oxygen reaction represents a situation with reduced steric repulsion and framework distorsion. The third reaction, ethylene + ketene,

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[†] Universita di Bologna.
[‡] King's College London.
[§] Wayne State University.
[‖] Instituto di Chimica Organica.

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