

Coupling Reactions of Fe(benzyne)⁺ and Fe(naphthylene)⁺ in the Gas Phase

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The gas phase ion–molecule reactions of Fe(benzyne)⁺ and Fe(naphthylene)⁺ with acetylene, allene, ethene, butadiene, buckminsterfullerene and cyclopropane are studied using Fourier transform ion cyclotron resonance mass spectrometry. In a previous study we proposed that the reaction of Fe(benzyne)⁺ with ethene proceeds by a mechanism in which a multiple carbon–carbon bond couples with a metal–carbon bond of Fe(benzyne)⁺ to form new carbon–carbon and metal–carbon bonds. In this study we include the reactions of Fe(naphthylene)⁺ in order to test the generality of this mechanism and to observe the non-metallic products formed in these reactions. Fe(benzyne)⁺, for example, reacts with acetylene to yield Fe⁺ and C₆H₄C₂H₂, exclusively. In contrast, the reaction of Fe(naphthylene)⁺ with acetylene produces Fe⁺, C₁₀H₆C₂H₂⁺ and a metallacyclic product Fe–C₁₀H₆–C₂H₂⁺. This lends support that the neutral product formed in the reaction of Fe(benzyne)⁺ with acetylene is an intact C₆H₄C₂H₂. Similarly, Fe(naphthylene)⁺ reacts with ethene to form a metallacyclic product Fe–C₁₀H₆–C₂H₄⁺. In the reaction with C₆₀, Fe(naphthylene)⁺ is observed to yield the C₆₀ derivatives C₆₀C₁₀H₆⁺ and Fe–C₁₀H₆–C₆₀⁺. These gas phase ion–molecule coupling reactions are analogous to the condensed phase coupling reactions of metallobenzynes with molecules containing multiple bonds. © 1997 John Wiley & Sons, Ltd.

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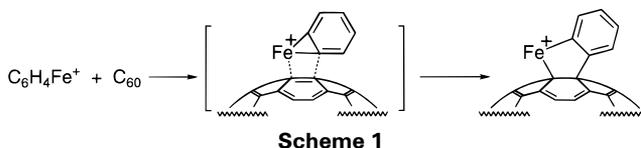
INTRODUCTION

Owing to its high degree of unsaturation and high reactivity,¹ benzyne cannot be isolated in solution. Coordination to a transition metal, however, can greatly increase its stability and, hence, metal–benzynes and metal complexes of small cycloalkynes have been widely investigated and used in a variety of synthetic processes.^{2–11} Nevertheless, isolating a metal–benzyne complex to study its reactivity is a formidable task and in most cases very large ligands are required to stabilize the benzyne structure.

Alternatively, gas phase ion–molecule reactions permit the study of the ‘intrinsic’ physical and chemical properties of a compound in the absence of complications due to solvation and the presence of other ligands. Some metal–benzyne ions, MC₆H₄⁺ (M = Fe, Co, Sc, Fe₂), have been successfully generated in the gas phase and their reactivities with various hydrocarbons have been examined.^{12–19} Ligated metal ions can undergo a variety of reactions depending on the metal

center, the ligand and the substrate. C–H bond oxidative insertions are common for late transition metals with singly bonded ligands reacting with alkanes, while low-valence species having d⁰ or d¹ metal centers undergo σ-bond metathesis.^{20,21} Olefin metathesis and migratory insertion are also frequently observed.^{20–23} Metal–benzyne ions exhibit several interesting reactions with alkenes and alkynes that can be considered coupling reactions. For instance, in a previous study on the reactions of Fe(benzyne)⁺ with various alkenes, Fe(benzyne)⁺ was observed to react with ethene to form C₈H₈ through a coupling mechanism, with Fe⁺ being observed as the only reaction product owing to its lower IE.¹⁶ Similarly, our recent studies of metal-ion-assisted derivatization of buckminsterfullerene indicated that the double bond of C₆₀ at the 6,6-ring junction can couple with Fe⁺–benzyne to form a C₆₀ metallacyclic derivative FeC₆₀C₆H₄⁺ (Scheme 1).^{24,25} This reaction mechanism is analogous to the commonly observed condensed phase cycloaddition reactions of metallobenzynes with alkenes and alkynes, as exemplified in Scheme 2.^{4–11}

In this paper, we report an extension of the above investigation to the reactions of Fe(benzyne)⁺ and Fe(naphthylene)⁺ with acetylene (C₂H₂), ethene (C₂H₄), allene (C₃H₄), butadiene (C₄H₆), buckminsterfullerene

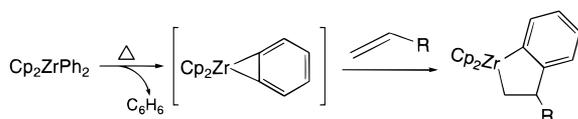


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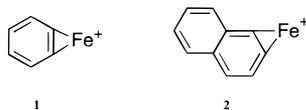


(C₆₀) and cyclopropane (*c*-C₃H₆). It should be pointed out that for all the coupling reaction products reported in this paper, determining whether the C—C bond is formed at the α - or β -position of the naphthalene was not possible using our methodology.

