Gas-Phase Reactions of Iron(I) Ions with Phenyl Halides. Observation of Metal-Catalyzed Oligomer Formation

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The reactions of iron ions with phenyl halides were studied with Fourier transform mass spectrometry (FTMS). The iron ions react in successive dehydrohalogenation reactions with fluorobenzene, chlorobenzene, and bromobenzene to form complex ions, $Fe(C_6H_4)_n^+$, with n as high as 7 for chlorobenzene and bromobenzene. These complex ions can lose the iron atom upon reactions with the neutral halide to form oligophenylene ions, $(C_6H_4)_n^+$, with n up to 5. These may be the first direct observations of metal-catalyzed organic oligomer formation in the gas phase. Iodobenzene, due in part to the weak C–I bond, reacts differently to form $Fe(C_6H_5)^+$, which in turn reacts to form $Fe(C_6H_5)_2^+$. Dehydroiodination is finally seen when $Fe(C_6H_5)_2^+$ reacts with iodobenzene to form $Fe(C_6H_5)_2(C_6H_4)^+$. The metal–ligand bond energy $D^0(Fe^+–C_6H_4)$ was found to be 83 ± 3 kcal/mol. A lower limit for the bond energy $D^0(Fe^+–C_6H_5)$ was found to be 65 kcal/mol.

Introduction

Metal-catalyzed synthesis of polymers is a widely used technique, but the details of the underlying mechanisms of these reactions are, in many cases, less well-known. Polyphenylenes, in particular poly(*p*-phenylenes), have received considerable attention in recent years due to their electrical conductive properties upon doping.[1] A number of different synthetic procedures have been used for the preparation of these compounds. With benzene or phenyl halides as reactants and metals or metal salts as catalysts, products of varying chain length and physical properties are produced.[2] A mass spectral method for the analysis of these compounds has been developed by Brown and co-workers.[3] In an effort to characterize the reactions of various transition-metal ions with aromatic compounds in the gas phase, we have observed the initial steps of the metal-catalyzed formation of polyphenylenes.

The reactions of metal ions with organic molecules in the gas phase have been studied by a number of researchers, particularly in the last 10 years. Solvent complications are avoided in the gas phase, and important thermochemical data can be acquired with ion cyclotron resonance (ICR) being the most extensively employed technique. The development of Fourier transform mass spectrometry (FTMS)[4] and the commercial availability of such instruments have greatly enhanced the interest in the studies of ion/molecule reactions and provide a versatile technique for these efforts. Other methods offer certain advantages, such as the ion beam apparatus developed by Armentrout, Hodges, and Beauchamp.[5] Armentrout and co-workers[6] have reported elegant state specific reactions of various transition-metal ions with small alkanes and hydrogen. Freiser and co-workers have developed a convenient technique for generating metal ions through the interaction of a laser pulse with metal targets in an FTMS[7] and have studied the reactions of a number of metal ions with various classes of organic compounds.[8] To date, most reports have concentrated on the primary reactions of the metal ions with the sample of interest, and the subsequent reactions of the product ions are often not reported.

Although the reactions of transition-metal ions with aromatic compounds in the gas phase are still largely unexplored, a few reports have appeared on this subject from several groups. Dietz, Chatellier, and Ridge[9] studied the reactions of Fe^+ with phenyl halides. Jones and Staley[10] examined the reactions of Cu^+ with benzene and chlorobenzene, and Uppal and Staley[11] reported reactions of Ti^+ with chlorobenzene. Jacobson, Byrd, and Freiser studied the reactions of Co^+ and Rh^+ with toluene, cycloheptatriene, and norbornadiene.[12] Chowdhury and Wilkins have reported the reactions of Au^+ with a few arenes,[13] and Stepnowski and Allison have studied the gas-phase chemistry of Ni^+ and nickel-containing ions with several aromatic compounds.[14] Bjarnason and Taylor[15,16]

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[6] See, for example: Schultz, R. H.; Elkind, J. L.; Armentrout, P. B. *J. Am. Chem. Soc.* **1988**, *110*, 411.

