92. Substituent Effects on Fe⁺-Mediated [4+2] Cycloadditions in the Gas Phase

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The Fe⁺-mediated [4 + 2] cycloaddition of dienes with alkynes has been examined by four-sector ion-beam and ion cyclotron resonance mass spectrometry. Prospects and limitations of this reaction were evaluated by investigating several Me-substituted ligands. Me Substitution at C(2) and C(3) of the diene, *i.e.*, 2-methylbuta-1,3-diene, 2,3-dimethylbuta-1,3-diene, hardly disturbs the cycloaddition. Similarly, variation of the alkyne by use of propyne and but-2-yne does not affect the [4 + 2] cycloaddition step, but allows for H/D exchange processes prior to cyclization. In contrast, Me substituents in the terminal positions of the diene moiety (*e.g.*, penta-1,3-diene, hexa-2,4-diene) induce side reactions, namely double-bond migration followed by [3 + 2] and [5 + 2] cycloadditions, up to almost complete suppression of the [4 + 2] cycloaddition for 2,4-dimethylhexa-2,4-diene. Similarly, alkynes with larger alkyl substituents (pent-1-yne, 3,3-dimethylbut-1-yne) suppress the [4 + 2] cycloaddition route. Stereochemical effects have been observed for the (*E*)- and (*Z*)-penta-1,3-diene ligands as well as for (*E*, *E*)- and (*E,Z*)-hexa-2,4-diene. A mechanistic explanation for the different behavior of the stereoisomers in the cyclization reaction is developed. Further, the regiochemical aspects operative in the systems ethoxyacetylene/pentadiene/Fe⁺ and ethoxyacetylene/isoprene/Fe⁺ indicate that substituents avoid proximity.

Introduction. – In addition to its widespread analytical applications, in the last two decades mass spectrometry developed to one of the most important techniques for the examination of ion-molecule reactions in the gas phase [1]. The particular notion of investigating processes under these 'artificial' conditions is that here intrinsic features of reactants can be uncovered, while, in the condensed phase, solvents, ligands, and counter ions largely complicate and obscure the mechanistic pattern. Of course, there are also problems even under the otherwise ideal gas-phase conditions; for example, an in-depth investigation of stereochemical properties by mass spectrometry (MS) is quite challenging [2]. In fact, the differentiation of stereoisomers by MS techniques is often not trivial. While in most cases stereo-differentiation concerns cyclic compounds [2] [3], strategies have been developed recently, which allow for stereochemical probes of acylic compounds by means of 'bare' transition-metal ions [4].

Transition-metal-ion-mediated coupling reactions have been already investigated in the gas phase [5] [6]. For example, butadiene/acetylene/M⁺ (M = Cr, Mn, Fe, Co) complexes undergo formal [4 + 2] cycloadditions and subsequently eliminate molecular hydrogen, H_2, to yield benzene/M⁺. The mechanisms and energetic features of these reactions as well as the particular electronic role of the metals have been discussed in some detail. An unexpected result is that, in addition to their *Lewis* acidity, covalent assistance of the metal ions is operative in the cycloaddition [6]. Due to the fact that cycloadditions are strongly influenced by electronic and steric effects, the present study intends to probe whether similar effects exist for metal-ion-mediated [4 + 2] cycloaddi-

tions in the gas phase. To this end, appropriately substituted diene/alkyne/Fe$^+$ complexes have been examined.

Results and Discussion. – As has been shown earlier, Fe$^+$ mediates the [4 + 2] cycloaddition of butadiene and acetylene leading to the formation of a cyclohexa-1,4-diene complex which subsequently looses H$_2$ to afford benzene/Fe$^+$ [5] [6]. To investigate the influence of substituents upon the product, regio- and stereoselectivity of the cyclization, the complexes **1–14** were generated, and the unimolecular decompositions of their metastable ions have been examined[1]). To render the discussion of the results more distinct, we will first describe in more general terms the influence of alkyl substituents on the cycloaddition. Next, the stereochemistry of the metal-mediated cyclization will be discussed for the stereoisomeric pentadiene and hexadiene complexes. To complete the mechanistic picture, the regiochemical outcome of the cycloaddition is examined exemplarily for the reactions of ethoxyacetylene/Fe$^+$ complexes with Me-substituted diene ligands.

The complexes **1** and **2** react *via* exclusive losses of H$_2$ (*Table 1*). The mechanism proposed for the reaction of **1** (*Scheme 1*) involves formation of the formal [4 + 2]-cycloaddition intermediate **11** and its dehydrogenation leading to toluene/Fe$^+$, **12**, in analogy to the earlier studied butadiene/acetylene/Fe$^+$ parent system [6]. This conjecture is supported by the MI/CA spectrum of [**1** – H$_2$] which is in good agreement with the CA spectrum of genuine toluene/Fe$^+$ (*Table 2*). Similarly, the comparison of the MI/CA spectrum of [**2** – H$_2$] with the CA spectrum of authentic xylene/Fe$^+$ isomers suggests that o-xylene/Fe$^+$ is indeed formed *via* a [4 + 2] cycloaddition (*Table 3*). In particular, the loss

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[1]) The experiments were performed with a modified *VG ZAB/HF/AMD 604* four-sector mass spectrometer of *BEBE* configuration (*B* stands for magnetic and *E* for electric sectors), which has been described in [7]. Organometallic cations were generated by chemical ionization (CI) of appropriate precursor mixtures; note that the generation of mixed metal complexes of the type [Fe(L)(L′)]$^+$ requires a careful optimization of the individual pressures of the components, because otherwise the homoligated complexes [Fe(L)$_2$]$^+$ or [Fe(L′)$_2$]$^+$ prevail. After acceleration to 8-keV kinetic energy, the ions of interest were mass-selected using $B(1)E(1)$ at a resolution of $m/\Delta m \geq 4000$, which was necessary in order to resolve isobaric ions. Some isobaric impurities are inherent to generation of Fe$^+$ complexes from the corresponding organic substrates and Fe(CO)$_5$. For example, the butadiene complex [^{56}Fe(C$_4$H$_6$)]$^+$ is isobaric to [^{54}Fe(CO)$_2$]$^+$. In some cases, the intensities of the ions of interest were that low that a complete resolution could not be achieved and small contributions of interfering CO complexes had to be taken into account. These interferences can, however, be monitored by losses of $\Delta m = 28$ which disappeared upon enhancing the resolution and also did not shift upon D labeling. Unimolecular dissociation of metastable ions (MI) in the field-free region preceding $B(2)$ was monitored by scanning this sector. MS/MS/MS Experiments [8] were performed by selecting the organometallic ions of interest with $B(1)$ only. The fragment ions resulting from unimolecular decompositions in the field-free region preceding $E(1)$ were selected using $E(1)B(2)$ in order to avoid the appearance of artifacts [9], subsequently collided with He (80% transmission, *T*), and the CA spectra were recorded by scanning $E(2)$. These experiments will be referred to as MI/CA spectra. For comparison to MI/CA results, collisional activation (CA) experiments were performed by using $B(1)E(1)B(2)$ to select the parent ions, colliding them with He as a target gas (80% *T*) and monitoring the fragment ions by means of $E(2)$. For the sake of brevity, only selected MS^3 spectra are reported in the *Tables*, and the complete set of data is available upon request. All spectra were accumulated and on-line processed with the *AMD/Intectra* data system; 5–50 scans were averaged to improve the signal-to-noise ratio.

