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Neutralization–reionization mass spectrometry as a novel probe to structurally characterize organic ligands generated in the Fe(I)-mediated oligomerization of acetylene in the gas phase

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ABSTRACT

Relatively detailed information on the structures of the ligands "$C_{2x}H_{2x}$" formed in the Fe^+-mediated oligomerization of acetylene ($xC_2H_2 \rightarrow C_{2x}H_{2x}$; $x = 2$–4) in the gas phase is provided by subjecting the resulting $Fe(C_{2x}H_{2x})^+$ systems to a neutralization–reionization mass spectrometry (NRMS) experiment. It is shown that for $x = 2$ the preferred structure corresponds to the $Fe(C_2H_2)_2^+$ complex **3**$^+$. Isomerization to Fe(cyclobutadiene)$^+$ **4**$^+$ or the formation of a ferracyclopentadiene ion **5**$^+$ are both negligible. The addition of a further C_2H_2 ligand to **3**$^+$ gives rise to a NR mass spectrum which clearly indicates that cyclotrimerization to a benzene ligand has occurred (**1**$^+ \rightarrow$ **2**$^+$) to some extent. Addition of a further C_2H_2 molecule to the $Fe(C_6H_6)^+$ complex **2**$^+$, however, does not result in the formation of a Fe(cyclooctatetraene)$^+$ complex **8**$^+$. Obviously, the barrier for the isomerization $Fe(C_2H_2)(C_6H_6)^+$ (**6**$^+$) $\rightarrow$ $Fe(C_8H_8)^+$ (**8**$^+$) is too high. It is suggested that NRMS may be superior to other mass spectrometric techniques to probe the structural features of the organic ligands attached to transition metal ions.

INTRODUCTION

As demonstrated repeatedly, the relatively recent technique of neutralization–reionization mass spectrometry (NRMS) (for leading references, see ref. 1) is ideally suited to generate and characterize a variety of elusive molecules including coordinatively unsaturated metal fragments [2] in the gas phase, species which are often not accessible in solution or in a matrix because of facile intermolecular processes. In addition, in a few case studies

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the method has proved quite valuable to distinguish ionic isomers (for instructive examples see ref. 3); the latter experiments are based on the concept that the propensity of isomerization reactions, as compared with dissociations, is for numerous systems much larger for ions than for their neutral counterparts. Here, we demonstrate for the first time that NRMS can also be used to obtain useful insight into the nature of the ligands[a] formed in the course of Fe^+-mediated oligomerization of acetylene in the gas phase (eqn. 1)[b], a reaction of scientific interest as well as of great economic value (for excellent reviews on many aspects of the fundamental problem of alkyne cyclo-oligomerization using more traditional approaches see ref. 7):

$$Fe^+(C_2H_2)_x \longrightarrow Fe^+(C_{2x}H_{2x}) \qquad (x = 2\text{–}4) \tag{1}$$

EXPERIMENTAL

The mass spectrometric experiments were carried out with a modified VG Instruments ZAB mass spectrometer. This is a four-sector instrument of BEBE configuration (B stands for magnetic sector and E for electric sector) which has been built by AMD Intectra, Harpstedt, Germany, by combining the BE part of a ZAB-HF-3F machine (MS I) with an AMD 604 double-focussing mass spectrometer (MS II) (for a full description of the machine and its operation see ref. 8). The ions $Fe(C_2H_2)_x^+$ ($x = 2$–4) were generated by 100 eV electron impact ionization of a mixture of C_2H_2 ($p \simeq 10^{-5}$ mbar) and 1 μl $Fe(CO)_5$, the latter introduced in the chemical ionization source via a heated septum inlet. Owing to the higher bond energy of C_2H_2 to Fe^+ (for thermochemical data see ref. 9), the CO ligands of $Fe(CO)_n^+$ ($n = 1$–5) are rapidly replaced by C_2H_2 (eqn. 2). Depending on the C_2H_2 pressure, the base peak in the ion source mass spectra corresponds to $Fe(C_2H_2)_x^+$ with $x = 3$ and 4.

$$Fe(CO)_5 \xrightarrow{EI} \underset{n = 1\text{–}5}{Fe(CO)_n^+} \xrightarrow{xC_2H_2} \underset{x = 1\text{–}4}{Fe(C_2H_2)_x^+} + nCO \tag{2}$$

