symmetric and antisymmetric modes, respectively, in going from the liquid to the gas phase. The model in Figure 10 shows that part of the NO_2 group is, in fact, exposed to the ambient, overlying (gas) phase.

Using the values of ϕ_{mz} for the ring modes only in order to avoid complications arising from the perturbed nitro modes, the average orientation of a nitrobenzoate group involves a 60° tilt of the ring plane away from the surface normal with an ~30° twist around the 1,4 ring axis. This is depicted in the model in Figure 10. This model also shows the C=O bonds of the ester groups oriented near parallel to the surface plane. The value of ϕ_{mz} of 67° indicates these bonds are canted, on average, at 23° from the surface plane. Caution must be used in interpreting this angle too quantitatively, however, since the C=O absorption frequencies and line shapes differ somewhat between those calculated and observed (see Figure 5 and Table IV), suggesting that there is some difference in the intermolecular environment of the ester group in the monolayer relative to the bulk crystalline phase.

Summary Conclusions

It has been shown that a variety of substituted disulfide molecules adsorb from solution onto gold surfaces to form densely packed, stable, and oriented monolayer structures. In all cases, the evidence is consistent with the strong attachment of the S–S bond in high density at the gold with the concurrent formation of an ambient-organic interface with the surface properties determined by the other functional groups of the molecules. The detailed structures of the assemblies involve intra- and intermolecular interactions similar to those of the bulk crystalline phases but with a few interesting differences. The ability to produce these model, multifunctional organic overlayers in a specific and controlled way suggests a number of significant applications to interfacial studies in important areas including electrochemistry, adhesion and wetting, biology, microelectronics, and materials science. These possibilities are now being actively pursued in these and other laboratories and will be described in forthcoming papers.

Acknowledgment. The authors gratefully acknowledge many valuable discussions with Professor George Whitesides and Dr. Barry Troughton during the course of this work. The authors also acknowledge David Hwang and Frank Padden for TEM and SEM analyses, respectively, and M. Green for the X-ray diffraction analyses of the gold substrates.

Registry No. DTT-H, 86023-22-5; DTT-F_p, 85977-44-2; DTT-hexadecanoate, 85995-15-9; DTT-PNBA, 85977-45-3; DTT-OAc, 86022-77-7; DTT-TFA, 85977-46-4; HDDS, 1561-75-7; $(HO_2C(CH_2)_2S)_2$, 1119-62-6; $(HO_2C(CH_2)_{10}S)_2$, 23483-56-9; $(H_2N(CH_2)_2S)_2$, 51-85-4; $(CH_3(CH_2)_{17}S)_2$, 2500-88-1; $(CH_3S)_2$, 624-92-0; $(CH_3(CH_2)_3S)_2$, 629-45-8; $(CH_3(CH_2)_7S)_2$, 822-27-5; $(CH_3(CH_2)_9S)_2$, 10496-18-1; $(CH_2CH(CH_2)_{20}S)_2$, 106712-20-3; Au, 7440-57-5.

On the Mechanism of Fe^+-Induced Hydrogen Migrations in Gaseous Octyne/Iron(I) Complexes

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Abstract: The study of D-labeled isomeric octynes provides a detailed insight into the gas-phase chemistry of this prototypic hydrocarbon with bare Fe^+. The results not only clearly establish that β-hydrogen transfer is indeed involved in many major decomposition routes, thus providing firm experimental evidence for this often invoked reaction, but also serve as evidence for some unprecedented reactions. Among these reactions is a site-specific 1,2-dehydrogenation of $Fe(2\text{-octyne})^+$, which serves as a further example for "remote functionalization" proceeding via metallacycles. Another of these reactions is the loss of ethylene from the $C_{(1)}/C_{(2)}$ of $Fe(4\text{-octyne})^+$, where, if described in terms of the traditional sequence of oxidative addition/β-hydrogen transfer/reductive elimination, the β-hydrogen transfer to the metal ion is not reversible nor does the reaction constitute the rate-determining step of the overall process. More likely is a process in which a metallacycle is involved. Evidence is presented that the metal ion not only inserts into the activated propargylic C–C bond but also inserts into the homopropargylic, to some extent, and even less activated C–C bonds. Ethylene loss from $Fe(4\text{-octyne})^+$ complexes is associated with an isotope effect of $k_H/k_D = 1.1$ per deuterium. The rarely observed β-alkyl migrations are not involved in the gas-phase chemistry of $Fe(\text{octyne})^+$ complexes.

Table I. Structures of Products Formed by Fe^+-Induced Rearrangement of Alkenes and Alkynes

	% products		
$Fe(\text{alkene})^+$	**4**	**5**	branching ratio a:b
3-octene	45	55	0.5
4-octene	30	70	0.4
5-decene	35	65	0.5
	% products		
Fe(alkyne)	**9**	**10**	branching ratio a:b
3-heptyne	60	40	1.5
3-octyne	75	25	3.0
4-octyne	60	40	1.5
3-nonyne	65	35	1.9

The activation of C–H and C–C bonds of hydrocarbons by transition-metal complexes is of fundamental importance in catalysis and has attracted considerable attention.[1] Whereas the direct activation of C–H bonds by an intermolecular process has been observed in solution only recently,[2] the activation of C–C and C–H bonds of hydrocarbons and many functionalized organic compounds by bare metal ions, M^+, in the gas phase has been demonstrated repeatedly during the last decade by using various techniques like ion cyclotron resonance (ICR) mass spectrometry,[3] Fourier transform mass spectrometry (FTMS),[4] ion beam experiments,[5] and collisional activation (CA) mass spectroscopy.[6] From the numerous reports[3-6] of the gas-phase chemistry of transition-metal ions with organic substrates, the sequence involving metal insertion/β-hydrogen shift/competitive ligand loss, suggested for the first time by Allison and Ridge,[3c] is now regarded as a principal route to account for the majority of reductive

