Reaction of Gas-Phase Iron(I) with Alkynes and Dienes: Mechanism of Rearrangement after Insertion into Propargylic or Allylic Carbon–Carbon Bonds

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The structures of $FeC_nH_{2n-2}^+$ species formed by reaction of $FeCO^+$ with alkynes (n = 3–8) and dienes (n = 3–6, 8) in a high-pressure source of a tandem mass spectrometer were determined by collisionally activating the adducts and examining the spectra of product ions. The alkyne complexes rearrange by insertion of Fe^+ into the propargylic C–C bond followed by abstraction of a β-H atom from the resulting alkyl fragment. New insight into the details of the H atom transfer process is provided by determining the structures of ions formed by reaction of Fe^+ with an isomeric set of octynes and octadienes. In contrast to the mechanism previously proposed for rearrangement of Fe(olefin)$^+$, the H atom is transferred primarily to C_3 of the propargyl fragment to produce a (1,2-diene)Fe(1-alkene)$^+$ complex. For diene adducts, transfer of a H atom occurs to C_1 of the π-allyl moiety to produce a smaller diene ligand. The structures of product ions were determined by comparing the collisionally activated decomposition (CAD) spectra of these ions with those of reference alkyne and diene complexes.

Introduction

In this paper, we are concerned with the reactivity of gas-phase Fe^+ with organic molecules containing double and triple bonds. In 1977, Allison and Ridge[1] reported the first examples of transition-metal ion species reacting with olefins. The technique of ion cyclotron resonance (ICR) mass spectrometry was employed to establish that $TiCl_x^+$ species (x = 1–3), formed by electron ionization of $TiCl_4$, react with olefins (≥C5) to form an adduct which eliminates smaller olefins. By using an ion beam apparatus, Beauchamp et al.[2] reported that Co^+ reacts with olefins in a similar fashion and proposed a mechanism to account for this behavior. Fourier transform mass spectrometry (FTMS) was used in subsequent studies to show that Fe^+ and Ni^+ also react with olefins.[3,4]

The mechanism of rearrangement of Fe(olefin)$^+$ complexes was confirmed recently by utilizing high-energy collision activated decomposition (CAD) spectroscopy[5,6] to probe the structures of the metal ion complexes.[7] The rearrangement proceeds by oxidative addition of Fe^+ to the allylic C–C bond followed by transfer of a β-H to produce a bis(olefin) complex (Scheme Ia) as originally proposed by Beauchamp and co-workers.[2] Upon collisional activation, the adduct dissociates by loss of the less strongly bound olefin. Although β-H abstraction by transition-metal ions[8] is now a well-established mechanism in the gas phase, the terminus of the migrating β-H (i.e., the site to which the H atom is transferred) following allylic insertion has never been fully established.

The reactions of Fe^+ with multiple bonds are sufficiently selective that location of the site of unsaturation can be deduced from the CAD spectrum of an Fe(olefin)$^+$ complex. The preferential insertion of transition-metal ions into allylic C–C bonds serves as the basis of an analytical method developed recently.[9] Fe^+ CI and tandem mass spectrometry were used for locating double and triple bonds in olefins, dienes, alkynes, fatty acid esters, and alkenyl acetates.

In this report, we extend the earlier mechanistic study[7] by investigating the mechanism of reaction of Fe^+ with dienes and alkynes. This was accomplished by interpreting both the CAD spectra of a series of alkynes and dienes complexed with Fe^+ and the spectra of decomposition products formed from rearrangements of the adducts. CAD spectra of isomeric octadiene and octyne complexes are presented as part of a deductive test of the proposed mechanism. New details of the mechanism are revealed by taking advantage of the good precision and high dynamic range of a sector tandem mass spectrometer. For example, the terminus of the migrating hydrogen atom could be determined by studying the nature of products formed in the β-H transfer process.

Experimental Section

CAD experiments were performed on a Kratos MS50 triple analyzer mass spectrometer.[10] Organometallic ions formed in the CI source were mass selected at a resolution of 5000–10 000 (10% valley definition) by using MS-I. Ions were then activated by collisions with helium target gas in a collision cell located after the double-focussing MS-I, and the CAD spectrum of resulting fragment ions was acquired by scanning MS-II. CAD spectra were acquired after the selected ion beam was suppressed 50% by using helium collision gas.

In a typical experiment, 10–20 (20 s) scans were signal averaged by using a Data General Nova-4X computer and software written in this laboratory. Average precision of CAD peak height measurements is ±8% relative standard deviation for small peaks (≤10% relative abundance) and ±6% rsd for major peaks (>10% RA). Precision of CAD measurements taken months apart is within ±10% rsd. Narrow scans of small peaks over a limited mass range (ESA voltage) were taken when peak heights were to be compared closely and give data with an average rsd of ±3%. Abundance ratios determined from such data have estimated rsd of ±5% or less.

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[1] Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1977**, *99*, 35–39.

[2] Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6623–6628.

[3] Jacobsen, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 7484–7491.

[4] Jacobsen, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 736–742.

[5] Cooks, R. G.; Glish, G. L. *Chem. Eng. News* **1981**, *59*, 40–52.

[6] Levson, K.; Schwarz, H. *Mass Spectrom. Rev.* **1983**, *2*, 77–148.

[7] Peake, D. A.; Gross, M. L.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 4307–4316.

[8] Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1976**, *98*, 7445–7447.

[9] Peake, D. A.; Gross, M. L. *Anal. Chem.* **1985**, *57*, 115–120.

[10] Gross, M. L.; Chess, E. K.; Lyon, P. A.; Crow, F. W.; Evans, S.; Tudge, H. *Int. J. Mass Spectrom. Ion Phys.* **1982**, *42*, 243–254.

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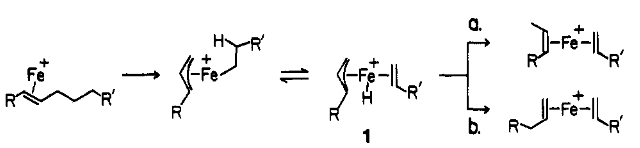
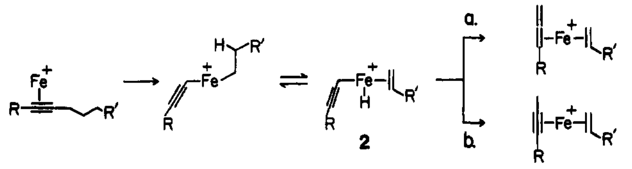
Scheme I



Scheme II



The $FeC_nH_{2n-2}^+$ were formed by reactions of $Fe(CO)_x^+$, produced by decompositions of $Fe(CO)_5^+$, and the appropriate alkyne or diene.[7,9] $Fe(CO)_5^+$ (30 μL of liquid) was injected into a 100-mL glass reservoir which was unheated and mounted on a direct insertion probe, and the flow adjusted using a fine metering valve (SS-22R54, Whitey Co.) to a pressure of approximately 10 mtorr in the source. A single injection of $Fe(CO)_5$ provided sufficient backing pressure to operate the source for 3–4 h. The olefin (10 μL) was introduced through a heated inlet, and the total pressure in the ion source was brought to 25–100 mtorr for 15–20 min.

The CI source was operated at 280-eV ionization energy with a total emission current of 500 μA. The accelerating voltage was 8000 V and the repeller was set to 0 V with respect to the source chamber. The source was operated at less than 100 °C to minimize thermal decomposition of $Fe(CO)_5$.