[7] (a) Burnier, R. C.; Carlin, T. C.; Reents, W. D.; Cody, R. B.; Lengel, R. K.; Freiser, B. S. *J. Am. Chem. Soc.* **1979**, *101*, 7127. (b) Cody, R. B.; Burnier, R. C.; Reents, W. D., Carlin, T. J.; McCrery, D. A.; Lengel, R. K.; Freiser, B. S. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *33*, 37.

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have reported isomer differentiation of disubstituted benzene derivatives through iron ion reactions in the gas phase, and this group has also studied the reactions of Fe^+ with several monosubstituted benzene derivatives.[17,18]

In their paper a decade ago, Dietz et al.[9] reported a study of the reactions of iron ions with phenyl halides in the gas phase obtained by using an ICR spectrometer. Reaction 1 was observed for fluorobenzene, chlorobenzene, and bromobenzene. In the case of chlorobenzene, two more

$$Fe^+ + C_6H_5X \rightarrow Fe(C_6H_4)^+ + HX \qquad (1)$$

steps of dehydrohalogenation were observed to form $Fe(C_{12}H_8)^+$ and $Fe(C_{18}H_{12})^+$. Iodobenzene, however, was found to react differently. Recent instrumental advances have allowed us to probe these reactions in more detail, and we wish to report a number of additional reactions for these systems, including the direct observation of iron-catalyzed phenylene oligomer formation.[17,18] In the process of completing this paper we became aware of the work of Huang and Freiser[19] that partially overlaps this effort.

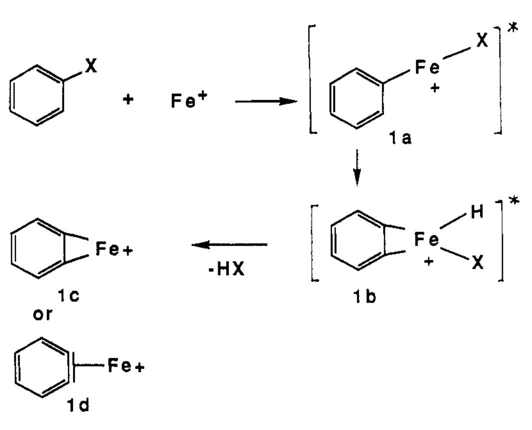
Experimental Section

The experimental approach used for these experiments has been described elsewhere.[16] Briefly, a Nicolet FTMS-2000 Fourier transform mass spectrometer equipped with a 3.0 T superconducting magnet was used. Iron ions were generated by using the laser ionization technique developed by Freiser and co-workers,[7] but a stainless-steel target on the direct insertion probe was employed with a pulsed CO_2 laser and a Nicolet desorption interface. The use of a stainless-steel target served two purposes. The magnetic properties of iron make it unsuitable for use in the high magnetic field near the cell of the mass spectrometer, and the other metals in the stainless steel can be studied as well as iron. Iron(I) ions were isolated by using double-ejection pulses, stored in the cell, and allowed to react with the sample during a delay event, which was varied from 0.003 to 25.6 s, prior to ion detection. All reaction paths were established by using double-resonance techniques.[20] Product ions were isolated and their reactions with the neutral phenyl halide monitored in the same manner as described above. Trapping voltages were kept at 0.8–1.0 V to trap only iron ions of low kinetic energy.

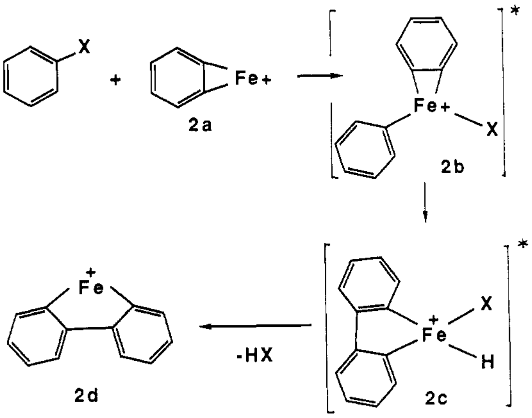
The reactant gas was introduced through the sample inlet system into the source side ICR cell, where reactions and ion detection also took place. The pressure of the reactant was usually around 2×10^{-7} Torr but, in the case of chlorobenzene, was varied from 2×10^{-8} to 1×10^{-6} Torr to examine the pressure dependence of the iron ion reactions. The low-pressure measurements were done after a bakeout of the instrument with background pressure on the order of 10^{-9} Torr.