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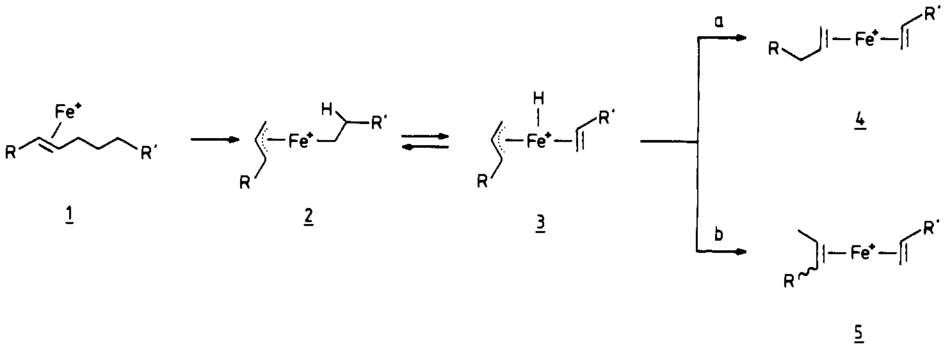
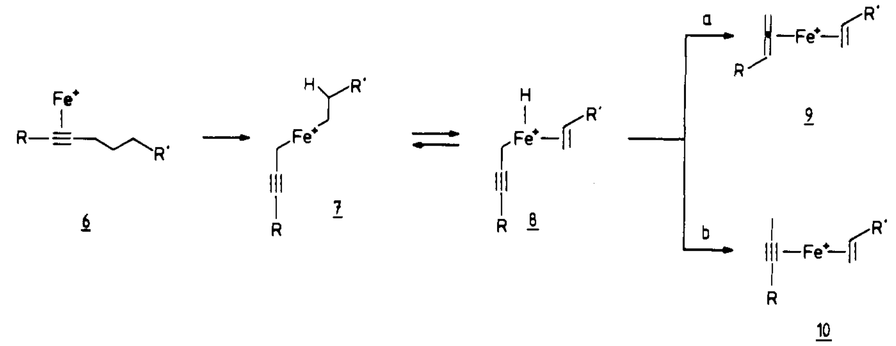
[‡] Nebraska.

Scheme I



Scheme II



elimination product ions, although there is also evidence that the first step in the interaction of the bare metal ion with saturated hydrocarbons involves oxidative addition of a C-H bond to the metal.[5h]

For unsaturated hydrocarbons, like olefins and acetylenes, the reaction commences with complexation of the respective π-bonds

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Table II. Partial CAD Spectra of Labeled Fe(octyne)$^+$ Complexes and Main Products Formed upon CA of $FeC_8H_{14}^{+a}$

	m/z																						
	Fe–C_8				Fe–C_6				Fe–C_5				Fe–C_4					Fe–C_3			
complex	167	166	165	164	141	140	139	138	127	126	125	124	114	113	112	111	110	99	98	97	96
11				17				30		100		43					19		25		31
(5,5-$^2H_2$)-**11**	11	17	6	7		32	3	8	100	27	24	10	<1	3	6	14	9	22		27	14
12				50				15		2		10			17		100				7
(1,1,1-$^2H_3$)-**12**	69	9	12	4	19		4	2	8	4	4	3	4	100	50	25	33		7	7	6
(4,4-$^2H_2$)-**12**		66	8	3		17	3	2		6	4	4	1	5	100	26	30	1			7
(5,5-$^2H_2$)-**12**		87	9	5		17	2	4		8	5	6	22	6	23	28	100				
(6,6-$^2H_2$)-**12**		63	8	7		15	4	5		2	5	8		20	13	100	31				
(7,7-$^2H_2$)-**12**		17	40	6		5	3	15		3	10	6	27	9	21	57	100			4	8
13				13				22				100			1		11		6		14
(7,7-$^2H_2$)-**13**		3	9			6	6	20		4	100	8	<1		3	3	11	5		9	9

^{a}Data are given in % base peak.

by the metal ions, followed by oxidative addition of the allylic or propargylic C–C bonds to the metal ion (Schemes I and II). The rearrangements are completed by β-hydrogen transfer to produce, starting from alkenes, bis(olefin)/metal ion complexes (**4**, **5**), as originally proposed by Beauchamp et al.[5d]

The specificity of the overall reaction is such that an unambiguous location of the double bond in alkenes can be achieved by monitoring the products formed upon collision-induced dissociations of the M(alkene)$^+$ complexes.[6b,c]

Similarly, Peake and Gross[6c,f] were able to locate triple bonds in alkynes by reacting the hydrocarbons with $Fe(CO)_x^+$ ($x = 1,2$) in a chemical ionization source and dissociate the mass selected Fe(hydrocarbon)$^+$ ions by using tandem mass spectrometry methodologies (MS-MS).[7] Moreover, details of the propargylic insertion mechanism could be elucidated by comparing the CA mass spectra of authentic Fe/hydrocarbon ions with those of products formed upon collision-induced dissociations of Fe/octyne$^+$ complexes. From these studies[6c,f] it was concluded that the propargylic C–C bond is oxidatively added to the π-complex/Fe$^+$ (**6** → **7**), followed by a β-hydrogen migration to the metal ions (**7** → **8**). The metal–hydrido complex **8** rearranges further by transferring the hydrogen to the propargyl moiety to produce either a 1,2-diene/alkene (**9**) or a 2-alkyne/alkene metal ion complex **10** (Scheme II). For alkynes, pathway a (transfer of H to the vinylic carbon atom to generate a diene/alkene complex) seems to be favored over path b (migration to the propargylic carbon atom to produce a 2-alkyne ligand).[6f] Typical branching ratios, taken from ref 6f, for the formation of products **4**/**5** and **9**/**10** (Schemes I and II) are given in Table I.

