

The dinuclear isonitrile complex **9** is synthesized most effectively by photolysis. Like other isonitrile complexes, it exhibits an intramolecular rearrangement corresponding to inversion of the bridging nitrogen. At higher temperatures, bridge-terminal exchange is observed but with a barrier about 20 kJ mol⁻¹ higher than for the corresponding carbonyl complex **6**.³⁶ All the isonitrile complexes exhibit more $\nu(\text{CN})$ bands in the IR than expected—the conformational (or Fermi resonance) effects underlying these features are not understood.

Conclusions

CpRh(C₂H₄)₂ is susceptible to a range of photochemical substitution reactions. The advantage of working at low temperature is valuable for the synthesis of labile complexes and for the identification of solvent complexes,

which play a significant role in the reaction mechanism. Most of the products are derived by simple substitution of ethene, but additional dinuclear products are formed with CO and BuⁿNC. The latter (**9**) shows two-stage fluxional behavior. The presence of an alternative pathway to substitution is demonstrated by photolysis in the presence of C₂D₄ which effects H/D exchange within the ligand, probably via a vinyl hydride mechanism.

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Reactions of Gas-Phase Iron(I) Ions with Neutral Allenes. Degenerate Double-Bond Isomerization versus Competitive Activation of Vinylic and Allenylic C-C Bonds

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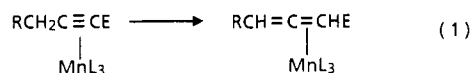
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The study of a large set of labeled allenes (4,5-nonadiene and isomeric 1,2-, 2,3-, and 3,4-octadienes) provides a quite detailed insight in the chemistry of bare Fe⁺ with these hydrocarbons in the gas phase. General features are the following: (i) Oxidative addition of a carbon-hydrogen bond to the metal ion is not associated with the rate-limiting step. This is more likely to correspond with the elimination of C₂H₄, as demonstrated in the case of, for example, Fe(4,5-nonadiene)⁺. (ii) The tendency of isomerization processes (presumably via multiple hydrogen migrations) is much more pronounced for Fe(allene)⁺ complexes than isomeric Fe(alkyne)⁺ counterparts. The position of the C=C=C unit seems to affect the extent of isomerization preceding unimolecular dissociations of the Fe⁺ complexes. The most complex pattern, which involves up to four(!) hydrogen shifts from one alkyl chain across the Fe⁺-complexed C=C=C unit to the other, is observed for 1,2- and 2,3-octadienes. (iii) Highly specific processes are demonstrated for Fe-(3,4-octadiene)⁺. Data are reported which are in keeping with the operation of an unprecedented degenerate isomerization. This process may question the conventional view that both vinylic and allylic C-C bond cleavages are operative in competition for Fe(allene)⁺ complexes. Labeling experiments are mandatory for an understanding of the reaction pathways.

It is well established¹ that the isomerization process allenes \rightleftharpoons alkynes, which for the first time was described a century ago by Favorskii,² can be accomplished under quite a variety of conditions including base catalysis or enzymatic, thermal, or electrochemical activation. Although it is known that both the substrate and the actual conditions used affect the rates of isomerization and the extent to which the equilibrium may be shifted from the C=C=C to the C=C=C system or vice versa, the understanding of the various factors is far from being complete.

In recent years it was demonstrated³ that transition-metal complexes (in particular those containing MnL₃ fragments) mediate the *irreversible* isomerization of substituted acetylenes (E denotes an electron-withdrawing

substituent) to allenes (eq 1).



Of particular interest, in quite a different context, are the reactions of allenes with *bare transition-metal ions*, like Fe⁺, as these studies provide some insight into the elementary steps of the activation of C-H and C-C bonds. Indeed, this topic has emerged as a most fascinating and promising one over the last decade.⁴ Moreover, a comparison of the gas-phase chemistry of complexes of unli-

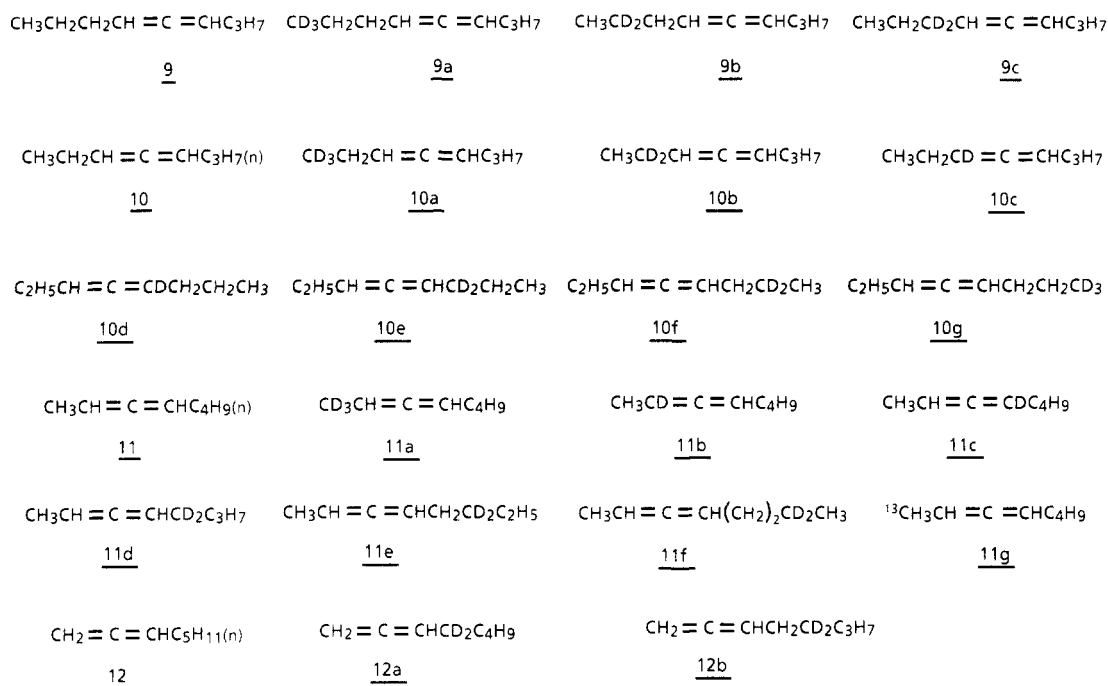
(1) Patai, S., Ed. *The Chemistry of Functional Groups: The Chemistry of Ketenes, Allenes, and Related Compounds*; Wiley: London, 1980; Chapters 2, 9, 10, 11, 12, 13, 15, and 20 and references cited therein.

(2) Favorskii, A. J. *Prakt. Chem.* 1888, 37, 382.

(3) Franck-Neumann, M. In *Organometallics in Organic Synthesis*; de Meijere, A., tom Dieck, H. Eds.; Springer-Verlag: Berlin, 1988; p 247.

