

Gas-Phase Chemistry between Fe⁺-Benzyne and Alkenes

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Abstract: The chemistry between Fe⁺-benzyne and several small alkenes in the gas phase is studied. The formation of Fe⁺ and Fe⁺-benzocyclobutene from the reaction of FeC₆H₄⁺ with ethylene can be explained by a rearrangement of a benzo-ironacyclopentene intermediate, which is in turn formed from the migratory insertion of the ethylene ligand across the C-C triple bond of the benzyne ligand. Alternatively, it can also be explained by the simple coupling between the ethylene and benzyne ligands. Two additional product ions generated from ethylene, FeC₈H₆⁺ and the hydrogenation product, Fe⁺-benzene, are formed presumably from initial Fe⁺ insertion into the ethylene C-H bond. Combined isotope labeling studies indicate that the reaction of FeC₆H₄⁺ with both propene and isobutene to form Fe⁺-toluene probably proceeds by a mechanism based on initial Fe⁺ insertion into a vinylic C-C bond or C-H bond, and not by a concerted ene mechanism followed by Fe⁺-facilitated fragmentation. All three linear butenes, 1-butene, *cis*-2-butene, and *trans*-2-butene, react very similarly with FeC₆H₄⁺, yielding a variety of product ions including Fe⁺-1-methyleneindene, which appears to have an ionization potential close to that of Fe, 7.870 eV. Both cyclopentene and cyclohexene react with FeC₆H₄⁺ to give mainly the hydrogenation product, Fe⁺-benzene, as well as a minor amount of product ions corresponding to ring cleavage of the cycloalkenes. The reaction of butadiene with FeC₆H₄⁺ yields Fe⁺-naphthalene and Fe⁺.

The high degree of unsaturation of benzyne renders it highly reactive and suitable for a wide variety of synthetic purposes.¹ Among its synthetically most versatile chemistry is its reactions with unsaturated hydrocarbons. Its reactions with alkenes generally fall into one of three categories: (i) cycloaddition reactions with monoenes by a generally agreed upon bisradical mechanism, (ii) ene reactions, and (iii) Diels-Alder-type reactions.² While the highly reactive nature of benzyne makes it difficult to isolate, its coordination to a transition-metal center can greatly increase its stability, and benzyne complexes of several transition metals have been isolated and crystallized.³⁻⁵

Gas-phase transition-metal cations exhibit very rich chemistry with many usually inert small organic molecules via their ability to oxidatively add into C-C and C-H bonds.⁶ Thus, studying Fe⁺-benzyne provides an opportunity to explore the mutual influence on reactivities between the metal center and the benzyne ligand. Our recent study on the chemistry of Fe⁺-benzyne with small alkanes indicates that the metal acts as an activation center by oxidatively adding into C-C and C-H bonds of alkanes, followed by migratory insertion of the alkyl group or hydrogen atom across the C-C triple bond of the benzyne ligand.⁷ In this paper we extend this work to the chemistry observed between Fe⁺-benzyne and several small alkenes in the gas phase. The chemistry of both Fe⁺ and benzyne with alkenes has been studied in great detail.^{1,8}

Experimental Section

All experiments were performed on a prototype Nicolet FTMS-1000 Fourier transform mass spectrometer.⁹ It is equipped with a 5.2-cm³ trapping cell situated between the poles of a Varian 15 in electromagnet maintained at 0.9 T. The cell utilizes two stainless steel screens of 80% transmittance as the transmitter plates, permitting the irradiation of the

interior with various light sources. Fe⁺ was generated by focusing the beam of a Quanta Ray Nd:YAG laser (operated at the fundamental wavelength 1.064 μm) onto a high-purity Fe target.¹⁰

Chemicals were obtained in high purity from commercial sources and used as supplied except for multiple freeze-pump-thaw cycles to remove noncondensable gases. Cell pressures were measured with an uncalibrated Bayard-Alpert ionization gauge and were typically (2-4) × 10⁻⁶ Torr for samples and (2-4) × 10⁻⁵ Torr for argon during collision-induced dissociation (CID) experiments.