In spite of numerous studies, there are several central, yet unanswered questions concerning the details of the mechanism of interactions of bare metal ions with organic substrates. For example, one question is related to the reversibility of the hydrogen migrations. Whereas it is often suggested that reactions such as **2** ⇄ **3** or **7** ⇄ **8** are reversible, there is also evidence that, for some systems (e.g., *saturated* hydrocarbons[5h]), both reversible and irreversible β-hydrogen transfers take place. Similarly, for many systems studied, the rate-determining step in the sequence of oxidative addition/β-hydrogen transfer/reductive elimination remains clouded. This also holds for the problem of β-alkyl transfer in competition with β-hydrogen transfer, a rarely observed process that does seem to be operative in few cases in solution[8] as well as in the gas phase.[5h]

In this contribution, we focus on these questions for the system Fe$^+$/isomeric octynes[9] by using specifically labeled 1-, 2-, 3-, and 4-octynes which were reacted with $Fe(CO)_x^+$ ($x = 1$, 2) and their collision-induced dissociations recorded with MS-MS methodologies.

Experimental Section

Collision experiments[10] were performed on either a Kratos MS50[11] or a Vacuum Generator ZAB-HF-3F triple sector mass spectrometer.[12] The former instrument has an *EBE* and the latter a *BEB* configuration (*B* magnetic and *E* electric sector). Organometallic ions formed in the CI source were mass selected at a resolution of 3000–10000 (10% valley definition) by using MSI. High kinetic energy ions (8 keV) were then activated by collisions with helium target gas in a collision cell located after the double-focussing MSI, and the CAD spectra (or, in the absence of helium, the spectra due to unimolecular dissociations) of resulting fragment ions were recorded by scanning MSII. The CAD spectra were acquired after the mass selected ion beam was suppressed 50% by using helium collision gas. In a typical experiment, 10–100 scans were signal averaged by using a Data General Nova-4X computer and software written for the Kratos MS50 instrument at the Nebraska-Lincoln laboratory or by using the VG 250/11 data system for the ZAB-HF-3F instrument (TU Berlin).

The mass resolution of daughter ion spectra with the EBE instrument is not sufficient by the separate completely ion signals that are differing by one mass unit. The results presented here are the result of deconvoluting the complex multiplets. This was done by assuming Gaussian peaks of constant width for each peak in the multiplet. Peak width, height, and position were varied, and the agreement between the calculated and observed peak profiles was assessed by using a least-squares comparison. When the agreement became better than a present limit, convergence was assumed. We found that the precision of assessing component peak heights in multiplets is better than ±3% relative for peaks greater than 20% of the height of the base peak of the multiplet and better than ±10% for peaks at least 3% of the base peak.

The Fe(alkyne)$^+$ ions were formed by reactions of $Fe(CO)_x^+$ ($x = 1$, 2[13]), produced by the decomposition of $Fe(CO)_5^+$,[14] and the appropriate alkyne with use of experimental conditions as described in ref 6f. The labeled alkynes (Chart I) were synthesized[15] by standard laboratory procedures and purified by preparative gas chromatography. Both deuterium position and labeling content (>95%) were determined by H NMR and mass spectrometry.

Results and Discussion

The main products of the collision-induced decomposition of $FeC_8H_{14}^+$ are given in Table II for the unlabeled 1-, 2-, and

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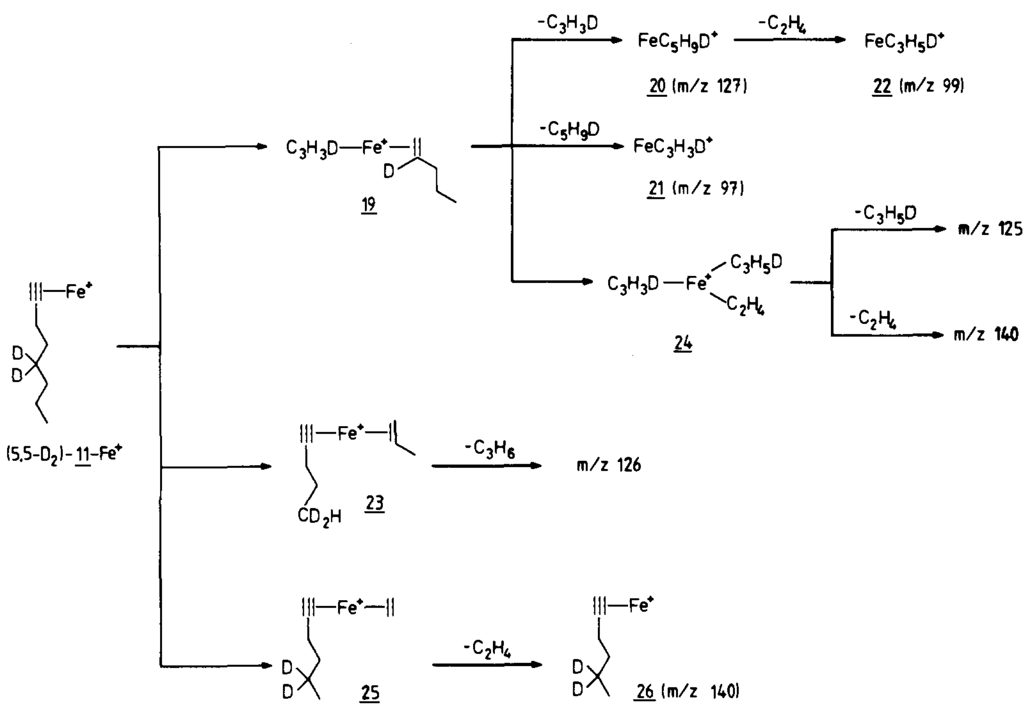
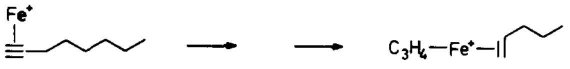
Scheme III