(4) (a) For example, more than 100 recent references are given in: Schulze, C.; Schwarz, H.; Peake, D. A.; Gross, M. L. *J. Am. Chem. Soc.* 1987, 109, 2368. For further leading reviews, see: (b) Beauchamp, J. L.; Stevens, A. E.; Corderman, R. R. *Pure Appl. Chem.* 1979, 51, 967. (c) Allison, J. *Prog. Inorg. Chem.* 1986, 34, 627. (d) Freiser, B. S. *Talanta* 1985, 32, 697. (e) Armentrout, P. B. In *Structure/Reactivity and Thermochemistry of Ions*; Ausloos, P., Lias, S. G., Eds.; NATO ASI, Reidel: Dordrecht, 1987; p 97. (f) Ridge, D. P. *Ibid.* 1987; p 165.

Chart I



gated transition-metal ions with isomeric allene/acetylene pairs contributes toward an understanding of the basic processes underlying the chemistry of these ionic systems in the absence of solvent and counterion effects which principally obscure the inherent properties of the system. However, even under the ideal situation which prevails in the gas phase, the reactions of $\text{Fe}(\text{allene})^+$ complexes seem to be more complex than those of the analogous $\text{Fe}(\text{alkyne})^+$ systems. While the latter are relatively well understood,⁵ the chemistry of the former is by no means uniform,⁶ in particular with respect to the problem of the unimolecular isomerization allene \rightleftharpoons alkyne preceding the gas-phase dissociations. For example, while the collisional activation (CA) mass spectra of $\text{Fe}(\text{1-pentyne})^+$ and $\text{Fe}(\text{2-pentyne})^+$ differ from that of $\text{Fe}(\text{1,2-pentadiene})^+$, the CA spectra of $\text{Fe}(\text{2-pentyne})^+$ and $\text{Fe}(\text{2,3-pentadiene})^+$ are practically indistinguishable. Similarly, the complexes of Fe^+ with 1- and 2-hexyne give rise to CA mass spectra quite different from those reported for the $\text{Fe}(\text{1,2-hexadiene})^+$ system. However, in spite of some differences the CA spectra of the $\text{Fe}(\text{C}_4\text{H}_6)^+$ complexes generated from either 1- and 2-butyne or 1,2-butadiene can only be accounted for by invoking extensive rearrangements preceding the collision-induced dissociations.⁶

While the studies of Peake and Gross⁶ clearly indicate that scission of a vinylic C–C bond constitutes a major reaction path for many $\text{Fe}(\text{allene})^+$ complexes (in distinct contrast to simple olefines or acetylenes for which formal allylic or propargylic bond cleavages dominate, while reactions involving the $\text{C}(\text{sp}^2)\text{--C}(\text{sp}^3)$ or $\text{C}(\text{sp})\text{--C}(\text{sp}^3)$ bonds are negligible^{5,7}), their investigations do not permit one to draw conclusions as to the detailed reaction mechanism. In particular, questions as to whether metal ion mediated *degenerate* isomerization of allenes may occur were not addressed. Similarly, the important problem concerning the rate-determining step in the multistep sequence which

according to the traditional explanation⁶ consists of CH/CC activation, β -hydrogen transfer or β -C–C cleavage, and reductive elimination, respectively, could not be solved.

In previous studies of $\text{Fe}(\text{acetylene})^+$ complexes⁵ we have demonstrated that this information can be provided by the analysis of labeled precursors. The investigation of deuterated isotopomers does not only prove which C–H and C–C bonds are actually activated by the bare transition-metal ions; more importantly, by choosing an appropriately symmetric precursor *intramolecular* kinetic isotope effects can be determined, which in turn characterize the rate-limiting step in the above-mentioned multistep sequence. Moreover, the problem of reversibility versus irreversibility of the various intramolecular hydrogen transfers can be addressed in a quite straightforward manner.

For example, in the reaction of bare Fe^+ with 4-octyne to eventually generate C_2H_4 from C(1) and C(2), the oxidative addition of a CH group to the metal ion is neither reversible nor associated with the rate-limiting step. The latter is ascribed to the (reductive) elimination of $\text{C}_2\text{H}_4\text{-D}_x$ ($x = 0, 2, 4$) which is associated with a kinetic isotope effect of $k_{\text{H}}/k_{\text{D}} = 1.1$ per deuterium atom.^{4a,5a}

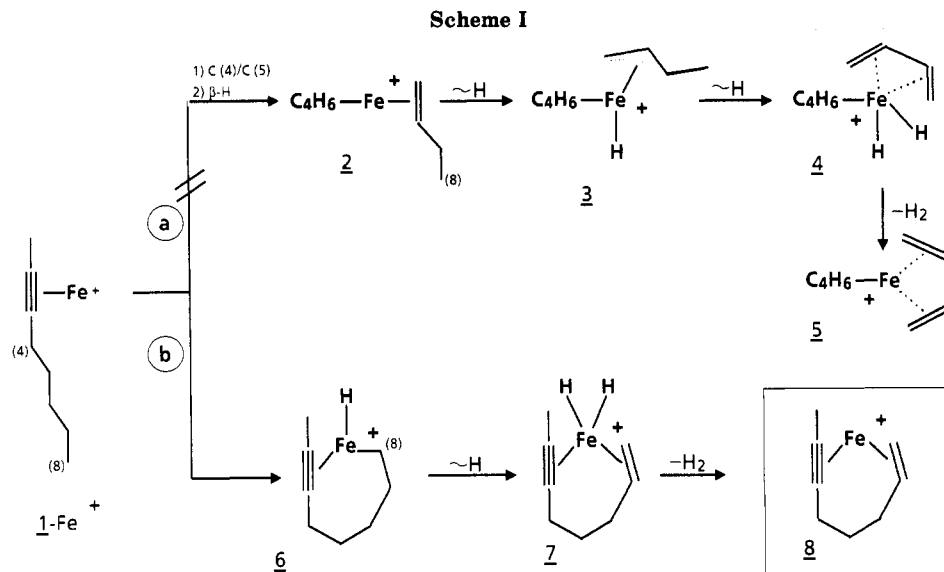
Furthermore, when labeling experiments were combined with a CA study of the products generated from the $\text{Fe}(\text{alkyne})^+$ complexes, an even more refined picture emerged; thus it was, for example, possible to demonstrate that the *site-specific* hydrogen loss from $\text{Fe}(\text{2-octyne})^+$ does *not* proceed via the conventional reaction path a (Scheme I) to eventually generate the $\text{C}_4\text{H}_6\text{-Fe}^+\text{-}\eta^4\text{-butadiene}$ complex 5; it rather follows a quite unique sequence (Scheme I, path b), which, for the first time was observed for $\text{Fe}(\text{nitrile})^+$ complexes.⁸ The reaction commences with the activation of a *remote* C–H bond and is terminated with the reductive elimination of H_2 to generate the bidentate Fe^+ complex 8.^{5c,9}

(5) (a) Schulze, C.; Weiske, T.; Schwarz, H. *Chimia* 1986, 40, 362. (b) Ref. 4a. (c) Schulze, C.; Schwarz, H. *Chimia* 1987, 41, 29.

(6) (a) Peake, D. A.; Gross, M. L. *Anal. Chem.* 1985, 57, 115. (b) Peake, D. A.; Gross, M. L. *Organometallics* 1986, 5, 1236.

(7) (a) Peake, D. A.; Gross, M. L.; Ridge, D. P. *J. Am. Chem. Soc.* 1984, 106, 4307. (b) Reference 4a,c,f.