The reactant ion, FeC₆H₄⁺, was prepared by the previously reported reaction of Fe⁺ with chlorobenzene¹¹ and isolated by swept double-resonance ejection pulses¹² before its reactions with a variety of different samples. The minor isotope peak ⁵⁴Fe⁺ was ejected prior to its reaction with chlorobenzene. To avoid interference from the secondary reactions of Fe⁺-benzyne,^{7,11,13} chlorobenzene was pulsed in through a General Valve Corp. Series 9 pulsed solenoid valve triggered simultaneously with the laser desorption pulse, filling the cell to a maximum pressure of ~10⁻⁵ Torr in about 150 ms and then being pumped away in about 300 ms by a 6-in. diffusion pump.¹⁴ The efficiency of the reactions observed was in general ≥10% of the collision rate.

The major product ion distributions are reproducible to ±10% absolute and ±15% for CID fragments. To ensure that the product branching ratios were collected primarily for ground-state Fe⁺-benzyne, a high background pressure of argon was maintained during the experiment to allow cooling of the reactant ions. However, a minor population of nonthermal species cannot be completely ruled out.

The major product ion structures were investigated by collision-induced dissociation (CID).¹⁵ The translational energy of the parent ions in the laboratory frame can be varied typically between 0 and 100 eV. The spread in kinetic energy is approximately 35% at 1 eV, 10% at 10 eV, and 5% at 30 eV.¹⁶

Results and Discussion

Quite different reaction patterns were observed for each of the smaller alkenes. Thus, the discussion will be grouped on the basis of the different alkenes.

The reaction of ethylene with FeC₆H₄⁺ is the simplest reaction system, but it presents some of the most interesting and intriguing

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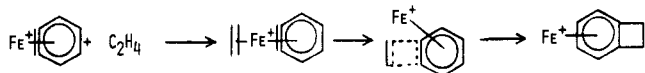
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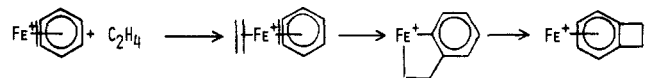
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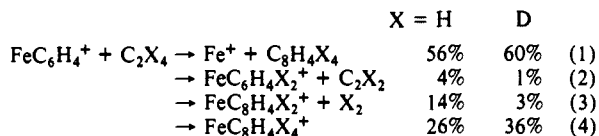
Scheme I



Scheme II



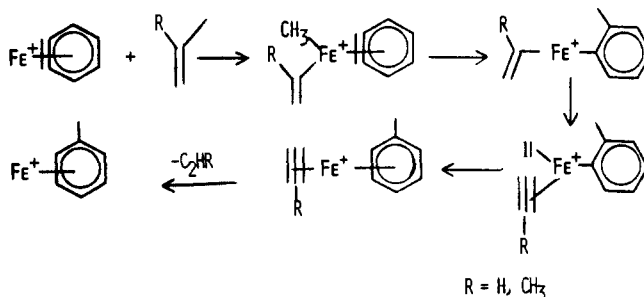
chemistry. Both ethylene and perdeuterated ethylene react with FeC₆H₄⁺ to form several product ions, reactions 1–4. There is



no H/D scrambling for perdeuterated ethylene. Repeated experiments confirmed the different relative abundances for the product ions, particularly the ones in reactions 2 and 3 for C₂H₄ and C₂D₄. The product ion in reaction 2 is presumably Fe⁺-benzene, as evidenced by exclusive loss of the ligand upon CID. CID on both FeC₈H₈⁺ from C₂H₄ and C₈H₄D₄⁺ from C₂D₄ from reaction 4 yields Fe⁺ and FeC₆H₄⁺ within the energy range studied (16–49 eV), with the relative abundance of Fe⁺ increasing with energy. The fragment distributions for FeC₈H₈⁺ are identical with that of Fe⁺-benzocyclobutene formed from Fe⁺-benzyne with ethane within experimental variations.⁷ These results suggest either an Fe⁺-benzocyclobutene structure or the simple condensation of ethylene onto the reactant ion. To probe this further, FeC₈H₈⁺ formed from reaction 4 was isolated and trapped in a low pressure of toluene, which yielded 78% of the displacement product Fe⁺-toluene and 22% of the condensation product Fe-(C₈H₈)(C₇H₈)⁺. This result excludes the ethylene condensation structure because, in that case, displacement of ethylene, instead of the whole ligand, is expected. It is likely that Fe⁺ in reaction 1 arises from the same intermediate leading to the formation of FeC₈H₈⁺. The exothermicity obtained from the formation of benzocyclobutene is sufficiently high that dissociation of the entire ligand from the metal center is feasible for the majority of the FeC₈H₈⁺ formed. Using a recently determined bond energy of D⁰(Fe⁺-benzyne) = 76 ± 10 kcal/mol,⁷ together with ΔH_f(C₆H₄) = 100 ± 5 kcal/mol,¹⁷ ΔH_f(C₂H₄) = 14.5 kcal/mol,¹⁸ and ΔH_f(benzocyclobutene) = 48 ± 1 kcal/mol, yields a heat of reaction for reaction 1 of 9 ± 16 kcal/mol, indicating that the reaction can be exothermic. One uncertainty for this estimate lies in the heat of formation of benzyne. An earlier report put it as high as 118 kcal/mol,¹⁸ which would result in reaction 1 being more exothermic. Considering the preparation of the reactant ion from chlorobenzene, Fe⁺ may be viewed as a catalyst for the conversion of chlorobenzene and ethylene to benzocyclobutene and HCl.