1

2

3

4

5

6

7

(*E*)-**8**

(*Z*)-**8**

(*E*)-**9**

(*Z*)-**9**

(*E,E*)-**10**

(*E,Z*)-**10**

11

12

13

14
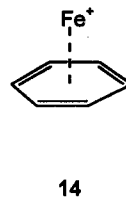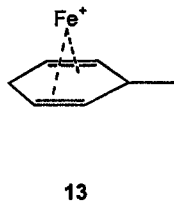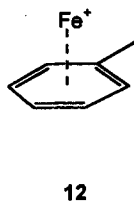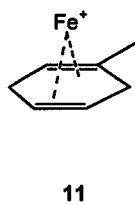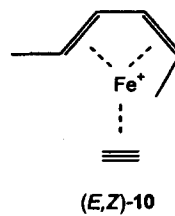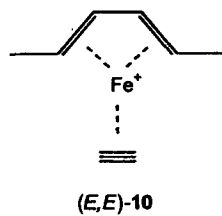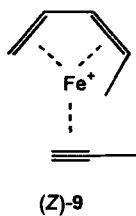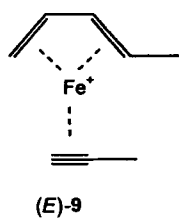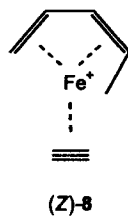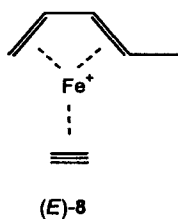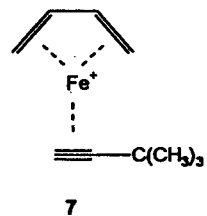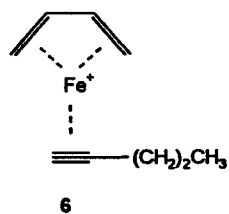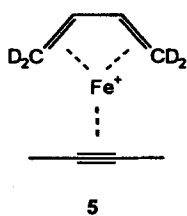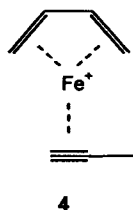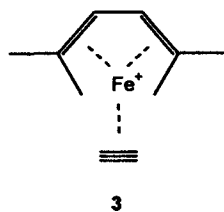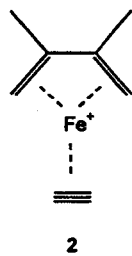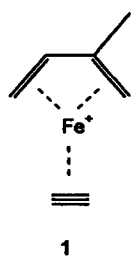
of ethane ($\Delta m = 30$) [10] is characteristic for *o*-xylene. Furthermore, examination of the isotopologous complexes[2]) isoprene/[D_2]acetylene/Fe^+, **1a**, and 2,3-dimethylbutadiene/[D_2]acetylene/Fe^+, **2a**, give no indication for the occurrence of H/D exchange reactions and exclusive losses of H_2 are observed (*Table 1*).

Complex **3** differs from the previously discussed systems in terms of the expected products. Owing to complete methylation at the terminal positions of the butadiene moiety, [1,4] elimination from the [4 + 2] cyclization intermediate should give rise only to C_2H_6 loss. However, explusion of C_2H_6 is a very minor side reaction (*Table 1*), and other reaction channels are preferred which eventually result in H_2 loss. Quite likely, peralkylation of the diene at the terminal positions drastically reduces the propensity for a metal-mediated [4 + 2] cycloaddition. We presume that steric congestion prevents the formation of a *cisoid* conformation which is a prerequisite for any *Diels-Alder*-type reaction. The reaction of **3** was not further investigated.

Table 1. *Mass Differences (Δm in amu) Observed in the Metastable Ion (MI) Mass Spectra of Diene/Alkyne/Fe^+ Complexes 1–5, 8–10, and 11 for Comparison*[a])

Complex	No.	Δm										
		2	3	4	16	17	18	19	26	28[b])	29	30
Isoprene/acetylene/Fe^+	**1**	100										
Isoprene/[D_2]acetylene/Fe^+	**1a**	100										
2,3-Dimethylbuta-1,3-diene/acetylene/Fe^+	**2**	100										
2,3-Dimethylbuta-1,3-diene/[D_2]acetylene/Fe^+	**2a**	100										
2,5-Dimethylhexa-2,4-diene/acetylene/Fe^+ [c])	**3**	77			5					4[d])		3
2,5-Dimethylhexa-2,4-diene/[D_2]acetylene/Fe^+ [c])	**3a**	56	22		2	3				2[d])	2	1
Buta-1,3-diene/propyne/Fe^+	**4**	100										
[1,1,4,4-D_4]Buta-1,3-diene/propyne/Fe^+	**4a**	7	31	62								
[1,1,4,4-D_4]Buta-1,3-diene/but-2-yne/Fe^+ [f])	**5**	29	46	15		3	2					
(*E*)-Penta-1,3-diene/acetylene/Fe^+	(*E*)-**8**	17			79				1	3[d])		
(*E*)-Penta-1,3-diene/[D_2]acetylene/Fe^+	(*E*)-**8a**	11	4		54	28				2[d])	1	
(*Z*)-Penta-1,3-diene/acetylene/Fe^+	(*Z*)-**8**	33			61				2	3[d])		
(*Z*)-Penta-1,3-diene/[D_2]acetylene/Fe^+	(*Z*)-**8a**	29	5		27	33				4[d])	2	
[5,5,5-D_3]Penta-1,3-diene/acetylene/Fe^+	**8b**	18	11			7	18	36	3	2[d])	3	2
(*E*)-Penta-1,3-diene/propyne/Fe^+	(*E*)-**9**	48			45							6
(*Z*)-Penta-1,3-diene/propyne/Fe^+	(*Z*)-**9**	54			37							7
(*E,E*)-Hexa-2,4-diene/acetylene/Fe^+	(*E,E*)-**10**	65			21				1			13
(*E,Z*)-Hexa-2,4-diene/acetylene/Fe^+	(*E,Z*)-**10**	62			20				3			14
3-Methylcyclohexa-1,4-diene/Fe^+	**13**	39			61							

[a]) Intensities are normalized to $\sum = 100$.
[b]) Loss of $\Delta m = 28$ was neglected, if not specified.
[c]) Additional losses of $\Delta m = 42$ (6%) and $\Delta m = 44$ (5%) are observed.
[d]) Loss of $m/z = 28$ can be interfered by isobaric impurity of CO^1).
[e]) Further, losses of $\Delta m = 31$ and $\Delta m = 43–46$ ($\sum = 10\%$) are observed.
[f]) Further losses corresponding to $C_4H_{6-n}D_n$: $n = 1–4$ are observed; $n = 2$ (2%), $n = 1, 3$, and 4 (< 1%).

