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Chemistry of Fe(arene)$^+$ Ions with Halobenzenes

Yongqing Huang,[†] Don Rufus A. Ranatunga, and Ben S. Freiser[*]

Contribution from the H. C. Brown Laboratory of Chemistry, Purdue University, West Lafayette, Indiana 47907

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Abstract: The gas-phase ion chemistry between a series of Fe(arene)$^+$ ions and halobenzene and dihalobenzene species was studied. Fe$^+$ in the arene complex acts as a reaction-initiating center to insert oxidatively into the phenyl–X bond (X = Cl, Br, I). The arene ligand then undergoes migratory insertion into the Fe$^+$–phenyl σ bond. Subsequent hydrogen abstraction from the organic moiety and HX elimination generate Fe(biphenyl)$^+$ ions. This reaction cycle may be repeated up to five times to give Fe(polyphenyl)$^+$. In contrast, Fe(fluorobenzene)$^+$ shows no reactivity with chlorobenzene, while CH_3 groups on the arene ligand sterically hinder the migratory insertion into the Fe$^+$–phenyl bond.

Introduction

Gas-phase monatomic transition metal cations are unique in their abilities to activate a variety of chemical species, most notably highly stable small hydrocarbons via oxidative insertion into C–C and C–H bonds.[1–8] A natural extension of bare transition metal ion chemistry is to study transition metal complex ions having a limited number of ligands. For example, a species such as ML$^+$ with a low formal oxidation state on the metal is highly coordinatively unsaturated and, like the bare metal ion, may insert oxidatively into an X–Y bond. The two σ-bonded moieties resulting from such an oxidative insertion, –X and –Y, are usually highly reactive in nature and may interact with the nearby L ligand. This opens up reaction pathways not associated with bare transition metal ions. The overall reaction process may be viewed as the metal acting as a reaction-initiating center to induce structure modifications to its ligand. Chemistry emerging from such studies has proven to be both interesting and diversified, depending on the specific ML$^+$ studied and the neutral reactants involved.[9–17] Results from such studies could also suggest synthetic pathways of tailor-designing complex ions of desired structures starting with an easily available ionic species. In this paper we report the unique reactivities between a series of Fe(arene)$^+$ ions and halobenzenes, particularly chlorobenzene, where Fe$^+$ facilitates chemical reaction on the arene ligands.

Experimental Section

Experiments were performed on a prototype Nicolet FTMS-1000 Fourier transform ion cyclotron resonance mass spectrometer (FTICRMS) and a standard Extrel FTMS-2000 FTICRMS instrument.[18] The FTMS-1000 instrument is equipped with a 5.2 cm cubic trapping cell situated between the poles of a Walker Scientific 15 in electromagnet maintained at 1.0 T. The FTMS-2000 instrument is equipped with a 3T Nicolet superconducting magnet and all experiments were performed on the analyzer side of a dual cell. Fe$^+$ was generated by focusing the beam of a Quanta Ray Nd:YAG laser (operated at 1.064 μm) onto a thin high-purity target of iron on both instruments.[19,20]

All chemicals were obtained in high purity from commercial sources and used as supplied except for multiple freeze–pump–thaw cycles to remove noncondensible gases. Sample pressures were measured with an uncalibrated Bayard-Alpert type ionization gauge and were typically 1×10^{-6} Torr for samples and 2×10^{-5} Torr for background argon serving as collision gas for collision-induced dissociation (CID) experiments and for cooling ions before ion–molecule reactions. The low vapor pressures of *o*-, *m*-, and *p*-terphenyl dictated that they be introduced into the instrument by a solids probe mounted on the analyzer side of the instrument in order to achieve a room temperature background pressure of 10^{-8}–10^{-7} Torr suitable for the experiments.