(8) (a) Lebrilla, C. B.; Schulze, C.; Schwarz, H. *J. Am. Chem. Soc.* 1987, 109, 98. (b) Lebrilla, C. B.; Drewello, T.; Schwarz, H. *Ibid.* 1987, 109, 5639. (c) Lebrilla, C. B.; Drewello, T.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* 1987, 79, 287. (d) Czekay, G.; Drewello, T.; Schwarz, H. *J. Am. Chem. Soc.*, submitted for publication. (e) Prüsse, T.; Lebrilla, C. B.; Drewello, T.; Schwarz, H. *Ibid.* 1988, 110, 5986.



In this paper we describe results of the reaction of bare Fe^+ with several neutral allenes. In particular, we discuss the chemistry of $\text{Fe}(4,5\text{-nonadiene})^+$ ¹⁰ and of the complexes of Fe^+ with isomeric 1,2-, 2,3-, and 3,4-octadienes, employing a large set of specifically labeled isotopomers (Chart I). These systems were chosen as suitable models on the following grounds: (a) Fe^+ -mediated cleavage of both formal "allylic" and "vinylic" C-C bonds can occur, and it may be interesting to see whether both reaction modes are realized and if so, what is the branching ratio. (b) Due to the symmetry of 4,5-nonadiene (9), labeling of one C_3H_7 alkyl chain permits the determination of intramolecular kinetic isotope effects. (c) The study of the octadiene isomers 10, 11, and 12, respectively, in comparison with the well-understood isomeric octynes⁵ may shed light on the pertinent question if, and to what extent, transition-metal ion mediated isomerization between C_8 allenes and C_8 alkynes occur.

Experimental Section

The experimental setup has been described in detail in earlier papers.^{4a,8} Briefly, Fe^+ is generated from $\text{Fe}(\text{CO})_5$ by electron-impact ionization. In a typical experiment $\text{Fe}(\text{CO})_5$ and the allene (in a ratio 1:10) were introduced simultaneously via the gas inlet system in the chemical ionization source of a Vacuum Generators ZAB-HF-3F triple sector mass spectrometer of BEB configuration (B denotes magnetic and E electric sector).¹² Experimental conditions were as follows: ionization energy, 100 eV; emission current, 0.5 mA; repeller voltage, 0 V; acceleration voltage, 8 kV; ion-source temperature, 200 °C; ion-source pressure, 10^{-6} mbar;

(9) Suggested structures are hypothetical in nearly all cases studied in mass spectrometry; they are based on plausible considerations using as much direct and indirect evidence as available from experiments and model considerations. Strictly speaking, none of the structures are proven. Nevertheless, the heuristic merits of such structural representations are undeniable in chemistry, as long as speculation remains within acceptable limits. In the case of distinguishing and "characterizing" structures, as, for example, 5 and 8 (Scheme I) and other $\text{Fe}(\text{C}_8\text{H}_{12})^+$ isomers, CA mass spectrometry proved extremely helpful as it did in many other studies of organometallic species in the gas phase (see ref 4a, 5, and 6).

(10) Preliminary results of this system were reported: Steinrück, N.; Schwarz, H. *Chimia*, 1988, 42, 263.

(11) Due to the orthogonal π systems of the $\text{C}=\text{C}=\text{C}$ unit "vinylic" cleavage of a $\text{C}(\text{sp}^2)/\text{C}(\text{sp}^3)$ bond is in allenes in fact comparable to the "allylic" bond cleavage of simple alkenes.

(12) For a description of the machine, see: (a) Weiske, T. Ph.D. Thesis, Technical University, Berlin, 1985. (b) Terlouw, J. K.; Weiske, T.; Schwarz, H.; Holmes, J. L. *Org. Mass Spectrom.* 1986, 21, 665.

Table I. Metastable Ion Spectra of Labeled $\text{Fe}(4,5\text{-nonadiene})^+$ Complexes^a

neutral	Fe^+ complex precursor		
	9a	9b	9c
C_2H_4	55	56	>98
$\text{C}_2\text{H}_3\text{D}$	3	3	<1
$\text{C}_2\text{H}_2\text{D}_2$	42	41	<1
C_3H_6	50	50	45
$\text{C}_3\text{H}_5\text{D}$	4	50	7
$\text{C}_3\text{H}_4\text{D}_2$	6	<1	48
$\text{C}_3\text{H}_3\text{D}_3$	40		

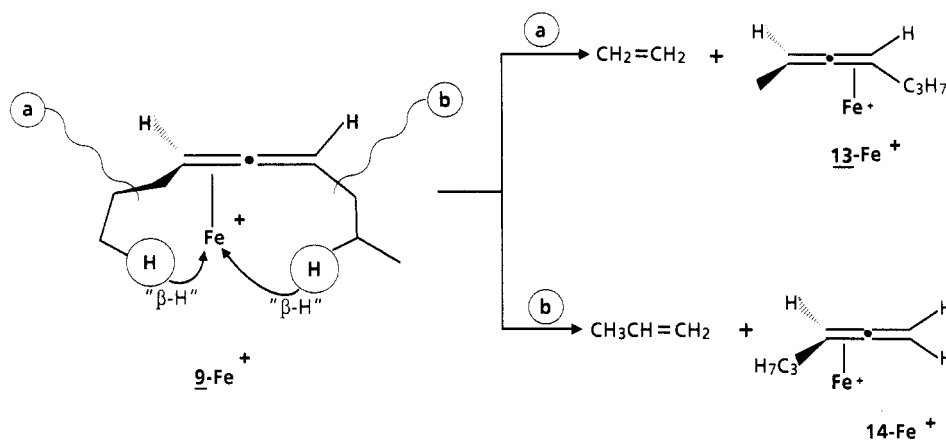
^a Intensities are given in % Σ neutral, for each class of neutrals formed.

mass resolution, 3000–5000 (10% valley definition). The $\text{Fe}(\text{hydrocarbon})^+$ complexes were formed by reactions of presumably $\text{Fe}(\text{CO})_x^+$ ($x = 1, 2$)¹³ and the appropriate hydrocarbon. It should be stated that the resolution is sufficient to distinguish between CO and C_2H_4 ; thus, the conceivable replacement of C_2H_4 by CO in the organometallic complexes can be excluded. The so-formed organometallic complexes, having 8-keV kinetic energy, were mass selected and focused with B(1)E, and the unimolecular dissociations occurring in the field-free region between E and B(2) were monitored by scanning B(2). The data reported correspond to the average of 20–30 scans which were accumulated by using the VG 11/250 data system. Errors are better than $\pm 2\%$ of reported data. Collisional activation experiments were performed by using helium as a neutral target gas. The pressure in the collision cell, which is located in the field-free region between E and B(2), was chosen such that the primary ion beam intensity was attenuated to 50%. This corresponds roughly to 2–2.5 collisions. In several experiments, CA mass spectra were not only recorded on ion source generated ions but, in addition, on fragment ions originating from dissociations of metastable ions during their transit.