Table 2. *Representative Mass Differences (Δm in amu) in the MI/CA Spectra of the Dehydrogenation Products of 1, 4, and 8 in Comparison to the CA Spectra of Other [Fe,C$_7$,H$_8$]$^+$ Isomers[a])*

Spectrum	Complex	No.	Δm								
			14	15	26	28	57	67	78	83	Fe$^+$
MI/CA	[Isoprene/acetylene/Fe$^+$ −H$_2$]	[1 −H$_2$]		42	2	15	100	23	1	2	30
MI/CA	[Buta-1,3-diene/propyne/Fe$^+$ − H$_2$]	[4 −H$_2$]		13	2	6	100	53	1	10	82
MI/CA	[(E)-penta-1,3-diene/acetylene/Fe$^+$ −H$_2$]	[(E)-8 −H$_2$]	6	6	100	6	38	14	8	3	32
MI/CA	[(Z)-penta-1,3-diene/acetylene/Fe$^+$ −H$_2$]	[(Z)-8 −H$_2$]	8	8	85	13	100	32	16	13	99
CA	Toluene/Fe$^+$	12		19	1	6	100	22	1	5	26
CA	Cyclohepta-1,3-5-triene/Fe$^+$	15	33	3	99	3	100	19	98	11	70
CA	6-Methylfulvene/Fe$^+$	17	1	4	100	5	14	12	5	2	25
CA	Cyclopenta-1,3-diene/acetylene/Fe$^+$	19	1	1	100	5	6	6	2		7
CA	Norbornadiene/Fe$^+$	20	1		100	1	7	7	4	2	30
CA	Cyclopentene/acetylene/Fe$^+$] −H$_2$[b])	[21 −H$_2$]	2	2	100	17	7	4	4	1	10

[a]) Intensities are given relative to the base peak (100); intensities < 1% are neglected.
[b]) This ion was generated in the ion source.

Table 3. *Representative Mass Differences (Δm in amu) of MI/CA Spectra of 2, 9, and 10 after Loss of H$_2$ in Comparison to the CA Spectra of [Fe,C$_8$,H$_{10}$]$^+$ Isomers[a])*

Spectrum	Complex	No.	Δm									
			15	28	29	30	41	57	67	71	81	Fe$^+$
MI/CA	[2,3-Dimethylbuta-1,3-diene/acetylene/Fe$^+$ −H$_2$]	[2 −H$_2$]	7	4	[b])	31	10	100	13	34	10	18
MI/CA	[(E)-Penta-1,3-diene/propyne/Fe$^+$ −H$_2$]	[(Z)-9 −H$_2$]	12	100	[b])	4	80	15	12	7	5	17
MI/CA	[(Z)-Penta-1,3-diene/propyne/Fe$^+$ −H$_2$]	[(Z)-9 −H$_2$]	11	100	[b])	2	75	15	15	6	7	26
MI/CA	[(E,E)-Hexa-diene/acetylene/Fe$^+$ −H$_2$]	[(E,E)-10 −H$_2$]	6	100	[b])	2	31	3	4	1	2	3
CA	o-Xylene/Fe$^+$		12	6	[b])	30	8	100	12	36	14	77
CA	m-Xylene/Fe$^+$		17	8	[b])	8	9	100	9	28	9	67
CA	p-Xylene/Fe$^+$		10	4	[b])	5	4	100	11	31	12	60
CA	Ethylbenzene/Fe$^+$		14	7	72	[b])	5	42	10	43	24	100
CA	Cycloocta-1,3,5-triene[c]/Fe$^+$		1	100	[b])			8	2	1		1	6

[a]) Intensities are given relative to the base peak (100%).
[b]) Mass resolution of the spectra measured in the 4th field-free region was too low to evaluate the intensities for small peaks close to more intense fragments.
[c]) Cycloocta-1,3,5-triene was used in an isomeric mixture together with bicyclo[4.2.0]octa-2,4-diene.

To examine the effect of alkyl groups attached to the alkyne, the complexes **4–7** have been studied. Complex **4**, for instance, reacts exclusively *via* dehydrogenation. Further, the MI/CA spectrum of [**4** −H$_2$] shows the same fragmentations like the CA spectrum of genuine **12**, indicating that cyclization has taken place. However, the metastable complex[3]) [1,1,4,4-D$_4$]buta-1,3-diene/propyne/Fe$^+$, **4a**, leads to losses of H$_2$, HD, and

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[3]) [1,1,4,4-D$_4$]Buta-1,3-diene (98% atom % D) was purchased from *Cambridge Isotope*.
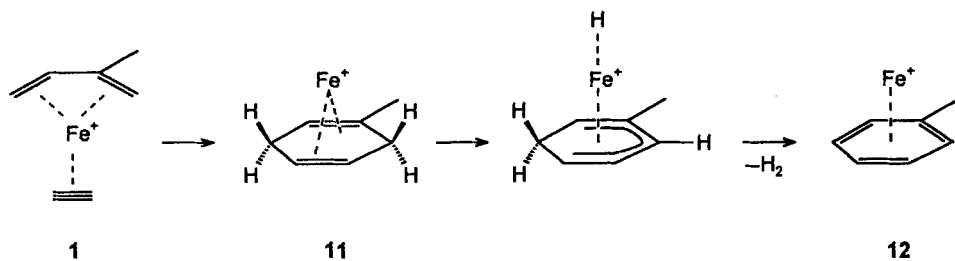
D$_2$ (7:31:62) as neutral fragments. According to the mechanistic proposal depicted in *Scheme 1*, one would expect exclusive loss of D$_2$ from **4a**. However, this result cannot be explained in terms of a statistical H/D exchange either, because loss of D$_2$ is still strongly preferred. Instead, partial H/D exchange from the 1,4-positions in the butadiene with the propargylic H-atoms is suggested to take place prior to the cyclization. The conjecture that H/D equilibration in **4a** occurs before, rather than after the cyclization step is further supported by the exclusive losses of H$_2$ from **1a** and **2a**; otherwise, these complexes should also give rise to (partial) H/D exchange. The butadiene/butyne/Fe$^+$ complex cannot be studied under CI conditions, because it is impossible to distinguish it from the isomeric complexes butyne/butyne/Fe$^+$ and butadiene/butadiene/Fe$^+$, respectively. Therefore, the labeled complex **5** has been examined, which shows predominately the loss of H$_2$, pointing towards cyclization. However, extensive H/D exchange processes, probably involving propargylic C–H bond activation, take place in analogy and even more extensive as compared to complex **4a**. In addition, elimination of CH$_4$ is observed as a side reaction. For alkynes bearing larger alkyl substituents as in **6** the unimolecular dissociation is rather unselective: ten different expulsions are observed; among them H$_2$ (57%) and butadiene (20%) represent the major reaction products. Probably, most of these fragmentations are not due to cyclization and elimination, but rather result from direct C–H bond activation of the pentyne ligand [11]. Similarly, in the reaction of **7** the expected dehydrogenation due to the [4+2] route is completely suppressed; instead losses of $\Delta m = 42$ (66%), $\Delta m = 54$ (10%), $\Delta m = 86$ (23%), and $\Delta m = 140$ (2%) are observed. Moreover, the most prominent peak ($\Delta m = 42$) can be attributed to consecutive losses of acetylene and CH$_4$ from the alkyne as is already known as a typical process for the 2,2-dimethylbut-3-yne/Fe$^+$ complex [11–13]. Thus, in complex **7** it appears that the buta-1,3-diene ligand serves as a mere spectator; the chemistry itself concerns exclusively the alkyne ligand. Summarizing these results, substitution of alkynes with higher alkyl groups opens up reaction channels at the expense of a [4+2]-type cyclization. Since the scope of this paper is the analysis of substituent effects on the metal-mediated [4+2] cyclization, this issue will not be further pursued here.

