near-zero values of both charge and charge flux during the stretching or of close values and opposite signs of the two parameters. The first hypothesis must be discarded because reasonable C–H deformation intensities require q°_{H} values far from zero, the charge flux on deformation being negligible[44,45] (eq 1b), so the second hypothesis should be the preferred one. The meaning of $\mathrm{CF(CH_{str})}$ having large values and opposite sign with respect to q°_{H} is that the hydrogen atom of the C–H group has a high deformable charge, which tends to release during the stretching, reaching neutrality at the dissociation limit: in other words, the $\equiv$C—H bond of the coordinated terminal alkynes dissociates into neutral atoms and not into ions. Among the free hydrocarbons, the alkanes and alkenes have high deformable charges, whereas on the alkynes the charge is practically fixed. This is further support for the model of the coordinated alkynes, which are supposed to be similar to olefins or to saturated hydrocarbons.

Even if the intensity value does not resolve the ambiguity of the sign of the charge on H atom (eq 1a), it seems likely that the charge is positive, as in the free alkynes. At the same time, the charge on the C alkynic atom should be negative because of the aforementioned relationship between the signs of charge and charge flux. As the negative charge on C atoms is mainly released by the π-back-donation from the metals, the greater the q°_{C} and, consequently, the q°_{H} values, the greater the π-effect. So we expect the greatest π-back-donation and the greatest q°_{H} with IVa and IVc complexes, because the π-effect increases as the number of the coordinating metals increases, and the lowest ones with complex IV′a, because its structure implies the lowest degree of π-interaction between the alkyne and the metal cluster. From Table IV, the *R*(CH) values suggest q°_{H} values in the following order: IVa > IIa > free $\mathrm{HC_2H}$ > IIIa $\approx$ III′a > IV′a for acetylene complexes; IVc $\approx$ IIIc > IIc > free $\mathrm{HC_2CH_3}$ for propyne complexes. This roughly parallels the expected order of the M-to-alkyne π-donation.

The $\mathrm{M_3}$ complexes require further comments. Their structures, usually indicated as $\mathrm{M_3}(\|)$alkyne with the C$\equiv$C axis parallel to an M—M bond, implies a low level of π-back-donation from metals to the alkyne, so the charge order for the acetylene complexes is reasonable. The $\mathrm{Os_3}$ propyne compound, according to its *R* value, appears to have greater q°_{H}, which in turn suggests greater π-back-donation. In the $\mathrm{M_3}$(alkyne) complexes the π-effect is increased if the structure moves from the $\mathrm{M_3}(\|)$ to the $\mathrm{M_3}(\perp)$; therefore, the *R* value of the $\mathrm{Os_3}$(propyne) complex is suggestive of a deformation of the symmetric structure, with $\mathrm{HC_2CH_3}$ moiety slightly rotated, such that the C$\equiv$C axis is no longer parallel to the Os—Os bond. Such a slightly distorted structure has already been reported for $\mathrm{Os_3H_2(CHCOC_2H_5)(CO)_9}$[47] and for $\mathrm{Os_3(CO)_9(C_2H_5C_2C_2H_5)P(C_6H_5)_3}$[14] and was ascribed to the asymmetric π-donation from the $\mathrm{OC_2H_5}$ group or to the steric demands of the phosphine ligand.

Very good agreement was reported on simple molecules between the q°_{H} values derived from experimental infrared intensities and those computed by quantum-mechanical calculations, suggesting agreement between the IR charge and the Mullikan electron population.[48] The agreement, however, is only evident if both parameters are the result of very sophisticated calculations (NCA on absolute intensities and "ab initio" MO analysis). Comparison is meaningless in our case because the Mullikan charges on C and H reported for alkyne–metal cluster complexes are approximate and one dependent on the calculation procedure. However, in agreement with the previous suggestion, MO analysis on model compounds such as $\mathrm{Co_2(CO)_6HC_2H}$,[49] $\mathrm{Co_2(CO)_6(CH_3)_3CC_2C(CH_3)_3}$,[12] $\mathrm{Fe_3(CO)_9HC_2H}$,[50] and $\mathrm{Co_4(CO)_{10}HC_2H}$[51] stressed the importance of the π-back-donation from metal to alkyne, suggesting carbanionic character for the ligand.

In conclusion, comparative analysis of the IR vibrational properties (frequencies and intensities) of the alkynes coordinated to metal clusters can suggest the following points.

(a) The C$\equiv$C and the $\equiv$C—H bonds are greatly affected by the coordination, whereas slight effects or no effect is observed on the other bonds of the alkyne.