The following ion source conditions were employed: ion source temperature, 200°C; repeller voltage, ≈ 0 V; acceleration voltage, 8 kV; mass resolution $m/\Delta m > 1500$ (10% valley definition). Collision-induced dissociations (for reviews see ref. 10), used to characterize the ions formed in the

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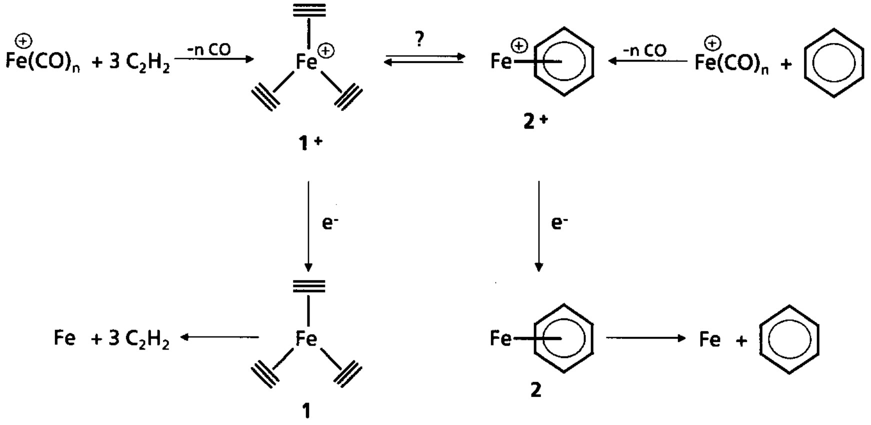
[a] For the application of other methods to characterize ionic products of transition metal ion-induced dissociations of organic molecules see ref. 4.

[b] For a detailed discussion of the unimolecular and collision-induced gas phase chemistry of M^+(alkyne) complexes (M = transition metal), see ref. 5. The cyclo-oligomerization of alkynes in matrices by first-row transition metal atoms is reviewed in detail in ref. 6.

source, were brought about by mass-selecting an 8 keV beam of the ions of interest by means of B(1)E(1) and colliding it with helium in a collision chamber located in the field-free region between E(1) and B(2) at a transmission, *T*, of 80%. Ionic products were recorded by scanning B(2). In the NRMS experiments, a beam of mass-selected $Fe(C_2H_2)_x^+$ ions (having 8 keV translational energy) was neutralized in the first cell of a differentially pumped tandem collision cell (located in the field-free region between E(1) and B(2)) by colliding the beam with xenon (80% *T*). Unreacted ions were deflected away from the beam of neutral species by applying a voltage of 1000 V on the deflector electrode; subsequent reionization occurred in the second collision cell by collision with oxygen (80% *T*). The resulting mass spectra were recorded by scanning B(2). In all experiments signal averaging techniques were used to improve the *S*/*N* ratio. The data were accumulated by on-line processing 5–30 spectra with the AMD-Intectra computer system DP10.

RESULTS AND DISCUSSION

The central problem we are addressing in this study concerns the structure of the $(C_2H_2)_x$ ligands generated in reaction 2: do the acetylene units, for example $x = 3$, remain distinct ($\mathbf{1}^+$) or do they undergo isomerization reactions such that cyclotrimerization to benzene ($\mathbf{1}^+ \rightarrow \mathbf{2}^+$) takes place at the metal centre (Scheme 1)?



Scheme 1.

An indication that the oligomerization $3C_2H_2 \rightarrow C_6H_6$ has indeed occurred, at least to some extent, is provided by the collisional activation (CA) mass spectrum of $Fe(C_2H_2)_3^+$. As shown in Table 1, this mass spectrum contains signals at *m*/*z* 78 ($C_6H_6^{+\cdot}$) and 77 ($C_6H_5^+$) which are due to the losses of Fe ($\Delta m = 56$) and FeH (the latter possibly as Fe and H). Though of low abundance, these signals leave no doubt that some fraction of the three, originally

TABLE 1

CA mass spectra of $Fe(C_2H_2)_3^+$ and $Fe(C_6H_6)^{+a}$

Ion	Loss of neutral(s) with Δm															
	1	2	26	27	28	29	39	40	41	52	53	54	56	57	66	78
$Fe(C_2H_2)_3^+$	3	1	100	7	4	< 1	< 1	< 1	–	18	8	1	1	1	< 1	14
$Fe(C_6H_6)^+$	60	8	< 1	20	6	3	2	3	2	3	27	1	4	3	< 1	100

[a] Intensities are given as % base peak.

separate C_2H_2 units was fused to a C_6H_6 unit. However, if the CA spectrum of $Fe(C_2H_2)_3^+$ is compared with that of an authentic $Fe(C_6H_6)^+$ ion, generated by reacting $Fe(CO_n^+$ with C_6H_6 in the ion source, the spectral differences are so pronounced that a complete transformation $3C_2H_2 \rightarrow C_6H_6$ can be ruled out with certainty.