The effects of the ejection pulses on the kinetic energy of the iron ions were of concern, as a kinetically excited ion may react differently (endothermic reactions) than those with low kinetic energy. This was addressed by allowing the laser-generated ions to react without the isolation of iron, and the results were compared. The reactions of the other metal ions from the steel target slightly complicate spectral interpretation, but the reactions of the unisolated iron ions were the same as the reactions of the isolated iron ions.

Scheme I



Scheme II



The distribution in internal energy of the laser-desorbed iron ions is unknown. The possibility that a significant fraction of the ions may be in excited states was of concern because ions in excited states may react differently than those in the ground state as recently shown by Armentrout and co-workers.[6] The reactions of the iron ions with chlorobenzene and bromobenzene were investigated with nitrogen collision gas present at tenfold the pressure of the sample. This pressure difference would cause the average iron ion collisions with sample molecules to occur after nearly ten collisions with nitrogen molecules, and these collisions would be expected significantly to reduce the fraction of iron ions in excited states. No significant differences in the reaction products or reaction rates were observed with or without the nitrogen present, suggesting that either the fraction of excited ions is low or that the ions in excited states react in the same manner as those in the ground state.

The phenyl halides were commercially obtained and used without further purification, except for a few freeze–pump–thaw cycles.

Results and Discussion

Iron ions reacted with fluorobenzene to yield $Fe(C_6H_4)_n{}^+$ with $n = 1$ or 2 whereas chlorobenzene and bromobenzene reacted through successive dehydrohalogenations to give $Fe(C_6H_4)_n{}^+$ with $n = 1$–7. These reactions all proceed according to (2). Reaction 3 appears to compete with the

$$Fe(C_6H_4)_n{}^+ + C_6H_5X \rightarrow Fe(C_6H_4)_{n+1}{}^+ + HX \qquad (2)$$

one above for certain values of n. The phenylene oli-

$$Fe(C_6H_4)_n{}^+ + C_6H_5X \rightarrow (C_6H_4)_n{}^+ + Fe(C_6H_5X) \qquad (3)$$

gomers are observed for fluorobenzene with $n = 2$ whereas reactions with $n = 2$–5 occur for chlorobenzene and bromobenzene. The oligophenylene ions are unreactive with the phenyl halides. At longer reaction times the tri-

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(15) Bjarnason, A.; Taylor, J. W. Iron Ion Chemistry and Isomer Discrimination using FTMS. Proceedings of the 35th ASMS Conference on Mass Spectrometry and Allied Topics, Denver, CO, May 1987, pp 335–336.