All compounds given in Chart I were synthesized by standard laboratory procedures, purified by preparative gas chromatog-

(13) Double-resonance experiments (ref 4a and 6 and also: Nibbering, N. M. M.; Schwarz, H., et al. unpublished results) by using FTICR indicate that FeCO^+ and $\text{Fe}(\text{CO})_2^+$ are the major precursors to $\text{Fe}(\text{alkyne})^+$ and $\text{Fe}(\text{RCN})^+$ complexes. It should, however, be emphasized that double-resonance experiments performed at 10^{-7} mbar may not strictly apply at the high pressure (10^{-5} mbar) used in the CI source. Similarly, the actual electronic state of Fe^+ in the $\text{Fe}(\text{hydrocarbon})^+$ complexes is unknown. It should, however, be mentioned that in contrast to reactions with H_2 , the reactivity of Fe^+ with larger molecules is insensitive to the state of Fe^+ . See, for example: (a) ref 4e and references cited therein. (b) Schultz, R. H.; Armentrout, P. B. *J. Phys. Chem.* 1987, 91, 4433. (c) Schultz, R. H.; Elkind, J. L.; Armentrout, P. B. *J. Am. Chem. Soc.* 1988, 110, 44.

Scheme II

Table II. Partial Collisional Activation (CA) Mass Spectra of $\text{Fe}(\text{C}_8\text{H}_{14})^+$ Complexes (m/z 166)^a

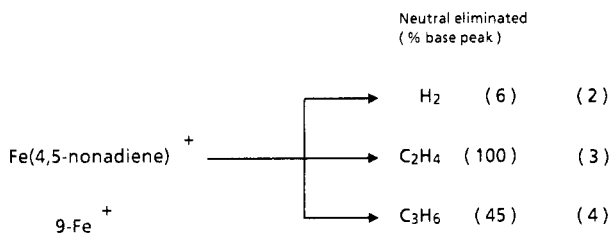
C ₈ H ₁₄ precursor	m/z								
	Fe - C ₈	Fe - C ₆		Fe - C ₆		Fe - C ₄	Fe - C ₃		Fe
	164	138	136	126	124	110	98	96	56
1-octyne (15) ^b	13 (14)	30 (41)	10	100 (100)	43 (57)	18 (11)	20	24	18
2-octyne (1) ^b	60 (82)	20 (27)			10 (27)	100 (100)		10	20
3-octyne (16) ^b	10 (11)	21 (15)			100 (100)	11		14	12
4-octyne (17) ^b		100 (100)			10	17		13	11
3,4-octadiene (10)	10 (16)	100 (100)			38 (28)	18		15	14
2,3-octadiene (11)	38 (37)	52 (30)			100 (100)	62 (40)		10	14
1,2-octadiene (12)	33 (71)	36 (40)		28 (14)	45 (51)	100 (100)	11	28	20

^aData are given in % base peak. Data given in parentheses refer to metastable ion decompositions. Signals with <10% relative intensities are not included. The complete set of data is available from the authors upon request. ^bThe data reported are similar to those published earlier by Gross, Schwarz, et al.^{4a,5a,6b}

raphy, and fully characterized by NMR spectroscopy.

Results and Discussion

A. The Fe(4,5-nonadiene)⁺ Complex. The metastable ion (MI) mass spectrum of 9-Fe⁺ is characterized by the branching ratios given in eq 2-4.¹⁴



The analysis of the labeling data of the Fe⁺ complexes of **9a**, **9b** and **9c**, given in Table I, is straightforward. We note the following: (a) C₂H₄ and C₃H₆ are generated in competition from 9-Fe⁺ favoring the activation of the formal allylic C-C bond (path a in Scheme II) by a factor of 2.2 in comparison to cleavage of the vinylic C-C bond (Scheme II: path b). (b) The study of the labeled isotopomers is quite revealing in many respects. Hydrogen exchange processes are minor for both reactions; the alkenes C₂H₄ and C₃H₆ are generated in a "clean" fashion

(14) It should be mentioned that the neutrals formed from the organometallic complexes are not structurally characterized but inferred indirectly from the mass differences between precursor and daughter ion masses. However, for energetic reasons there cannot be any possible doubt that the mass differences of 2, 28, and 42 daltons must refer to molecular hydrogen, ethylene, and propene, respectively. Due to the relatively low abundance of the hydrogen loss reaction, this process will not be included in the discussion of the labeled isotopomers of **9**. The complete data set is given in ref 10.

with specific hydrogen transfers from a position "β" to the C-C bond to be cleaved. (c) Oxidative addition of a carbon-hydrogen (deuterium) bond to the π-complexed metal ion is not associated with a kinetic isotope effect. This is evidenced by comparing the isotope distribution for the generation of ethylene and propene from **9a-Fe**⁺ and **9b-Fe**⁺. (d) The only isotope effect observed is associated with the ligand detachment of ethylene ($k_{\text{C}_2\text{H}_4}/k_{\text{C}_2\text{H}_2\text{D}_2} = 1.33$; thus $k_{\text{H}}/k_{\text{D}} = 1.15$ per deuterium atom is comparable to the data reported for ethylene loss from Fe(4-octyne)⁺ with $k_{\text{H}}/k_{\text{D}} = 1.11$ ⁵). (e) The absence of any significant hydrogen scrambling products makes it highly unlikely that unimolecular dissociation of Fe(4,5-nonadiene)⁺ is preceded by extensive double-bond migrations. (f) Attempts to unambiguously characterize the products formed upon losses of C₂H₄ or C₃H₆ from 9-Fe⁺ by CA mass spectrometry proved unsuccessful. It should, however, be mentioned that in view of the earlier studies of Peake and Gross,⁶ structures 13 and 14 are not unreasonable.¹⁵ The

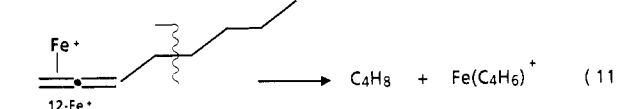
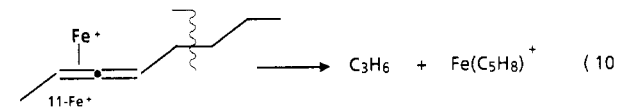
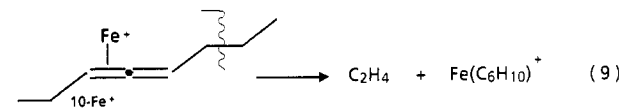
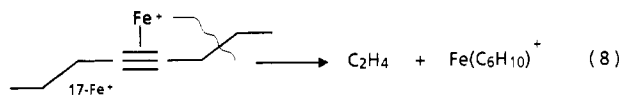
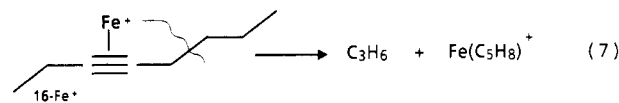
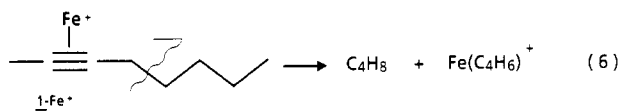
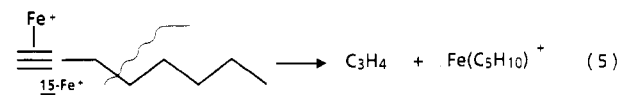
(15) The fluxional behaviour of both neutral and ionic allene metal complexes in solution has been studied.¹⁶ Depending on the nature of the transition metal and the substitution pattern of the allenes, activation energies for the concerted 1,2 shift of the metal fragment were found to span the range of 9-23 kcal/mol. Interestingly, for ligated iron complexes, the metal ion is preferentially attached to the less substituted double bond of the allene. As this preference has been explained in terms of steric effects (repulsive interaction of the allene substituents with the ligands of the metal complex), this preference must not necessarily hold true for bare transition-metal ions. In fact, the binding energy between bare transition-metal ions and π-donors (e.g. olefins, alkynes) is the larger the more electron-rich the π-ligand is.¹⁷ In this paper the bare Fe⁺ is, for consistency, always attached to the higher substituted C=C bond of the allene unit.