To investigate stereochemical effects on these metal-mediated [4+2] cycloadditions, several stereoisomeric complexes (**8–10**) were examined. The isomers (*E*)-**8** and (*Z*)-**8**[4]) both give rise to the same unimolecular decompositions, but in terms of relative intensities the dehydrogenation is favored for (*Z*)-**8**. However, as will be shown later, there are

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[4]) (*Z*)-Penta-1,3-diene (97%) and (*E*)-penta-1,3-diene (98%) were purchased from *Aldrich Chemicals*.

some side reactions besides the [4 + 2] cycloaddition which deserve special mentioning. First, let us discuss some aspects of the [4 + 2] reaction of (E)-8 as a representative for both stereoisomers. Assuming that the reaction sequence depicted in Scheme 1 holds true as well for (E)-8, two different elimination processes are expected: the intermediate 3-methylcyclohexa-1,4-diene/Fe$^+$, 13, should eliminate either H_2 or CH_4 to give toluene/ Fe$^+$, 12, and benzene/Fe$^+$, 14, respectively. Both losses are indeed observed in the unimolecular decomposition of (E)-8, and also genuine metastable 13[5]) undergoes these reactions, thus, further supporting the formation of this species as an intermediate. Comparison of the MI/CA spectrum of [(E)-8 – CH$_4$] with the CA spectrum of authentic benzene/Fe$^+$, 14, suggests that the latter is indeed formed by demethanation of (E)-8, because both spectra are very similar [17]; the remaining differences can be traced back to different amounts of internal energy stored in the ions depending on the method of generation, as has been analyzed previously [6]. In marked contrast, the MI/CA spectrum of [(E)-8 – H$_2$] reveals significant differences as compared to the CA spectrum of authentic 12 (Table 2). In particular, the losses of C_2H_2 ($\Delta m = 26$) and C_6H_6 ($\Delta m = 78$) are much more intense for [(E)-8 – H$_2$] than for 12, whereas loss of FeH ($\Delta m = 57$) is more pronounced in the latter. Consequently, competing reaction pathways contribute to the unimolecular dehydrogenation of (E)-8 giving rise to $[Fe,C_7,H_8]^+$ isomers other than 12.

Therefore, in addition to the [4 + 2] cycloaddition to afford a six-membered ring, alternative routes for the dehydrogenation of (E)-8 have to be taken into consideration. One alternative resulting in a seven-membered ring is depicted in Scheme 2. In the first step, an (E/Z)-isomerization of the pentadiene within the complex is involved. Similar (E/Z)-isomerizations have been proposed earlier [18] [19] and are suggested to occur inter alia via reversible allylic C–H bond activations. Once (Z)-8 is formed, Fe$^+$ activates a C–H bond to yield the conjugated pentadienyl system [19–21]; the latter can undergo a formal [5 + 2] cycloaddition with the acetylene ligand. Upon dehydrogenation the cyclohepta-1,3,5-triene/Fe$^+$ complex, 15, is formed.

Scheme 2

(E)-8   15
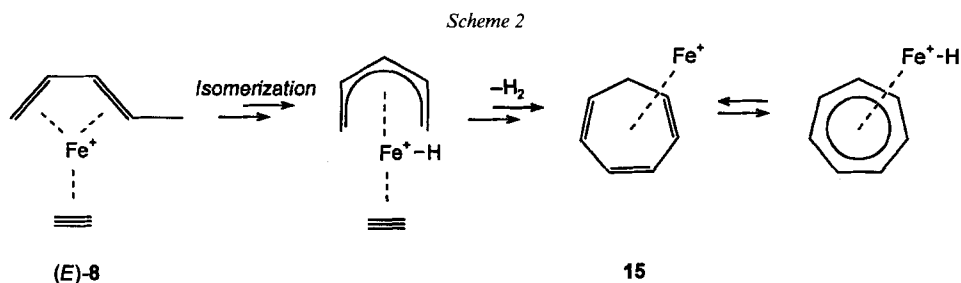
In addition, at least two plausible mechanistic pathways can lead to substituted cyclopentadiene/Fe$^+$ complexes. The mechanism depicted in Scheme 3 involves an initial allylic C–H bond activation of the diene, followed by a formal [3 + 2] cycloaddition with

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[5])   3-Methylcyclohexa-1,4-diene was prepared from benzoic acid which was transformed to cyclohexa-2,5-diene-1-carboxylic acid by Birch reduction [14]. Cyclohexa-2,5-diene-1-carboxylic acid was reduced with LiAlH$_4$ to cyclohexa-2,5-diene-1-methanol [15], which, on treatment with TsCl [15], followed by reaction with LiAlH$_4$, gave the desired 3-methylcyclohexa-1,4-diene [16].

acetylene. This route is completed by dehydrogenation to yield **16**, which may isomerize [22] to the 6-methylfulvene complex, **17** [23]. Similarly, after (E/Z)-isomerization of the pentadiene ligand as described above, an allylic C—H bond activation may afford an internal cyclization of pentadiene, in which the acetylene ligand serves as a spectator giving rise to a C_5-building block complexed to acetylene/Fe^+ (*Scheme 4*). Subsequent loss of molecular hydrogen leads to the cyclopenta-1,3-diene/acetylene/Fe^+, **19**, which may eventually undergo another [4 + 2] cycloaddition affording norbornadiene/Fe^+, **20**. The proposed reaction sequence **18** → **19** → **20** has been verified by examination of **21**, which was generated by CI of a mixture of acetylene, cyclopentene, and $Fe(CO)_5$. The resulting dehydrogenation product $[21 - H_2]$ was considered to correspond to the structure **19** [21], and in fact the CA spectra of $[21 - H_2]$ and **19** are practically identical. In agreement with earlier work [24] [25] which provided evidence for an equilibrium between **19** and **20**, also the CA spectra of **19** and **20** reveal no major differences except for the more pronounced Fe^+ signal ($\Delta m = 94$) from **20** due to loss of the complete norbornadiene ligand.