EXPERIMENTAL

All the experiments were performed on a Finnigan FT/MS-2000 Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer equipped with a 3 T superconducting magnet.²³ The ion-trapping potential was set at 2 V. A Bayard–Alpert ion gauge was used to monitor pressures. Fe⁺ was generated by laser desorption of a pure iron metal target using a Quanta-Ray Nd:YAG laser operated at its fundamental IR output (1064 nm).²⁶ Argon at a pressure of about 5.0×10^{-6} Torr was used as the collision gas for thermalization and collision-induced dissociation (CID)²⁷ experiments. Standard FT-ICR ion ejection techniques²⁸ and SWIFT excitation²⁹ were used to study ion–molecule reaction pathways and to isolate an ion prior to CID experiments. Sustained off-resonance irradiation (SORI)³⁰ was also employed in some experiments to determine the lowest-energy fragmentation pathways. Chemicals were obtained commercially and used as supplied. Electron impact ionization was used to verify the purity of the reagents and, for the liquid samples, freeze–pump–thaw cycles were employed to remove air before sample introduction.

Fe(benzynes)⁺ **1**^{12,14,31} and Fe(naphthynes)⁺ **2**³² were prepared via the dehydrohalogenation reactions of Fe⁺ with chlorobenzene and 1-fluoronaphthalene, respectively [reactions (1) and (2)]. The two neutrals were introduced into the vacuum system through a Varian leak valve at about 1×10^{-7} Torr. In the case of Fe(benzynes)⁺, chlorobenzene-*d*₆ was used to generate Fe(C₆D₄)⁺ to verify the ion masses and to study the reaction mechanism further. However, deuterated chemical for Fe(naphthynes)⁺ is not commercially available. One minor difficulty is that when Fe⁺ reacts with 1-fluoronaphthalene, the condensation product FeC₁₀H₇F⁺ dominates.



To enhance the intensity of **2**, therefore, SORI at $\Delta f = 2$ kHz from the cyclotron frequency of FeC₁₀H₇F⁺ was applied for 500 ms during reaction (2) to promote elimination of HF from the adduct ion. The reactions of **1** and **2** with selected neutrals, introduced using

solenoid pulsed valves (General Valve Corporation Series 9),³³ were then studied.

RESULTS AND DISCUSSION

The reactions of **1** with various alkenes have been previously examined.¹⁶ Its reactions with ethene and propene represent two uniquely different mechanisms. The former yields major products Fe⁺ and FeC₈H₈⁺ through a coupling mechanism and the latter yields FeC₇H₈⁺ via a C—C bond insertion mechanism. Guided by these two types of reactions, we selected some molecules containing multiple bonds, and no sp³ carbons, to study the coupling reactions of **1**. In some coupling reactions, only Fe⁺ was observed as the ion–molecule reaction product, presumably because Fe has a lower ionization energy than that of the neutral ligand formed. The reactions of **2** are found to be analogous to those of **1**. However, the coupled ligand has a more extended π -system and thus a competitive or lower ionization energy than that of Fe. In this way we are able to observe and study the coupled ligand product which could only be proposed for **1**.

Reactions with acetylene

As shown in Fig. 1, **1** reacts with acetylene to form Fe⁺, exclusively [reaction (3)]. In contrast, **2** undergoes both addition–demetalation and condensation reactions with acetylene to form Fe⁺, C₁₀H₆C₂H₂⁺ (*m/z* 152) and C₁₀H₆FeC₂H₂⁺ (*m/z* 208) respectively [reactions (4)–(6), Fig. 2]. Also seen in Fig. 2 is that C₁₀H₆FeC₂H₂⁺ [generated in reaction (6)] undergoes a secondary reaction with another molecule of acetylene to form C₁₄H₁₀⁺ [reaction (7)]. Both CID (20 eV center-of-mass energy *E_{cm}*) and low-energy SORI on C₁₀H₆FeC₂H₂⁺ yield