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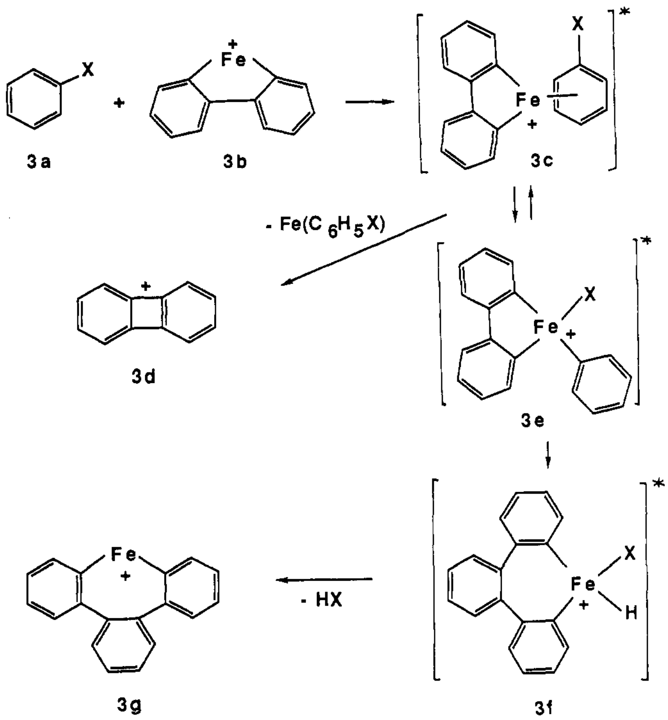
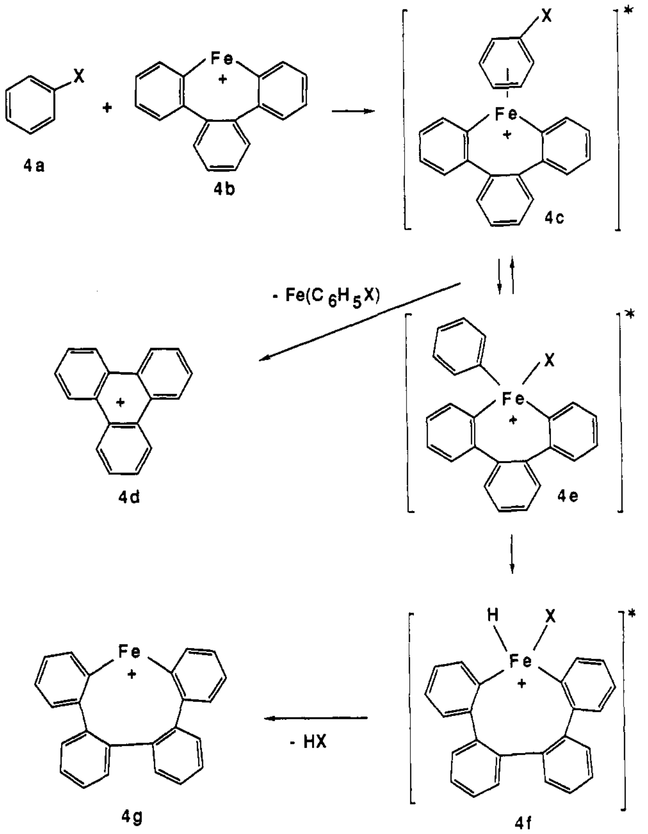
(20) (a) Comisarow, M. B.; Grassi, V.; Parisod, G. *Chem. Phys. Lett.* **1978**, *57*, 413. (b) Marshall, A. G.; Comisarow, M. B.; Parisod, G. *J. Chem. Phys.* **1979**, *71*, 4434. (c) Parisod, G.; Comisarow, M. B. *Adv. Mass Spectrom.* **1980**, *8*, 212.

Scheme III



Scheme IV



phenylene ion becomes one of the most abundant of all of the ions observed, which points to its relative stability. To the best of our knowledge, these are the first observations of metal-catalyzed organic oligomer formation in the gas phase.[17,18]

The initial step in the oligomer formation is the formation of the iron–phenylene complex ion $Fe(C_6H_4)^+$. The insertion of metal ions into C–X bonds has been observed by several researchers,[9,10,21] and Scheme I is proposed as a possible mechanism for the formation of the complex ion. The reaction product $Fe(C_6H_4)^+$ may react again with the neutral halide to form $Fe(C_6H_4)_2^+$ according to Scheme II. This ion alternatively can either react to form the next larger complex ion $Fe(C_6H_4)_3^+$ or lose the iron to form the dimer (biphenylene) ion $(C_6H_4)_2^+$. A possible mechanism for these reactions is shown in Scheme III. The next step is shown in Scheme IV, where $Fe(C_6H_4)_3^+$ reacts with the phenyl halide to form $Fe(C_6H_4)_4^+$ and the trimer (triphenylene) ion $(C_6H_4)_3^+$. These steps are then repeated to form successively larger complex ions and oligomer ions.