Two mechanisms may be postulated to account for the formation of FeC₈H₈⁺, a ligand-centered mechanism, Scheme I, and a metal-centered mechanism, Scheme II. While it is difficult to obtain conclusive evidence to support either one, some points related to the mechanisms are worthy of discussion. The ligand-centered mechanism is basically a π₂ + π₂ cycloaddition reaction between benzyne and ethylene, which is generally believed to occur through a stepwise biradical mechanism. Crystallographic data on mononuclear transition-metal benzyne complexes indicate that the metal center is coplanar with the benzyne ligand, with the resonance structures metal-benzyne and benzometallacyclopentene cation both contributing to the stabilization.^{3,4} It seems likely that this should also be the structure in Fe⁺-benzyne, and the high value of D⁰(Fe⁺-C₆H₄) = 76 ± 10 kcal/mol⁷ seems to support this configuration, since a π structure with the metal ion

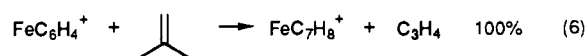
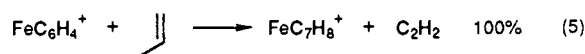
Scheme III



center on top of the benzyne ring would be expected to have a bond energy similar to that of D⁰(Fe⁺-C₆H₆) = 55 ± 5 kcal/mol.¹⁹ In the coplanar structure, the immediate space beside the C–C triple bond in the benzyne ligand available for the cycloaddition reaction with ethylene is blocked by the metal center. The cycloaddition via Scheme I would have to occur after the metal center is pushed out of the plane of the benzyne ligand, incurring sacrifice in the bond energy of about 20 kcal/mol. However, the energy gained from the ion/induced-dipole interaction between the reactant ion and the ethylene molecule, plus whatever chemical interaction is available between Fe⁺ and ethylene, should be enough to compensate for the loss in the bond energy associated with the dislodging of the Fe⁺ from the benzyne plane. In Scheme II, the reaction simply occurs via the migratory insertion of the ethylene ligand across the C–C triple bond of the benzyne ligand to form a benzoironacyclopentene intermediate, which then rearranges to form Fe⁺-benzocyclobutene. One result consistent with such a mechanism comes from the reaction of Ni(η²-C₆H₄)(Cy₂PCH₂CH₂PCy₂) (Cy = cyclohexyl) with ethylene where the species with the benzonickelacyclopentene structure is stable enough to be crystallized and structurally studied by X-ray.³

It is interesting to note that FeC₈H₈⁺ and the hydrogenation product FeC₆H₆⁺ are not observed from the CID fragmentation of Fe⁺-benzocyclobutene. In view of the similarity between the low-energy CID fragmentation and those involved in ion-molecule reactions, it is likely that these product ions do not come from the further fragmentation of Fe⁺-benzocyclobutene, suggesting that reactions 2 and 3 occur via a mechanism different from that of reactions 1 and 4, possibly initiated with the metal center inserting into a vinylic C–H bond. The observed difference in product branching ratios for ethylene and perdeuterated ethylene would seem to support this notion. There should be no isotope effect present for reactions 1 and 4 because neither of the two schemes involves direct participation of carbon–hydrogen bonds. Thus, the lower product abundances in reactions 2 and 3 for C₂D₄ as compared to that of C₂H₄ can only be attributed to the presence of an isotope effect, implying the direct involvement of carbon–hydrogen bonds in a key reaction step, most likely in the Fe⁺ oxidative insertion into a vinylic C–H bond. Finally, the absence of H/D exchange products, FeC₆H_{4-x}D_x⁺, in reactions 1–4 suggests that vinylic insertion is irreversible.