CID experiments were performed on product ions of structural importance.[21,22] CID in the FTICRMS is known to be a multiple collision process.[21] Thus, the collision energy, given in the laboratory frame throughout the paper, corresponds to the maximum translational energy achievable and was varied typically in the range of 0–100 eV. The spread in kinetic energy depends on the average kinetic energy and is less than 5% at the energies used in this study.[23]

Fe(arene)$^+$ complex ions were prepared from the condensation reactions of Fe$^+$ with the corresponding arene neutrals pulsed in through a pulsed solenoid valve.[24] The Fe(arene)$^+$ ions were then carefully isolated by swept double resonance experiments[25] and trapped in the background pressure of neutral reactant for further reaction. The reproducibility of the results obtained under different background pressures and cooling times using the two different instruments suggests that the results are representative of the thermalized species. However, a contribution due

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[†] Current Address: Department of Drug Disposition, Central Research, Rhone Poulenc Rorer, Collegeville, PA 19426.

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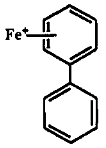
to unthermalized ions cannot be completely ruled out. The relative percentage ratios reported were reproducible with a ±5% absolute uncertainty.

Results and Discussion

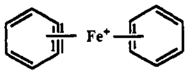
Reactions 1 and 2 occur upon reacting Fe(benzene)$^+$ with chlorobenzene. Reaction 1 indicates that the metal center in $FeC_6H_6^+$ undergoes facile oxidative insertion into the Ph–Cl bond of chlorobenzene. Dehydrochlorination has been observed for the reaction of bare Fe$^+$ with chlorobenzene to give Fe(benzyne)$^+$.[26,27] However, underneath the seemingly identical HCl elimination of chlorobenzene by Fe$^+$ and $FeC_6H_6^+$ are very different mechanisms by which the elimination is achieved, as demonstrated by the corresponding reaction of perdeuterated chlorobenzene, C_6D_5Cl, where HCl and DCl eliminations account for 80% and 20% of the product ions in reaction 1, respectively. A simple HCl elimination of the incoming neutral reactant by the metal center would give 100% DCl elimination, with the benzene ligand acting as a mere spectating ligand. Instead, the results imply the active participation of the benzene ligand throughout the reaction. The labeling experiment reveals that the hydrogen in the eliminated HCl comes largely from the benzene ligand and suggests the formation of Fe(biphenyl)$^+$, structure I, while a simple HCl elimination would yield $Fe(C_6H_4)(C_6H_6)^+$, structure II. An alternative structure, $Fe(C_6H_5)_2^+$, is unlikely considering the secondary reactions discussed later, where the Fe center would have to assume an unfavorably high oxidation state. In fact, as discussed below, we believe that a previously suggested $Fe(C_6H_5)_2^+$ product ion generated by an alternative route is actually Fe(biphenyl)$^+$, structure I.[26]

$$FeC_6H_6^+ + C_6H_5Cl \longrightarrow FeC_{12}H_{10}^+ + HCl \quad 98\% \quad (1)$$

$$\longrightarrow FeC_{12}H_{11}Cl^+ \quad 2\% \quad (2)$$



I

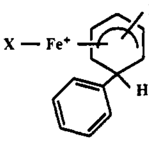


II

Reactions 3–5 list the CID results of the product ion from reaction 1 at 36 eV, as well as those of structures I and II, which are formed from the condensation reactions of biphenyl with Fe$^+$ and of benzene with Fe(benzyne)$^+$, respectively.[27] The results in reactions 3–5 may be explained by the presence of two isomeric structures for the product ion from reaction 1. Since the parent ions are dissociated completely under these CID conditions, the relative contributions of structures I and II are easily estimated by assuming that the CID branching ratios are a linear combination of the two structures, giving 92% of structure I and 8% of structure II. The minor amount of structure II is due to simple HCl elimination.