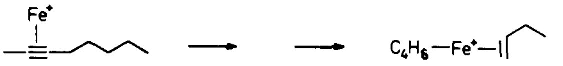


3-octyne (**11–13**). The decompositions of $FeC_8H_{14}^+$ species induced by collision (Table II) are consistent with propargylic insertion of Fe^+ followed by β-hydrogen transfer to produce alkene–diene adducts. For example, $FeC_8H_{14}^+$ formed by reaction of $FeCO^+$ and $Fe(CO)_2^+$ [13] with 1-octyne (**11**) rearranges following propargylic insertion to **15** (reaction 1). Upon collisional activation, **15** dissociates to $FeC_5H_{10}^+$ (100%) and $FeC_3H_4^+$ (31%). Other major fragment ions can be explained by invoking further rearrangement of **15** according to Scheme I. After loss of C_3H_4, rearrangement of Fe(1-pentene) results in formation of $FeC_3H_6^+$ (25%) and $FeC_2H_4^+$ (7%). This is best explained by the formation of a (propene)Fe(ethylene)$^+$ complex.



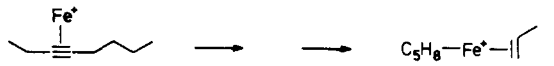
(1)

11-Fe^+ 15



(2)

12-Fe^+ 16



(3)

13-Fe^+ 17

In a similar fashion, **12** and **13** react with Fe^+ and, upon collisional activation, produce mainly C–C cleavage products according to reactions 2 and 3. Note the remarkably high contribution of H_2 loss from the Fe(2-octyne)$^+$ complex (50%), which will be discussed in detail below.

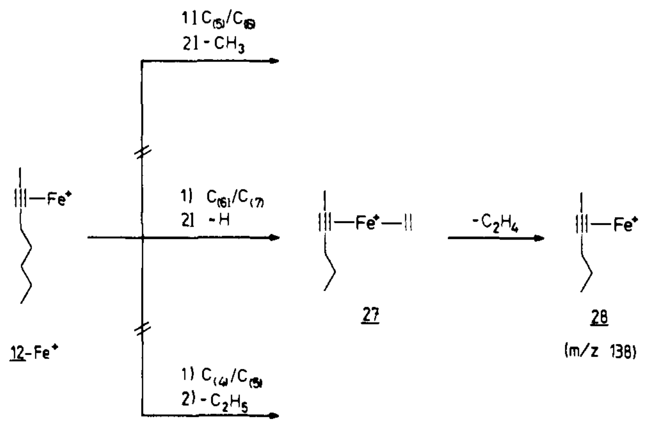
The labeling data given in Table II are, to a first approximation, by and large consistent with site-specific processes (i.e., β-hydrogen transfers following oxidative insertion of the Fe^+ into a C–C bond). In the following we will discuss each octyne isomer separately.

Chart I

$HC\equiv C(CH_2)_5CH_3$ 11	$HC\equiv C(CH_2)_2CD_2(CH_2)CH_3$ $(5,5-D_2)$-11	
$CH_3C\equiv C(CH_2)_4CH_3$ 12	$CD_3C\equiv C(CH_2)_4CH_3$ $(1,1,1-D_3)$-12	$CH_3C\equiv CCD_2(CH_2)_3CH_3$ $(4,4-D_2)$-12
$CH_3C\equiv CCH_2CD_2(CH_2)_2CH_3$ $(5,5-D_2)$-12	$CH_3C\equiv C(CH_2)_2CD_2CH_2CH_3$ $(6,6-D_2)$-12	$CH_3C\equiv C(CH_2)_3CD_2CH_3$ $(7,7-D_2)$-12
$CH_3CH_2C\equiv C(CH_2)_3CH_3$ 13	$CH_3CH_2C\equiv C(CH_2)_2CD_2CH_3$ $(7,7-D_2)$-13	
$CH_3(CH_2)_2C\equiv C(CH_2)_2CH_3$ 14	$CD_3(CH_2)_2C\equiv C(CH_2)_2CH_3$ $(1,1,1-D_3)$-14	$CH_3CD_2CH_2C\equiv C(CH_2)_2CH_3$ $(2,2-D_2)$-14
$CH_3CH_2CD_2C\equiv C(CH_2)_2CH_3$ $(3,3-D_2)$-14	$CD_3CD_2CH_2C\equiv C(CH_2)_2CH_3$ $(1,1,1,2,2-D_5)$-14	

Fe(1-octyne)$^+$. The study of $(5,5-^2H_2)$-**11** provides clear insight into the formation of the major C–C cleavage products (Scheme III). In line with the formation of an intermediate **19**, products of *m/z* 127 and 97 are formed from this bis(olefin) complex. The former is, in agreement with earlier studies,[6f] assigned as a complex of Fe^+ with $(2-^2H)$pentene-1, which further decomposes (according to Scheme I) to split off specifically C_2H_4, thus forming an ion of *m/z* 99. The signal for the ion $FeC_5H_8^+$ (*m/z* 124) in the spectrum of unlabeled 1-octyne (43%) is for $(5,5-^2H_2)$-**11** found at *m/z* 124, 125, and 126 (see Table II); we interpret this as an indication for the operation of two processes to generate the $FeC_5H_8^+$ complex. One consists of an insertion of Fe^+ into the $C_{(5)}/C_{(6)}$ bond of 1-octyne, followed by hydrogen transfer (formation of **23**, Scheme III). The olefin/alkyne complex **23** may then fall apart (loss of C_3H_6) to give an ion of *m/z* 126. The signal at *m/z* 125 can be explained by further rearrangement of **19** to