Propene and Isobutene. Both propene and isobutene react with FeC₆H₄⁺ to form the methanation product ion Fe⁺-toluene exclusively, reactions 5 and 6. CID on both product ions yields



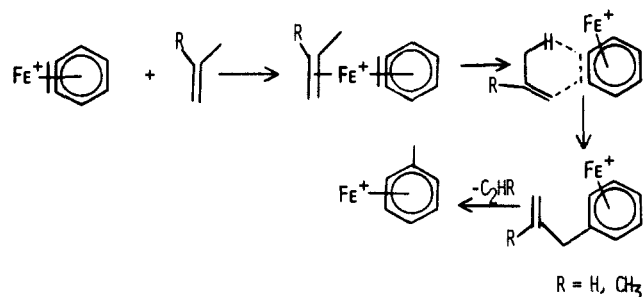
Fe⁺ exclusively over the energy range studied (17–53 eV), consistent with the Fe⁺-toluene structure. When propene is reacted with FeC₆D₄⁺ prepared from perdeuterated chlorobenzene, FeC₇H₄D₄⁺ is formed exclusively, indicating no H/D exchange or scrambling. Scheme III may be easily envisioned to explain

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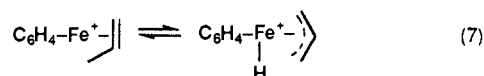
Scheme IV



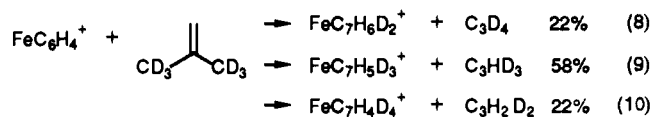
the formation of Fe^+ -toluene. In this mechanism, the reaction proceeds via initial insertion of Fe^+ into a vinylic C-C bond, followed by a methyl migratory insertion onto the benzyne ring across the C-C triple bond and subsequent β -H abstraction of the vinyl group. The migratory coupling of the H radical and the *o*-methylphenyl group to form toluene and the elimination of the alkyne molecule complete the reaction. Alternatively, the reaction could also proceed by initial vinylic C-H insertion, followed by H migration to the benzyne ligand, and subsequent β -methyl abstraction and its coupling with the phenyl group. If this were the mechanism, one might expect initial insertion into a vinylic C-H bond, followed by a β -H abstraction rather than a β -methyl abstraction, yielding Fe^+ -benzene, but this is not observed. However, although β -H abstraction is in general more favorable than β -methyl abstraction, in this case the vinylic C-CH₃ bond is estimated to be weaker than the vinylic C-H bond by about 10 kcal/mol²⁰ and, therefore, β -methyl abstraction would be thermodynamically favored. Thus, either mechanism is possible.

An alternative mechanism, Scheme IV, which is essentially a ligand-centered mechanism based on the so-called ene reaction, can also be proposed to explain reactions 5 and 6. It is conceivable that the fragmentation of Fe^+ -phenylallyl occurs via initial insertion of Fe^+ into the vinylic C-C bond to form the vinylbenzyliron cation, which undergoes β -H abstraction from the vinyl group, coupling between the H and benzyl radicals, and elimination of the alkyne ligand to form Fe^+ -toluene in sequence. One result consistent with such a mechanism is that CID on Fe^+ -phenylallyl, the key intermediate from Scheme IV, forms Fe^+ -toluene and Fe^+ over the energy range studied (17–53 eV). It is likely that the exothermicity for formation of Fe^+ -phenylallyl is low enough that fragmentation at this energy gives Fe^+ -toluene exclusively. Also, the reaction of Fe^+ with phenylallyl forms Fe^+ -toluene exclusively. Additionally, CID on Fe^+ -2-methyl-3-phenylpropene, the key intermediate expected from the reaction of FeC_6H_4^+ with isobutene via the ligand-centered ene mechanism, yields Fe^+ -toluene and Fe^+ .