Iron pentacarbonyl and 1,3-butadiene iron tricarbonyl were purchased from Strem Chemicals. Alkyne and diene samples were obtained from Wiley Organics or Aldrich Chemicals and were reported to be 97–99% pure. Propyne (85%, stabilized with allene) was obtained from Farchan Laboratories, and cyclobutane (99%) was obtained from Columbia Organics. The 1,2-hexadiene sample was purified by using preparative GC with a 4 m × 6 mm stainless-steel column packed with 20% TCEP coated on 60/80 mesh Chromosorb (Supelco) and operated at 80 °C.

Reactions of Fe^+ with Octynes and Octadienes

The CAD spectra of $FeC_8H_{14}^+$ species (Table I) are consistent with propargylic or allylic insertion of Fe^+ followed by β-H transfer to produce alkene–alkyne or alkene–diene adducts (Schemes I and II). For example, $FeC_8H_{14}^+$ formed by reaction of $FeCO^+$ and $Fe(CO)_2^+$ with 1-octyne[11] rearranges following propargylic insertion to **3** (reaction 1). Upon collisional activation, **3** dissociates to $FeC_5H_{10}^+$ (100% RA) and $FeC_3H_4^+$ (31% RA). Despite the rich chemistry exhibited by a species which is initially 1-octyne complexed with Fe^+, it is not yet possible to specify when the rearrangement occurs. Nevertheless, we will refer to complexes of this nature by using the name of the reacting olefin, e.g., Fe(1-octyne)$^+$.

Other major fragment ions can be explained by invoking further rearrangement of **3**. After loss of C_3H_4, rearrangement of Fe(1-pentene)$^+$ results in formation of $FeC_3H_6^+$ (25%) and $FeC_2H_4^+$ (7%). The structure of the $FeC_5H_{10}^+$ produced from reaction of Fe^+ with 1-octyne in the ion source is determined by comparing its CAD spectrum to that of Fe(1-pentene)$^+$.[7] Since their CAD spectra are identical within experimental error (Figure 1a,b), the $FeC_5H_{10}^+$ is assigned the Fe(1-pentene)$^+$ struc-

Table I. CAD Spectra of $FeC_8H_{14}^+$

complex	product ions																	
	Fe-C_8H_{12}	Fe-C_8H_{10}	Fe-C_7H_{10}	Fe-C_7H_8	Fe-C_6H_{10}	Fe-C_6H_8	Fe-C_6H_6	Fe-C_5H_{10}	Fe-C_5H_8	Fe-C_5H_5	Fe-C_4H_8	Fe-C_4H_6	Fe-C_3H_6	Fe-C_3H_4	Fe-C_2H_3	Fe-C_2H_2	Fe-CH_3	Fe
1,4-octadiene	1.6	0.5	0.3		100		2.5		11.2	3.8		4.1	2.0	6.5	3.5	3.8	1.9	7.4
4-octyne	1.8	0.4	1.0	0.9	100		2.6		7.3	3.9		16.0	1.8	11.8		3.2	2.2	10.4
1-octyne	16.9	12.2	2.8	4.8	29.5	15.0	9.9	100	43.3	9.7		18.5	25.0	30.9	7.0[a]	8.3	4.6	28.6
1,3-octadiene	20.5	5.0	3.2	1.5	21.8	5.3	3.1		100	8.0	1.3	10.7	6.5	6.1		10.2	3.1	12.4
1,7-octadiene	3.3	6.4	1.7	2.3	19.2		1.8		100	8.5		15.6	6.5	8.0	8.2	10.9	3.4	16.5
2,4-octadiene	2.1	0.5	0.6		51.4				100	7.4		5.5	6.5	8.4		9.6	3.4	12.6
3-octyne	13.3	0.8	1.8	1.1	22.0	4.2	2.3		100	6.6	1.1	10.5	5.6	14.0		7.6	3.5	14.2
cyclooctene	8.0	12.2	8.2	4.5	41.4		4.6		100	7.7		25.2	5.7	6.4	7.3	9.5	3.2	16.7
2,6-octadiene	6.0				0.5	0.9			2.8	1.3	8.5	100			9.7		3.0	16.8
2-octyne	50.9	8.0	4.0	5.0	15.2	2.1	1.9	2.2	9.5	2.9	17.0	100		7.0	8.7		3.5	21.5

[a] Fe(1-octyne)$^+$: $FeC_2H_4^+$, 6.6% RA.

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[11] Double-resonance experiments obtained by using FTMS indicate that $FeCO^+$ and $Fe(CO)_2^+$ are the major precursors to Fe(alkyne)$^+$ and Fe(diene)$^+$ complexes. For example, Fe(1-pentyne)$^+$ is formed from $FeCO^+$ (50%) and $Fe(CO)_2^+$ (50%), Fe(1,3-pentadiene)$^+$ [>90% $FeCO^+$], and Fe(1-heptyne)$^+$ and Fe(1,3-octadiene)$^+$ [≥90% $Fe(CO)_2^+$]. It must be emphasized that double-resonance experiments performed at 1 × 10^{-7} torr give results that may not strictly apply at the high pressures (0.1 torr) used in the CI source.

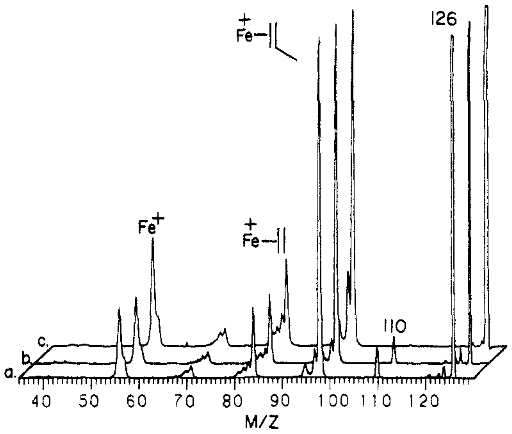
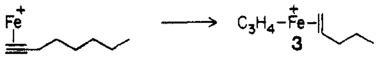


Figure 1. CAD spectra of $FeC_5H_{10}^+$, *m/z* 126, from (a) reaction of Fe^+ with 1-octyne, (b) Fe(1-pentene)$^+$, and (c) reaction of $Fe(CO)_2^+$ with ethylene and propene.

ture. Although Fe(1-pentene)$^+$ rearranges primarily to (propene)Fe(ethylene)$^+$, the CAD spectrum of Fe(1-pentene)$^+$ is not identical with that of the $FeC_5H_{10}^+$ formed by reaction of ethylene and propene with $Fe(CO)_2^+$ (Figure 1c). For example, Fe(1-pentene)$^+$ loses H_2 and CH_4, whereas (propene)Fe(ethylene)$^+$ does not. Thus, a distinction has to be made between Fe(1-pentene)$^+$ and (propene)Fe(ethylene)$^+$. Allylic insertion into C–C bonds and other insertion reactions such as those leading to losses of H_2 and CH_4 from Fe(1-pentene)$^+$ can be viewed as a signature of the structure of the initial olefin complex.