The structure of the complex ions and the oligophenylene ions are depicted here as ringlike, and in the case of the complex ions, the iron ion is connected to two phenylene units. No direct evidence has been obtained to support this picture, and the ring may have rearranged to form an open chain. The unusual stability of the trimer $(C_6H_4)_3^+$ does, however, point to a ring structure, and, indeed, Dietz et al.[9] calculate ΔH°_{298} for the formation of the triphenylene ring from chlorobenzene to be −38 kcal/mol. A ring with four phenylene units would be expected to be strained, and it is observed in less abundance in these reactions. The competing reaction, the formation of $Fe(C_6H_4)_5^+$, is favored. The pentaphenylene ion is only observed in minor abundance. No evidence was found for the existence of the hexaphenylene ion $(C_6H_4)_6^+$ or larger oligomer ions despite attempts to produce them from the corresponding iron complex ions. After isolation of the iron hexaphenylene complex ion, $Fe(C_6H_4)_6^+$, using double-resonance techniques, its reactions with the neutral phenyl halide were found only to yield the iron heptaphenylene complex ion, $Fe(C_6H_4)_7^+$, and the iron hexaphenylene phenyl halide complex ion, $Fe(C_6H_4)_6(C_6H_5X)^+$. Both were produced at very low rates compared with the production of the smaller complexes that were produced at rates near collision rates. No evidence could be found for the production of $Fe(C_6H_4)_8^+$ or larger complex ions.

Some support for the suggested structures comes from Wittig and Klar,[22] who have reported the iron-catalyzed synthesis of *o*-oligophenylenes from biphenyl anions. They present cyclic structures for tetra- and hexaphenylene produced from iron complex ions with the cyclic structures similar to those suggested in the schemes presented above.

Using heat of formation values from ref 23 (ΔH_f in kcal/mol, Fe^+ 281; C_6H_5Br, 24.9; HBr, −9), one can obtain, using the value $n = 0$ in reaction 2, that $\Delta H_{f298}(Fe(C_6H_4)^+) < 315$ kcal/mol (assuming that the reaction is exothermic). From this limit and using the value for the $\Delta H_f(C_6H_4) = 115$ kcal/mol (from ref 23), one can deduce that $D^0(Fe^+–C_6H_4) > 81$ kcal/mol. Dietz et al.[9] calculate this value to be 66 kcal/mol by using older values for the heats of formation. Most dramatic is the difference in the value for $\Delta H(C_6H_4)$, 100 vs 115 kcal/mol here. Photodissociation studies[19] suggest that $D^0(Fe^+–C_6H_4) \leq 86$ kcal/mol. Using this value and the value calculated above, the bond energy is assigned 83 ± 3 kcal/mol.

Iron ions also react to form molecular ion clusters of the type $Fe(C_6H_5X)_n^+$ which are observed for fluorobenzene ($n = 1, 2$) and $n = 1$ for chlorobenzene and bromobenzene. It is of interest to note that $Fe(C_6H_5F)^+$ and $(C_6H_4)_2^+$ both have nominal mass of 152, but the resolution of the mass spectrometer, even in the low-resolution mode used in

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(21) (a) Allison, J.; Ridge, D. P. *J. Organomet. Chem.* **1975**, *99*, C11. (b) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1976**, *98*, 7445.

(22) Wittig, G.; Klar, G. *Justus Liebigs Ann. Chem.* **1967**, *704*, 91.

(23) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl.1.

these experiments, was sufficient to resolve those two peaks. Ions of the form $Fe(C_6H_5X)(C_6H_4)_n^+$ were also detected for fluorobenzene (n = 1, 2) and chlorobenzene and bromobenzene (n = 2–6). These ions are formed according to reaction 4. These reactions compete with reactions 2 and 3 above but proceed at a lesser rate. No ions of this type were observed for iodobenzene. A comparison of reactions 2 and 4 reveals that the reaction of $Fe(C_6H_4)_n^+$ with the neutral phenyl halide can yield two products (aside from the oligomer formation). The formation of $Fe(C_6H_4)_{n+1}^+$ with the elimination of HX is believed to involve the insertion of Fe into the C–X bond. The formation of $Fe(C_6H_4)_n(C_6H_5X)^+$ possibly involves a bond between the iron atom and the benzene ring of the phenyl halide.

$$Fe(C_6H_4)_n^+ + C_6H_5X \rightarrow Fe(C_6H_5X)(C_6H_4)_n^+ \quad (4)$$

Only in the case of $Fe(C_6H_4)_3^+$ (for chlorobenzene and bromobenzene) is reaction 5 observed.

$$Fe(C_6H_4)_3^+ + C_6H_5X \rightarrow XFe(C_6H_4)_3^+ + C_6H_5^\bullet \quad (5)$$

The bond enthalpy of the C–X bond in the phenyl halide is 81 kcal/mol for bromobenzene and 95 kcal/mol for chlorobenzene (calculated by using enthalpy values from ref 23). The bond energy of the Fe–X bond in the iron complex ion must, therefore, be higher for this reaction to be exothermic.