In order to probe which mechanism is operating here, FeC_6H_4^+ was reacted with [1-¹³C]propene. If the ene mechanism is occurring for reaction 5, then FeC_7H_8^+ should be formed exclusively in the ¹³C-labeled experiment. In contrast, the exclusive formation of $\text{Fe}^{13}\text{CC}_6\text{H}_8^+$ would be expected if the metal-centered mechanism is operating. Surprisingly, the reaction of FeC_6H_4^+ with [1-¹³C]propene gives 47% FeC_7H_8^+ and 53% $\text{Fe}^{13}\text{CC}_6\text{H}_8^+$. While it is tempting to suggest that both mechanisms are operating here, the observed products can also be explained by complete C1-C3 scrambling, which could occur by reaction 7, before the actual reaction leading to the formation of Fe^+ -toluene.



To further probe the mechanism, the reaction of FeC_6H_4^+ with selectively deuterated isobutene was studied, reactions 8–10. For the metal-centered mechanism, $\text{FeC}_7\text{H}_5\text{D}_3^+$ is the expected product ion. If a scrambling mechanism similar to reaction 7 occurs once,



the isobutene $\text{CD}_2=\text{C}(\text{CH}_2\text{D})(\text{CD}_3)$ would be formed, and its reaction with FeC_6H_4^+ via the metal-centered mechanism would form $\text{FeC}_7\text{H}_6\text{D}_2^+$ and $\text{FeC}_7\text{H}_4\text{D}_4^+$ in equal intensity without considering any isotope effect. This is roughly the case in reactions 8 and 10, assuming that 58% of the reaction occurs without scrambling. For the ene mechanism, $\text{FeC}_7\text{H}_6\text{D}_2^+$ is the expected product ion for the reaction without H/D scrambling. For the scrambled isobutene $\text{CD}_2=\text{C}(\text{CH}_2\text{D})(\text{CD}_3)$, three product ions, $\text{FeC}_7\text{H}_6\text{D}_2^+$, $\text{FeC}_7\text{H}_5\text{D}_3^+$, and $\text{FeC}_7\text{H}_4\text{D}_4^+$, should be formed in the ratio 1:2:3. Clearly, this does not account for the distributions in reactions 8–10. Interestingly, if complete scrambling by reaction 7 is involved, the reaction product intensities predicted for reactions 8–10 are 21%, 58%, and 21%, respectively, which is a close fit of the experimental results.²¹

Linear Butenes. FeC_6H_4^+ reacts with 1-butene, *cis*-2-butene, and *trans*-2-butene to give a wide variety of product ions, reactions 11–16. All three linear butenes react very similarly, with *cis*-

	1-butene	<i>cis</i> -2-butene	<i>trans</i> -2-butene	
$\text{FeC}_6\text{H}_4^+ + \text{butene} \rightarrow \text{FeC}_6\text{H}_6^+ + \text{C}_4\text{H}_6$	7	5	3	(11)
$\rightarrow \text{FeC}_7\text{H}_8^+ + \text{C}_3\text{H}_4$	41	25	27	(12)
$\rightarrow \text{FeC}_8\text{H}_{10}^+ + \text{C}_2\text{H}_2$	7	8	7	(13)
$\rightarrow \text{FeC}_8\text{H}_{10}^+ + \text{C}_2\text{H}_2$	7	4	3	(14)
$\rightarrow \text{FeC}_{10}\text{H}_8^+ + 2\text{H}_2$	14	13	12	(15)
$\rightarrow \text{FeC}_{10}\text{H}_{10}^+ + \text{H}_2$	24	45	48	(16)

and *trans*-2-butene being virtually identical within the experimental variation. CID on the product ion $\text{FeC}_{10}\text{H}_{10}^+$ gives a wide variety of product ions. For example, CID on the $\text{FeC}_{10}\text{H}_{10}^+$ from *cis*-2-butene at 26 eV gives 21% Fe^+ , 20% $\text{C}_{10}\text{H}_8^+$, 5% FeC_6H_6^+ , 7% FeC_7H_8^+ , 8% FeC_8H_8^+ , and 39% $\text{FeC}_{10}\text{H}_8^+$. This is in contrast to the isomeric ferrocene cation, which fragments by consecutive loss of C_5H_5 .²² CID at 27 eV on the $\text{FeC}_{10}\text{H}_8^+$ ion, regardless of the starting butene, yields about 40% Fe^+ and 60% $\text{C}_{10}\text{H}_8^+$. The large abundance of the organic ion from CID indicates that the C_{10}H_8 ligand probably has an ionization potential very close to, or even slightly lower than $\text{IP}(\text{Fe}) = 7.870$ eV.¹⁸ CID at 27 eV on Fe^+ -naphthalene formed from naphthalene condensation with Fe^+ yields 89% Fe^+ and 11% $\text{C}_{10}\text{H}_8^+$, presumably naphthalene cation, consistent with a higher IP for naphthalene of 8.14 ± 0.01 eV.¹⁸ These results indicate that the $\text{FeC}_{10}\text{H}_8^+$ ion formed from the three linear butenes is probably not Fe^+ -naphthalene. The only other isomer with an experimentally determined IP lower than that of Fe is azulene, which has an IP of 7.41 ± 0.02 eV.¹⁸ Since we have not as yet found any evidence for any ring-expansion reactions, it is unlikely that this would be the structure. Interestingly, while we are not aware of any experimental IP values for 1-methyleneindene, one calculation has placed its IP at 8.36 eV.²³ Considering that the method used for the calculation has a positive error of up to 0.45 eV for similar compounds with experimentally available values, it is not unreasonable to suggest that it has an IP close to that of Fe. A feasible, but speculative, mechanism can be proposed to explain the formation of Fe^+ -1-methyleneindene, Scheme V.