(b) The charge on the acetylenic H is positive and that on acetylenic C is negative and both mainly depend on the metal-to-alkyne π-back-donation.

(c) The $\equiv$C—H bond has prevailing covalent character, and it is expected to dissociate into neutral atoms.

(d) The charge distribution on the coordinated alkyne molecule affects the group bonded to the alkynic carbon atoms.

(e) Both frequency and intensity of the IR bands offer some insight into structure predictions.

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The Chemistry of Iron–Alkene Ions with Chlorobenzene

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The chemistry of $\mathrm{Fe^+}$–alkene ions with chlorobenzene is studied in the gas phase by laser-desorption Fourier transform mass spectrometry. The reaction between $\mathrm{Fe^+}$–ethylene and chlorobenzene occurs via initial insertion of $\mathrm{Fe^+}$ into the Cl–C bond, followed by ethylene migratory insertion into the $\mathrm{Fe^+}$–phenyl bond. Subsequent β-hydrogen abstraction and HCl elimination completes the reaction. In the case of $\mathrm{Fe^+}$–propene, a remarkable selectivity governing the migratory insertion step is present, resulting in the formation of $\mathrm{Fe^+}$–β-methylstyrene.

Recent studies on transition-metal ions in the gas phase have provided a great deal of insight into their reaction mechanisms, kinetics, and thermochemistry.[1] Attachment of one or more ligands to such a transition-metal center can have little or major effects on the reactivity of the metal ion center. This depends on the nature of the ligand and the interaction between the metal center and the ligand, as well as on the neutral reacting species selected for the reaction process.[2,3] Thus, results obtained from

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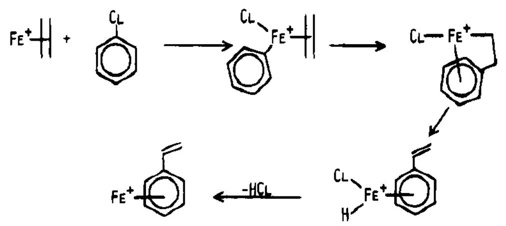
Scheme I



the gas-phase study of ML$^+$ (L = ligand), as compared to that of M$^+$, are potentially very useful in revealing the intrinsic ligand effect on the reactivity, as well as the extent to which the ligand influences the reaction.

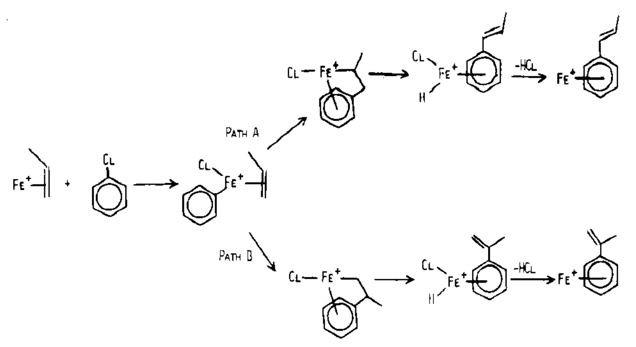
Gas-phase Fe$^+$ reacts with chlorobenzene by dehydrochlorination to form Fe$^+$–benzyne, which reacts further to form a series of product ions corresponding to iron–polyphenylene and polyphenylene cations.[4-6] Fe$^+$–alkene ions also react with chlorobenzene via elimination of HCl. However, detailed studies show that the chemistry of Fe$^+$–alkene ions is different from that of bare Fe$^+$, with the alkene ligand often actively participating in the reaction.[7] Here we report the results from such a study. All experiments were performed on a prototype Nicolet FTMS-1000 spectrometer. Details of the laser-desorption Fourier transform mass spectrometry experiments have been reported previously.[8,9]

Fe$^+$–ethylene, which is prepared from the reaction of Fe$^+$ with propane,[10] reacts with chlorobenzene, yielding $FeC_8H_8^+$ as the sole product. Collision-induced dissociation (CID)[11,12] of the product ion yields exclusive loss of the ligand from the metal center over the energy range studied (16–49 eV, laboratory frame), suggesting that the product ion has an Fe$^+$–styrene structure.[6] The product ion in reaction 1 could conceivably have been formed