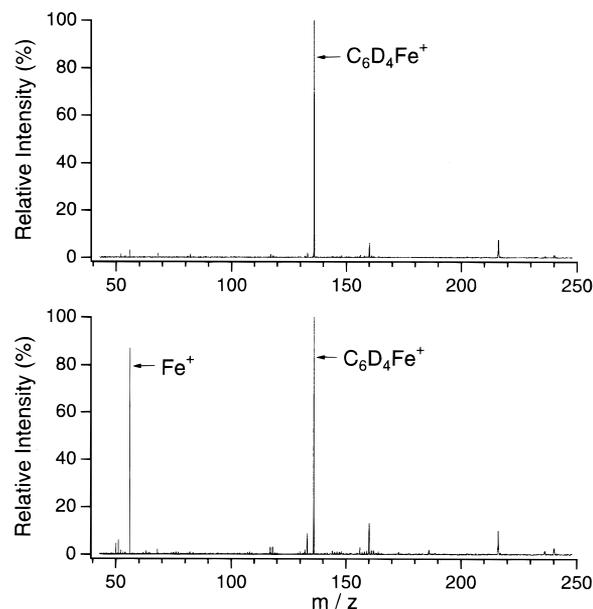


Figure 1. Isolation of Fe⁺–benzynes, allowing a 400 ms delay time as reaction blank (top). Acetylene pulsed in to a maximum pressure of about 1×10^{-6} Torr, reaction time 400 ms (bottom).

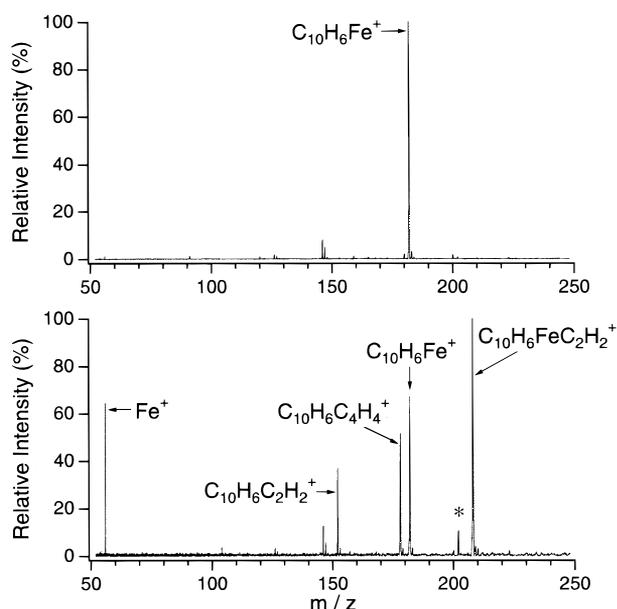
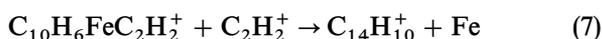
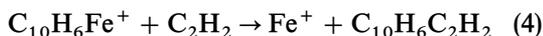
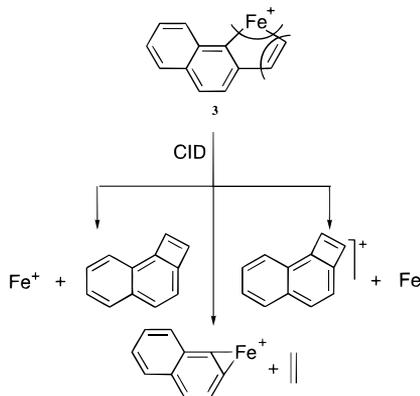


Figure 2. Isolation of Fe^+ -naphthylene, allowing a 400 ms delay time as reaction blank (top). Acetylene pulsed in to a maximum pressure of about 1×10^{-6} Torr, reaction time 400 ms (bottom). The peak (m/z 202) with an asterisk is from the further condensation reaction of Fe^+ with 1-fluoronaphthalene.

mainly Fe^+ and $\text{C}_{10}\text{H}_6\text{Fe}^+$, with $\text{C}_{10}\text{H}_6\text{C}_2\text{H}_2^+$ being observed as a minor product.

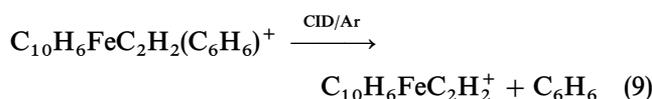
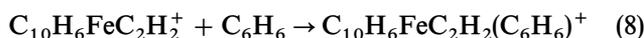
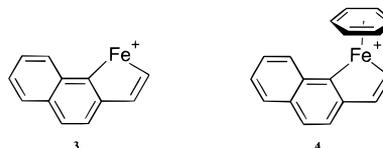


These fragment ions appear and rise in a parallel fashion, which suggests that the $\text{C}_{10}\text{H}_6\text{FeC}_2\text{H}_2^+$ has structure 3. Collisional activation cleaves either two $\text{Fe}-\text{C}$ bonds to yield Fe^+ and $\text{C}_{10}\text{H}_6\text{C}_2\text{H}_2^+$ or a $\text{C}-\text{C}$ bond and an $\text{Fe}-\text{C}$ bond to yield $\text{C}_{10}\text{H}_6\text{Fe}^+$ (Scheme 3). Note that while a 2 + 2 cycloaddition will initially generate the naphthocyclobutadiene-type structure shown in Scheme 3 and elsewhere in the paper, we do not rule out the possibility of rearrangement to acenaphthalene or ethynyl-naphthalene structures. Sequential fragmentation would be expected if the ion had two separate ligands