Cyclopentene and Cyclohexene. For the acyclic alkenes discussed above, there is extensive C-C bond cleavage involved in the reaction. Thus, it is interesting to see if the same occurs for the small cycloalkenes. Both cyclopentene and cyclohexene give mainly the hydrogenation product ion, Fe^+ -benzene, with a small

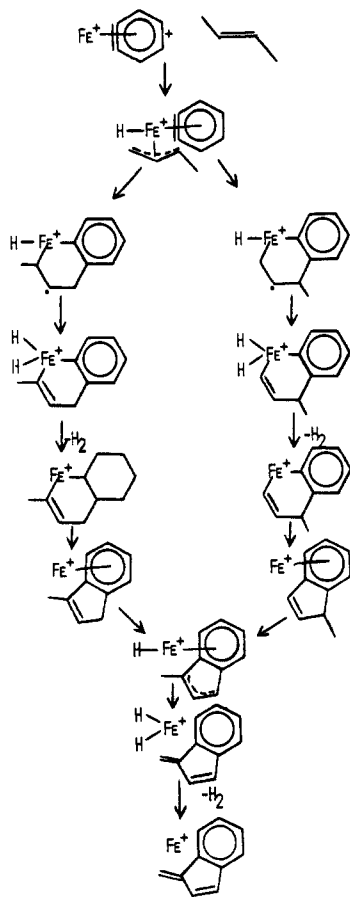
(21) The number of combinations of n different things taken r at a time, denoted ${}_nC_r$, is given by the equation of ${}_nC_r = n!/[r!(n-r)!]$. Assuming complete scrambling, the ratio of the products in reactions 8–10 is the same as the ratio of $\text{CD}_4:\text{CD}_3\text{H}:\text{CD}_2\text{H}_2$, respectively, from $\text{C}_4\text{H}_2\text{D}_6$. This ratio would be ${}_6\text{C}_4:{}_6\text{C}_3 \times 2:{}_6\text{C}_2 \times 2:{}_6\text{C}_2$ or 15:40:15, which gives the percentages reported.

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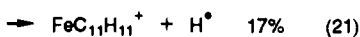
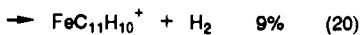
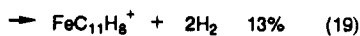
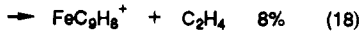
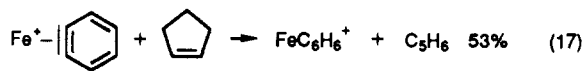
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Scheme V



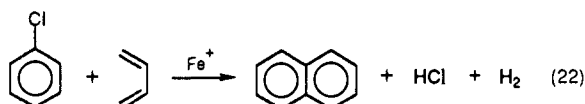
amount of product corresponding to ring cleavage also observed. For example, the product ions resulting from the reaction of FeC₆H₄⁺ with cyclopentene are shown in reactions 17–21. Loss