In a similar fashion, 2- and 3-octyne react with Fe^+ and, upon collisional activation, produce minor amounts of $FeC_4H_8^+$ and $FeC_3H_6^+$, respectively (reactions 2 and 3). The CAD spectra of the alkene products from reactions 2 and 3 are consistent with the expected structures. As illustrated above, this can be established by comparing the spectra of $FeC_nH_{2n}^+$ products with those of reference Fe(alkene)$^+$ adducts.[7]

In contrast, $FeC_4H_6^+$, $FeC_5H_8^+$, and $FeC_6H_{10}^+$ are the major products from reactions 2–4 and appear to exist as mixtures of structures on the basis of their CAD spectra. The structures of these product ions are the key to a missing detail in the β-hydrogen abstraction mechanism, i.e., to which site is the β-H atom ultimately transferred?



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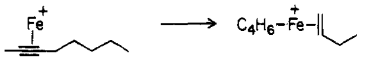

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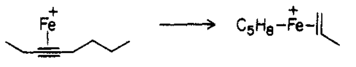
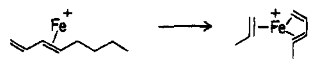


(3)

(4)

The major CAD products from reaction of Fe^+ with the octadiene isomers (Table I) are consistent with insertion of Fe^+ into the allylic C-C bond. For example, Fe(1,3-octadiene)$^+$ and Fe(1,7-octadiene)$^+$ species rearrange to pentadiene–propene complexes (reactions 5 and 6). Although Fe(2,4-octadiene)$^+$ rearranges to a hexadiene–ethylene complex (Table I), partial isomerization to Fe(1,3-octadiene)$^+$ appears to be facile, since $FeC_5H_8^+$ (100%) is more abundant than the expected $FeC_6H_{10}^+$ (51%). This is the only example reported here where isomerization occurs more readily than allylic insertion and subsequent rearrangement.



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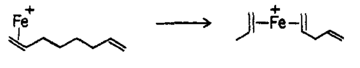

(6)

Table II. Abundance Ratio of FeC_2H^+ (*m/z* 81) to $FeCH_2^+$ (*m/z* 70) from $FeC_3H_4^+$

complex	81/70[a]	complex	81/70[a]
allene	2.0 ± 0.1	1,2-pentadiene	3.4 ± 0.1
1-pentyne	2.4 ± 0.1	1,5-hexadiene	3.5 ± 0.2
1-hexyne	2.5 ± 0.2	1,2-hexadiene	3.8 ± 0.2
1-heptyne	2.8 ± 0.2	propyne	4.1 ± 0.2
1-octyne	3.0 ± 0.2	1,3-hexadiene	4.2 ± 0.3

[a] CAD data acquired over a mass range of *m/z* 65–85.

In order to determine unequivocally the nature and origin of the $FeC_nH_{2n-2}^+$ products (reactions 1–6), it is necessary to examine the behavior of small alkynes and dienes when complexed to Fe^+. Given the probability of H transfer to either the carbon bonded to Fe^+ (C_1) or to C_3, both 1,2-diene (Scheme IIa) and 2-alkyne (Scheme IIb) products are expected from reactions of Fe^+ with the octyne isomers. If Fe(2-alkyne)$^+$ and Fe(1,2-diene)$^+$ complexes can be distinguished from each other and from other isomeric forms, such as 1-alkynes or 1,3-dienes, then the terminus of the migrating H atom can be determined without isotopic labeling. The CAD spectra of alkyne (propyne to heptyne) and diene (allene to hexadiene) adducts are presented next and interpreted so that they may serve as references for determining the structures of the $FeC_nH_{2n-2}^+$ products from reactions 1–6.

Reactions of Fe^+ with C_3H_4–C_7H_{12}

$FeC_3H_4^+$. Propyne and allene do not rearrange extensively when complexed to Fe^+. Instead, they primarily dissociate upon CA by loss of C_3H_4 to give back Fe^+ as the most abundant fragment. Nevertheless, reproducible differences in the abundances of FeC_2H^+ (*m/z* 81) and $FeCH_2^+$ (*m/z* 70) do exist and permit isomeric adducts to be distinguished (Table II). Since the FeC_2H^+ and $FeCH_2^+$ fragments correspond to losses of methyl and C_2H_2 radicals, it seems likely that decomposition occurs via direct cleavage of the C–C bonds of the complexed C_3H_4 ligand. Such fragmentations may not involve metal ion insertions but result from rupture of C–C bonds by the high-energy collision process. In fact, allene and propyne radical cations also fragment by cleavage of the double or carbon–carbon single bond, respectively.[12]

$FeC_4H_6^+$. Although Fe^+ is the dominant fragment (100% RA), the abundances of other fragment ions allow the $FeC_4H_6^+$ structures to be differentiated. Characteristic high-energy fragments are reasonably $FeC_2H_3^+$ from Fe(1,3-butadiene)$^+$ and FeC_2H^+ from Fe(1-butyne)$^+$. The ratio of abundances of $FeC_2H_3^+$ (*m/z* 83) and FeC_2H^+ (*m/z* 81) is particularly indicative of the $FeC_4H_6^+$ structure (Table III). 1-Butyne, 2-butyne, and 1,2-butadiene adducts also lose $\cdot CH_3$ and CH_4 to form $FeC_3H_3^+$ and $FeC_3H_2^+$. Fe(2-butyne)$^+$ gives $FeC_3H_3^+$ more readily than do Fe(1-butyne)$^+$ and Fe(1,3-butadiene)$^+$.

The two important $FeC_4H_6^+$ structures to be differentiated are Fe(2-butyne)$^+$ and Fe(1,2-butadiene)$^+$. Fe(2-butyne)$^+$ fragments to give $FeC_2H_3^+$ (*m/z* 83) and FeC_2H^+ (*m/z* 81). Neither of these products can be formed directly from fragmentation of Fe(2-butyne)$^+$. Since the *m/z* 83/81 abundance ratio of Fe(2-butyne)$^+$ is intermediate between those of Fe(1-butyne)$^+$ and Fe(1,3-butadiene)$^+$, it is pos-

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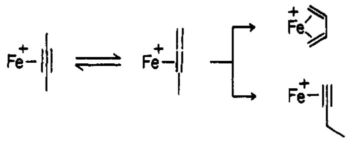
[12] Wagner, W.; Levson, K.; Lifshitz, C. *Org. Mass Spectrom.* **1980**, *15*, 271.

Table III. Abundance Ratio of $FeC_2H_3^+$ (*m/z* 83) to FeC_2H^+ (*m/z* 81) from $FeC_4H_6^+$

complex	83/81	complex	83/81
1,3-butadiene	1.7 ± 0.1	1,2-hexadiene	1.2
2,6-octadiene	1.7[a]	2-octyne	1.3
cyclooctene	1.7	2-heptyne	1.2
1-heptyne	1.7	2-hexyne	1.3
2-butyne	1.2 ± 0.1	3-hexyne	1.3
1,2-butadiene	1.2 ± 0.1	1-butyne	0.6 ± 0.03

[a] Single determination from full CAD spectrum.

sible that the Fe(2-butyne)$^+$ isomerizes to 1-butyne and 1,3-butadiene complexes. Furthermore, Fe(2-butyne)$^+$ probably isomerizes via a 1,2-butadiene intermediate (reaction 7) because the *m/z* 83/81 abundance ratios of Fe(2-butyne)$^+$ and Fe(1,2-butadiene)$^+$ are identical (Table III). Presumably, a 1,3-shift of a hydrogen atom takes place via the metal ion to give Fe(1,2-butadiene)$^+$. A second 1,3-H shift would produce 1-butyne or 1,3-butadiene complexed to Fe$^+$.