<div align="center"><i>Scheme 3</i></div>

(*E*)-**8**   **16**   **17**
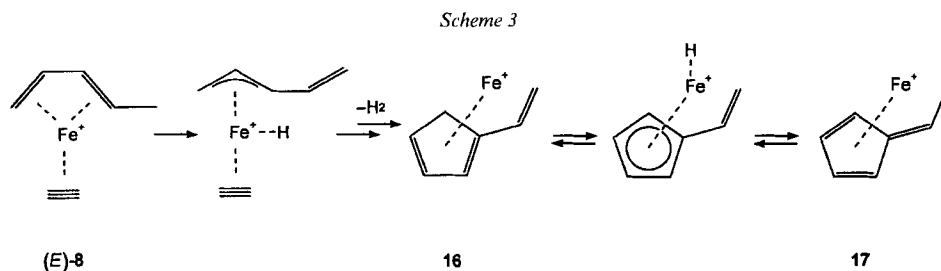
To clarify which products are formed from (*E*)-**8** by the various conceivable dehydrogenation pathways, the MI/CA spectrum [(*E*)-**8** $- H_2$] was compared to the CA spectra of several plausible $[Fe, C_7, H_8]^+$ isomers (*Table 2*). The CA spectrum of **15** displays the same fragmentation pattern as observed in the spectrum of [(*E*)-**8** $- H_2$], but again significant intensity differences for the characteristic fragments corresponding to $\Delta m = 14$, 57, and 78 are found. Consequently, the product of dehydrogenation of (*E*)-**8** may in part correspond to **15**, but by no means exclusively. Similarly, none of the other isomers examined can explain the MI/CA results alone. Thus, a mixture of isomers is formed from (*E*)-**8**, *e.g.*, the formal [4 + 2] cycloaddition product **12** as well as the [5 + 2] product **15**. Nevertheless, even a mixture of **12** and **15** alone cannot explain the intense loss of $\Delta m = 26$ (C_2H_2), and, thus, further $[Fe, C_7, H_8]^+$ isomers must be considered. Among these, isomers with five-membered rings appear quite likely as the CA spectra of **17**[6]), **19**, **20**, and $[21 - H_2]$ are very similar except for the more pronounced C_7H_8 losses from **17** and **20**. The base peaks in these CA spectra correspond to $\Delta m = 26$ (C_2H_2). Hence, the MI/CA spectrum of [(*E*)-**8** $- H_2$] can be rationalized by the formation of a mixture consisting of **12**, **15**, and at least one additional isomer related to substituted cyclopentadiene/Fe^+ as depicted in *Scheme 4*.

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[6])   6-Methylfulvene [26] was prepared from AcCl and acetaldehyde which formed, under catalysis of $ZnCl_2$, 1-chloroethyl acetate. Reaction of 1-chloroethyl acetate with sodium cyclopentadienide gave, after treatment with Et_3N, 6-methylfulvene.

Scheme 4

(E)-8   18   19   21   20
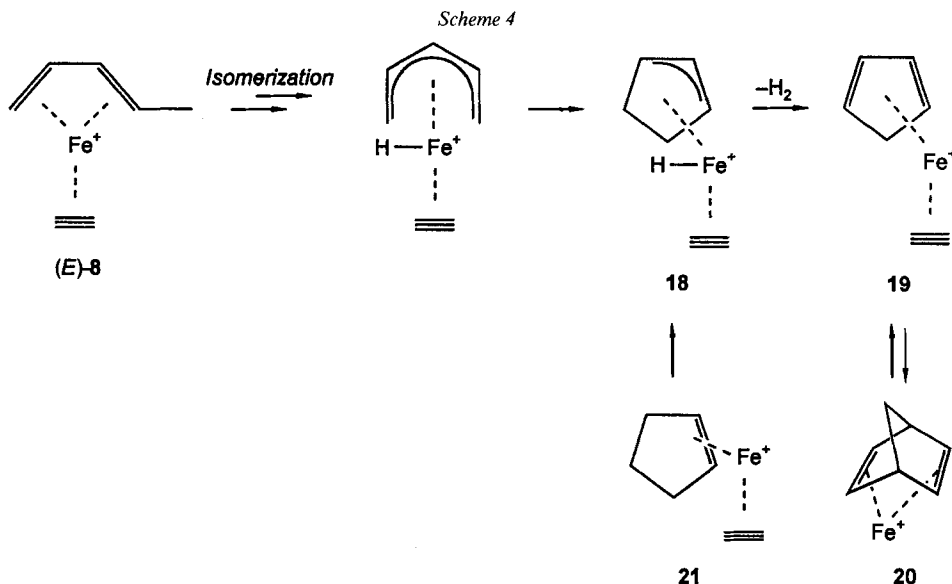
In summary, the complex (E)-8 reacts with much less selectivity than the unsubstituted system buta-1,3-diene/acetylene/Fe$^+$ as well as the methylated complexes 1–5, for which the formal [4 + 2] cycloaddition path prevails. Thus, Me substitution in the terminal position of the diene hinders the [4 + 2] route, to the extent that the metastable ions undergo other cyclizations instead. In particular, the penta-1,3-diene skeleton allows for the initial generation of a pentadienyl complex which directs part of the reactive ions from the [4 + 2] pathway towards the [3 + 2] and/or [5 + 2] cycloaddition routes.