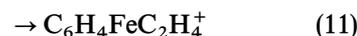
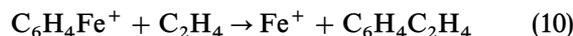
Scheme 3

(naphthylene- Fe^+ -acetylene), owing to the apparent differences in the bond energies of Fe^+ -naphthylene and Fe^+ -acetylene. To further verify structure 3, $\text{C}_{10}\text{H}_6\text{FeC}_2\text{H}_2^+$ was isolated and reacted with benzene. Instead of ligand displacement of the C_2H_2 moiety by benzene, a condensation product $\text{C}_{10}\text{H}_6\text{FeC}_2\text{H}_2(\text{C}_6\text{H}_6)^+$ was observed [reaction (8)]. CID of $\text{C}_{10}\text{H}_6\text{FeC}_2\text{H}_2(\text{C}_6\text{H}_6)^+$ at $E_{\text{cm}} = 10$ eV yields loss of the benzene ligand [reaction (9)]. This is analogous to the CID of the condensation product of 2 with benzene, where loss of neutral benzene is observed. 4 represents a possible structure for the product $\text{C}_{10}\text{H}_6\text{FeC}_2\text{H}_2(\text{C}_6\text{H}_6)^+$ in reaction (8). This further supports the structure 3 for $\text{C}_{10}\text{H}_6\text{FeC}_2\text{H}_2^+$, because if the C_2H_2 moieties in 3 and 4 were not coupled to the naphthylene, CID of 4 would also yield loss of acetylene ligand, since $D(\text{Fe}^+-\text{C}_6\text{H}_6) = 49.6 \pm 2.3$ kcal mol $^{-1}$ ³⁴ > $D(\text{Fe}^+-\text{C}_2\text{H}_2) = 36 \pm 2$ kcal mol $^{-1}$.³⁵



Reactions with ethene

As reported earlier,¹⁶ 1 reacts with ethene to form mainly Fe^+ and $\text{C}_6\text{H}_4\text{FeC}_2\text{H}_4^+$ by condensation, with a small amount of $\text{C}_6\text{H}_4\text{FeC}_2\text{H}_2^+$ via dehydrogenation and FeC_6H_6^+ by elimination of C_2H_2 [reactions (10)–(13)]. In analogy to 1, 2 undergoes a condensation reaction with ethene to form $\text{C}_{10}\text{H}_6\text{FeC}_2\text{H}_4^+$ [reaction (14)] and a dehydrogenation reaction yielding $\text{C}_{10}\text{H}_6\text{FeC}_2\text{H}_2^+$ [reaction (15)]. Among the reactions of 2, however, condensation is the major reaction and Fe^+ is not formed [reactions (14) and (15)], Fig. 3.



In analogy to the CID of 3 and the benzyne counterpart $\text{C}_6\text{H}_4\text{FeC}_2\text{H}_4^+$,^{14,16} CID of $\text{C}_{10}\text{H}_6\text{FeC}_2\text{H}_4^+$ at $E_{\text{cm}} = 12.5$ eV yields mainly Fe^+ and $\text{C}_{10}\text{H}_6\text{Fe}^+$, with $\text{C}_{10}\text{H}_6\text{FeC}_2\text{H}_2^+$ and unmetalated $\text{C}_{10}\text{H}_6\text{C}_2\text{H}_x^+$ ($x = 2-4$) being minor products. $\text{C}_{10}\text{H}_6\text{FeC}_2\text{H}_4^+$ reacts with benzene to form an adduct product and no displacement of ethene is seen. As shown in Fig. 4, low-energy SORI on the adduct ion yields back $\text{C}_{10}\text{H}_6\text{FeC}_2\text{H}_4^+$. These results suggest a metallacyclic structure 5 for $\text{C}_{10}\text{H}_6\text{FeC}_2\text{H}_4^+$, formed via a coupling mechanism.