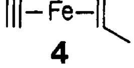

(7)

$FeC_5H_8^+$. Quite unlike $FeC_3H_4^+$ and $FeC_4H_6^+$ structures, C_5H_8 complexes, on the basis of Fe$^+$ abundance (<100%, see Table IV), rearrange preferentially instead of dissociating. For example, Fe(1-pentyne)$^+$ rearranges via propargylic insertion. Upon collisional activation, $FeC_3H_4^+$ (100%) and $FeC_2H_4^+$ (21%) are produced. The $FeC_3H_4^+$ is probably Fe(allene)$^+$ because the abundance ratio of *m/z* 81/70 from the $FeC_3H_4^+$ product (Table II) is similar to that of Fe(allene)$^+$.

On the basis of their CAD spectra, Fe(1,2-pentadiene)$^+$ can be readily distinguished from Fe(2-pentyne)$^+$. However, we must still confront the question of whether Fe(1,2-pentadiene)$^+$ has a unique structure. The spectrum of Fe(1,2-pentadiene)$^+$ is not a linear combination of CAD spectra of the 1- and 2-pentyne Fe$^+$ adducts. $FeC_3H_4^+$ from reaction of 1,2-pentadiene with Fe$^+$ appears to be a mixture of Fe(propyne)$^+$ and Fe(allene)$^+$ (Table II). Since isomerization to a mixture of Fe(pentyne)$^+$ isomers is unlikely, Fe(1,2-pentadiene)$^+$ must have a unique structure. Reaction of Fe$^+$ with Fe(1,2-pentadiene)$^+$ may proceed principally by vinylic insertion and to a lesser extent by allylic insertion.

The CAD spectra of Fe(2-pentyne)$^+$ and Fe(2,3-pentadiene)$^+$ are nearly identical (Table IV), which is interpreted to indicate that a 1,3-H shift via the metal ion may be facile. Furthermore, the major CAD fragments are in accord with subsequent isomerization to a 1,3- or 1,4-pentadiene complex followed by decomposition to give $FeC_2H_2^+$ (100%) and $FeC_3H_6^+$ (~60%). Recall that the spectrum of Fe(2-butyne)$^+$ may also be consistent with triple-bond isomerization (reaction 7).

The adducts of Fe$^+$ with 1,3- and 1,4-pentadiene rearrange primarily to (propene)Fe(acetylene)$^+$ (4). Since there are no allylic C–C bonds, insertion into a vinylic bond must occur. Vinylic insertions appear to be important only when allylic insertion or isomerization prior to allylic insertion is not possible. The 1,3- and 1,4-pentadiene complexes with Fe$^+$ can be distinguished from each other on the basis of abundance ratios of $FeC_3H_6^+$ (*m/z* 98) to $FeC_3H_5^+$ (*m/z* 97) and $FeC_3H_5^+$ to $FeC_3H_4^+$ (*m/z* 96) (see Table V).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The structure of Fe(isoprene)$^+$ is clearly different than other $FeC_5H_8^+$ species because the isoprene adduct undergoes a very abundant loss of methane (58%), probably by insertion of Fe$^+$ into the vinylic methyl bond. Alternatively, insertion into the other vinylic C–C bond followed by H atom transfer may produce a propene–acetylene complex, 4, which would dissociate to give $FeC_2H_2^+$ and $FeC_3H_6^+$. In addition to rearrangement, Fe(isoprene)$^+$ dissociates readily to produce Fe$^+$ (100%).

Unlike isomeric $FeC_3H_4^+$ and $FeC_4H_6^+$ which primarily decompose to Fe$^+$, isomeric $FeC_5H_8^+$ species yield highly informative fragment ions upon CA. This is true for a complete set of linear, acyclic C_5H_8 isomers. Except for Fe(2-pentyne)$^+$ and Fe(2,3-pentadiene)$^+$, it is possible to differentiate clearly the structures of all $FeC_5H_8^+$ studied.

$FeC_6H_{10}^+$. Fe(4-octyne)$^+$ should fragment to give either Fe(2-hexyne)$^+$ or Fe(1,2-hexadiene)$^+$. A systematic study of the Fe$^+$ complexes with available C_6H_{10} isomers was conducted to determine whether the various hexyne adducts could be distinguished from hexadienes complexed with Fe$^+$. As expected, Fe(1-hexyne)$^+$ primarily rearranges after propargylic insertion to (propene)Fe(C_3H_4)$^+$ which dissociates to give $FeC_3H_4^+$ (100%) and $FeC_3H_6^+$ (67%) (Table VI). The $FeC_3H_4^+$ product, like that from Fe(1,2-pentadiene)$^+$, is a mixture of Fe(allene)$^+$ and some Fe(propyne)$^+$ (see Table II).

The spectrum of Fe(1,2-hexadiene)$^+$ is clearly different than those of 2-hexyne or other C_6H_{10} complexes. As expected, allylic insertion produces (C_4H_6)Fe(ethylene)$^+$ which dissociates to give $FeC_4H_6^+$ (56%). The $FeC_4H_6^+$ product is either Fe(1,2-butadiene)$^+$ or Fe(2-butyne)$^+$ (Table III). However, the most abundant ion in the CAD spectrum is $FeC_3H_4^+$. The $FeC_3H_4^+$ product has a *m/z* 81/70 abundance ratio that is identical with that of Fe(propyne)$^+$ (Table II). Two possible pathways are likely for the formation of (C_3H_4)Fe(propene)$^+$: a 1,3-H shift and isomerization of the double bond occur to produce either

Table IV. Partial CAD Spectra of $FeC_5H_8^+$

	product ions[a]								
complex	FeC_5H_6	FeC_5H_5	FeC_4H_4	FeC_3H_6	FeC_3H_4	FeC_3H_3	FeC_2H_4	FeC_2H_2	Fe
1-pentyne	1.2	2.1	1.4	2.5	100	10.7	20.7	5.6	23.9
1,2-pentadiene	4.9	8.4	7.8	26.2	100	13.6	5.7	44.4	28.0
3-heptyne	10.5	12.4	13.0	45.2	100	20.2	6.2	76.6	50.3
3-octyne	8.3	10.5	10.9	33.8	100	17.7	6.4	54.8	46.4
3-nonyne	9.2	13.1	11.5	34.7	100	22.6	6.4	59.8	57.2
2-pentyne	14.6	7.3	18.9	55.0	34.1	18.1	2.8	100	61.7
2,3-pentadiene	5.6	11.3	20.4	61.4	33.8	17.5	3.0	100	57.2
1,3-pentadiene	9.1	19.5	4.7	57.6	12.6	13.9		100	60.3
1,4-pentadiene	5.3	12.4	3.1	59.7	10.5	14.7		100	53.3
isoprene	17.6	10.5	58.2	37.5	41.1	22.6	2.9	61.8	100

[a] Full CAD spectra available from authors on request.