	Rxn 1	I	II	
$FeC_{12}H_{10}^+ \longrightarrow Fe^+ + C_{12}H_{10}$	92%	97%	23%	(3)
$\longrightarrow FeC_6H_4^+ + C_6H_6$	6%		77%	(4)
$\longrightarrow C_{12}H_{10}^+ + Fe$	2%	3%		(5)

The formation of Fe(biphenyl)$^+$ may be explained by Scheme 1 (R = H, X = Cl). The reaction is initiated by the oxidative insertion of Fe$^+$ into the phenyl–chloro bond. The benzene ligand then undergoes migratory insertion into the Fe$^+$–phenyl bond to give the key intermediate, structure III, which then undergoes a H abstraction and HCl elimination to give Fe(biphenyl)$^+$. The mechanism is analogous to the one proposed by Corderman and Beauchamp for the methylation of M(cyclopentadienyl)$^+$, M = Fe and Ni, by CH_3Br.[28]



III

It is interesting that the 20% of DCl elimination in the deuterated experiment is higher than the 8% estimation of simple HCl elimination. The discrepancy cannot be explained by H/D isotope effects involved in the reaction as any such effect would decrease the relative importance of DCl elimination. Instead, it may be explained by the H/D scrambling suggested in Scheme 1, where rearrangement of intermediate III occurs by the migration of a hydrogen atom from one C_6 moiety to the next, which may then undergo rearrangement via hydrogen fluxional behavior. Loss of DCl from intermediate III would explain the higher than expected intensity of the DCl elimination product ion in the reaction of $FeC_6H_6^+$ with C_6D_5Cl, since it would result in the presence of both isomers I and II. In order to confirm this hypothesis, the HCl and DCl elimination product ions generated from the reaction of $FeC_6H_6^+$ with C_6D_5Cl were permitted to react to completion with toluene. Indeed, this resulted in the formation of 8% of the ligand displaced product $Fe(C_6D_4)(C_6H_5CH_3)^+$ arising from $Fe(C_6D_4)(C_6H_6)^+$, structure II, and a total of 92% of the condensation products, $FeC_{19}H_{14}D_4^+$ and $FeC_{19}H_{13}D_5^+$, arising from the two isotopologs of structure I. Further confirmatory evidence was obtained from the reactions of toluene with the authentic ions produced from the condensation of biphenyl with Fe$^+$ to form I and of benzene with $Fe(C_6D_4)^+$ to form II. As expected, Fe(biphenyl)$^+$ and $Fe(C_6D_4)(C_6H_6)^+$ reacted with toluene to yield exclusively $FeC_{19}H_{18}^+$, the condensation product, and $Fe(C_6D_4)(C_6H_5CH_3)^+$, the displacement product, respectively.

Reactivities similar to reaction 1 were also observed for bromobenzene and iodobenzene. However, the only reaction for fluorobenzene is the condensation process to give Fe(benzene)(fluorobenzene)$^+$, which yields $FeC_6H_6^+$ exclusively upon CID at 21 eV. The difference in reactivities may be due to the inability of Fe$^+$ to activate the stronger Ph–F bond, which has a bond energy of 125 kcal/mol compared to 95 kcal/mol for Cl–Ph.[29] Thus, the benzene ligand has lowered the reactivity of Fe$^+$, as bare Fe$^+$ is able to insert oxidatively into both F–Ph and Cl–Ph bonds.[27] Both bromobenzene and iodobenzene have even lower X–Ph bond energies (77 and 62 kcal/mol, respectively). The energies required for C_6H_5X to form C_6H_4 and HX are 68, 70, 71, and 59 kcal/mol for X = F, Cl, Br, and I, respectively, further suggesting that the ability of the metal center to insert into the C_6H_5–X bond, not the overall reaction exothermicity, is the key to the feasibility of reaction 1 by the mechanism shown in Scheme 1.

The product ion formed in reaction 1 readily reacts further to give a secondary product ion, reaction 6. The operation of Scheme 1 (R = Phenyl, X = Cl) is suggested by a deuterium labeling experiment, where DCl and HCl elimination each account for about 50% of the product ions upon reacting C_6D_5Cl with

$$FeC_{12}H_{10}^+ + C_6H_5Cl \rightarrow FeC_{18}H_{14}^+ + HCl \quad 100\% \quad (6)$$