(16) (a) Ben-Shoshan, R.; Pettit, R. *J. Am. Chem. Soc.* **1967**, *89*, 2231. (b) Foxman, B.; Marten, D.; Rosan, A.; Raghu, S.; Rosenblum, M. *Ibid.* **1977**, *99*, 2160.

actual mechanism of activation of the C–C and C–H bonds of **9** by bare Fe⁺ remains to be elucidated. Nevertheless, the high specificity is notable in particular with reference to the data reported earlier⁶ and the systems to be described in the next section.

B. The Fe(C₈H₁₄)⁺ Complexes. The data given in Table II for both the unimolecular (MI) and collision-induced dissociations of several Fe⁺-octyne and Fe-octadiene⁺ complexes leave no doubt that the ion source generated Fe(C₈H₁₄)⁺ species dissociate such that the major reactions seem to reflect the structural integrity of the neutral C₈H₁₄ isomers. Although both the CA and MI spectra of the various isomeric complexes have most fragmentation processes in common, the branching ratios are so different that common intermediates are very unlikely (see, however, below). Quite interesting is the fact that the often reported isomerization allenes \rightleftharpoons alkynes does not seem to hold for the Fe⁺-complexed octyne/octadiene isomers. This is clearly indicated not only by the data given in Table II and the labeling results (to be described below) but also by the finding that from the Fe⁺(octadiene)⁺ complexes, upon collisional activation, CH₄ is eliminated (5–9% relative intensities); this reaction is either absent or of very minor importance in the CA spectra of isomeric Fe(octyne)⁺ species.^{4a,5,6b} For the major dissociation processes (eq 5–11) one is tempted to interpret

Major reaction channels



the results in terms of the traditional mechanism, i.e. insertion of the metal ion in that particular C–C bond which is activated by the π -system; the reactions, which involve β -hydrogen transfers,¹⁸ are terminated by the elimination

(17) (a) Müller, J. *The Organic Chemistry of Iron*; Academic Press: New York, 1978; Vol. 1, p 145. (b) Kappes, M. M.; Staley, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 1813. (c) Jacobson, D. B.; Freiser, B. S. *Ibid.* **1983**, *105*, 736, 5197, 7484. (d) Jacobson, D. B.; Freiser, B. S. *Organometallics* **1984**, *3*, 513. (e) Hettich, R. L.; Jackson, T. C.; Stanko, E. M.; Freiser, B. S. *J. Am. Chem. Soc.* **1986**, *108*, 5086. (f) Hanratty, M. A.; Beauchamp, J. L.; Illies, A. J.; Koppen, P. v.; Bowers, M. T. *Ibid.* **1988**, *110*, 1 and references cited therein. (g) Schulze, C.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes*, in press.

Table III. Unimolecular Losses of Hydrogen, Ethylene, and Propene from Fe(3,4-octadiene)⁺ Isotopomers^a

	Fe ⁺ complex precursor						
	10a	10b	10c	10d	10e	10f	10g
H ₂	56	70	100	100	95	60	68
HD	44	30			5	40	32
C ₂ H ₄	74	69	98	97	97	29	27
C ₂ H ₃ D	2	7	2	3	3	6	7
C ₂ H ₂ D ₂	24	24				65	66
C ₃ H ₆	82	84	89	91	5	7	6
C ₃ H ₅ D	10	14	11	9	15	82	9
C ₃ H ₄ D ₂	5	2			80	11	16
C ₃ H ₃ D ₃	3						69

^a See footnote a in Table I.

of an alkene unit.¹⁹ As already noted by Peake and Gross⁶ and also observed for the Fe(4,5-nonadiene)⁺ system described above, the data in Table II suggest that activation of the formal allylic and vinylic C–C bonds by the metal ion occurs in competition, favoring the former in a ratio 2–3:1. Further inspection of the data reveals, however, the presence of decomposition modes which cannot be explained in terms of the traditional concept but rather points to either more complicated reactions or the operation of mechanisms similar to the one described for H₂ loss from Fe(2-octyne)⁺ (Scheme I). Among these processes are the quite abundant losses of hydrogen and ethylene from the Fe⁺ complexes of 1,2- and 2,3-octadienes or of C₃H₆ from 1,2-octadiene. While these reactions may in principle be explained without invoking a prior double-bond isomerization, the elimination of C₄H₈ from 3,4-octadiene or C₅H₁₀ from 2,3-octadiene requires at least multiple hydrogen transfer. In the following, we will focus on some major aspects, and we shall demonstrate that an understanding of the gas-phase chemistry can only be achieved by extensive labeling studies.

For the sake of clarity the organization of the discussion is such that octadiene isomers will be described separately.

I. The Fe(3,4-octadiene)⁺ Complex 10-Fe⁺. Out of the many unimolecular and collision-induced processes of this system (Table II), we will describe the losses of H₂, C₂H₄, and C₃H₆ (presumably propene¹⁹), respectively.

With regard to the unimolecular loss of a hydrogen molecule from 10-Fe⁺, the analysis of the deuterated isotopomers (Table III) proves that hydrogen is generated from both the “ethyl” and the “propyl” part of 3,4-octadiene. Due to the operation of a significant kinetic isotope effect,²⁰ it is not possible, in spite of the many labeled precursors studied, to quantify the contribution of either alkyl chain. (See below and ref 23.) However, the following observations are noteworthy: (i) Hydrogen loss does not follow a 1,1-elimination mode. The data reported are, however, in keeping with a 1,2-elimination. (ii) The hydrogens attached to the double bonds, i.e. C(3)/C(5), are

(18) The course of the reaction sequence, i.e. addition of a C–C bond to the metal ion followed by β -hydrogen transfer or vice versa, is for most systems studied not known. For references and recent examples, see ref 8e.

(19) The nature of the neutral alkenes, i.e. C₂H₄, C₃H₆, and C₄H₈, is unknown. For sensitivity reasons the otherwise powerful technique of neutralization-reionization mass spectrometry (NRMS) in its variant of collision-induced dissociative ionization (CIDI) cannot be applied in the present case. For leading references 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) Holmes, J. L. *Mass Spectrom. Rev.*, submitted for publication. (d) Burgers, P. C.; Holmes, J. L.; Mommers, A. A.; Terlouw, J. K. *Chem. Phys. Lett.* **1983**, *102*, 1.