Scheme IV



a tris(olefin) complex **24**, from which C_3H_5D could be split off. The minor component at m/z 124 is likely to be due to some H/D scrambling occurring in the course of the multi-step processes. Dehydrogenation of $FeC_5H_{10}^+$ to generate $FeC_5H_8^+$ can be ruled out as a major contributing pathway because authentically synthesized $FeC_5H_{10}^+$ eliminates H_2 to only 4%.[6b]

The m/z of the ion formed by loss of ethylene from Fe(1-octyne)$^+$ (m/z 138 for **11**) is nearly completely shifted to m/z 140 for (5,5-$^2H_2$)-**11**, demonstrating that the label is retained in the ionic fragment. By using the traditional interpretation, this result can be accounted for by assuming either that this fragment is specifically generated from the tris(olefin) complex **24** (Scheme III: **24** → m/z 140) or that oxidative insertion of Fe^+ into the $C_{(6)}/C_{(7)}$ bond of 1-octyne is operative (formation of **25**), followed by loss of C_2H_4 (**25** → **26**). The present results do not allow these alternatives to be distinguished.

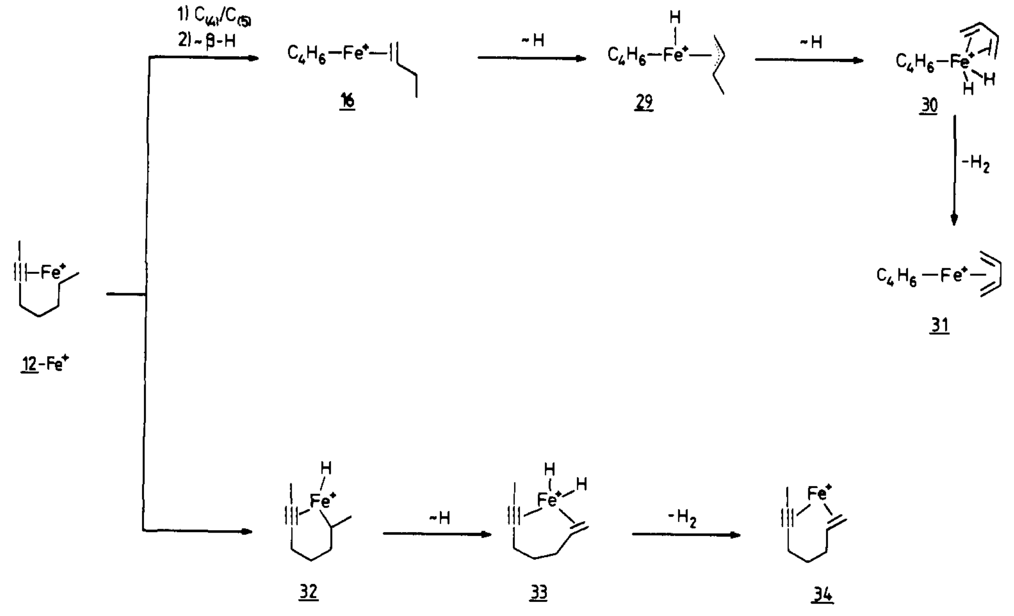
Fe(2-octyne)$^+$. According to reaction 2, two of the principal fragments of the Fe(2-octyne)$^+$ complex should be $FeC_4H_8^+$ (m/z 112) and $FeC_4H_6^+$ (m/z 110) which are, indeed, observed experimentally. If these two ions were only formed via intermediate **16** (reaction 2) and if no H/D scrambling would occur, one should observe the following in the CAD spectra of the deuteriated isotopomers: The fragment $FeC_4H_8^+$ should not undergo a mass shift when the hydrogens at positions $C_{(1)}$ or $C_{(4)}$ are replaced with deuteriums, whereas deuteriation of $C_{(5)}$ and $C_{(7)}$ should cause a shift to m/z 114. Labeling of $C_{(6)}$ should give rise to a fragment at m/z 113 if β-D transfer pertains. Analogously, the $FeC_4H_6^+$ fragment (m/z 110) would be expected to be subject to specific mass shifts, i.e., to m/z 113 for (1,1,1-$^2H_3$)-**12**, m/z 112 for (4,4-$^2H_2$)-**12**, and m/z 111 for (6,6-$^2H_2$)-**12**; labeling at positions $C_{(5)}$ and $C_{(7)}$ should have no effects. The data for the labeled 2-octynes (Table II) leave no doubt that reality is more complex and that the ion $FeC_4H_6^+$ to some extent is generated via dehydrogenation of the $FeC_4H_8^+$ species. This is not surprising as earlier experiments[4f] had already shown that (1) dehydrogenation of Fe(1-butene)$^+$ is a dominant decomposition route and (2) that the product $FeC_4H_8^+$ formed from intermediate **16** is indeed that of Fe(1-butene)$^+$.[6c,f] In spite of the quite extensive labeling, we have not been able, unfortunately, to sort out the various mechanistic components from the isotope distribution in the relevant m/z 110–114 region (Table II).