Table V. Abundance Ratio of $FeC_3H_6^+$ (*m/z* 98) and $FeC_3H_4^+$ (*m/z* 96) to $FeC_3H_5^+$ (*m/z* 97) from $FeC_5H_8^+$

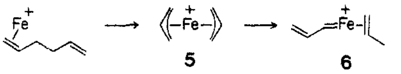
complex	98/97	97/96
1,3-pentadiene	6.1 ± 0.5	0.8 ± 0.6
1,3-octadiene	4.6	0.6[a]
2,4-octadiene	3.6	0.8
1,4-pentadiene	3.1 ± 0.1	1.8 ± 0.1
1,7-octadiene	2.5	2.1
cyclooctene	2.0	2.1

[a] Single determination from full CAD spectrum.

a hexyne or 1,3-hexadiene ligand or Fe^+ inserts into the vinylic C–C bond. Since the spectrum of Fe(1,2-hexadiene)$^+$ is unique and is not a linear combination of any other two $FeC_6H_{10}^+$ spectra, isomerization is ruled out. Allene moieties appear to react differently with Fe^+ than dienes where each double bond reacts with the metal ion as if it were isolated. Both 1,2-pentadiene and 1,2-hexadiene complexes give products that most likely result from a vinylic insertion. In fact, one may view this insertion as vinylic to the 2,3 bond or allylic to the 1,2 bond.

In contrast to Fe(1-hexyne)$^+$, the 2- and 3-hexyne complexes dissociate to form $FeC_4H_6^+$ (100%). The abundance ratios of *m/z* 83/81 produced by collisionally activating the $FeC_4H_6^+$ products (Table III) are identical to those of Fe(2-butyne)$^+$ and Fe(1,2-butadiene)$^+$. The spectrum of Fe(2-hexyne)$^+$ is consistent with rearrangement to (C_4H_6)Fe(ethylene)$^+$. Since β-H transfer is not possible after propargylic insertion of Fe^+ into 3-hexyne, an isomerization is necessary so that the observed products can be formed. This is also true for 2-pentyne and 2-butyne complexes. A second 1,3-H shift may produce a 2-hexyne or hexadiene complex which would dissociate to yield $FeC_4H_6^+$ and $FeC_3H_4^+$.

The various $FeC_6H_{10}^+$ species originating from isomeric hexadienes dissociate by loss of propene to give $FeC_3H_4^+$ (100% RA). Since the major features of their CAD spectra are virtually identical, hexadiene adducts rearrange via a common intermediate, possibly **5** (reaction 8). Rearrangement of (π-allyl)$_2$Fe$^+$ (**5**) to a C_3H_4–propene complex must involve transfer of a H atom from one π-allyl group to the other. Although the $FeC_3H_4^+$ product from reaction of 1,5-hexadiene with Fe^+ has an *m/z* 81/70 abundance ratio which is approaching that of Fe(propyne)$^+$ (Table II), formation of Fe(propyne)$^+$ requires several vinylic H atom shifts. A more efficient mechanism involving a carbene species, **6**, formed by transfer of a single vinylic hydrogen, is chemically more attractive. If the carbene species is formed, then Fe(propyne)$^+$ and the $FeC_3H_4^+$ from **6** must have distinguishable abundance ratios.



(8)

$FeC_7H_{12}^+$. The CAD spectra of the $FeC_7H_{12}^+$ investigated here (Table VII) are consistent with rearrangement via propargylic insertion. Fe(1-heptyne)$^+$ rearranges to (C_3H_4)Fe(butene)$^+$ which decomposes to give $FeC_4H_8^+$ (100%) and $FeC_3H_4^+$ (49%). Subsequent rearrangement of the $FeC_4H_8^+$ and loss of H_2 produces $FeC_4H_6^+$ (99.8%). As expected, the CAD spectrum of the $FeC_4H_8^+$ is identical with that of Fe(butene)$^+$,[13] and the abundance ratio of *m/z* 83/81 from the $FeC_4H_6^+$ product is the same as that of Fe(1,3-butadiene)$^+$ (Table III). Fe(2-heptyne)$^+$ rearranges to (propene)Fe$(C_4H_6)^+$, and Fe(3-heptyne)$^+$ rearranges to (C_5H_8)Fe(ethylene)$^+$, as expected.

Determination of Mechanism

Structure of Products from Reactions of Fe^+ and Octynes. Adducts of Fe^+ and octynes rearrange to $(C_nH_{2n-2})Fe(C_nH_{2n})^+$ (reactions 1–4). The structures of the $FeC_nH_{2n-2}^+$ and $FeC_nH_{2n}^+$ species may be investigated by collisionally activating those ions formed by unimolecular decompositions in the CI source. We showed earlier that source-formed product ions have the same structures as those produced by collisional activation of the Fe(olefin)$^+$.[7] The structures of product ions from reactions of Fe^+ and octynes will now be assigned by comparing their CAD spectra with the reference spectra of $FeC_3H_4^+$, $FeC_4H_6^+$, $FeC_5H_8^+$, and $FeC_6H_{10}^+$.

$FeC_3H_4^+$ from Fe(1-octyne)$^+$ (reaction 1) can be assigned qualitatively as a 1:1 mixture of Fe(allene)$^+$ and Fe(propyne)$^+$ (Table II). It must be emphasized that the method of determining mixtures of $FeC_3H_4^+$ structures is not as reliable as calculating linear combinations of CAD spectra, since mixtures are detected only as small, although reproducible, changes in the ratio of two high-energy fragment ions. Nevertheless, the conclusion that the $FeC_3H_4^+$ from Fe(1-octyne)$^+$ occurs as a mixture is strengthened since Fe^+ also reacts with 1-hexyne and 1-heptyne to give mixtures of $FeC_3H_4^+$ structures.

$FeC_4H_6^+$ from Fe(2-octyne)$^+$ (reaction 2) is Fe(2-butyne)$^+$ and/or Fe(1,2-butadiene)$^+$ (Table III), and not any other linear $FeC_4H_6^+$ structure. Since the CAD spectra of Fe(2-butyne)$^+$ and Fe(1,2-butadiene)$^+$ are identical, we cannot determine the relative contribution of each to the $FeC_4H_6^+$ spectrum. Reactions of Fe^+ with 2-hexyne and 2-heptyne also produce Fe(2-butyne)$^+$ or Fe(1,2-butadiene)$^+$.

As mentioned above, $FeC_5H_8^+$ from Fe(3-octyne)$^+$ (reaction 3) exists as a mixture of structures. Its CAD spectrum is best modeled as a linear combination of the spectra of Fe(1,2-pentadiene)$^+$ (75%) and Fe(2-pentyne)$^+$ (25%). Although Fe(2-pentyne)$^+$ and Fe(2,3-pentadiene)$^+$ have nearly identical CAD spectra, formation of a 2,3-pentadiene ligand is not likely because this would require both a β-H transfer and a multiple-bond shift. Moreover, the $FeC_5H_8^+$ from Fe(3-heptyne)$^+$ is best viewed as a mixture of Fe(2-pentyne)$^+$ (40%) and Fe(1,2-pentadiene)$^+$ (60%) (Table VIII).

$FeC_6H_{10}^+$ from Fe(4-octyne)$^+$ (reaction 4) appears to be a mixture of Fe(2-hexyne)$^+$ and a Fe(hexadiene)$^+$ (Table VI). In view of the mixtures of 1,2-diene and 2-alkyne complexes identified above, one would expect these $FeC_6H_{10}^+$ products to exist as a mixture of 2-hexyne and 1,2-hexadiene complexed with Fe^+. Indeed, the CAD spectrum of the $FeC_6H_{10}^+$ product is best modeled as a mixture of Fe(1,2-hexadiene)$^+$ (60%) and Fe(2-hexyne)$^+$ (40%).