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Scheme 1

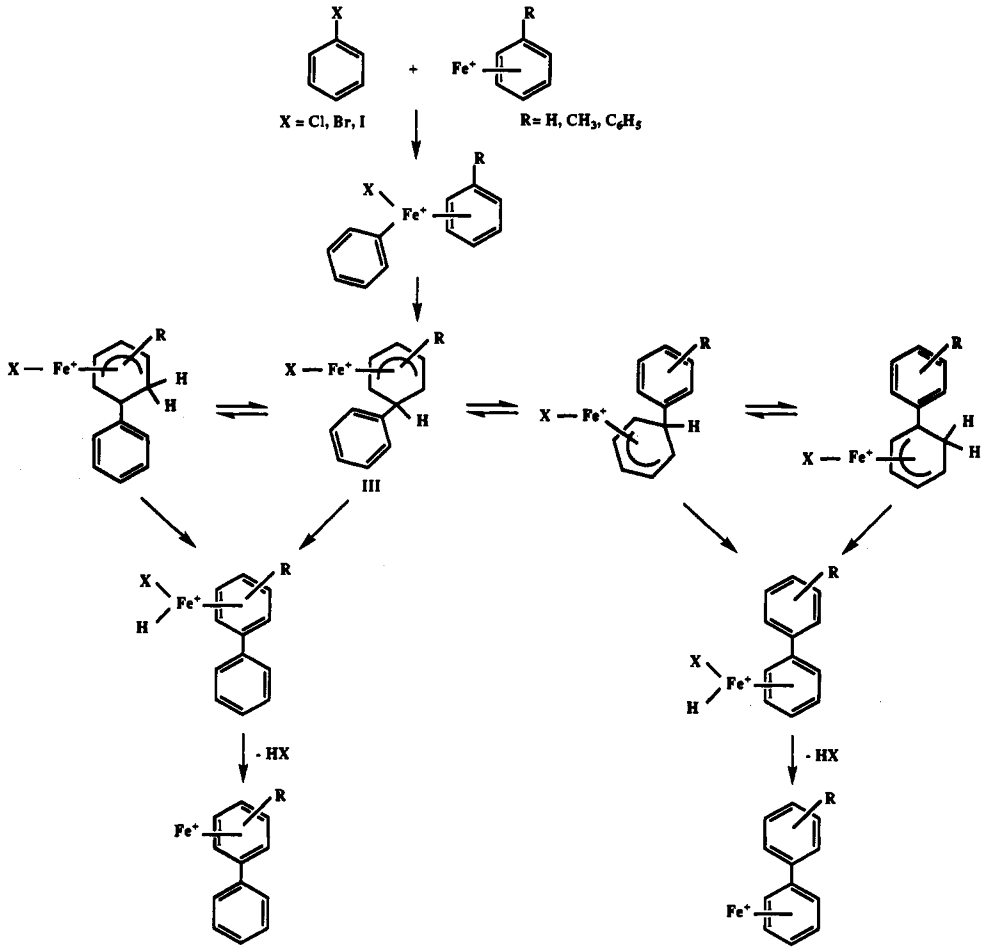


Table 1. CID at 67 eV on $FeC_{18}H_{14}^+$ Formed from Different Reactions

	Fe^+	$FeC_6H_4^+$	$C_{16}H_{10}^+$	$C_{17}H_{11}^+$	$C_{18}H_{12}^+$	$C_{18}H_{14}^+$
Fe^+ + *o*-terphenyl	3		6	10	72	9
Fe^+ + *m*-terphenyl	24		5	6	48	17
Fe^+ + *p*-terphenyl	26		5	7	48	14
$FeC_6H_6^+ + 2C_6H_5Cl$	8		7	9	73	3
$Fe(biphenyl)^+ + C_6H_5Cl$	14		7	9	65	5
$Fe(C_6H_4)(C_6H_6)^+ + C_6H_5Cl$	19	13	4	8	54	2
$Fe^+ + 3C_6H_5I$	11		6	9	63	11