(20) In fact, the data in Table III indicate that the isotope effects seem to be different for the insertion of the metal ion in the methyl versus methylene carbon–hydrogen (deuterium) bonds.

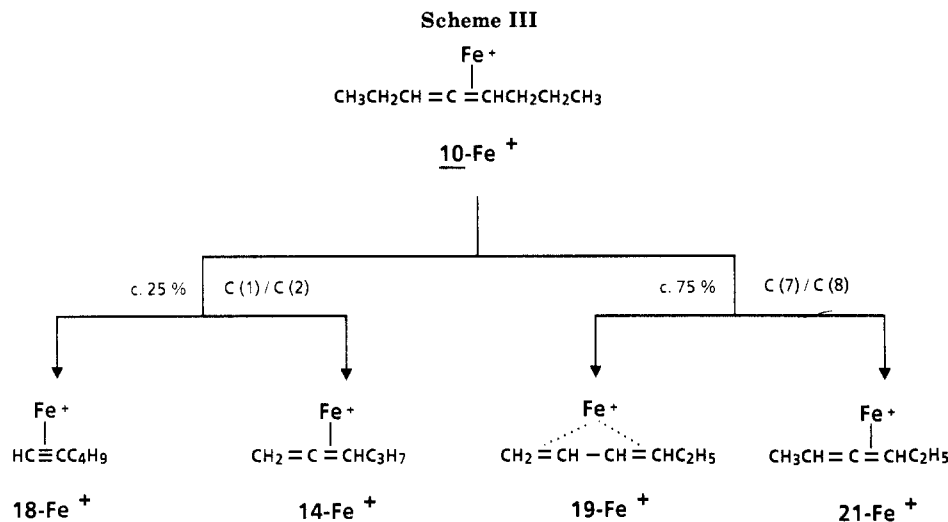


Table IV. Partial CA Mass Spectra of Fe(C₆H₁₀)⁺ Complexes (m/z 138)^a

C ₆ H ₁₀ precursor	Fe - C ₆		Fe - C ₅			Fe - C ₄			Fe - C ₃			Fe - C ₂			Fe - C ₁	Fe		
	136	135	134	122	121	112	111	110	109	98	96	95	83	82	81	71	57	56
1-hexyne (18) ^b	7							15		57	100	11			5			27
1,2-hexadiene (14) ^b	6							46	5		100	7						25
1,3-hexadiene (19) ^b	15					5		15			100	5	6					17
2,3-hexadiene (21)	8			5		5		100	6		82	6	5	7	5			22
3,4-octadiene (10)	9	8	8		13	7	6	62	10	6	100	11	10	13	10	6	10	50
3,5-octadiene (20)	13	15	9		14	12	11	37	8	5	100	13	13	17	9	7	7	49
4-octyne (17) ^b	6							100	7	7	66	7	5	5				29

^aData are given in % base peak; signals with <5% relative intensities are omitted. The complete spectra are available upon request.

^bThe CA spectra of the Fe⁺ complexes of 14, 17, 18, and 19 are also reported in ref 6b.

not involved. (iii) The absence of D₂ loss does rule out not only a 1,1-elimination mode but also scrambling reactions; this may indicate that the oxidative additions of the C-H (C-D) bonds to the metal ion are irreversible.²¹ (iv) The involvement of the methyl group C(8) in the generation of hydrogen is another example for the *remote functionalization* of *nonactivated* C-H bonds by (bare) transition-metal ions.^{4a,5,8}

Next, we will discuss the generation of ethylene from Fe(3,4-octadiene)⁺, which is the major component of both MI and CA spectra. The study of the labeled analogues of 10 clearly proves that the neutral originates from both the ethyl and the propyl parts of the molecule in a ratio of ca. 1:3, favoring again the cleavage of a formal allylic C-C bond. We note that in contrast to the hydrogen loss, scrambling processes are gaining slight importance; even the "vinyllic" C-H bonds as well as the methylene group C(6), which should be "inert" if the traditional mechanism is operative, already contribute to the formation of the neutral.

In previous studies,^{4a,6} it was demonstrated that the comparison of CA spectra of authentic molecules with those of ions generated in the course of a metal ion mediated fragmentation process may be extremely helpful in supporting suggested mechanisms. As outlined in Scheme III, due to the many possible products, the prospects of gaining insight into the mechanism of C₂H₄ loss from 10-Fe⁺ by analyzing the CA spectra of Fe(C₆H₁₀)⁺ species are not very promising. Although the CA spectra of Fe⁺ with the C₆H₁₀ isomers of 1-, 2-, and 3-hexyne and the 1,2-, 1,3-, and 2,3-hexadienes are different (Table IV and Ref 6b), indicating no or minor mutual isomerization, it is impos-

sible to reproduce the CA spectra of Fe(C₆H₁₀)⁺, generated by C₂H₄ loss from 10-Fe⁺, by any linear combination of the CA spectra given in Table IV.²² We note, however, that the fraction of 18-Fe⁺, contributing to the product(s) formed from 10-Fe⁺, must be very small; this follows directly from the minor signal at m/z 98 (loss of C₃H₄) in the CA spectrum of Fe(C₆H₁₀)⁺ generated from 10-Fe⁺. In the CA spectra of authentic Fe(1-hexyne)⁺ (18-Fe⁺), this process corresponds to 57% (relative intensity).

We further note from the data in Table IV that the Fe(C₆H₁₀)⁺ species generated from 3,5-octadiene (20) and from 3,4-octadiene 10 have very similar CA spectra. Indeed, there cannot exist any possible doubt that the reaction of 10-Fe⁺ is preceded by an isomerization which is unparalleled in gas-phase organometallic chemistry. This is evidenced by the following experiments. If one takes CA mass spectra of Fe(C₆H₁₀)⁺, generated by losses of C₂H₄ from 10-Fe⁺ and C₂H₂D₂ from either 10b-Fe⁺ or 10f-Fe⁺, the spectra are *identical* in any respect (Figure 1). This result can hardly be explained by assuming that an *intact* 3,4-octadiene undergoes Fe⁺-mediated direct cleavages of formal vinyllic and allylic C-C bonds. If this were the case, the spectra shown in Figure 1 should be different, as loss of C₂H₂D₂ from intact 10b is expected to mainly generate 14-Fe⁺; in contrast, loss of C₂H₂D₂ from the "propyl" part of 10f should result in species different from 14-Fe⁺. The indistinguishability of the CA spectra requests that in competition with the direct cleavage of the "allylic" C-C bond the *ethyl and propyl chains* of 10-Fe⁺ *must equilibrate*. While we cannot rule out that Fe(3,5-octadiene)⁺ (20-Fe⁺) is involved in the degenerate isomerization of 10-Fe⁺ (Scheme IV), the isomeric Fe(4-octyne)⁺ complex (17-Fe⁺) does *not* serve as an intermediate. This is also

(21) It is open to question whether the minor loss of HD from 10e (5%) is due to scrambling or, more likely, to a specific 1,2 elimination involving the "allylically" activated C(6) position.