What happens if the two isomeric systems $Fe(C_2H_2)_3^+$ ($\mathbf{1}^+$) and $Fe(C_6H_6)^+$ ($\mathbf{2}^+$) are subjected to a NRMS experiment? Before presenting the experimental results let us try to analyse the situation. Common to the two isomers is a significant loss of binding energy between the metal and the organic ligand(s) when comparing the ions $\mathbf{1}^+$ and $\mathbf{2}^+$ with their neutral counterparts **1** and **2**. Consequently, we should expect that a substantial fraction of the neutral species $Fe(C_2H_2)_3$ (**1**) and $Fe(C_6H_6)$ (**2**) will fall apart to iron and the organic ligand(s) when derived from neutralization of the corresponding ions. As a result, and in line with previous findings [2cdi], the recovery signals in the NR mass spectra are predicted to be of low intensity. However, the species Fe, C_2H_2 and C_6H_6 formed in the neutralization of $\mathbf{1}^+$ and $\mathbf{2}^+$ upon entering the second collision cell will be reionized with cross-sections, σ, following the qualitative order: $\sigma(C_6H_6) > \sigma(Fe) > \sigma(C_2H_2)$ (for leading references on this aspect and procedures to estimate cross-sections of electron transfer processes in beam experiments see ref. 11). If the acetylene units of $Fe(C_2H_2)_3^+$ have remained distinct (i.e. $\mathbf{1}^+ \nrightarrow \mathbf{2}^+$) one would not expect to observe hydrocarbon ion signals above m/z 26 ($C_2H_2^{+\cdot}$) in the NR spectrum. However, if trimerization to C_6H_6 has taken place, the NR mass spectrum of $Fe(C_2H_2)_3^+$ must contain a signal at m/z 78 (together with ionic fragments formed thereof by further dissociation of $C_6H_6^{+\cdot}$). The analysis of the two NR mass spectra (Figs. 1 and 2) is quite revealing.

Let us first discuss the NR mass spectrum of $Fe(C_6H_6)^+$ (Fig. 1). We note the nearly quantitative absence of a recovery signal at m/z 134. The reasons are twofold. (i) The bond energy $D°(Fe^+\text{-}C_6H_6)$ for $\mathbf{2}^+$ of 55 kcal mol^{-1} [12] is significantly smaller for the neutral system **2**. Although no accurate experimental data exist for $D(Fe\text{–}C_6H_6)$, preliminary ab initio MO calculations using pseudo-potentials for Fe suggest that for the neutral system **2** the bond energy is more than 30 kcal mol^{-1} smaller when compared with $Fe(C_6H_6)^+$ [13]. (ii) Differences in the geometries of $Fe(C_6H_6)^+$ and $Fe(C_6H_6)$ may result in small Franck–Condon factors for the vertical electron transfers in the neutralization and reionization steps [2d].

The NR mass spectrum of $Fe(C_6H_6)^+$ is dominated by a signal at m/z 78 ($C_6H_6^{+\cdot}$) and hydrocarbon fragment ions formed by further dissociation. We also note an intense signal for reionized Fe m/z 56), while $Fe(C_xH_y)^+$ species are either absent or of minor abundance. All these findings confirm our expectations of the properties of $Fe(C_6H_6)$.

Most interesting is the result obtained when $Fe(C_2H_2)_3^+$ ($\mathbf{1}^+$) is subjected