Mechanistic Implications. On the basis of structural studies of $FeC_nH_{2n-2}^+$ formed by propargylic insertion, we are able to show that a mixture of 2-alkyne and 1,2-diene complexes are formed from decompositions of the various octyne isomers complexed to Fe^+. The mixtures of $FeC_nH_{2n-2}^+$ structures result from transfer of a H atom primarily to the first carbon atom (C_1) and to a lesser extent to C_3 of the alkyne moiety, **2**, to give either a 1,2-diene or a 2-alkyne complex, respectively (Scheme II).

Further evidence is provided by obtaining the CAD spectrum of $FeC_5H_8^+$ from reaction of Fe^+ and 3-nonyne (Table V). The 3-nonyne system was chosen because the structure determination of $FeC_5H_8^+$ products is nearly unequivocal. The $FeC_5H_8^+$ exists as a mixture of 66% Fe(1,2-pentadiene)$^+$ and 34% Fe(2-pentyne)$^+$ (Table VIII),

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[13] Larsen, B.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 1912–1922.

Table VI. Partial CAD Spectra of $FeC_6H_{10}^+$

complex	product ions[a]							
	FeC_6H_8	FeC_5H_6	FeC_4H_8	FeC_4H_6	FeC_3H_6	FeC_3H_4	FeC_2H_3	Fe
1-hexyne	11.1	1.0	2.7	16.1	66.5	100	3.5	30.1
1,2-hexadiene	18.2	1.9	5.7	55.7	9.3	100	4.6	21.4
1,3-hexadiene	21.1	2.3	10.4	22.7	6.3	100	7.4	24.4
2,4-hexadiene	21.0	2.9	11.0	22.9	6.5	100	7.4	25.8
1,4-hexadiene	12.9	1.6	10.0	19.2	6.6	100	9.0	25.6
1,5-hexadiene	16.3	2.3	15.0	31.4	14.9	100	17.0	43.9
1,4-octadiene	19.5	4.2	16.9	34.7	9.8	100	15.3	45.5
2,4-octadiene	26.2	3.4	13.6	27.6	7.3	100	9.9	36.0
2-hexyne	2.1	1.1	1.0	100	0.7	8.3	4.0	13.5
3-hexyne	16.3	6.7	6.8	100	4.0	58.5	4.8	20.1
4-octyne	13.5	2.8	4.3	100	6.1	61.3	5.9	31.5
cyclooctene	4.3	0.4	0.7	100	0.8	6.2	7.6	15.3

[a] Full CAD spectra available from authors on request.

Table VII. Partial CAD Spectra of $FeC_7H_{12}^+$

complex	product ions[a]							
	FeC_7H_{10}	FeC_6H_8	FeC_5H_8	FeC_4H_8	FeC_4H_6	FeC_3H_6	FeC_3H_4	Fe
1-heptyne	25.4	4.7	25.3	100	99.8	3.9	48.7	32.5
2-heptyne	9.2	1.4	18.5		100	10.1	5.3	18.3
5-decyne	23.7	5.8	39.7	10.8	100	7.9	38.0	20.6
3-heptyne	2.7	2.8	100	0.4	8.6	2.6	8.0	7.6

[a] Full CAD spectra available from authors on request.

Table VIII. Structures of Products Formed by Rearrangement of Alkene and Alkyne Adducts

	$FeC_nH_{2n-2}^+$	
$Fe(alkyne)^+$	C1 (%)	C3 (%)
3-octyne	2-pentyne (25)	1,2-pentadiene (75)
3-nonyne	2-pentyne (35)	1,2-pentadiene (65)
4-octyne	2-hexyne (40)	1,2-hexadiene (60)
3-heptyne	2-pentyne (40)	1,2-pentadiene (60)
	$FeC_nH_{2n}^+$	
$Fe(alkene)^+$	C1 (%)	C3 (%)
3-octene	2-pentene (55)	1-pentene (45)
5-decene	2-heptene (65)	1-heptene (35)
4-octene	2-hexene (70)	1-hexene (30)

in good agreement with the product compositions from $Fe(3\text{-heptyne})^+$ and $Fe(3\text{-octyne})^+$. Thus, all available evidence is consistent with formation of the products generalized in Scheme II.

As a final test of mechanism, $Fe(1\text{-decyne})^+$ and $Fe(5\text{-decyne})^+$ were investigated (Figure 2). If the mechanism outlined in Scheme II is correct, one would predict that $FeC_7H_{14}^+$ formed from reaction of Fe^+ and 1-decyne is $Fe(1\text{-heptene})^+$. Indeed, the spectrum of the $FeC_7H_{14}^+$ is identical with that of $Fe(1\text{-heptene})^+$.[9] The spectrum of the $FeC_7H_{12}^+$ from $Fe(5\text{-decyne})^+$ is similar to, but not identical with that of $Fe(2\text{-heptyne})^+$ (Table VII), and dissimilar to the other $FeC_7H_{12}^+$ spectra. By analogy with the $FeC_5H_8^+$ and $FeC_6H_{10}^+$ products, the $FeC_7H_{12}^+$ is assigned to be a mixture of 1,2-heptadiene and 2-heptyne complexes. Although quantitative modeling requires the availability of all reference diene and alkyne isomers, the qualitative features of the $Fe(allene)^+$ CAD spectrum can be predicted to be similar to that of the corresponding $Fe(2\text{-alkyne})^+$ adduct.

Structure of Products from Reactions of Fe^+ with Octadienes and Cyclooctene. In contrast to the mixtures of 1,2-diene and 2-alkyne complexes from $Fe(octynes)^+$, the $FeC_nH_{2n-2}^+$ produced by reaction of Fe^+ with octadienes and cyclooctene appear to exist as 1,3- or 1,4-dienes complexed with Fe^+. For example, Fe^+ reacts with 2,6-octadiene and cyclooctene to produce $FeC_4H_6^+$ species which decompose to give *m/z* 83/81 abundance ratios identical with that of $Fe(1,3\text{-butadiene})^+$ (Table III). The $Fe(1,3\text{-butadiene})^+$ products are clearly different than the $FeC_4H_6^+$ produced from reaction of Fe^+ with 2-octyne (reaction 2).

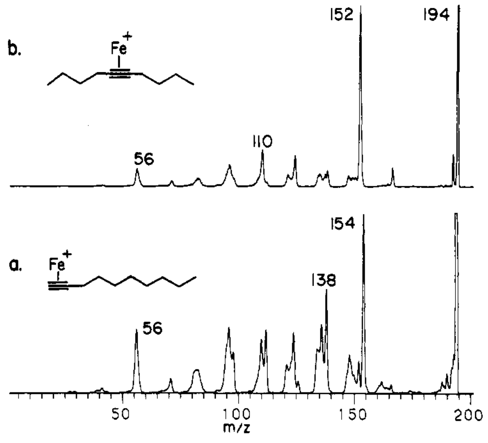


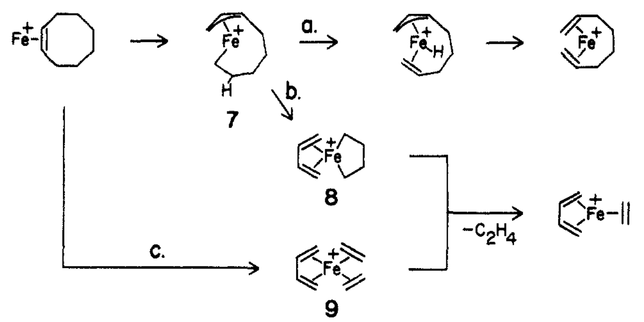
Figure 2. CAD spectra of $FeC_{10}H_{18}^+$, *m/z* 194, from (a) $Fe(1\text{-decyne})^+$ and (b) $Fe(5\text{-decyne})^+$.