In the case of fluorobenzene, $Fe(C_6H_5F)_2(C_6H_4)^+$ is observed and formed from $Fe(C_6H_5F)_2^+$ in the dehydrofluorination reaction (6).

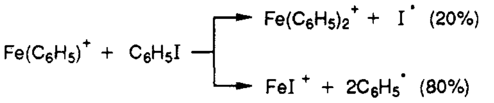
$$Fe(C_6H_5F)_2^+ + C_6H_5F \rightarrow Fe(C_6H_5F)_2(C_6H_4)^+ + HF \quad (6)$$

Iron ions react with iodobenzene according to (7).

$$Fe^+ + C_6H_5I \rightarrow Fe(C_6H_5)^+ + I^\bullet \quad (7)$$

A lower limit for the bond energy $D^0(Fe^+–C_6H_5)$ can be calculated, assuming that reaction 7 is exothermic by using heat of formation values from ref 23 (ΔH_f in kcal/mol; Fe^+, 281; C_6H_5I, 39.4; I, 25.5). From these values one can conclude that ΔH_f $(Fe(C_6H_5)^+) < 295$ kcal/mol. Using $\Delta H(C_6H_5)$ = 79 kcal/mol,[23] one can deduce that $D^0(Fe^+–C_6H_5) > 65$ kcal/mol which is in good agreement with Dietz et al.,[9] who reported a lower limit of 64 kcal/mol for this bond energy.

Double-resonance studies show that FeI^+ is efficiently produced from $Fe(C_6H_5)^+$ reacting with neutral iodobenzene according to reactions 8 and 9. Continuous ejection of $Fe(C_6H_5)^+$ at m/z 133 during the entire reaction time does result in the formation of small amounts of FeI^+. This indicates that some FeI^+ is formed directly in the primary reactions of iron ions with iodobenzene. From thermodynamic arguments the phenyl entities possibly leave as biphenyl ($C_6H_5–C_6H_5$) rather than as phenyl radicals. Experiments were performed to probe this reaction in more detail. The formation of FeI^+ may occur in one step according to reaction 9a or in two steps according to reactions 9b and 9c or reactions 9d and 9e. A method suggested by Cody[24] of Nicolet Analytical Instruments (Madison, WI) provided evidence supporting the one-step reaction in (9a). This was done by applying a continuous ejection pulse during the entire reaction time. Any ionic species at m/z 260, and in another run any species at m/z 337, that might have been present in the cell were ejected from the cell. Products from the reaction intermediate are not observed in the mass spectrum collected in this manner if the lifetime of the reaction intermediate is longer than the time required for its ejection from the cell. The ejection time varies with the power of the ejection pulse but can be as short as a few microseconds for these species. No reduction in the abundance of FeI^+ was observed when this technique was used. This indicates that FeI^+ is produced via the one-step process (9a) involving the formation of $(C_6H_5)_2$ or that the lifetime of the intermediate (in (9c) or (9e)) is shorter than the ejection time (a few microseconds). It should be pointed out that the ejection time is about 10^5 times shorter than the time between collisions at the pressure used in these experiments.