Products from losses of propene and ethylene from Fe(2-octyne)$^+$, although of minor importance in comparison with products formed via insertion of Fe^+ in the propargylic C–C bond, are also observed (10 and 15% relative abundance, Table II). For the propene loss, the results for the labeled compounds (Table II) suggest, as a major pathway, insertion in the homopropargylic $C_{(5)}/C_{(6)}$ bond followed by β-hydrogen (deuterium) transfer. Some H/D scrambling seems to take place. For ethylene loss from Fe(2-octyne)$^+$, the process of oxidative addition to the $C_{(6)}/C_{(7)}$ bond /β-hydrogen transfer/dissociation of the bis(olefin) complex is more specific, as demonstrated by the characteristic and clean mass shifts in the m/z 138–141 region. Moreover, the results clearly demonstrate that *no* β-alkyl transfer following insertion in either $C_{(5)}/C_{(6)}$ or $C_{(4)}/C_{(5)}$ is operative, in contrast to the chemistry of saturated alkanes.[5h] A likely mechanism (see, however, below) for ethylene loss from Fe(2-octyne)$^+$ is formulated in Scheme IV.

The CAD spectrum of Fe(2-octyne)$^+$ contains a very abundant signal due to loss of H_2 (50%). How can we explain the preferred formation of this fragment and account for the label distribution reported in Table II? A conceivable mechanism might start from intermediate **16**, the product formed by oxidative insertion in the activated propargylic bond of 2-octyne. **16**, being a (C_4H_6)–Fe(1-butene)$^+$ complex, might then undergo dehydrogenation of the 1-butene ligand as described in the upper part of Scheme V. That Fe(1-butene)$^+$ undergoes abundant H_2 loss has already been observed by Freiser,[4f] and the $FeC_4H_8^+$ fragment generated from **12**, which has the structure of Fe(1-butene)$^+$,[6f,15] also undergoes loss of H_2.

The analysis of the data for X_2 loss (X = H, D) from labeled Fe(2-octyne)$^+$ complexes clearly reveals that an unprecedented mechanism is operative. Before discussing this it is worth recalling that dehydrogenation of Fe(butene)$^+$ is associated with a nearly complete loss of positional identity of all hydrogens, irrespective of whether the complex is generated from Fe^+ and butene[4f] or

Scheme V



Scheme VI

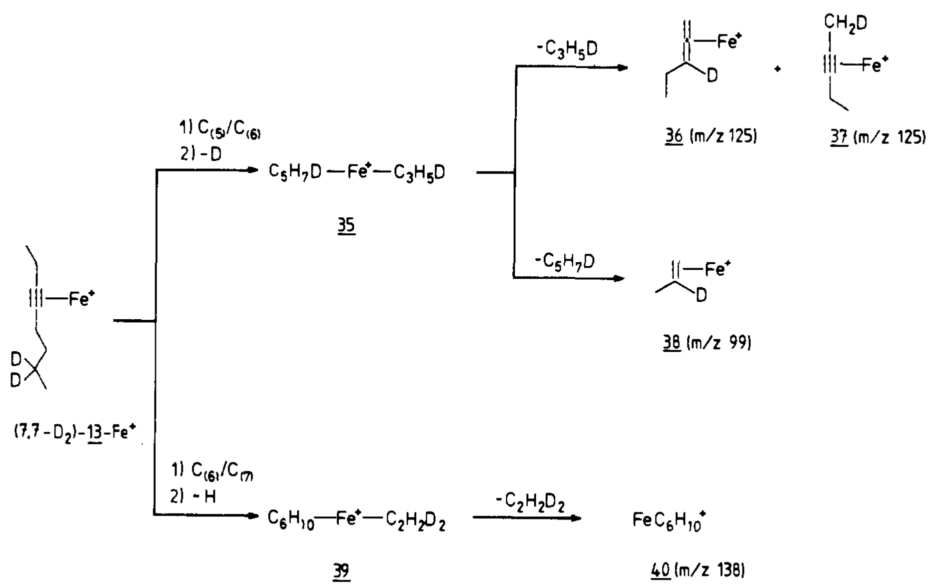


Table III. Unimolecular Loss of C_2X_4 (X = H, D) from Labeled Fe(4-Octyne)$^+$ Complexes[a]

C_2X_4	$C_3H_7C{\equiv}CC_3H_7$ **14**	$C_2H_5CD_2C{\equiv}CC_3H_7$ (3,3-$^2H_2$)-**14**	$CH_3CD_2CH_2C{\equiv}CC_3H_7$ (2,2-^2H)-**14**	$CD_3(CH_2)_2C{\equiv}CC_3H_7$ (1,1,1-$^2H_3$)-**14**	$CD_3CD_2CH_2C{\equiv}CC_3H_7$ (1,1,1,2,2-$^2H_5$)-**14**
C_2H_4	100	100	54.5	54.8	59.1
C_2H_3D					
$C_2H_2D_2$			45.5	45.2	
C_2HD_3					
C_2D_4					40.9
$k_{C_2H_4}/k_{C_2X_4}$			1.20	1.21	1.44

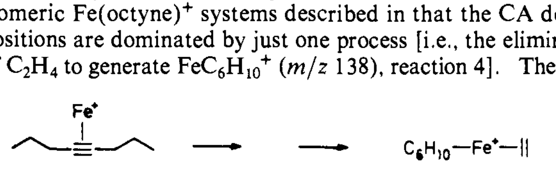
[a] Data are given in % $\sum C_2X_4$. Errors are ±3% of reported data.

from 2-octynes labeled in position $C_{(5)}$, $C_{(6)}$, or $C_{(7)}$.[15] Inspection of the data in Table II clearly demonstrates the deviating behavior of Fe(2-octyne)$^+$ in the dehydrogenation reaction, in that H/D scrambling contributes to only a minor extent. Deuteriation of the methylene positions $C_{(5)}$ and $C_{(6)}$ does not yield significant losses of HD or D_2 (the major process is due to loss of H_2, i.e., *m/z* 166); on the other hand, labeling of $C_{(7)}$ brings about loss of HD (*m/z* 165), which, as inferred from the relative intensities, seems to be associated with a kinetic isotope effect. These results suggest that dehydrogenation follows a formal 1,2-hydrogen elimination, involving $C_{(7)}/C_{(8)}$ (the latter position is indirectly inferred from the labeling data of the isotopomers of **12**). The labeling results imply that, if dehydrogenation proceeds via the bis(olefin) complex **16**, the presence of the C_4H_6 ligand effectively suppresses the hydrogen scrambling within the butene ligand.