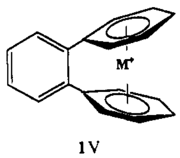
$FeC_{12}H_5D_5^+$ formed from the primary reaction of Fe(benzene)$^+$ with perdeuterated chlorobenzene. Scheme 1 predicts Fe(terphenyl)$^+$ for the product ion in reaction 6. Surprisingly, its CID at 67 eV gives neutral eliminations corresponding to FeH_2, $FeCH_3$, and FeC_2H_4, as well as Fe. The terphenyl structure of the product ion from reaction 6 was supported by comparing its CID fragmentation pattern with that of known structures of Fe(terphenyl)$^+$ isomers, which were prepared by reacting Fe^+ with the individual isomers of terphenyl. All three Fe(terphenyl)$^+$ isomers give CID results similar to that of the product ion from reaction 6, as listed in Table 1.

Also included in Table 1 are the CID results of the $FeC_{18}H_{14}^+$ ions formed from the reactions of chlorobenzene with known structures I and II, respectively. It is evident that $FeC_{18}H_{14}^+$, formed from the reaction of Fe(biphenyl)$^+$ with chlorobenzene, is similar to the product ion in reaction 6, providing further evidence of a mostly Fe(biphenyl)$^+$ structure for the product ion from reaction 1. In contrast, $FeC_{18}H_{14}^+$, formed from the reaction of structure II with chlorobenzene, gives a distinctive $FeC_6H_4^+$ CID fragment.

An earlier study examined the reaction of C_6H_5I with $Fe(C_6H_5)_2^+$ to give $Fe(C_6H_5)_2(C_6H_4)^+$ and HI, where $Fe(C_6H_5)_2^+$ was prepared from the sequential reaction of Fe^+ with two molecules of iodobenzene.[26] With no evidence in that study to support the structures of either the reactant ion or the product ion in this case, it is possible that the reactant ion is actually Fe(biphenyl)$^+$ and it represents a variation of reaction 6 with iodobenzene as the neutral reactant. This indeed seems to be the case. When the system with iodobenzene was studied, the reactant ion, $FeC_{12}H_{10}^+$, gave Fe^+ exclusively upon CID at 57 eV, which is the same as the Fe(biphenyl)$^+$ formed in reaction 1. Furthermore, CID experiments performed on the $FeC_{18}H_{14}^+$ product ion yield results similar to those obtained from the different Fe(terphenyl)$^+$ isomers, Table 1.

It is interesting to speculate on the structure of the ion generated by loss of FeH_2 from Fe(terphenyl)$^+$ during CID. While a terphenyl cation containing one benzyne ring is reasonable, the triphenylene cation is also a possibility, especially for Fe(*o*-terphenyl)$^+$ where loss of FeH_2 could lead to its formation directly. Formation of triphenylene from the meta and para isomers, however, would require initial rearrangement to the ortho isomer via reversible C–C insertion and β-hydrogen abstraction steps. This latter possibility, however, seems unlikely considering that structures I and II do not interconvert appreciably during CID as indicated by the product distributions for reactions 3–5.

Reactions 1 and 6 raise the tantalizing possibility of preparing a bead-like polyphenyl structure where the beads are individual phenyl rings threaded together by phenyl–phenyl bonds. While minor intensities of $FeC_{24}H_{18}^+$ and $FeC_{30}H_{22}^+$ were indeed observed, only 12% of the $FeC_{18}H_{14}^+$ intensity reacted away even at extended reaction times. There are two possibilities for the terminations of the reactions. The accumulated electronic effects of the polyphenyl ligands might inhibit the metal center from activating phenyl–chloro bonds and the higher order products are from slow endothermic reactions. An alternative explanation may involve the structure(s) of the product ions from reaction 6, which may be *o*-, *m*-, or *p*-terphenyl. For example, Fe(*o*-terphenyl)$^+$ might adopt structure IV where the metal center is flanged by the two terminal phenyl groups which are perpendicular to the plane of the middle phenyl ring. Such a geometry would put Fe^+ in an environment resembling that of the sandwich structure of $Fe(benzene)_2^+$ which is itself unreactive with chlorobenzene. It is thus likely that no further reaction occurs if reaction 6 gives only Fe(*o*-terphenyl)$^+$. To probe this point, the reactions of chlorobenzene with the corresponding Fe^+ complex ions of *o*-, *p*-, and *m*-terphenyl were studied. No reaction was observed between Fe(*o*-terphenyl)$^+$ and chlorobenzene. Somewhat surprisingly, only about 12% of the meta isomer and 33% of the para complex ions react to form $FeC_{24}H_{18}^+$ and $FeC_{30}H_{22}^+$ under a high-pressure pulse of chlorobenzene. This offers the interesting possibility that the meta and para isomers might themselves be a mixture of positional isomers with the metal attached to the central or terminal phenyl rings. Thus, both the ligand structure and its coordination geometry with the metal center are important in determining the reactivity.