$$Fe(C_6H_5)^+ + C_6H_5I \rightarrow Fe(C_6H_5)_2^+ + I^\bullet \ (20\%) \quad (8)$$

$$Fe(C_6H_5)^+ + C_6H_5I \rightarrow FeI^+ + 2C_6H_5^\bullet \ (80\%) \quad (9)$$

$$Fe(C_6H_5)^+ + C_6H_5I \rightarrow FeI^+ + (C_6H_5)_2 \quad (9a)$$

$$Fe(C_6H_5)^+ + C_6H_5I \rightarrow IFe(C_6H_5)^{+*} \ (m/z\ 260) + C_6H_5^\bullet \quad (9b)$$

$$IFe(C_6H_5)^{+*} \rightarrow FeI^+ + C_6H_5^\bullet \quad (9c)$$

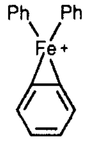
$$Fe(C_6H_5)^+ + C_6H_5I \rightarrow C_6H_5I{\cdot}Fe(C_6H_5)^{+*} \ (m/z\ 337) \quad (9d)$$

$$C_6H_5I{\cdot}Fe(C_6H_5)^{+*} \rightarrow FeI^+ + (C_6H_5)_2 \quad (9e)$$

FeI^+ reacts with the neutral iodobenzene to form the cluster ion $Fe(I)(C_6H_5I)^+$, which in turn forms $Fe(I)(C_6H_5I)_2^+$ at longer reaction times. Dehydroiodination can finally be seen when $Fe(C_6H_5)_2^+$, produced in reaction 8, reacts further with iodobenzene as shown in reaction 10.

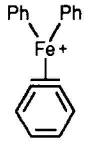
$$Fe(C_6H_5)_2^+ + C_6H_5I \rightarrow Fe(C_6H_5)_2(C_6H_4)^+ + HI \quad (10)$$

The product ion in reaction 10 may have structure **5a** or **5b**. Another step of dehydroiodination follows to produce $Fe(C_6H_5)_2(C_6H_4)_2^+$, which may be of the form shown in structure **6**. No evidence could be found for the production of the biphenylene ion from this complex ion.

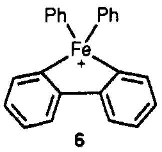


5a

or



5b



6

In the reaction of iron ions with any of the phenyl halides, the presence of the phenylene ion, $C_6H_5^+$, can be detected in minor quantities. This ion is probably formed in reactions involving halide extraction as shown below.

$$Fe^+ + C_6H_5X \rightarrow C_6H_5^+ + FeX \quad (11)$$

At longer reaction times, the phenyl ion reacts to form the stable biphenylene ion $(C_6H_5)_2^+$.

Conclusions

The study reported here highlights a methodology that may become useful in probing the fundamental processes of metal-catalyzed polymerization. By controlling pressure and reaction time before acquiring the mass spectrum, each step in a multistep process, as these reactions inherently are, can be analyzed. Studies of ion/molecule reactions in the gas phase avoid solvent complications and thus give a clearer picture of the interplay between the reactants. The presence of reaction intermediates not directly observed in the mass spectrum may be confirmed or dismissed provided that their lifetimes are longer than the

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[24] Cody, R. B.; Bjarnason, A., work in progress.

times required for their ejection (typically a few microseconds). Studies are continuing on other metal-catalyzed polymerization processes further to examine this phenomenon in the gas phase.

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Registry No. Fe^+, 14067-02-8; C_6H_5F, 462-06-6; C_6H_5Br, 108-86-1; C_6H_5I, 591-50-4; $(Fe(C_6H_4)^+)$, 119208-09-2; chlorobenzene, 108-90-7.

Unsaturated Carbene Ligands: (η^2-Vinyl)-, (Vinylcarbene)-, and (η^4-Butadienyl)tungsten Dithiocarbamate Complexes