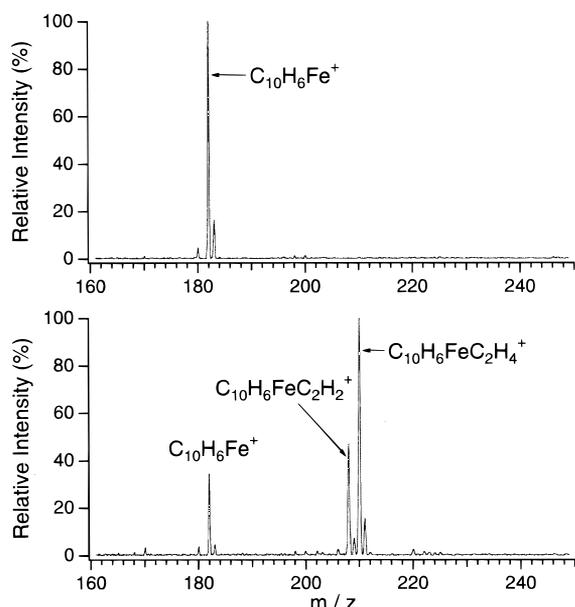


Figure 3. Isolation of Fe⁺-naphthylene, allowing a 400 ms delay time as reaction blank (top). Ethene pulsed in to a maximum pressure of about 1×10^{-6} Torr, reaction time 400 ms (bottom).



Interestingly, CID ($E_{cm} = 10$ eV) and SORI on $C_{10}H_6FeC_2H_2^+$ formed in reaction (15) yield only Fe⁺ (70%) and $C_{10}H_6C_2H_2^+$ (30%). $C_{10}H_6Fe^+$ was not observed. This indicates that $C_{10}H_6FeC_2H_2^+$ formed in reaction (15) is an isomer of the ion formed in reaction

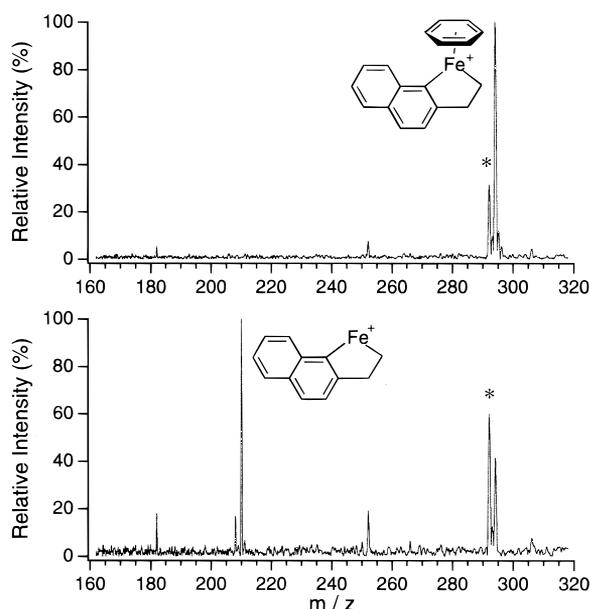
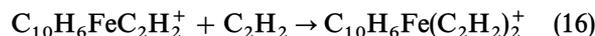


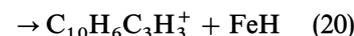
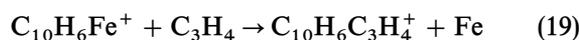
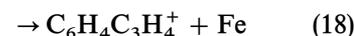
Figure 4. Isolation of $C_{10}H_6FeC_2H_4(C_6D_6)^+$ with a 40 ms delay as blank for subsequent SORI experiment (top). Formation of $C_{10}H_6FeC_2H_4^+$ upon SORI at $\Delta f = 1$ kHz for 400 ms (bottom). The peak with an asterisk is from the reaction of $C_{10}H_6FeC_2H_2^+$ (see Fig. 3), which was not ejected before allowing the reaction with benzene.

(6), which is postulated to have structure 3. This was further verified by reacting this ion with acetylene. Instead of the coupling–demetalation reaction (7) observed for 3, this $C_{10}H_6FeC_2H_2^+$ undergoes condensation with acetylene [reaction (16)] and CID on the condensation product yields loss of C_2H_2 . Based on these results, we propose structure 6 for the $C_{10}H_6FeC_2H_2^+$ formed in reaction (15).



Reactions with allene

As shown in Fig. 5, 1 reacts with allene to form about 85% Fe⁺ and about 15% $C_6H_4C_3H_4^+$ by addition–demetalation [reactions (17) and (18)]. These results suggest $IE(Fe) < IE(C_6H_4C_3H_4)$. In contrast, as shown in Fig. 6, 2 reacts with allene to yield the unmetalated products $C_{10}H_6C_3H_4^+$ and $C_{10}H_6C_3H_3^+$ [reactions (19) and (20)]. These reactions may follow the mechanism proposed in Scheme 4, but owing to the lower IE of the ligands, Fe⁺ is not formed.