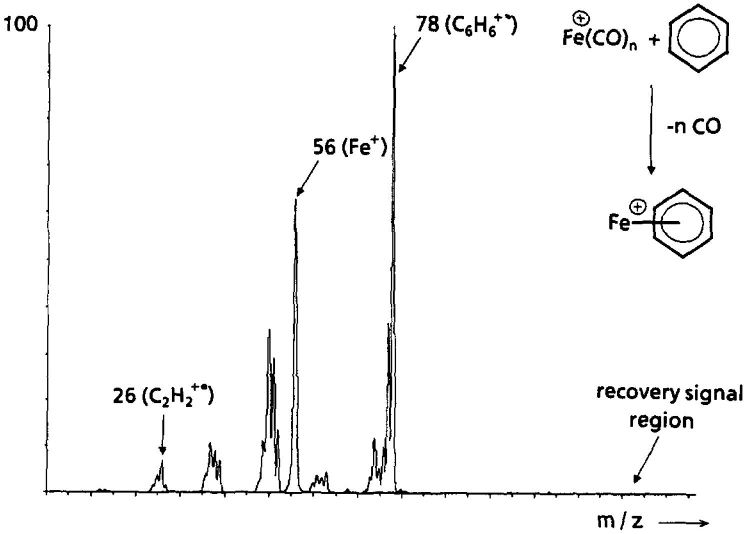


Fig. 1. NR mass spectrum (Xe/O_2) of *m*/*z* 134, $Fe(C_6H_6)^+$.

to an NR experiment (Fig. 2). In addition to the expected signals for Fe^+, $Fe(C_xH_y)^+$ and $C_2H_2^{+\cdot}$ we obtain an intense signal at *m*/*z* 78 ($C_6H_6^{+\cdot}$) and hydrocarbon signals which originate from further dissociation of $C_6H_6^{+\cdot}$. These signals can only be accounted for by the presence of an intact C_6H_6 unit in the $Fe(C_2H_2)_3^+$ ions. Thus, part of the $Fe(C_2H_2)_3^+$ population has indeed isomerized to $Fe(C_6H_6)^+$. This conclusion is further substantiated by inspecting

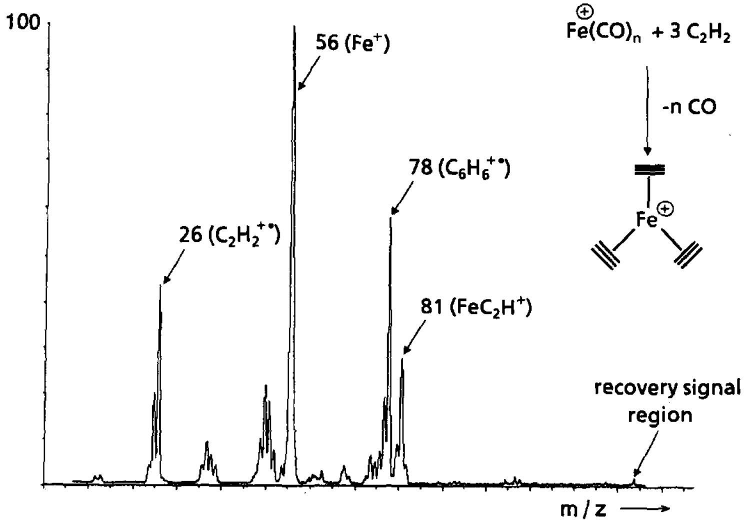


Fig. 2. NR mass spectrum (Xe/O_2) of *m*/*z* 134. $Fe(C_2H_2)_3^+$.

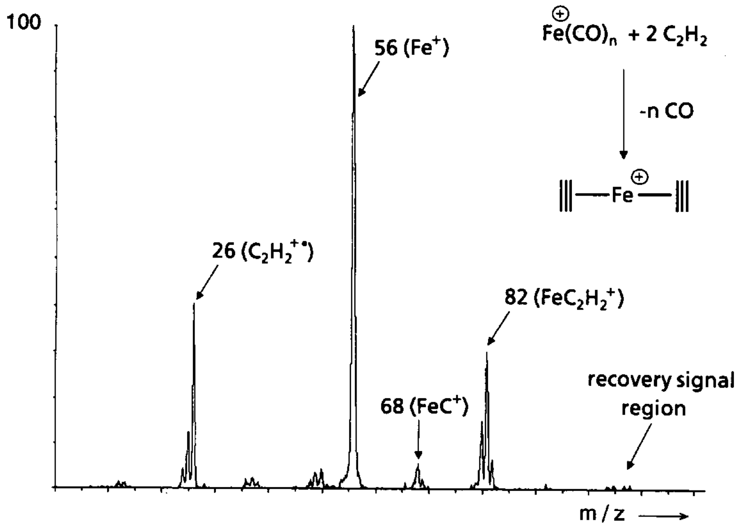


Fig. 3. NR mass spectrum (Xe/O$_2$) of *m*/*z* 108, Fe(C$_2$H$_2$)$_2^+$.