Let us now turn towards the stereochemical effect observed in the unimolecular reactions of (E)-8 and (Z)-8. In particular, the ratios of H$_2$ and CH$_4$ losses change remarkably; i.e., from 18:82 for the (E)-isomer to 35:65 for the (Z)-isomer. Due to the fact that different internal energies of the metastable ions may interfere CA experiments, the reactions were also carried out under FTICR conditions[7]). The ion/molecule reac-

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[7]) Fourier transform ion cyclotron resonance (FTICR) experiments were performed with a Spectrospin CMS 47X FT-ICR mass spectrometer equipped with an external ion source and a superconducting magnet (Oxford Instruments, 7.05 Tesla) [13] [27]. Here, Fe$^+$ ions were generated via laser desorption/laser ionization by focusing the beam of a Nd:YAG laser (1064 nm) onto an iron target [28]. The cations were extracted from the ion source and transferred to the analyzer cell by a system of electric potentials and lenses. The isolation of the ^{56}Fe$^+$ isotope and all subsequent isolation steps were performed by using FERETS [29], a computer controlled ion-ejection protocol which combines single-frequency ion-ejection pulses with frequency sweeps to optimize ion isolation. Subsequently, the ions were thermalized by collisions with pulsed-in Ar and carefully re-isolated to avoid off-resonance excitation [30]. Thermalization was assumed to be complete, if no further changes in reactivity occurred upon increasing the number of collisions with Ar [31]. Pentadiene/Fe$^+$ complexes were generated by reaction of bare Fe$^+$ with pulsed-in propene affording a mixture of (C$_2$H$_4$)Fe$^+$ and (C$_3$H$_6$)Fe$^+$ which were then converted to (C$_5$H$_8$)Fe$^+$ by pulsing-in (E)- or (Z)-penta-1,3-diene, respectively. The latter ion was then allowed to react with acetylene which was leaked into the ICR cell at a constant pressure of ca. 10^{-8} mbar. Analogously, acetylene/Fe$^+$ was generated and reacted with pentadiene. All functions of the instrument were controlled by a Bruker Aspect 3000 minicomputer.

tions of penta-1,3-diene/Fe$^+$ with acetylene give ratios of H_2/CH_4 20:80 and 40:60 for the (E)- and (Z)-complexes, respectively. Similarly, the reactions of acetylene/Fe$^+$ with penta-1,3-dienes give ratios of 20:80 and 35:65 for (E)- and (Z)-isomers. These results are in excellent agreement with those of metastable ions and demonstrate that the different ratios for H_2 and CH_4 are not due to instrumental effects, but indicate a certain degree of stereoselectivity in the Fe$^+$ mediated [4+2] cycloaddition of (E)-**8** and (Z)-**8**.

To rationalize the origin of the different behavior of the two penta-1,3-diene isomers, let us briefly consider the stereochemical constraints of a [4+2] cycloaddition. A simple explanation for the favored loss of H_2 from metastable (Z)-**8**, as compared to (E)-**8**, is based on the mechanism depicted in *Scheme 5*. A stereochemical constraint arises already from the fact that both ligands, penta-1,3-diene and acetylene, are complexed to the Fe$^+$ cation. Consequently, acetylene has to attack the pentadiene ligand from the same side of the Fe$^+$ ion; an approach to the diene from the opposite face is not possible. As a result, the Me group of (Z)-**8** is rotated away from the Fe$^+$ center, when the acetylene approaches the diene in the transition structure associated with the cyclization. Hence, *anti*-**13** is formed as an intermediate. As the metal ion cannot move from one π face to its opposite [32], *via* a multi-step process [33] *anti*-**13** gives rise to loss of H_2 resulting in the formation of **12**.

Scheme 5

(Z)-**8**   *anti*-**13**   **12**
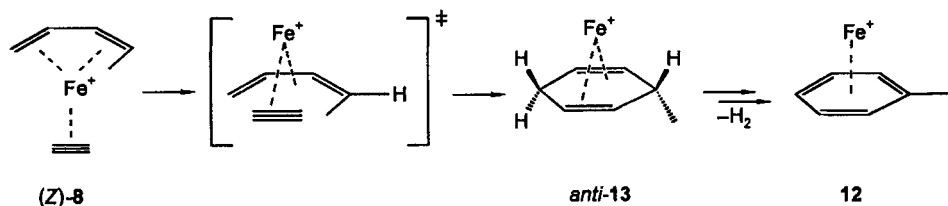
An analogous mechanism can be formulated for (E)-**8** (*Scheme 6*). However, following the same line of reasoning in the course of the cycloaddition, the Me group will end up at the same face of the ring as the complexing Fe$^+$ ion. Thus, *via* intermediate *syn*-**13**, loss of CH_4 is preferred.

Scheme 6

(E)-**8**   *syn*-**13**   **14**
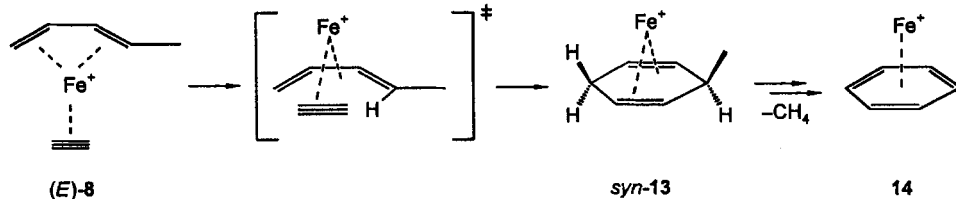
The stereochemical course of the reactions depicted in *Schemes 5* and *6* would result in the exclusive losses of H_2 from (Z)-**8** and of CH_4 from (E)-**8**. Experimentally, a preference for these two channels is indeed observed for the respective stereoisomers, but the existence of either pathway for the two stereoisomers is quite obvious. While

dehydrogenation may occur *via* the [5 + 2] and [3 + 2] routes as discussed above, the expulsion of CH_4 from (Z)-**8** can only be due to a [4 + 2] cycloaddition because the product corresponds to benzene/Fe^+; this follows from the similarity of the MI/CA spectrum of [(Z)-**8** $-CH_4$] and the CA spectrum of genuine benzene/Fe^+. Further, the analysis of the MI/CA spectrum of the product [(E)-**8** $-H_2$] reveals that *inter alia* toluene/Fe^+, **12**, is formed; consequently, part of the H_2 loss from (E)-**8** can be traced back to a formal [4 + 2] cycloaddition. Quite likely, Fe^+-mediated partial (E/Z)-isomerization of the diene (see above) precedes the cycloaddition step, but this isomerization cannot be complete as significant differences persist in the reactivities of (E)-**8** and (Z)-**8**. In addition, the fact that (E)-penta-1,3-diene is more stable than the (Z)-isomer may account for the favored losses of CH_4 from both complexes. Assuming that the complexation energies of Fe^+ to benzene and toluene are similar, the loss of CH_4 concomitant with formation of **14** is thermodynamically favored by 10 kcal/mol compared to dehydrogenation.