However, there is an alternative to be considered which is formulated in the lower part of Scheme V and in which we suggest that dehydrogenation is *not* preceded by C–C activation but rather involves a metallacycloalkyne (**32**) as an intermediate. From **32**, via β-hydrogen transfer (**32** → **33**), H_2 can be eliminated in a formal 1,2-elimination involving $C_{(7)}/C_{(8)}$ of 2-octyne. Although the data do not permit a distinction between the two fundamentally different mechanisms, we should like to draw attention to a precedent[3m,6g] for the "remote functionalization"[16] of nonactivated C–H bonds. The gas-phase reaction of bare Fe$^+$ with linear alkyl nitriles commences with an "end-on" complexation of the nitrogen lone pair with Fe$^+$, followed by *specific, geometry-governed* oxidative addition to a remote unactivated C–H bond; the so-formed intermediate serves as precursor for both reductive 1,2-elimination of a hydrogen molecule and loss of olefin. If this reaction is also operative for the Fe(2-octyne)$^+$ system, one could easily explain the highly specific 1,2-dehydrogenation of the acetylene without being forced to make the unjustified assumption that the presence of a second ligand (i.e., C_4H_6) suppresses hydrogen scrambling in Fe(butene)$^+$. It has not escaped our notice that in analogy to the Fe/nitrile system,[6g] **33** might also serve as an intermediate for loss of C_2H_4 involving $C_{(7)}/C_{(8)}$ of 2-octyne, thus adding an attractive mechanistic variant to Scheme IV.

Fe(3-octyne)$^+$. The dominant C–C cleavage product of this complex corresponds to $FeC_5H_8^+$ (*m/z* 124), and CA spectrometry demonstrates that the product formed via intermediate **17** (reaction 3) is best modelled as a mixture of ca. 75% Fe(1,2-pentadiene)$^+$ and 25% Fe(2-pentyne)$^+$.[6f] The study of (7,7-$^2H_2$)-3-octyne confirms the earlier suggestion that insertion of Fe$^+$ in the propargylic C–C bond is followed by β-hydrogen transfer which results in a nearly quantitative mass shift *m/z* 124 → *m/z* 125 (Table II). We also note the mass shift for the Fe(propene)$^+$ fragment (*m/z* 98 → *m/z* 99) and the fact that most of the ethylene eliminated from Fe(3-octyne)$^+$ involves $C_{(7)}$ (likely together with $C_{(8)}$). The likely intermediates involved in the various C–C cleavage reactions of the Fe(3-octyne)$^+$ system are described in Scheme VI for (7,7-$^2H_2$)-**13**. The relatively high ratio of HD vs. H_2 loss (3:1) is perhaps due to the operation of a process comparable to that described in Scheme V for the Fe(2-octyne)$^+$ system and involves metallacycles as intermediates.

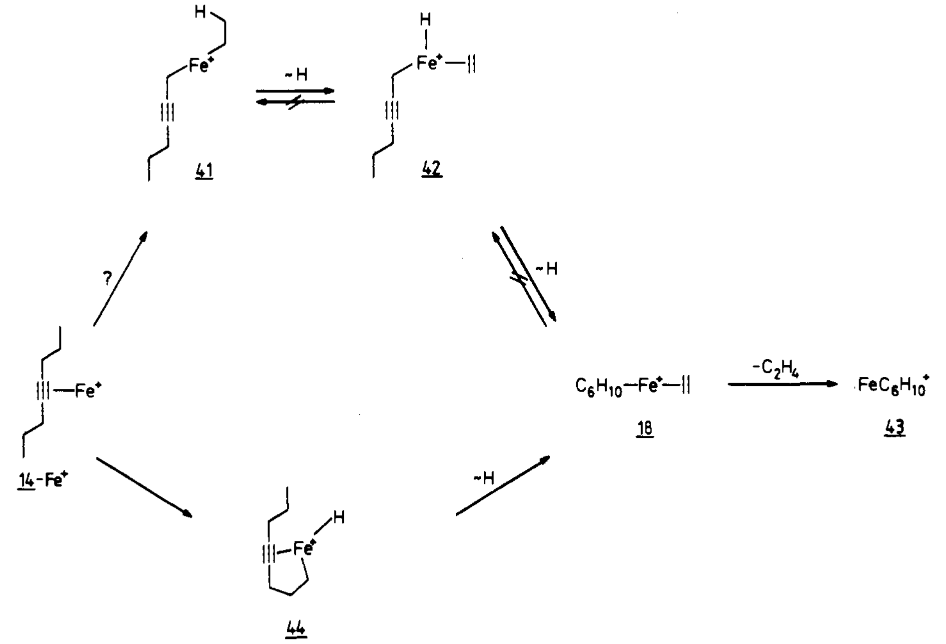
Fe(4-octyne)$^+$. This complex is distinct from all the other isomeric Fe(octyne)$^+$ systems described in that the CA decompositions are dominated by just one process [i.e., the elimination of C_2H_4 to generate $FeC_6H_{10}^+$ (*m/z* 138), reaction 4]. The latter is formed from intermediate **8** (Scheme II: R = C_3H_7; R′ = H) via hydrogen migration to either the vinylic carbon atom (**8** → **9**) or the propargylic carbon atom (**8** → **10**), followed by elimination of C_2H_3R' (R′ = H). The CA analysis of the $FeC_6H_{10}^+$ products formed suggests that pathway **8** → **9** is favored by a factor 1.5 over the route **8** → **10**.[6f]



(4)

We now address the following questions: (1) Is the β-hydrogen transfer **7** → **8** reversible, and does the insertion of the metal ion into the C–H bond constitute the rate-determining step? (2) Is

Scheme VII



an isotope effect discernible when deuteriated precursors are used, and if so, what are the mechanistic implications? Answers are provided by the analysis of the data reported in Table III for the unimolecular losses of C_2X_4 (X = H, D) from labeled Fe(4-octyne)$^+$ complexes. Unimolecular dissociations rather than collision-induced ones were used to obtain better reproducibility.