(1)

from the interaction of the ethylene ligand and the benzyne ligand, with the latter being formed from the Fe$^+$ dehydrochlorination of chlorobenzene, as is the case for bare Fe$^+$. In such a case, the ethylene ligand would have been a mere "spectating" ligand during the whole dehydrochlorination process. This pathway appears to be ruled out when it is compared with the chemistry of Fe$^+$–benzyne with ethylene. The reaction between Fe$^+$–benzyne and ethylene yields several product ions, with bare Fe$^+$ and Fe$^+$–benzocyclobutene being the major product ions.[13] In this reaction, the benzyne ligand is attached to the metal center first, with the reaction occurring upon encountering the incoming ethylene ligand. It is unlikely that the reaction should be completely different simply by first attaching the ethylene ligand to the metal center with the benzyne ligand brought in next, despite some difference in the energetics involved. This is easily confirmed from the reaction of Fe$^+$–ethylene with perdeuterated chlorobenzene, which yields exclusive elimination of HCl, not the DCl elimination expected from simple dehydrochlorination of chlorobenzene. This immediately suggests that the mechanism in Scheme I, rather than the simple dehydrochlorination, is operating here. In this mechanism, the reaction is initiated by Fe$^+$ insertion into the Cl–C_6H_5 bond, followed by migratory insertion of the ethylene ligand into the Fe$^+$–phenyl bond to form an intermediate η^7-(2-phenylethyl)chloroiron ion. Alternatively, the latter step might also proceed by phenyl migratory insertion into the alkene ligand across the C–C double bond. The proposed intermediate then undergoes a β-hydrogen migration to the Fe$^+$ center and subsequent HCl elimination to form Fe$^+$–styrene. Thus, the overall reaction can be simply regarded as the phenylation of the ethylene ligand by chlorobenzene.

Scheme II



In order to gain more mechanistic insight into Scheme I, chlorobenzene was reacted with Fe$^+$–ethylene-*1,1-d*$_2$ which was prepared from the reaction of Fe$^+$ with propane-*2,2-d*$_2$ by methane elimination. This reaction yielded ~48% $FeC_8H_7D^+$ and ~52% $FeC_8H_6D_2^+$. The almost identical intensities of these two ions indicates a minimal isotope effect, suggesting that the rate-limiting step is not the β-hydrogen abstraction process but more likely is the Fe$^+$ insertion into the phenyl–chloro bond.

Fe$^+$–propene, which is also prepared from the reaction of Fe$^+$ with propane,[10] reacts with chlorobenzene, yielding $FeC_9H_{10}^+$, exclusively. Use of perdeuterated chlorobenzene again indicates that the hydrogen atom in the eliminated HCl comes from the propene ligand. CID on the product ion from the reaction of Fe$^+$–propene with chlorobenzene yields Fe$^+$ and Fe$^+$–toluene. According to the aforementioned mechanism, Fe$^+$–β-methylstyrene and Fe$^+$–α-methylstyrene might be formed depending on the carbon atom of the C–C double bond to which the phenyl group is attached during the migratory insertion step, as shown in Scheme II. CID on Fe$^+$–α-methylstyrene, prepared from the displacement reaction of α-methylstyrene with Fe$^+$–benzene, gives Fe$^+$ and $FeC_8H_6^+$ fragments over the energy range studied (9–45 eV). CID on authentic Fe$^+$–β-methylstyrene, prepared from the displacement reaction of β-methylstyrene with Fe$^+$–benzene, yields Fe$^+$ and Fe$^+$–toluene over the same energy range. Comparison of the CID results indicates that the phenyl group is surprisingly selective in attaching exclusively to the terminal carbon atom not having a methyl substitution. Fe$^+$–propene-*2-d*, prepared from reacting Fe$^+$ with propane-*2,2-d*$_2$, reacts with chlorobenzene by exclusively eliminating HCl, again demonstrating the remarkable selectivity of path A over path B in Scheme II. While it seems reasonable that the demonstrated selectivity arises from the steric effect of the methyl group on phenyl during the migratory insertion step, the existence of electronic factors cannot be ruled out.

As is shown in Scheme II, path A, the hydrogen that is α to the phenyl group and β to the Fe$^+$ center migrates to the metal center and eventually gets eliminated as HCl. However, the hydrogen atoms on the terminal methyl group are also β to the metal center and available for abstraction. Migration of one of these hydrogens would lead to the formation of Fe$^+$–phenylallyl. Unfortunately, CID on a known structure of Fe$^+$–phenylallyl gives the same CID results as that of Fe$^+$–β-methylstyrene, indicating that they probably interconvert under activation and fragment through a common intermediate. While our experiments could not distinguish the two structures, it is reasonable to expect that the reaction will yield the β-methylstyrene structure preferentially. This is because β-hydrogen abstraction should occur more readily

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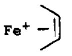
for the benzyl hydrogens, which have a weaker C–H bond strength, than for those on the terminal methyl group. Attempts to use deuterium-labeled alkene ligands to characterize such selectivity was, unfortunately, unsuccessful because of the difficulty of preparing the required precursor ion without H/D scrambling. As an example, the displacement reactions of 2-(methyl-d_3)-propene-*3,3,3*-d_3 with a FeL^+ (L = alkene ligand) always resulted in H/D exchange between the two ligands.