This mechanistic scenario is further supported by the labeled complexes (E)-penta-1,3-diene/[D_2]acetylene/Fe^+, (E)-**8a**, and (Z)-penta-1,3-diene/[D_2]acetylene/Fe^+, (Z)-**8a**, for which the stereochemical features of the unlabeled complexes remain conserved; yet, both labeled stereoisomers show eliminations of HD and CH_3D besides the H_2 and CH_4 losses, expected for an exclusive [4 + 2] cycloaddition route (*Table 1*). Note, however, that the MI/CA spectra of the ions formed by CH_4 and CH_3D losses, respectively, are in accordance with the formation of (labeled) benzene/Fe^+. The MI/CA spectra of the dehydrogenation products (*Table 4*) again indicate the formation of mixtures of five-, six-, and seven-membered rings. Notably, for [(E)-**8a** $-H_2$]$^+$ the abundances of acetylene ($\Delta m = 26$ and 27) and benzene losses ($\Delta m = 80$), respectively, are somewhat larger than for [(Z)-**8a** $-H_2$]$^+$ for which the loss of FeH ($\Delta m = 57$) to yield a $C_7H_7D_2^+$ cation predominates. This difference can be traced back to competing processes. Thus, while for (Z)-**8** the [4 + 2] process to yield **12** is not impeded by steric congestion, dehydrogenation of (E)-**8a** *via* the [4 + 2] route requires isomerization prior to ring formation or has to follow other cyclization pathways to yield, *e.g.*, five- and seven-membered rings. In line with this reasoning, the differences in the MI/CA spectra are much less pronounced for [(E)-**8a** $-HD$]$^+$ and [(Z)-**8a** $-HD$]$^+$. Furthermore, the finding that H_2 and HD losses give rise to isomeric mixtures, implies that either all mechanisms for the formation of five-, six-, and seven-membered rings allow H/D equilibration or that H/D exchange occurs prior to cyclization. The second alternative seems more plausible,

Table 4. *Representative Mass Differences (Δm in amu) in the MI/CA Spectra of Pentadiene/[D_2]Acetylene/Fe^+ Complexes after Losses of H_2 and HD, Respectively*[a])

Complex	Δm						
	26	27	57	69	79	80	Fe^+
[(E)-**8a**$-H_2$]	48	100	85	27		19	99
[(Z)-**8a**$-H_2$]	55	51	100	24		7	96
[(E)-**8a**$-HD$]	100	63	71	18	12		70
[(Z)-**8a**$-HD$]	100	43	58	19	9		53

[a])   Intensities are given relativ to the base peak (100%).

because it can be explained by simple activation of allylic C—H bonds by iron and transfer to the acetylene ligand [24], while in particular for the [4 + 2] route H/D equilibration following cycloaddition seems quite unlikely regarding the results of **1a** and **2a**.

The MI spectrum of the complex[8]) [5,5,5-D$_3$]penta-1,3-diene/acetylene/Fe$^+$, **8b** (*Table 1*) reveals expulsion of H$_2$, HD, and CH$_3$D, CH$_2$D$_2$, and CHD$_3$; nevertheless, the observed intensities do not correlate with a statistical H/D exchange. The ratio of isotopomeric hydrogen-to-methane losses (29:61) from **8b** lies in-between the one observed for the unlabeled complexes (*E*)-**8** and (*Z*)-**8**. Thus, the presence of a mixture of stereoisomers as well as the operation of a kinetic isotope effect, which will influence the branching ratios of the competing processes, are indicated. In any case, the extensive H/D equilibration supports the conjecture that allylic C—H bond activation of the diene precedes cyclization; this notion explains why we have not further attempted to generate **8b** in a stereoselective manner.

The reactions of the (*E*)- and (*Z*)-isomers the penta-1,3-diene/propyne/Fe$^+$ systems are rather intriguing. In their unimolecular reactions, (*E*)-**9** and (*Z*)-**9** show the expulsions of H$_2$ and CH$_4$ as expected for a [4 + 2] cycloaddition with some differences in the ratios of H$_2$ to CH$_4$. In analogy to the findings for (*E*)-**8** and (*Z*)-**8** (see above), (*Z*)-**9** yields more H$_2$ than CH$_4$ in comparison to (*E*)-**9**. Thus, to a first approximation we can attribute the difference between the (*E*)- and (*Z*)-isomers to the stereochemical course of the [4 + 2] cycloaddition. In addition, loss of $\Delta m = 30$ is observed which is probably due to consecutive elimination of H$_2$ and ethene as indicated by the MI/CA spectra of [(*E*)-**9** – H$_2$] and [(*Z*)-**9** – H$_2$] (*Table 3*). Further, these MI/CA spectra reveal that xylene/Fe$^+$, the expected product of a [4 + 2] cyclization and a subsequent dehydrogenation, is not formed exclusively, because the losses of C$_2$H$_4$ ($\Delta m = 28$) and C$_3$H$_5$· ($\Delta m = 41$) are much too intense compared to the CA spectra of the genuine Fe$^+$ complexes of the xylene isomers. These intensity differences have to be due to other products formed by unimolecular reaction of **9**. To identify these product(s), CA spectra of several [Fe,C$_8$,H$_{10}$]$^+$ isomers were compared to the MI/CA spectra of [(*E*)-**9** – H$_2$] and [(*Z*)-**9** – H$_2$]. While ethylbenzene/Fe$^+$ cannot account for the intense losses of $\Delta m = 28$ and $\Delta m = 41$, the CA spectrum of cycloocta-1,3-5-triene/Fe$^+$, used as a mixture with the equilibrated bicyclo[4.2.0]octa-2,4-diene/Fe$^+$ [34], exhibits an intense loss of $\Delta m = 28$. This result suggests that **9** undergoes cyclization to an eight-membered ring which can possibly equilibrate with a bicyclic species. The losses of $\Delta m = 41$ in the spectra of [(*E*)-**9** – H$_2$] and [(*Z*)-**9** – H$_2$] can be explained by involving the formation of a five-membered ring as proposed in *Schemes 2* and *4* for the lower homologue.

For the formation of six-membered rings *via* [4 + 2] cycloadditions, for the complexes (*E,E*)-**10** and (*E,Z*)-**10**[9]), one expects the eliminations of H$_2$, CH$_4$, and C$_2$H$_6$ which are indeed all observed in the unimolecular reactions. However, the MI/CA spectrum of [(*E,E*)-**10** – H$_2$] supports only minor formation of xylene/Fe$^+$; rather, eight-membered

[8]) [5,5,5-D$_3$]Penta-1,3-diene/Fe$^+$ was prepared by Fe$^+$-induced elimination of H$_2$O in the ion source from [5,5,5-D$_3$]pent-1-en-3-ol, which was synthesized by reacting CD$_3$CH$_2$MgBr with acroleine. As the stereochemical course of the metal-mediated dehydration is unknown, we assume that a mixture of (*E*)- and (*Z*)-isomers is formed.

[9]) (2*Z*,4*E*)-Hexa-2,4-diene and (*E,E*)-Hexa-2,4-diene were isolated from a commercially available mixture of isomers by distillation followed by preparative gas chromatography (*CP Wax 51/CW 20M*).

and possibly five-membered rings are produced, as deduced from the losses of C_2H_4 and $C_3H_5{}^{\cdot}$ in the MI/CA spectrum.