IV

The stability of structure III is obviously of fundamental importance to the overall feasibility of the reaction depicted in Scheme 1. The chemistry of chlorobenzene with several methylated arene ligand complex ions was studied to further probe the mechanism. The introduction of a single methyl group on the benzene shows little effect, as is indicated by reactions 7 and 8 for Fe(toluene)$^+$ with chlorobenzene. The corresponding

$$FeC_7H_8^+ + C_6H_5Cl \longrightarrow FeC_{13}H_{12}^+ + HCl \quad 98\% \quad (7)$$

$$\longrightarrow FeC_{13}H_{13}Cl^+ \quad 2\% \quad (8)$$

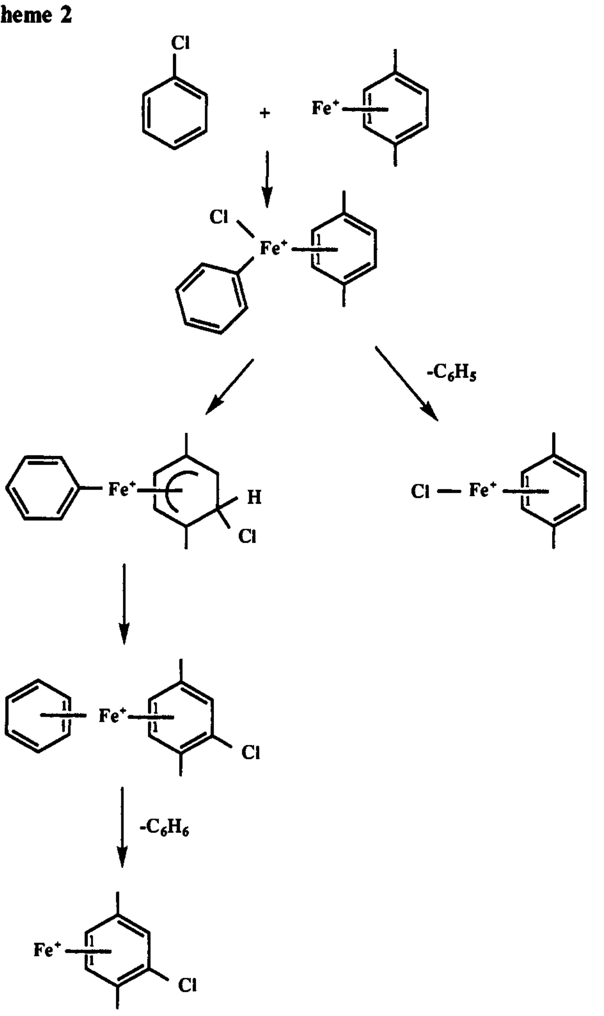
reaction with perdeuterated chlorobenzene gives 22% DCl and 78% HCl elimination, again indicating the predominance of the mechanism in Scheme 1. $FeC_{13}H_{12}^+$ gives efficient secondary reaction to form $FeC_{19}H_{16}^+$, but the relative intensity of $FeC_{25}H_{20}^+$ is very limited even at extended reaction times.