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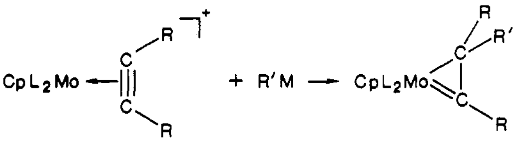
Carbene complexes with unsaturation in the carbene organic substituent have been prepared from $[(S_2CNR_2)_2W(\eta^4\text{-}C_4Ph_4H)][BF_4]$. Addition of one dithiocarbamate ligand to this cationic butadienyl complex results in dechelation of the olefin tail to form a neutral tris(dithiocarbamate) complex containing a vinyl-substituted η^2-vinyl ligand, $(S_2CNR_2)_3W(\eta^2\text{-}CPh{=}CPhCPh{=}CHPh)$. Spectroscopic properties (C_α, 262 ppm) and structural data (W–C_α, 1.94 Å) support formulation of the metal–η^2-vinyl unit as a metallacyclopropene. Protonation of this neutral η^2-vinyl complex produces a cationic complex containing a vinylcarbene ligand, $[(S_2CNR_2)_3W{=}CPhCPh{=}C(Ph)CH_2Ph][BF_4]$. The α-carbon retains its carbene character as evidenced by ^{13}C NMR (257 ppm). Reaction of the cationic η^4-butadienyl complex $[(S_2CNR_2)_2W(\eta^4\text{-}C_4Ph_4H)][BF_4]$ with $Li[Et_3BH]$ produces a terminal sulfide ligand while retaining the η^4-butadienyl ligand in $(S_2CNR_2)(\eta^4\text{-}C_4Ph_4H)W{=}S$. An X-ray structure of the (dithiocarbamato)(butadienyl)tungsten sulfide monomer provides confirmation of the strong bonding between tungsten and both the α-carbon (W–C_α, 1.96 Å) and the terminal sulfide (W–S, 2.10 Å).

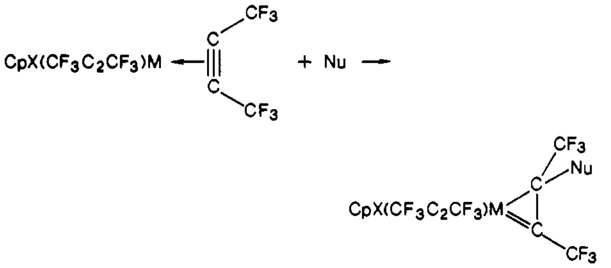
Introduction

Organic ligands which can be generically formulated as $\eta^n\text{-}C_nR_{n+1}$ with n = 2, 3 and 4 are an important class of carbene derivatives. Representative complexes containing η^2-vinyl (n = 2), η^3-vinylcarbene (n = 3), and η^4-butadienyl (n = 4) ligands have been prepared during the 1980s. In each case alternative bonding modes are available to the ligand.

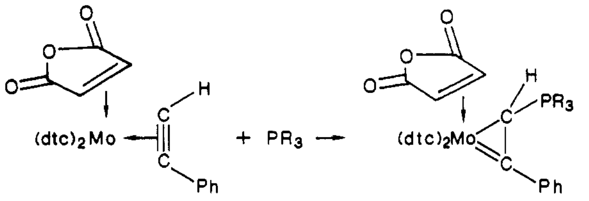
Several groups have prepared η^2-vinyl complexes by nucleophilic addition to four-electron alkyne ligands. Green and co-workers have reacted cationic alkyne complexes of the type $[(\pi\text{-}Cp)L_2Mo(RC{\equiv}CR)]^+$ with carbon-based nucleophiles and hydride transfer reagents to form neutral η^2-vinyl complexes $(\pi\text{-}Cp)L_2Mo(\eta^2\text{-}RC{=}CRR')$ (eq 1).[1] Davidson and co-workers have added heteroatom nucleophiles to complexes containing electron-poor hexafluorobutyne ligands to form η^2-vinyl products (eq 2).[2] We have utilized phosphorus-based nucleophiles to convert terminal alkyne ligands in olefin–alkyne complexes to η^2-vinyl ligands (eq 3).[3] In all of these cases a d^4 metal configuration characterizes both the alkyne reagent complex and the η^2-vinyl product monomer.[4]



(1)



(2)



(3)

Vinylcarbene complexes of the type $L_nM(\eta^3\text{-}CR{-}CR{=}CR_2)$ may form from metal carbene–alkyne coupling; a metallacyclobutene formulation is also possible for complexes with this stoichiometry. Cyclopropene is another source of C_3R_4 ligands. Reaction of metal-bound C_3R_4 moieties with carbon monoxide has been postulated as a route to vinylketene ligands of the type $\eta^4\text{-}R_2C{=}CR{-}CR{=}C{=}O$.[5,6]

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