Fe^+–isobutene, prepared from the reaction of Fe^+ with neopentane,[10] reacts with chlorobenzene to form $FeC_{10}H_{12}^+$. Its CID yields Fe^+ and Fe^+–toluene, which is the same as that of the known structure of Fe^+–β,β-dimethylstyrene, in accordance with Schemes I and II.

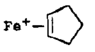
Fe^+–2-butene, prepared from the displacement reaction of *cis*-2-butene with Fe^+–propene, also reacts with chlorobenzene to give an HCl elimination product ion, as well as an additional dehydrogenation product ion (reactions 2 and 3). Both Fe^+–2-methyl-2-butene and Fe^+–2,3-dimethyl-2-butene can also be prepared from the displacement reactions of their respective ligands with Fe^+–propene. The reactions of these ions with chlorobenzene become much slower and less specific, although $FeC_{11}H_{14}^+$ and $FeC_{11}H_{12}^+$ are still observed as significant product ions for Fe^+–2-methyl-2-butene. In one sense, this is not unexpected from the above results because of the additional methyl groups on the C–C double bond. Especially in the case of Fe^+–2,3-dimethyl-2-butene, there is no benzyl hydrogen for β-hydrogen abstraction after initial Fe^+ insertion into the phenyl–chloro bond. The lack of specificity and slowness of these reactions, coupled with the added difficulty of preparing these specific reacting species, prevented further structural studies on these product ions.



$$+ C_6H_5Cl \longrightarrow FeC_{10}H_{10}^+ + H_2 + HCl \qquad 18\% \qquad (2)$$

$$\longrightarrow FeC_{10}H_{12}^+ + HCl \qquad 82\% \qquad (3)$$

The same reaction pattern also occurs for cyclic alkene ligands. For example, Fe^+–cyclopentene, prepared from Fe^+ dehydrogenation of cyclopentane, reacts with chlorobenzene to form HCl elimination and further dehydrogenation product ions (reactions 4–6). The observation of reaction 5 is interesting because the loss of a H• is unusual. A product ion of the same formulation has been observed from the reaction of Fe^+–benzyne with cyclopentene.[13] One of the likely structures for the ligand includes 1-phenylcyclopentenyl. Fe^+–cyclohexene, prepared from Fe^+ dehydrogenation of cyclohexane, reacts with chlorobenzene to form 90% of the HCl elimination product ion $FeC_{12}H_{14}^+$, as well as 5% $FeC_{12}H_{12}^+$ and 5% $FeC_{12}H_{10}^+$.



$$+ C_6H_5Cl \longrightarrow FeC_{11}H_{10}^+ + H_2 + HCl \qquad 12\% \qquad (4)$$

$$\longrightarrow FeC_{11}H_{11}^+ + H\cdot + HCl \qquad 8\% \qquad (5)$$

$$\longrightarrow FeC_{11}H_{12}^+ + HCl \qquad 80\% \qquad (6)$$

It is interesting that Fe^+–diene ions give very similar reactions. For example, Fe^+–cyclopentadiene reacts with chlorobenzene to form $FeC_{11}H_{10}^+$, exclusively. In the case of Fe^+–butadiene, 56% $FeC_{10}H_{10}^+$ and 44% of the further dehydrogenation product ion $FeC_{10}H_8^+$ are observed.

In summary, this study suggests that the mechanisms outlined in Schemes I and II accurately describe the reactions of Fe^+–alkene with chlorobenzene, with the alkene ligand actively participating in the reactions. Although one might have expected similar product ions to be generated from the reaction of Fe^+–benzyne with alkenes and Fe^+–alkene ions with chlorobenzene following HCl elimination, differences are observed that can readily be explained by the fact that the HCl is not eliminated directly from the chlorobenzene. Interestingly, the propene methyl group in the reaction of $FeC_3H_6^+$ with chlorobenzene results in a remarkable selectivity during the migratory step. Reactivity studies of Fe^+–alkene ions with other alkyl and aryl halides are currently underway.

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