The chemistry becomes somewhat more complicated as multiple methyl groups are attached to the benzene ligand. For example, reactions 9–11 were observed upon reacting chlorobenzene with

		p	*m*	*o*	
$FeC_8H_{10}^+ + C_6H_5Cl$	$\rightarrow FeC_8H_9Cl^+ + C_6H_6$	17%	11%	3%	(9)
	$\rightarrow FeC_8H_{10}Cl^+ + C_6H_5$	13%	8%	3%	(10)
	$\rightarrow FeC_{14}H_{14}^+ + HCl$	70%	81%	94%	(11)

the complex ions of Fe^+ with *p*-, *m*-, and *o*-xylene, respectively. Using C_6D_5Cl, DCl and HCl eliminations account for 20% and 80% of the product ions, respectively, in reaction 11 for the *p*-xylene isomer, once again verifying the generality of the mechanism in Scheme 1. The labeling experiments also indicate exclusive loss of C_6D_5H and C_6D_5 for reactions 9 and 10, respectively. Scheme 2 is proposed to explain these labeling results. Upon the initial Fe^+ insertion into the phenyl–chloro bond, the methyl groups on the arene ligand make it less favorable to undergo subsequent migratory insertion and, consequently, phenyl detachment from the metal center becomes competitive, reaction 10. Alternatively, migratory insertion of the arene ligand into the less sterically demanding Fe^+–Cl bond can occur. A subsequent hydrogen transfer to the metal center and arene elimination completes reaction 9. The maximum number of open carbon positions between the two methyl groups is 2, 3, and 4 for the para, meta, and ortho isomer, respectively. This order coincides with the decreased significance of reactions 9 and 10 and is consistent with an argument based on the steric effect of the phenyl group on the incoming arene ligand. This is strongly supported by the results of Fe(1,3,5-trimethylbenzene)$^+$, reactions 12–14. In this case, the steric effect becomes such a dominant factor that the mechanism in Scheme 2 is favored over that in Scheme 1. Isotope labeling experiments with C_6D_5Cl for reactions 12–14 are again consistent with Schemes 1 and 2.

Scheme 2



$$FeC_9H_{12}^+ + C_6H_5Cl \rightarrow FeC_9H_{11}Cl^+ + C_6H_6 \quad 49\% \quad (12)$$

$$\rightarrow FeC_9H_{12}Cl^+ + C_6H_5 \quad 42\% \quad (13)$$

$$\rightarrow FeC_{15}H_{16}^+ + HCl \quad 9\% \quad (14)$$

In contrast to the methyl groups whose cumulative effects modify the reactivity in Scheme 1 by opening reactivity according to Scheme 2, a fluorine substituent group on the arene ligand inhibits reaction 1 altogether. This is indicated by the lack of reaction between chlorobenzene and Fe(fluorobenzene)$^+$, which is prepared from the condensation reaction of Fe^+ with fluorobenzene. Interestingly, a somewhat related reaction has been reported between C_6H_5F and $Fe(C_6H_5F)_2^+$ to give presumably $Fe(C_6H_5F)_2(C_6H_4)^+$ and HF, although no structural characterization was attempted on the product ion.[26] We subsequently studied the chemistry of this system to examine the involvement of Scheme 1. CID on the product ion gives initial elimination of an intact C_6H_5F ligand to give $Fe(C_{12}H_9F)^+$, which subsequently eliminates HF to give $FeC_{12}H_8^+$ and eventually $C_{12}H_8^+$ at increasingly higher energies. The retention of the positive charge on the organic moiety suggests a biphenylene structure, which is the only isomer of $C_{10}H_8$ that has an ionization potential lower than that of Fe. In addition, HF elimination and eventually $C_{12}H_8^+$ formation from the CID of $Fe(C_{12}H_9F)^+$ is very similar to the CID products from Fe(*o*-chlorodiphenyl)$^+$ formed in reaction 15, discussed below. All of these results suggest only one intact fluorobenzene molecule in the previously reported $Fe(C_6H_5F)_2(C_6H_4)^+$ species. Instead, the CID results suggest a $Fe(C_6H_5F)(C_6H_5{-}C_6H_4F)^+$ structure. Unfortunately, attempts to form Fe(chlorobenzene)$^+$ to study its behavior failed due to the propensity for this ligand to lose HCl and form Fe(benzyne)$^+$.