the data given in Table 2. We note the following. (i) There is excellent agreement between the intensities of the $C_xH_y^+$ signals ($x = 3$–6; $y = 0$–6) for both NR mass spectra. Thus, we conclude that a benzene ligand is formed in the course of trimerization of acetylene.[c] (ii) In the NR spectrum of $Fe(C_2H_2)_3^+$ we observe that the signal for $C_2H_2^{+\cdot}$ is much too abundant when compared with $Fe(C_6H_6)^{+\cdot}$. This indicates that the trimerization of acetylene to benzene is not quantitative. Unfortunately, the present data do not permit us to quantify the extent of the trimerization reaction.

When comparing the CA data (Table 1) with the results obtained in the NRMS experiments (Figs. 1 and 2; Table 2), at first sight one is inclined to view these as contradictory. We do not think this is necessarily true as the proper structural assignments of the ligands of organometallic systems by CA of the ions may be hampered on the following grounds. (i) Many organometallic complexes exhibit pronounced unimolecular dissociations (metastable ion spectra). These energetically favoured processes are often strongly

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[c] We have also addressed the problem of whether part of the acetylene already isomerizes in the ion source to C_6H_6 and, in a further step, if it is the latter which replaces CO from $Fe(CO)_n^{+\cdot}$ to generate directly $Fe(C_6H_6)^+$ rather than substituting C_2H_2 for CO followed by trimerization of the acetylene units at the iron centre. However, this is not likely to happen as an NR mass spectrum of ion source generated $C_6H_6^{+\cdot}$ (formed by electron impact ionization of benzene) is distinctly different from an NR mass spectrum of *m*/*z* 78, generated by bombarding acetylene with electrons in the ion source. In addition, this observation questions previous generalizations [14] based on photoionization studies of acetylene trimer clusters, that the benzene ion is invariably a sink for all $C_6H_6^{+\cdot}$ ions.

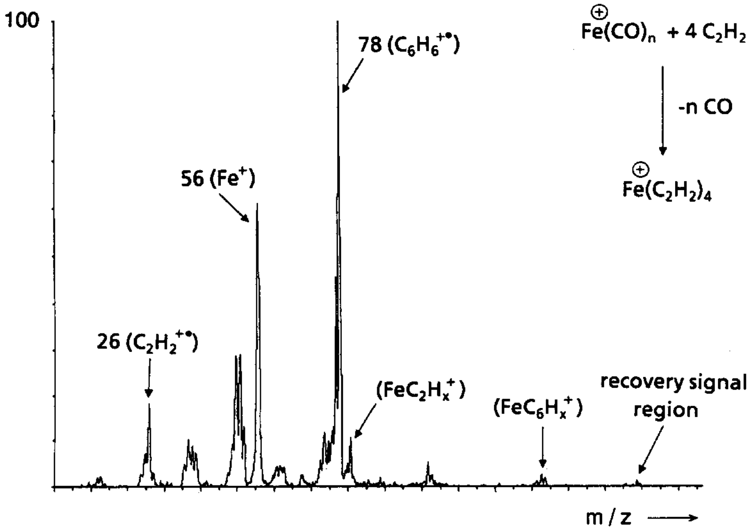


Fig. 4. NR mass spectrum (Xe/O_2) of *m/z* 160, $Fe(C_2H_2)_4^+$.

enhanced under CA conditions without generating new, structure-indicative decomposition pathways of the ligands; thus, the analytical significance of the "pure" CA spectra is diminished. (ii) Owing to the low ionization energies of metal ions, the charge prefers to stay on the organometallic fragments; consequently, structure-indicative processes involving the (organic) ligands are the exception rather than the rule.

Therefore, we recommend NRMS as a tool, clearly more powerful than CA in this study, to probe the structural properties of organic ligands generated in organometallic reactions. We have tested this conjecture by also subjecting the $Fe(C_2H_2)_x^+$ species ($x = 2$ and 4) to an NRMS experiment (Figs. 3 and 4).