Reactions with butadiene

As reported previously,¹⁶ 1 reacts with butadiene to yield about 66% Fe⁺ and about 34% $FeC_6H_4C_4H_4^+$. CID of $FeC_6H_4C_4H_4^+$ gives 93% Fe⁺ and 7% $C_6H_4C_4H_4^+$. $FeC_6H_4C_4H_4^+$ was concluded to be Fe⁺-naphthalene, formed by a Diels–Alder coupling mechanism and subsequent dehydrogenation. Similarly, 2 reacts with butadiene to form about 27% $C_{10}H_6C_4H_4^+$

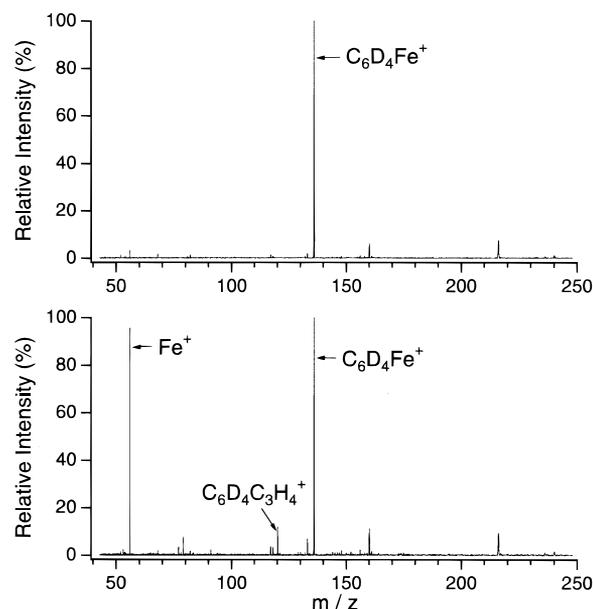


Figure 5. Isolation of Fe⁺-benzyne, allowing a 400 ms delay time as reaction blank (top). Allene pulsed in to a maximum pressure of about 1×10^{-6} Torr, reaction time 400 ms (bottom).

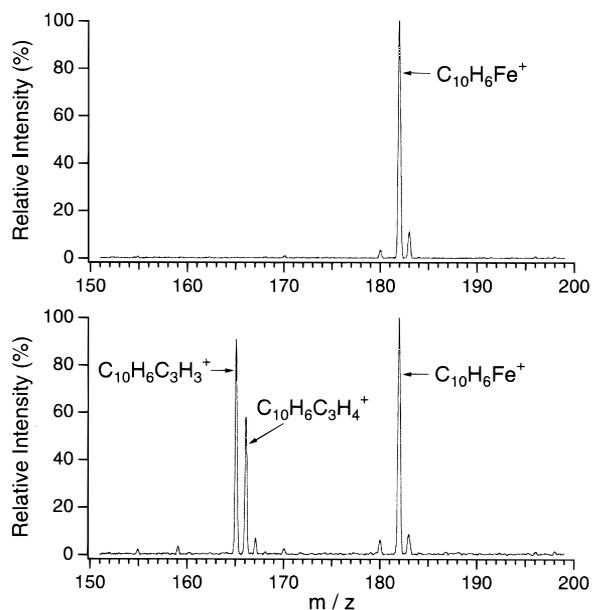
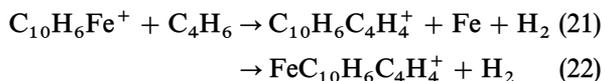


Figure 6. Isolation of Fe^+ -naphthylene, allowing a 400 ms delay time as reaction blank (top). Allene pulsed in to a maximum pressure of about 1×10^{-6} Torr, reaction time 400 ms (bottom).

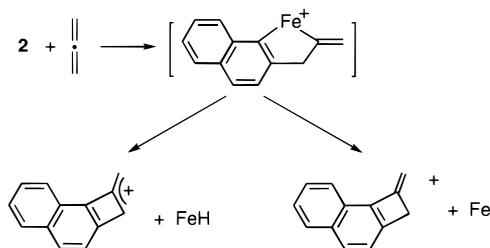
[reaction (21)] and about 73% $\text{FeC}_{10}\text{H}_6\text{C}_4\text{H}_4^+$ [reaction (22)]. The former is assumed to be phenanthrene ion formed through the dehydrogenation of $\text{C}_{10}\text{H}_6\text{C}_4\text{H}_6^+$ or loss of FeH_2 directly in the reaction.