The reaction mechanism described in Scheme 1 for chlorobenzene may also be observed for other substituted chlorobenzene species, although the reactivity may be less specific because of alternative reaction pathways made possible by the presence of the other substituent groups. This complication is exemplified by the reaction of *p*-chloro(trifluoromethyl)benzene with Fe(benzene)$^+$, which gives only about 19% of the HCl elimination predicted from Scheme 1, along with 55% condensation product and 26% $C_{13}H_9F_2^+$. The latter species is a dissociation product of the substituted biphenyl complex $Fe(C_6H_5C_6H_4CF_3)^+$ by the loss of FeF, as verified by CID. However, several dihalobenzene species still react efficiently with $FeC_6H_6^+$ via Scheme 1 exclusively. For example, reaction 15 occurs upon reacting $FeC_6H_6^+$ with *o*-dichlorobenzene, with exclusive DCl elimination observed from $FeC_6D_6^+$. CID on the product ion at 39 eV from reaction 15 gives 22% $C_{12}H_8^+$ and 78% $FeC_{12}H_8^+$. In contrast to chlorobenzene, however, no secondary products were observed at extended reaction times. *p*-Dichlorobenzene gives a primary product ion of the same formula as that in reaction 15, $FeC_{12}H_9Cl^+$, as well as an efficient secondary product ion, $FeC_{18}H_{12}Cl_2^+$, in contrast to the ortho isomer. The corresponding reaction of *m*-dichlorobenzene is less specific than its ortho and para isomers, as demonstrated in reactions 16–18.

$$FeC_6H_6^+ + o\text{-}C_6H_4Cl_2 \rightarrow FeC_{12}H_9Cl^+ + HCl \quad 100\% \qquad (15)$$

$$\begin{aligned} FeC_6H_6^+ + m\text{-}C_6H_4Cl_2 &\rightarrow FeC_6H_6Cl^+ + C_6H_4Cl && 17\% && (16)\\ &\rightarrow C_{12}H_{10}^+ + FeCl_2 && 14\% && (17)\\ &\rightarrow FeC_{12}H_9Cl^+ + HCl && 69\% && (18) \end{aligned}$$

Study of a mixed dihalobenzene species is particularly interesting as it provides a direct comparison of the relative reactivities of different functional groups. For example, reaction 19 was observed exclusively between $FeC_6H_6^+$ and 1,4-chlorofluorobenzene, with the primary product ion reacting further to form $FeC_{18}H_{12}F_2^+$. Only a minor amount of the tertiary product ion, $FeC_{24}H_{15}F_3^+$, was observed even at extended reaction time. These results are not surprising considering the different reactivities of chlorobenzene and fluorobenzene discussed earlier. However, the corresponding reactions of *p*-chlorobromobenzene are much less specific, with HCl elimination, presumably proceeding by Scheme 1, and Br elimination being two of the most prominent neutral eliminations from such reactions.

$$FeC_6H_6^+ + p\text{-}C_6H_4ClF \rightarrow FeC_{12}H_9F^+ + HCl \quad 100\% \qquad (19)$$

Summary

This study examined the chemistry between a series of Fe(arene)$^+$ ions and halobenzene and dihalobenzene species to give Fe(biphenyl)$^+$. The key to these reactions is the ability of Fe^+ to activate phenyl–halo bonds via oxidative insertion. The arene ligand then undergoes migratory insertion into the resulting Fe^+–phenyl bond. Subsequent hydrogen abstraction from the organic moiety and HCl elimination results in the formation of Fe(biphenyl)$^+$ for $FeC_6H_6^+$ with chlorobenzene. Further sequential reactions with chlorobenzene up to five times were observed to give Fe(polyphenyl)$^+$. Methyl groups on the arene ligands exert a steric effect on the phenyl group during the migratory insertion and induce alternative reaction pathways. In contrast, a fluoro-substituting group on the arene ligand blocks the reaction pathway altogether. The general significance of such a mechanism is evident by its operation in many reactions involving various substituted chlorobenzene species.

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