Common to both systems are the following features. (i) The recovery signals are practically absent, thus pointing to favoured dissociation processes of the neutrals. (ii) Signals for $C_4H_x^+$ ($x \geqslant 3$) in the $Fe(C_2H_2)_2^+$ system (Fig. 3) and for $C_8H_x^+$ ($x \geqslant 6$) in the $Fe(C_2H_2)_4^+$ complex (Fig. 4) are either absent or very weak. (iii) In the $Fe(C_2H_2)_2^+$ system, the NR spectrum is dominated by signals for Fe^+, $C_2H_2^{+\cdot}$ and $Fe(C_2H_x)^+$ ($x = 0$–2). These spectral features are in keeping with a bis-acetylene structure **3**$^+$, rather than an Fe^+(cyclobutadiene) complex **4**$^+$ or the metallacycle **5**$^+$. (iv) The NR mass spectrum of $Fe(C_2H_2)_4^+$, however, is dominated by signals at *m/z* 78 ($C_6H_6^{+\cdot}$) and *m/z* 56 (Fe^+). Though of low abundance, the signals for $Fe(C_2H_x)^+$ and $Fe(C_6H_x)^+$ are structure indicative and point—together with the above mentioned signals—to the structure of an $Fe(C_2H_2)(C_6H_6)^+$ complex **6**$^+$ rather than **7**$^+$ or **8**$^+$. For **7**$^+$ one must not expect the presence of *m/z* 78, while for **8** an

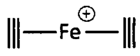
TABLE 2

NR mass spectra of $Fe(C_2H_2)_3^+$ ($\mathbf{1}^+$) and $Fe(C_6H_6)^+$ ($\mathbf{2}^+$)[a]

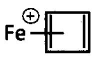
Ion	*m/z*	$Fe(C_2H_2)_3^+$ ($\mathbf{1}^+$)	$Fe(C_6H_6)^{+\cdot}$ ($\mathbf{2}^+$)	Δ[b]
Recovery ion region	134	1	< 1	+ 1
	133	–	< 1	–
	132	–	< 1	–
$FeC_2H_x^+$	82	5	–	+ 5
	81	47	1	+ 46
	80	14	1	+ 13
$C_6H_x^+$	78	100	100	–
	77	33	36	− 3
	76	12	13	− 1
	75	7	6	+ 1
	74	10	12	− 2
	73	3	4	− 1
$FeCH_x^+$	69	2	–	+ 2
	68	7	< 1	+ 7
$C_5H_x^+$	63	4	4	0
	62	2	3	− 1
	61	3	4	− 1
	60	2	2	0
Fe^+	56	170	60	+ 112
$C_4H_x^+$	52	12	12	0
	51	31	31	0
	50	37	38	− 1
	49	16	9	+ 7
	48	3	3	0
$C_3H_x^+$	39	7	8	− 1
	38	10	8	+ 2
	37	16	11	+ 5
	36	7	4	+ 3
$C_2H_x^+$	27	3	2	+ 1
	26	76	8	+ 68
	25	35	4	+ 31
	24	7	3	+ 4
CH_x^+	13	3	1	+ 2
	12	3	2	+ 1

[a] Data are given in % of signal *m/z* 78 = 100%.

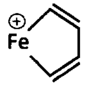
[b] In this column the deviation, Δ, between the two NR spectra is given.



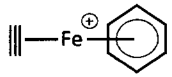
3+



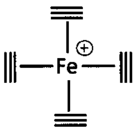
4+



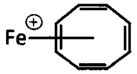
5+



6+



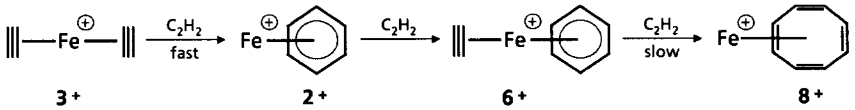
7+



8+

abundant signal for $C_8H_8^{+\cdot}$ should be observed. These features are not observed experimentally.

The observation that $Fe(C_2H_2)_2^+$ prefers to form the bis(acetylene)Fe^+ complex **3**$^+$ while for the trimer $Fe(C_2H_2)_3^+$ (**1**$^+$) a substantial fraction has isomerized to $Fe(C_6H_6)^+$ (**2**$^+$), and the fact that the propensity of $Fe(C_2H_2)(C_6H_6)^+$ (**6**$^+$) to isomerize to $Fe(C_8H_8)^+$ (**8**$^+$) is small, indicate that the Fe(benzene)$^+$ structure **2**$^+$ serves as a sink in the oligomerization of acetylene. This is readily formed when three C_2H_2 units are assembled around the metal ion centre but resists further oligomerization when a fourth C_2H_2 molecule is added (Scheme 2).



Scheme 2.

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