$FeC_5H_8^+$ products from reactions of various octadienes and cyclooctene with Fe^+ are $Fe(1,3\text{-pentadiene})^+$ or $Fe(1,4\text{-pentadiene})^+$ (Table V), in accord with the allylic insertion mechanism. The $FeC_5H_8^+$ from reaction of Fe^+ and 2,4-octadiene is a mixture of $Fe(1,3\text{-pentadiene})^+$ and $Fe(1,4\text{-pentadiene})^+$. Note that the *m/z* 97/96 abundance ratio is similar to that of $Fe(1,3\text{-pentadiene})^+$ whereas the *m/z* 98/97 ratio is closer to that of $Fe(1,4\text{-pentadiene})^+$.

The $FeC_6H_{10}^+$ products from reaction of Fe^+ with 1,4- and 2,4-octadiene are clearly hexadiene and not hexyne complexes (Table VI). Although the spectrum of $FeC_6H_{10}^+$ from $Fe(cyclooctene)^+$ is very similar to that of $Fe(2\text{-hexyne})^+$, comparison of the spectrum of $FeC_4H_6^+$ produced stepwise from $Fe(cyclooctene)^+$ with those of reference $FeC_4H_6^+$ reveals that the structures are different (Table III). Whereas $Fe(2\text{-hexyne})^+$ rearranges to $(2\text{-butyne})Fe(ethylene)^+$, loss of ethylene from $Fe(cyclooctene)^+$ produces $(1,3\text{-butadiene})Fe(ethylene)^+$.

Mechanistic Implications. In general, the structures of ions produced by reaction of Fe^+ and octadienes are consistent with rearrangement by the mechanism outlined

Scheme III



in Scheme Ia. The reactions of Fe^+ with compounds containing two double bonds proceed in identical fashion to reactions of Fe^+ and alkenes. The major CAD fragment ion from Fe(cyclooctene)$^+$, $FeC_5H_8^+$, may be rationalized by invoking an initial insertion of Fe^+ into the allylic bond to form **7** (Scheme III). Then, a β-H atom is abstracted by Fe^+ and ultimately transferred to give Fe(1,7-octadiene)$^+$ which rearranges to a propene–1,4-pentadiene complex (reaction 6).

A second pathway is required to explain losses of ethylene (25%) and C_4H_8 (41%), because these fragment ions are produced more readily from Fe(cyclooctene)$^+$ than from Fe(1,7-octadiene)$^+$. One possible mechanism would involve a metallacycle intermediate, **8** (Scheme IIIb). A second allylic insertion would directly convert **7** to a metallacyclopentane–butadiene ion, **8**. Another possibility is an electrocyclic reaction to produce **9**, which should lose one and two molecules of ethylene readily (Scheme IIIc). The loss of ethylene and C_4H_8 can be explained by either mechanism. Models of species **8** and **9** were prepared by reacting $FeC_4H_6(CO)_x^+$ from ionized 1,3-butadiene iron tricarbonyl with cyclobutane and ethylene, respectively. If the Fe(cyclooctene)$^+$ spectrum is assumed to be a linear combination of Fe(1,7-octadiene)$^+$ and either **8** or **9**, then the best approximation is obtained with 90% Fe(1,7-octadiene)$^+$ and 10% of **9**. This result suggests that allylic insertion competes favorably with a metal ion catalyzed electrocyclic reaction.

In prior work, olefins complexed to Fe^+ were reported to rearrange primarily by H atom transfer to C_1 of the π-allyl intermediate **1** to give predominantly a Fe(2-alkene)$^+$.[2,7] Since β-H transfer to the propargyl moiety **2** gives a mixture of the two possible products, one would expect that β-H transfer from **1** (Scheme Ib) to the π-allyl fragment produces both 2-alkene and 1-alkene ligands. Indeed, reexamination of the CAD spectra of several Fe(2-alkene)$^+$ species produced by allylic insertion reveals that a measurable amount of Fe(1-alkene)$^+$ is also produced. For example, Fe(4-octene)$^+$ decomposes to give a mixture of Fe(2-hexene)$^+$ (70%) and Fe(1-hexene)$^+$ (30%) (Table VIII). This subtle point of the allylic insertion in olefins was overlooked until now because most structural determinations have been of the $FeC_nH_{2n}^+$ which contains the alkyl fragment from which the β-H atom is abstracted. These products are exclusively Fe(1-alkene)$^+$ complexes.

Effects of Internal Energy. The conclusions of this study are based on the premise that changes in relative abundances of CAD fragment ions reflect ion structures and not internal energy effects due to differences in the ions' origin [from $FeCO^+$, $Fe(CO)_2^+$, etc.]. Kim and McLafferty demonstrated that *high-energy* CAD spectra are nearly insensitive to internal energies of the selected ions.[14] In order to test whether this insensitivity applies to decompositions of Fe(alkyne)$^+$ complexes, we attempted to vary the internal energy of Fe(1-hexyne)$^+$ by using the consecutive reaction technique.[7,15] For example, another route to $FeC_6H_{10}^+$ species is a consecutive reaction path such as reaction 9.

$$Fe(C_6H_{10})_2^+ \xrightarrow[\text{CA}]{} FeC_6H_{10}^+ \xrightarrow[\text{CA}]{} \text{products} \qquad (9)$$

The CAD spectra of $FeC_6H_{10}^+$ species formed by collisional activation of $Fe(C_6H_{10})_2^+$, $Fe(C_6H_{10})(CO)^+$, and $Fe(C_6H_{10})(CO)_2^+$ can be compared with the spectrum of Fe(1-hexyne)$^+$ reported in Table VI. No change was found for Fe(1-hexyne)$^+$ formed from the $Fe(C_6H_{10})_2^+$ dimer compared to Fe(1-hexyne)$^+$ formed in the ion source. The spectra of the $FeC_6H_{10}^+$ formed by loss of one or two carbonyl ligands are identical with each other but are slightly different from the Fe(1-hexyne)$^+$ spectrum. For example, the relative abundances of major fragment ions ($FeC_3H_4^+$ and $FeC_3H_6^+$) remain unchanged, while the abundances of minor fragments ($FeC_4H_6^+$, FeC_2H^+, and Fe^+) increase by a factor of 1.2–2.0.

If internal energy effects are an issue, then processes with low critical energies, such as the propargylic insertion resulting in the formation of $FeC_3H_4^+$, will be dependent on internal energy.[6] Indeed, this may be what is observed for $FeC_6H_{10}^+$ species formed from precursors containing carbonyl ligands. The differences in the $FeC_6H_{10}^+$ spectra are interpreted in terms of higher internal energy for complexes formed by collisional activation of $Fe(C_6H_{10})CO^+$ and $Fe(C_6H_{10})(CO)_2^+$ precursors. The abundance of low-energy fragments decreases relative to the sum of all collision-induced fragment ions. However, the observed increases in the relative abundance of higher energy fragments involving nonpropargylic insertions or other decomposition pathways are not sufficient to alter the assignment of ion structures. A possible explanation for the variations in the spectra of $FeC_6H_{10}^+$ from carbonyl precursors is that in the loss of a small neutral fragment such as CO, excess internal energy is not effectively partitioned away from the metal ion complex. In contrast, loss of neutrals (e.g., C_6H_{10}) with a comparable number of degrees of freedom as the product ion more effectively removes excess internal energy from the ion.