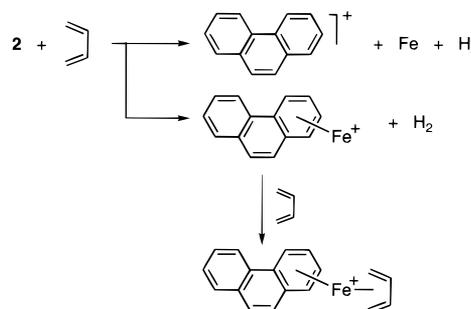
CID of $\text{FeC}_{10}\text{H}_6\text{C}_4\text{H}_4^+$ at $E_{\text{cm}} = 4$ eV yields about 60% $\text{C}_{10}\text{H}_6\text{C}_4\text{H}_4^+$ [IE(phenanthrene) = 7.86 eV]³⁶ and about 40% Fe^+ [IE(Fe) = 7.87 eV]³⁶, consistent with the neutrals of the two fragment ions having almost the same ionization energies. $\text{FeC}_{10}\text{H}_6\text{C}_4\text{H}_4^+$ undergoes a further condensation reaction with butadiene to form $\text{C}_4\text{H}_6\text{FeC}_{10}\text{H}_6\text{C}_4\text{H}_4^+$, which is unreactive with butadiene and gives back $\text{FeC}_{10}\text{H}_6\text{C}_4\text{H}_4^+$ upon CID ($E_{\text{cm}} = 3.5$ eV). As summarized in Scheme 5, these results suggest a butadiene- Fe^+ -phenanthrene structure for $\text{C}_4\text{H}_6\text{FeC}_{10}\text{H}_6\text{C}_4\text{H}_4^+$.

Reactions with C_{60}

As discussed in the Introduction, **1** has previously been observed to react with C_{60} to form a metallacyclic derivative $\text{FeC}_{60}\text{C}_6\text{H}_4^+$.^{24,25} Similarly, as shown in Fig. 7, **2** reacts with C_{60} to give both C_{60}^+ and a condensation product $\text{FeC}_{60}\text{C}_{10}\text{H}_6^+$. An unmetallated C_{60} naphthalene derivative $\text{C}_{60}\text{C}_{10}\text{H}_6^+$ is also formed through a slow reaction of $\text{FeC}_{60}\text{C}_{10}\text{H}_6^+$ with background fluoro-



Scheme 4

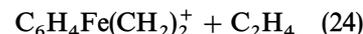
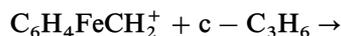


Scheme 5

naphthalene. CID of $\text{FeC}_{60}\text{C}_{10}\text{H}_6^+$ at $E_{\text{cm}} = 4$ eV yields mainly $\text{C}_{10}\text{H}_6\text{Fe}^+$, with $\text{C}_{60}\text{C}_{10}\text{H}_6^+$ being observed as a minor product. Similar to the $\text{FeC}_{60}\text{C}_6\text{H}_4^+$,^{24,25} $\text{FeC}_{60}\text{C}_{10}\text{H}_6^+$ is observed to react with another C_{60} molecule to form $\text{C}_{60}\text{FeC}_{60}\text{C}_{10}\text{H}_6^+$. This rules out a structure of $\text{C}_{60}\text{-Fe}^+$ -naphthylene, which is not expected to react with another C_{60} owing to steric effects. In analogy to the $\text{FeC}_6\text{H}_4^+/\text{C}_{60}$ system, Scheme 6 is proposed to explain the above observations.

Reactions with cyclopropane

1 undergoes sequential reactions with cyclopropane to form $\text{C}_6\text{H}_4\text{FeCH}_2^+$ and $\text{C}_6\text{H}_4\text{Fe}(\text{CH}_2)_2^+$ [reactions (23) and (24)].



$\text{C}_6\text{H}_4\text{Fe}(\text{CH}_2)_2^+$ does not react with cyclopropane further. Similarly, **2** reacts with cyclopropane to form the analogous products $\text{C}_{10}\text{H}_6\text{FeCH}_2^+$ and

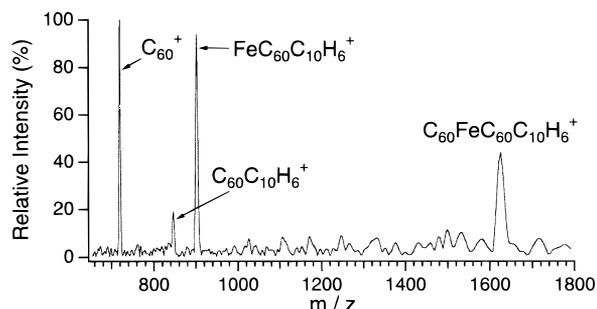
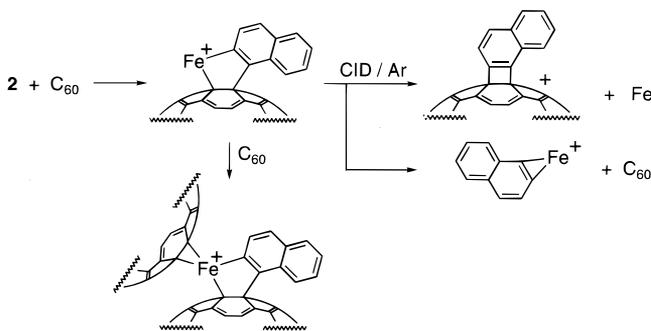
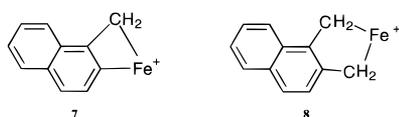


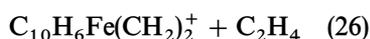
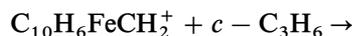
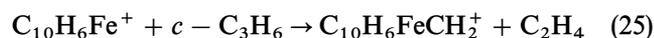
Figure 7. Partial mass spectrum illustrating reaction of Fe^+ -naphthylene with background C_{60} (pressure $< 0.5 \times 10^{-8}$ Torr), reaction time 6 s.