In the last section, we will address the regioselectivity involved in the Fe^+-mediated [4 + 2] cycloaddition. To this end, we first had to find a system which fulfills the following prerequisites. Obviously, the diene and the alkyne need to bear at least one substituent each to allow for the formation of different regioisomers. Further, the resulting isomers have to be distinguishable by mass spectrometry; this is not trivial at all, because substituted arenes often give rise to similar fragmentation patterns. Consequently, for comparison the expected products have to be accessible as reference compounds. Finally, the formal [4 + 2] cycloaddition should be relatively effective and possibly not interfered by other cyclization processes. Based on earlier MS studies, it is well known that the different regioisomers of dimethoxybenzene/M^+ can be distinguished [10]. In analogy, the *ortho-*, *meta-*, and *para-*isomers[10]) of ethoxytoluene/Fe^+ should be distinguishable; indeed, this is evidenced by the different fragmentations of their Fe^+ complexes (*Table 5*). Thus, the *ortho-*ethoxytoluene/Fe^+ differs from the other isomers by its characteristic enhanced loss of ethane ($\Delta m = 30$), and the *meta-* and *para-*complexes are distinguishable by the different ratios of the losses $\Delta m = 44$ $\Delta m = 58$, and $\Delta m = 70$ $\Delta m = 85$, respectively.

Let us first consider the [4 + 2] cycloaddition with an alkoxy substituent on the alkyne for the parent system. Ethoxyacetylene is known as an electron-rich dienophile in *Diels-Alder* reactions [35]. In fact, it favors cyclization in that the reaction of buta-1,3-diene/ethoxyacetylene/Fe^+, **22**, leads to the exclusive elimination of H_2. The MI/CA spectrum of [**22** $- H_2$] is very similar to the CA spectrum of phenetole/Fe^+ [17] which leads to the conclusion that **22** reacts selectively *via* a formal [4 + 2] cycloaddition. Thus, the use of ethoxyacetylene as a dienophile seems promising as similar results can be expected

Table 5. *Representative Mass Differenes (Δm in amu) in the MI/CA Spectra of* **23** *and* **24** *after Loss of H_2 in Comparison to Regioisomeric Ethoxytoluene/Fe^+ Complexes[a])*

Spectrum	Complex	No.	Δm									
			28	30	44	58	70	85	101	Fe^+	44/58[b])	70/85[b])
MI/CA	Isoprene/ethoxyacetylene/Fe^+	**23**	100	<3[c])	17	17	6	11	10	6	1.0	0.6
MI/CA	(*E*)-Penta-1,3-diene/ethoxy-acetylene/Fe^+	**24**	100	6[d])	15	18	5	4	5	2	0.8	1.2
CA	*o*-Ethoxytoluene/Fe^+		100	32	23	27	7	12	17	23	0.9	0.6
CA	*m*-Ethoxytoluene/Fe^+		100	4	20	30	10	9	12	4	0.7	1.1
CA	*p*-Ethoxytoluene/Fe^+		100	4	19	21	6	15	8	3	0.9	0.4

[a]) Intensities are given relative to the base peak (100%).
[b]) Structure indicative fragment ratios for losses of $\Delta m = 44$, 58, 70, 85, respectively; see text.
[c]) Mass resolution of the spectra measured in the 4th field-free region was too low to evaluate the intensities of peaks closed to more intense fragments.
[d]) Mass resolution was achieved by interpretation of a MS^3 spectra scanned by $B(2)$.

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[10]) The ethoxytoluenes were synthesized from the corresponding cresol and EtBr.

for the systems with one Me substituent at the diene moiety. Indeed, the unimolecular reaction of the isoprene/ethoxyacetylene/Fe$^+$, **23**, gives rise to loss of H$_2$ (> 99%), and for (E)-penta-1,3-diene/ethoxyacetylene/Fe$^+$, **24**, the most prominent peaks are the expected losses of H$_2$ (85%) and CH$_4$ (12%) besides some minor side reactions ($\Delta m = 44$, 1%; $\Delta m = 45$, 2%). For the (Z)-penta-1,3-diene/ethoxyacetylene/Fe$^+$ the same fragmentations in similar ratios are observed; consequently, stereochemical differences seem to be negligible in this case. Comparison of the characteristic fragment ratios in the MI/CA spectra of [**23** – H$_2$] and [**24** – H$_2$] with the CA spectra of the different regioisomers of ethoxytoluene/Fe$^+$ (*Table 5*) reveals that dehydrogenation of **23** leads predominately to the *para*-isomer while complex **24** forms the *meta*-ethoxytoluene/Fe$^+$ product. Hence, in both cases the sterically less hindered product is formed. For instance, frontier orbital theory predicts that the metal-free *Diels-Alder* reaction on an electron-rich diene with an electron-rich dienophile leads to the corresponding *meta*-isomer [36]. Even if there are few known examples of such *Diels-Alder* reactions, the present regioselectivity for the Fe$^+$-induced cyclization clearly deviates from this expectation. This finding can be traced back either to the modified electronical environment by the electron-withdrawing Fe$^+$ or simply the substituents avoid to approach each other, and the observed regioselectivity is mostly governed by steric effects.

22   23   24
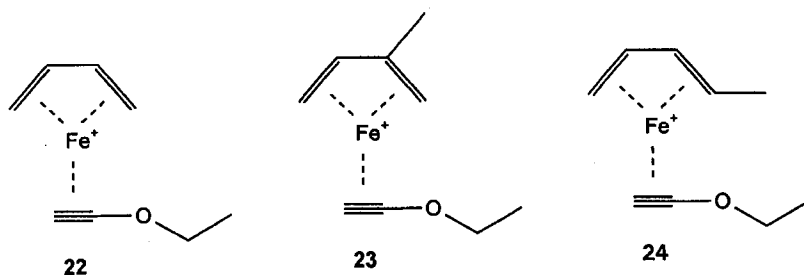
In conclusion, Fe$^+$-mediated [4 + 2] cycloadditions are influenced by the position of the Me substitution: the effect of Me groups at C(2) and C(3) of the diene is negligible. Similarly, Me substituents at the alkyne have a minor influence on the cycloaddition, whereas sterically more demanding alkynes disfavor cyclization. Increasing number of Me substituents on the terminal positions of the diene leads up to an almost complete suppression of the [4 + 2] cycloaddition route, and other pathways prevail. Nevertheless, substituents in the terminal position of the diene reveal stereochemical effects depending on the configuration of the C=C bond. The analysis of the regiochemistry reveals that in the cycloaddition reaction the alkyne and the diene moiety approach each other in a fashion such that steric interactions of the substituents are minimized.

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