As discussed earlier, the CAD spectra of Fe(alkene)$^+$ species formed as products from the reaction of Fe^+ with larger alkenes and alkynes are the same as those of Fe(alkene)$^+$ adducts formed directly. For example, $FeC_5H_{10}^+$ from reaction of Fe^+ and 1-octene or 1-octyne in the ion source has a spectrum that is identical with that of Fe(1-pentene)$^+$ (Figure 1). Since ions formed in the source should have less internal energy due to collisional stabilization than ions formed by high-energy collisional activation, it is reasonable that there are no internal energy effects for the Fe(alkene)$^+$ products formed in the ion source. Thus, all available evidence strongly suggests that the composite CAD spectra identified in this work result from mixtures of ion structures.

Summary and Conclusions

Whenever possible, Fe^+ oxidatively adds to the propargylic or allylic C–C bond of alkynes, dienes, and alkenes. Subsequently, a β-H atom is abstracted by the metal ion and transferred to the π-allyl or propargyl moiety to produce two unsaturated ligands bound to the metal ion. For alkyne complexes, the H atom is transferred primarily to C_3 of the propargyl fragment, **2**, to produce a 1,2-diene

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[14] Kim, M. S.; Mclafferty, F. W. *J. Am. Chem. Soc.* **1978**, *100*, 3279–3282.

[15] Burinsky, D. J.; Cooks, R. G.; Chess, E. K.; Gross, M. L. *Anal. Chem.* **1982**, *54*, 295–299.

ligand (Scheme IIa) and to a lesser extent to C_1 of **2** to produce a 2-alkyne ligand (Scheme IIb). For diene and alkene adducts, the H atom is transferred predominantly to C_1 of the π-allyl group (**1**, Scheme Ia). Alkene complexes also rearrange to a lesser extent by H transfer to C_1 of the π-allyl fragment (Scheme Ib). Allene complexes probably rearrange after vinylic and allylic insertions.

If no β-H is available after allylic insertion, several higher energy pathways become accessible. The iron ion probably causes isomerization of the multiple bond via a 1,3-H shift so that upon allylic insertion, β-H abstraction is possible or inserts into vinylic bonds when no alternative pathways exist.

The abundance of Fe^+ relative to other fragment ions formed upon collisional activation is a measure of the propensity of the metal ion to add oxidatively to C–C bonds. A relatively low abundance of Fe^+ (50% or less) is indicative of the presence of a highly reactive propargylic or allylic bond. If the allylic bond is deactivated because it is also a vinylic or terminal C–C bond and isomerization is not possible, then less oxidative addition occurs as signaled by a relative abundance of Fe^+ between ca. 50 and 100%. Dienes or alkynes with vinylic bonds and a limited number of carbon atoms are relatively inert toward oxidative addition, and Fe^+ becomes the most abundant CAD product (100%). The other CAD products obtained from these stable adducts probably result from high-energy processes involving direct decompositions of the organic ligand.

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Registry No. Fe^+, 14067-02-8; $FeCO^+$, 35038-14-3; $Fe(CO)_2{}^+$, 35038-15-4; 1,4-octadiene, 5675-25-2; 4-octyne, 1942-45-6; 1-octyne, 629-05-0; 1,3-octadiene, 1002-33-1; 1,7-octadiene, 3710-30-3; 2,4-octadiene, 13643-08-8; 3-octyne, 15232-76-5; cyclooctene, 931-88-4; 2,6-octadiene, 4974-27-0; 2-octyne, 2809-67-8; allene, 463-49-0; 1-pentyne, 627-19-0; 1-hexyne, 693-02-7; 1-heptyne, 628-71-7; 1,2-pentadiene, 591-95-7; 1,5-hexadiene, 592-42-7; 1,2-hexadiene, 592-44-9; propyne, 74-99-7; 1,3-hexadiene, 592-48-3; 1,3-butadiene, 106-99-0; 2-butyne, 503-17-3; 1,2-butadiene, 590-19-2; 2-heptyne, 1119-65-9; 2-hexyne, 764-35-2; 3-hexyne, 928-49-4; 1-butyne, 107-00-6; 3-heptyne, 2586-89-2; 3-nonyne, 20184-89-8; 2-pentyne, 627-21-4; 2,3-pentadiene, 591-96-8; 1,3-pentadiene, 504-60-9; 1,4-pentadiene, 591-93-5; isoprene, 78-79-5; 1,4-hexadiene, 592-45-0; 5-decyne, 1942-46-7.

Proposed Mechanism for Nucleophilic Attack in $[(\eta\text{-}C_5H_5)Re(NO)(CO)(PPh_3)]^+$

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A molecular orbital analysis of $[(\eta\text{-}C_5H_5)Re(NO)(CO)(PPh_3)]^+$ and its reduction to $[(\eta\text{-}C_5H_5)Re(NO)(CHO)(PPh_3)]$ shows that the site of nucleophilic attack is not the one suggested by the product. It is proposed that the nitrosyl ligand is the energetically favored position for attack, which leads to formation of $[(\eta\text{-}C_5H_5)Re(NHO)(CO)(PPh_3)]$. We further contend that this kinetic product is thermodynamically unstable and it rearranges to form the formyl complex.

Introduction

In the past few years there has been a considerable amount of work done on the synthesis, characterization, and reactivity of a variety of pseudotetrahedral organorhenium complexes, Gladysz being one of the principal investigators.[1-8] In particular, neutral formyls have generated a great deal of interest because of their presumed role in catalytic processes.[9,10] The rhenium formyl $[(\eta\text{-}C_5H_5)Re(CHO)(NO)(PPh_3)]$ has been investigated in more than one laboratory[11-13] and especially by Gladysz, who has found two different routes to synthesize it from its precursor $[(\eta\text{-}C_5H_5)Re(NO)(CO)(PPh_3)]^+$.[14] This carbonyl cation has also been used by Gladysz as the starting material in a series of reactions involving alternating nucleophilic and electrophilic attacks.[14]

Both of these studies are interesting from a theoretical point of view since the chemistry involved is relatively straightforward and yet presents some challenging questions. This paper will be devoted to an analysis of the

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[1] Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865.

[2] Merrifield, J. H.; Gladysz, J. A. *Organometallics* **1983**, *2*, 782.

[3] Kiel, W. A.; Buhro, W. E.; Gladysz, J. A. *Organometallics* **1984**, *3*, 879.

[4] Buhro, W. E.; Wong, A.; Merrifield, J. H.; Lin, G.-Y.; Constable, A. G.; Gladysz, J. A. *Organometallics* **1983**, *2*, 1852.

[5] Merrifield, J. H.; Fernandez, J. M.; Buhro, W. E.; Gladysz, J. A. *Inorg. Chem.* **1984**, *23*, 4022.

[6] Merrifield, J. H.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1204.

[7] Nakazawa, H.; Johnson, D. L.; Gladysz, J. A. *Organometallics* **1983**, *2*, 1846.

[8] Kiel, W. A.; Lin, G.-Y.; Bodner, G. S.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 4958.

[9] Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61.

[10] Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479.

[11] Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Rinz, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 1927.

[12] Casey, C. P.; Andrews, M. A.; Rinz, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 741.

[13] Sweet, J. R.; Graham, W. A. G. *J. Organomet. Chem.* **1979**, *173*, C9.

[14] Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.