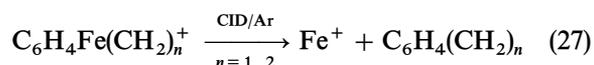
Scheme 6



$C_{10}H_6Fe(CH_2)_2^+$ [reactions (25) and (26)]. Once again, whether the CH_2 moieties are bound to the metal center as carbene or bound to both the metal and a ring carbon is the key issue here.



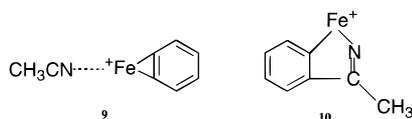
CID of both $C_6H_4FeCH_2^+$ and $C_6H_4Fe(CH_2)_2^+$ yields Fe^+ [reaction (27)]. CID of the two naphthylene counterparts, however, yields several fragments.



For $C_{10}H_6FeCH_2^+$ the major fragments are Fe^+ and $C_{10}H_6CH_2^+$, with $C_{10}H_6^+$ and $C_{10}H_6Fe^+$ being minor fragments. This suggests that $C_{10}H_6FeCH_2^+$ has structure 7, with the C—C bond being formed in the reaction. Similarly, CID of $C_{10}H_6Fe(CH_2)_2^+$ yields the major fragments Fe^+ and $C_{10}H_6Fe^+$ and minor products $C_{10}H_6FeC_2H_2^+$ and $C_{10}H_6C_2H_x^+$ ($x = 2-4$). This is almost identical to the fragmentation of 5. Therefore $C_{10}H_6Fe(CH_2)_2^+$ is proposed to have structure 5. The recovery of $C_{10}H_6Fe^+$ in the CID experiment also rules out structure 8.

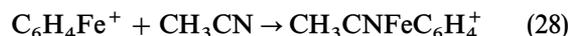
Miscellaneous

As reported previously in condensed phase studies,⁴⁻⁶ reactions of metallobenzynes with N_2 , O_2 and CH_3CN , all of which contain multiple bonds, also follow the cycloaddition mechanism illustrated in Scheme 2. Thus our investigation on the coupling reactions of 1 and 2 was extended to these molecules. Interestingly, no reactions were observed for 1 and 2 with N_2 . However,



both 1 and 2 react with O_2 to yield Fe^+ . The neutral products can be postulated as quinones owing to their high stability and relatively high IE (>9.5 eV).

$Fe(\text{benzyne})^+$ reacts with CH_3CN to form $CH_3CNFeC_6H_4^+$ exclusively [reaction (28)].



CID of $CH_3CNFeC_6H_4^+$ yields loss of CH_3CN exclusively to give back $FeC_6H_4^+$ over the entire energy range studied (3–54 eV center-of-mass energies). The CID results suggest that the reaction is a simple condensation and we propose that $CH_3CNFeC_6H_4^+$ has structure 9. If CH_3CN were coupled to $Fe(\text{benzyne})^+$ to give structure 10, for example, CID of 10 would be expected to fragment to some extent through both Fe—C and Fe—N bond cleavages to yield either Fe^+ and/or $C_6H_4CH_3CN^+$, in analogy to the CID of other reaction products formed from the coupling mechanism. Finally, $CH_3CNFeC_6H_4^+$ was observed to react further with CH_3CN to form $(CH_3CN)_2FeC_6H_4^+$, which also yielded loss of CH_3CN upon CID. Thus the second CH_3CN ligand is believed to remain uncoupled and simply ligated to the ion center in structure 9.

SUMMARY

In this paper we further demonstrate the coupling reactions of $Fe(\text{benzyne})^+$ and $Fe(\text{naphthylene})^+$ with unsaturated hydrocarbons. The proposed reaction mechanism is analogous to that observed for metallobenzynes in the condensed phase, where the reactions result in the formation of new carbon–carbon and metal–carbon bonds. For the benzyne reactions, the coupled product has an ionization energy above that of Fe and thus only Fe^+ is observed. The use of naphthylene, however, results in demetalated products which retain the charge. In this way we were able to observe and study the coupled ligand products.

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