of a hydrogen atom in reaction 21 is highly unusual. Surprisingly, CID on the product ion at 61 eV gives 13% Fe⁺, 51% FeC₃H₅⁺, and 36% FeC₆H₆⁺, eliminating cyclopentadienyl-benzene ion as its structure. The latter ion is prepared from the hydrogen displacement reaction of benzene with hydridocyclopentadienyliron ion formed from the rearrangement reaction of Fe⁺-cyclopentadiene.^{22,24} Its CID at the same energy only gives Fe⁺ and FeC₃H₅⁺. Certainly this is consistent with a cyclopentadienyliron-benzene cation structure, since $D^\circ(\text{Fe}^+ - \text{C}_5\text{H}_5) = 92 \pm 7$ kcal/mol is considerably greater than $D^\circ(\text{Fe}^+ - \text{C}_6\text{H}_6) = 55 \pm 5$ kcal/mol.^{19,24} Finally, the reaction of cyclohexene gives 80% FeC₆H₆⁺, 13% FeC₁₂H₁₀⁺, and, surprisingly, 7% FeC₈H₈⁺. It is interesting to note that the formation of FeC₈H₈⁺ from cyclohexene and FeC₉H₈⁺ from reaction 18 both involve cleavage of the ring structure. Unfortunately, no structural studies could be

performed on these species because of their low abundances.

Butadiene. The reaction of FeC₆H₄⁺ with butadiene forms 66% Fe⁺ and 34% FeC₁₀H₈⁺. CID of the latter at 27 eV gives 93% Fe⁺ and 7% C₁₀H₈⁺, which is virtually the same as that of Fe⁺-naphthalene within experimental variation, suggesting the structure of Fe⁺-naphthalene. Again, the reaction may proceed by Fe⁺ insertion into a terminal C-H bond, but it is also possible that the reaction occurs by a Diels-Alder mechanism to form Fe⁺-1,4-dihydronaphthalene and subsequent dehydrogenation. Formation of Fe⁺ and naphthalene from FeC₆H₄⁺ and butadiene is estimated to have a heat of reaction of -14 ± 15 kcal/mol.^{17,18} Finally, Fe⁺ can be viewed as a catalyst in reaction 22, which is exothermic by 25 kcal/mol.¹⁸



Conclusion

Interesting chemistry is observed between Fe⁺-benzyne and several small alkenes. Unfortunately, mechanistic probes could not conclusively distinguish whether the reactions observed for FeC₆H₄⁺ occur by the active participation of the Fe⁺ center through its oxidative addition into C-C and C-H bonds or by the direct interaction between the benzyne ligand and the incoming alkene ligand.

Two separate reaction pathways are required to explain the four product ions observed between FeC₆H₄⁺ and ethylene. FeC₈H₆⁺ and the hydrogenation product, FeC₆H₆⁺, may be explained by a pathway based on initial Fe⁺ insertion into a C-H bond, while two mechanisms can account for the formation of Fe⁺ and Fe⁺-benzocyclobutene. One possible mechanism involves the rearrangement of a benzoironacyclopentene intermediate formed from the migratory insertion of the incoming ethylene ligand across the C-C triple bond of the benzyne ligand. The other mechanism simply involves the direct $\pi_2 + \pi_2$ cycloaddition reaction between benzyne and ethylene ligands.

Both propene and isobutene react with FeC₆H₄⁺ to form the methanation product, Fe⁺-toluene, exclusively. While not conclusive, the mechanistic study with deuterium and ¹³C isotope labeling does suggest that the reactions most likely proceed via initial insertion of the Fe⁺ center into the vinylic C-C or C-H bond, not by the direct interaction between the benzyne and propene or isobutene ligands via a concerted six-membered pathway, with subsequent fragmentation through the Fe⁺ center.

All three linear butenes, 1-butene, *cis*-2-butene, and *trans*-2-butene, react with FeC₆H₄⁺ to form the same type of product ions, with the two 2-butenes virtually identical with respect to product distribution. CID on the product ion FeC₁₀H₈⁺ suggests that it probably has a structure of Fe⁺-1-methyleneindene and that the ionization potential of the indene should be very similar to that of Fe, 7.870 eV.¹⁸

Both cyclopentene and cyclohexene mainly undergo hydrogenation of the benzyne ligand, yielding FeC₆H₆⁺. However, the formation of FeC₉H₈⁺ from cyclopentene and FeC₈H₈⁺ from cyclohexene suggests Fe⁺ insertion into the C-C bond of the ring structure during the reaction.

Reactions of butadiene with the FeC₆H₄⁺ lead to the formation of Fe⁺-naphthalene, with the majority of the product ion having enough energy left to detach the ligand from the metal center, leading to the appearance of Fe⁺.

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