(22) No significantly better match is achieved for linear combinations by using the much larger basis set described by Gross et al.^{6b}

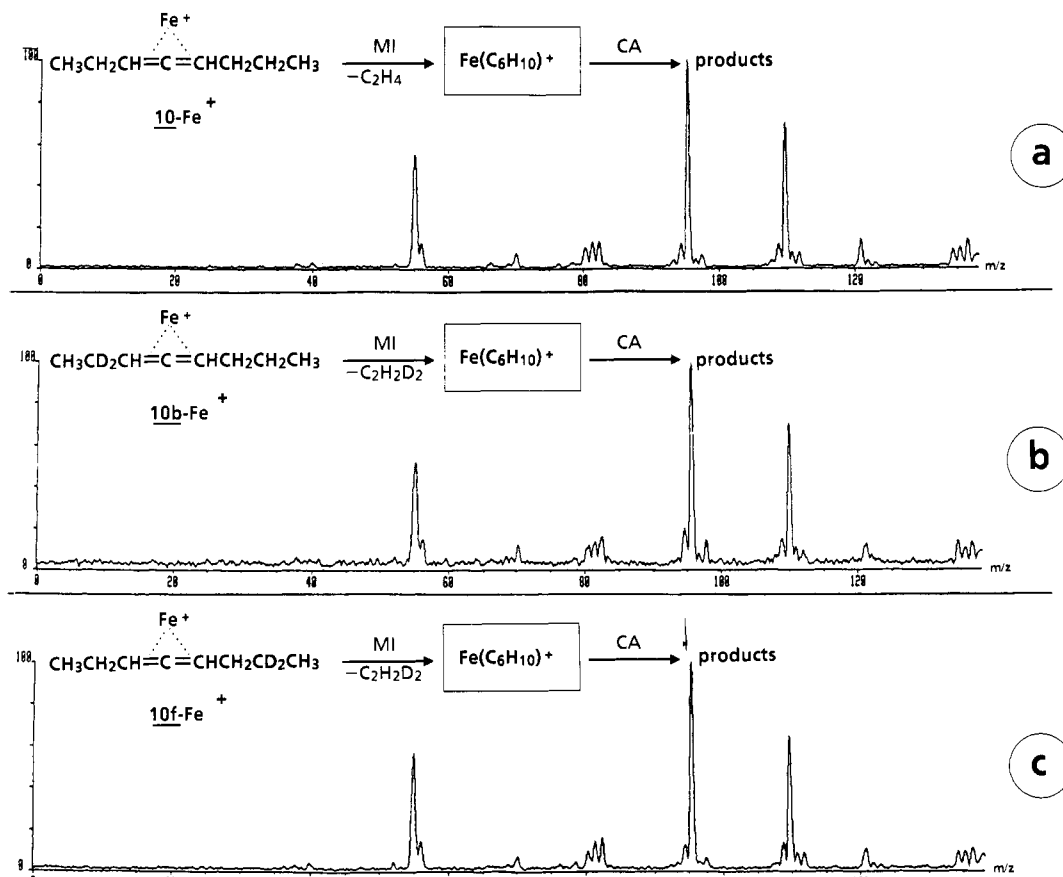


Figure 1. CA mass spectra of $\text{Fe}(\text{C}_6\text{H}_{10})^+$ species generated by unimolecular dissociations of metastable precursor ions: (a) loss of C_2H_4 from 10-Fe^+ ; (b) loss of $\text{C}_2\text{H}_2\text{D}_2$ from 10b-Fe^+ ; (c) loss of $\text{C}_2\text{H}_2\text{D}_2$ from 10f-Fe^+ .

Scheme IV

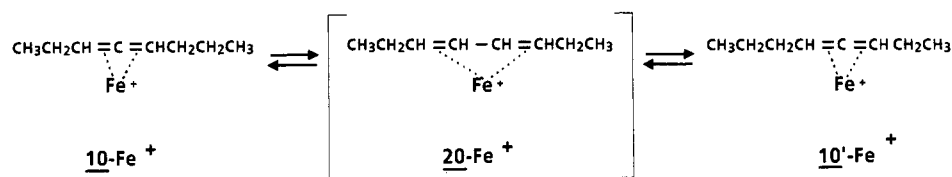


Table V. Unimolecular Losses of Hydrogen, Ethylene, Propene, and Butene from $\text{Fe}(3,4\text{-octadiene})^+$ Isotopomers^a

	Fe^+ Complex Precursor						
	11a	11b	11c	11d	11e	11f	11g
H_2	75	88	95	89	89	66	100
HD	25	12	5	11	11	34	
C_2H_4	71	79	91	84	67	23	82
$\text{C}_2\text{H}_3\text{D}$	6	21	9	9	18	19	
$\text{C}_2\text{H}_2\text{D}_2$	23			7	15	58	
$^{12}\text{C}^{13}\text{CH}_4$							18
C_3H_6	70	80	72	70	11	9	96
$\text{C}_3\text{H}_5\text{D}$	21	20	23	23	29	84	
$\text{C}_3\text{H}_4\text{D}_2$	9			7	60	7	
$^{12}\text{C}_2^{13}\text{CH}_6$							4
C_4H_8	24	49	51	16	15	14	60
$\text{C}_4\text{H}_7\text{D}_1$	27	51	49	40	60	56	
$\text{C}_4\text{H}_6\text{D}_2$	32			44	25	30	
$\text{C}_4\text{H}_6\text{D}_3$	17						
$^{12}\text{C}_3^{13}\text{CH}_8$							40

^a See footnote a in Table I.

supported by the very close resemblance of the CA spectra of $\text{Fe}(\text{C}_6\text{H}_{10})^+$ generated from 10-Fe^+ and 20-Fe^+ (see Table IV) and the distinct CA spectrum of $\text{Fe}(\text{C}_6\text{H}_{10})^+$ generated from 17-Fe^+ . The rate for the degenerate isomerization

$10\text{-Fe}^+ \rightleftharpoons 10'\text{-Fe}^+$ must be equal if not faster than that for C_2H_4 loss.

Further support for double-bond isomerization of 10-Fe^+ is provided by the data for propene loss from the labeled $\text{Fe}(3,4\text{-octadiene})^+$ isotopomers. If the reaction would exclusively involve the propyl part of 10 (i.e. cleavage of the vinylic C(5)/C(6) bond, hydrogen transfer from C(7)), one would expect complete retention of the labeling for 10a-d , losses of $\text{C}_3\text{H}_4\text{D}_2$ from 10e, $\text{C}_3\text{H}_5\text{D}$ from 10f, and $\text{C}_3\text{H}_3\text{D}_3$ from the Fe^+ complex of 10g. While the formation of these products is indeed largely favoured (Table III), the data, nevertheless, convincingly demonstrate that not only the "ethyl" group of 3,4-octadiene but also the vinylic C-H bonds participate in the formation of propene. Again, the results are in keeping with the assumption that the C-C activation is ca. 15–20% accompanied (or preceded) by hydrogen migrations.²³ Attempts to gain further in-

(23) In view of the tendency of 3,4-octadiene to undergo facile Fe^+ -induced double-bond migration it is worth recalling the hydrogen loss from $\text{Fe}(3,4\text{-octadiene})^+$. The fact, that the hydrogen molecule originates from both C(1)/C(2) and C(7)/C(8) does not rule out prior hydrogen migrations involving C(3)–C(6). Unfortunately, all attempts to prove the operation of such a "hidden" hydrogen migration failed for the present case. For references concerning this concept, see: Schwarz, H. *Top. Curr. Chem.* 1981, 97, 1.