The interpretation of the data seems to be straightforward and the following conclusions are drawn: (1) The absence of any scrambling products demonstrates that the hydrogen transfer from the propyl part of the C–C insertion intermediate to the metal ion is irreversible. (2) Comparison of the data for $(2,2\text{-}^2H_2)$-**14** and $(1,1,1\text{-}^2H_3)$-**14** proves that the β-hydrogen transfer does *not* constitute the rate-determining step in the overall reaction; if this would be the case one should observe a primary kinetic isotope effect,[17] discriminating against D transfer, which is not observed. (3) Ethylene elimination from the bis(olefin)/Fe$^+$ complex **18** to form eventually $FeC_6H_{10}^+$ is, not surprisingly, associated with a secondary kinetic isotope effect, favoring C_2H_4 over $C_2H_2D_2$ and C_2D_4 by factors of 1.20 and 1.44, respectively; thus, there operates an isotope effect $k_H/k_D = 1.1$ per deuterium atom.

It is obvious that these results are difficult to be reconciled with Scheme II. For example, if β-hydrogen transfer requires more energy than bond dissociation of the bis(olefin) complexes (e.g., **9** and **10**), then one might expect the β-hydrogen transfer to be rate determining, which it is not, and largely irreversible, which it is. On the other hand, if the β-hydrogen transfer is less energy-demanding[18] than dissociation of the bis(olefin) complex[19] then this step would be reversible and *not* be rate determining.

One way to resolve these contradictions would be to propose that the ethylene fragment of **42** is unsymmetrically bound and rotation around the Fe–C_2H_4 bond requires more energy than does the dissociation of **18** to C_2H_4 and **43**. Under these circumstances, **41** → **42** may well take place without H/D scrambling. Although no data are available for **42**, maintaining unsymmetrical bonding is unlikely because NMR measurements indicate[20] that the rotational barrier for (CO)$_4$Fe–olefin complexes lies in the 10–15-kcal/mol range, substantially *below* the barrier for loss of C_2H_4 from the metal ion/olefin complexes.

A mechanism in lieu of the propargylic insertion/β-hydrogen transfer process is proposed here that does resolve the inconsistencies noted above. A similar mechanism was proposed to account for the losses of hydrogen and olefin from Fe$^+$/nitrile complexes,[6g] e.g., and already has been used in this paper to describe the specific 1,2-dehydrogenation of Fe(2-octyne)$^+$ via metallacycles (i.e., Scheme V: **12**-Fe$^+$ → **32** → **33** → **34**). In other words, the reaction of Fe$^+$ and alkynes may not follow the traditional pattern of oxidative addition to a C–C bond/β-hydrogen transfer/reductive elimination (Scheme VII: **14**-Fe$^+$ → **41**), but instead the process begins with metal insertion into a C–H bond to form, in the case of a 4-octyne, the metallacycle **44**.

Conclusion

The major features of the reaction of Fe$^+$ and alkynes, as revealed by isotopic labeling, can be explained in terms of the traditional mechanism of oxidative addition to a propargylic C–C bond, β-hydrogen transfer, and reductive elimination for 1- and 3-octyne. The behavior of 2-octyne is also consistent with this process, but other decomposition chemistry, probably that of the [complex–H_2]$^+$, complicates the picture. However, the 4-octyne system presents an opportunity to look more closely at the traditional mechanism. Specifically, the apparent irreversibility of the β-hydrogen transfer process is in conflict with the traditional mechanism, and another mechanism involving C–H bond insertion and metallacycle formation is suggested as an alternative. Experiments aimed at testing this proposal will be the subject of future studies.

Acknowledgment. The generous support of our work by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the National Science Foundation (Grants CHE 8211164 and 8320388) is gratefully acknowledged. We are indebted to Dr. Thomas Weiske for technical assistance and Dr. Carlito B. Lebrilla for comments and discussions.

Note Added in Proof. The mechanism of dehydrogenation of Fe(2-octyne)$^+$ (Scheme V) could be distinguished recently by demonstrating that the product $(FeC_8H_{12})^+$ formed is best described as **34** not by Fe$(C_4H_6)_2^+$ complexes like **31**.[21]

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(17) Kinetic isotope effects $2 < k_H/k_D < 6$ (depending on the excess internal energy of the chemically activated organometallic compounds) were reported for β-hydrogen (deuterium) transfer by: Bomse, D. S.; Woodin, R. L.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 5503.

(18) For pertinent examples see ref 3c, 4k, and 5e.

(19) Binding energies of group 8 metal ions to ethylene are in the range 40–70 kcal/mol, ref 5d, g, h.

(20) (a) Kruczynski, L.; Li Shing Man, L. K. K.; Takats, J. *J. Am. Chem. Soc.* **1974**, *96*, 4006. (b) Wilson, S. T.; Coville, N. J.; Shapley, J. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 4038. (c) Segal, J. A.; Johnson, B. F. G. *J. Am. Chem. Soc., Dalton Trans.* **1975**, *677*, 1990.

(21) Schulze, C.; Schwarz, H. *Chimia*, in press.