Table VI. Unimolecular Losses of Hydrogen, Ethylene, Propene, and Butene from Fe(1,2-octadiene)⁺ Isotopomers^a

	Fe ⁺ Complex Precursor	
	12a	12b
H ₂	90	86
HD	10	14
C ₂ H ₄	75	78
C ₂ H ₃ D	17	21
C ₂ H ₂ D ₂	8	<1
C ₃ H ₆	50	28
C ₃ H ₅ D	38	61
C ₃ H ₄ D ₂	12	11
C ₄ H ₈	19	14
C ₄ H ₇ D	44	52
C ₄ H ₆ D ₂	37	34

^a See footnote a in Table I.

sight into the reaction mechanism of C₃H₆ loss from 10-Fe⁺ by taking CA mass spectra of the resulting Fe(C₅H₈)⁺ products proved unsuccessful. This is not surprising in view of the data reported earlier for this system by Gross et al.^{6b}

II. The Fe(2,3-octadiene)⁺ Complex 11-Fe⁺. As evidenced by the data of the labeled isotopomers of 11 (Table V), the hydrogen molecule seems to originate from *all* C-H bonds of 2,3-octadiene, and the high selectivity which was observed for the isomeric 3,4-octadiene does not any longer prevail. It is impossible to decide whether the label distribution is due to rapid scrambling processes or competing 1,2-eliminations.

That double-bond migration is operative in this system is demonstrated by the data for losses of C₂H₄, C₃H₆, and C₄H₈, respectively. Let us begin with the discussion of the generation of C₄H₈, which amounts to 40% (relative intensity) in the MI spectrum. Although we do not know the structure of the neutral C₄H₈, the data reveal an astonishing result. While one might have expected the neutral to originate from C(5)-C(8), the ¹³C-labeled isotopomer 11g proves that 40% of the neutral must involve C(1)! The carbon atoms C(2) and C(4) are also largely (>40%) incorporated in the neutral as indirectly indicated by the losses of C₄H₇D₁ from 11b and 11c. No doubt that prior to the generation of "butene" three (!) hydrogen atoms must be transferred from the butyl chain of 11 to the unsaturated C=C=C skeleton. Although a quantitative analysis is not yet possible, the data set indicates that in the "right → left" transfer of hydrogens, positions C(6) and C(7) participate to a larger extent than does C(5). We note, however, from the losses of C₄H₈, C₄H₇D₁, C₄H₆D₂, and C₄H₅D₃ from 11a-Fe⁺ that the actual mechanism must be quite complex. A simple degenerate isomerization, 11-Fe⁺ ⇌ 11'-Fe⁺, would, for example, not account for the label distribution of 11a-Fe⁺.

The base peak in the MI spectrum of Fe(2,3-octadiene)⁺ is due to loss of C₃H₆. In contrast to the elimination of C₄H₈, the unsaturated part of the 2,3-octadiene is much less involved in the generation of C₃H₆. According to the ¹³C labeling, C(1) is involved to 4% only. However, the hydrogens attached to C(1), C(2), and C(4) are quite mobile; this follows directly from the fact that these positions are involved to up to 20%. Although the major fraction of the C₃H₆ neutral originates from C(6)-C(8) (the involvement of the latter is, strictly speaking, not proven but only indirectly inferred), the label distribution for the isotopomers leaves no doubt that substantial hydrogen

migrations must precede the dissociation.

A similar situation prevails for the generation of C₂H₄ from Fe(2,3-octadiene)⁺. Here, C(1) amounts to 18% of the total label neutral amount formed. Hydrogen exchange reactions are extensive again.

In view of the quite complex isomerization/dissociation behavior of Fe(2,3-octadiene)⁺ we refrained from further probing the structures of the ionic products by, for example, CA mass spectrometry.

III. The Fe(1,2-octadiene)⁺ Complex 12-Fe⁺. The unimolecular eliminations of H₂, C₂H₄, C₃H₆, and C₄H₈ are preceded by extensive hydrogen exchange processes (Table VI); the limited basis set does not permit any definitive conclusions. Perhaps noteworthy are the facts that the activated CH positions of C(4) and C(5) participate quite extensively in all four reactions. What is obvious is the fact, that for the 1,2-octadiene complex, the gas-phase chemistry cannot be accounted for in terms of direct, simple C-C activation processes.

Conclusions

The present study, though by no means definitive with regard to all questions raised in the introduction, nevertheless provides the basis for a much better understanding of the gas-phase chemistry of Fe(allene)⁺ complexes. A few general trends emerge from the investigation of the labeled isotopomers: (i) The tendency of isomerization processes preceding dissociation is much more pronounced for allene than for isomeric (alkyne)Fe^I complexes. (ii) The location of the C=C=C unit seems to affect the tendency of isomerization. The most complex pattern is observed for 1,2- and 2,3-octadienes. For Fe(3,4-octadiene)⁺ not only highly specific processes were established; more importantly, for the first time data are reported which are in keeping with an unprecedented degenerate isomerization. This reaction may shed some doubt on the conventional notion that both vinylic and allylic C-C bond cleavages are operative in competition in allenes. It might well be that only the latter are involved at least for the 3,4-octadiene system. (iii) The study of labeled Fe(4,5-nonadiene)⁺ complexes permits, due to the symmetry of the hydrocarbon, a detailed insight in several fundamental aspects of the activation of allenes by bare Fe⁺. Most notable is the fact that the oxidative activation of the CH bond to the metal ion is not associated with the rate-limiting step. On the basis of the analysis of the kinetic isotope effects the latter is assigned to the elimination of C₂H₄. (iv) The prime role of studying labeled compounds as a major tool in elucidating mechanistic aspects of the chemistry of ionic organometallic systems is emphasized.

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Registry No. 1-Fe⁺, 107135-45-5; 9, 821-74-9; 9a, 118539-10-9; 9b, 118539-11-0; 9c, 118539-12-1; 10, 34511-01-8; 10-Fe⁺, 118597-15-2; 10a, 118539-13-2; 10b, 118539-14-3; 10c, 118539-15-4; 10d, 118539-16-5; 10e, 118539-17-6; 10f, 118539-18-7; 10g, 118539-19-8; 11, 16487-68-6; 11-Fe⁺, 118597-16-3; 11a, 118539-20-1; 11b, 118539-21-2; 11c, 118539-22-3; 11d, 118539-23-4; 11e, 118539-24-5; 11f, 118539-25-6; 11g, 118539-26-7; 12, 1072-19-1; 12-Fe⁺, 118575-37-4; 12a, 118539-27-8; 12b, 118539-28-9; 15-Fe⁺, 107135-43-3; 16-Fe⁺, 107135-51-3; 17-Fe⁺, 118575-36-3; 20-Fe⁺, 118575-39-6; 21-Fe⁺, 118575-38-5; Fe⁺, 14067-02-8; D₂, 7782-39-0.