Formation of Metallacyclic C_{60} Derivatives *via* Gas-Phase Ion−Molecule Reactions

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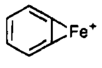
Received August 22, 1994

Since their discovery in 1985,[1] fullerenes have drawn much attention. In 1990, Kratschmer and Huffman[2] developed a method that made it possible to produce C_{60} and C_{70} in macroscopic quantities. Since then, the research on fullerene chemistry has boomed.[3−5] In particular, a large effort has been focused on the production of fullerene derivatives through reactions involving carbon−carbon bond formation. Several routes have been taken to synthesize these derivatives including reacting C_{60} with carbon radicals, nucleophilic reagents, and electrophilic reagents. These have led to the formation of carbon bridges and cycloadditions with fullerenes.[3] In particular, C_{60} derivatives of benzene and naphthalene have been synthesized.[6,7] Organometallic complexes containing C_{60} ligands have also been prepared and characterized.[8]

Paralleling these studies in the condensed phase are gas-phase studies. Although some ionic fullerene derivatives such as $C_{60}(NCC_2H_5)_{1-3}^{2+}$,[9,10] $C_{60}NO_2^-$,[11] exohedrally bound MC_{60}^+ (M = Fe, Co, Ni, Cu, Rh, La, and VO),[12,13] and endohedral $M@C_{60}^+$ (M = He, Ne, Y)[14−18] have been prepared in the gas phase, only a few examples have been reported on the production of gas-phase C_{60} derivatives formed through C−C bonds.[19−21] We have previously demonstrated that metalated and unmetalated buckminsterfullerene methylene derivatives, $CoC_{60}(CH_2)_{1-5}^+$ and $C_{60}(CH_2)_{1-3}^+$, respectively, can be prepared from CoC_{60}^+.[22] In this paper, we report the gas-phase reactions of C_{60} with Fe(benzyne)$^+$ and Fe(biphenylene)$^+$ in which metallacyclic C_{60} derivatives are formed.

All experiments were performed on an Extrel FTMS-2000 dual cell Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR-MS) equipped with a 3 T superconducting magnet.[23] The ion-trapping potential was set at 2 V. A Bayard−Alpert ion gauge was used to monitor pressure. Fe^+ was generated by laser desorption of the pure iron metal target using a Quanta-Ray Nd:YAG laser operated at its fundamental output (1064 nm).[24] C_{60} was introduced into the source side of the dual cell using a solids probe at 350 °C. The temperature of the trapping cell was kept at 200 °C to maintain a static background C_{60} pressure at $\sim 1.0 \times 10^{-8}$ Torr. At this temperature, the observation of a slow reaction suggests that the process is near thermoneutral or somewhat endothermic. Chlorobenzene was introduced using a Varian leak valve into the vacuum system at a static pressure of 7.9×10^{-7} Torr measured using standard procedures for calibrating the ion gauge for the sensitivity toward the neutral molecule.[25] Background argon pressure at $\sim 5.0 \times 10^{-6}$ Torr was used as the collision gas for thermalization and for collision-induced dissociation[26] (CID) experiments. Since a large percentage of the Fe^+ generated by laser desorption underwent a charge transfer reaction with background C_{60} to form C_{60}^+, a solenoid pulsed valve[27] was also used to introduce additional chlorobenzene to a maximum pressure of $\sim 10^{-5}$ Torr to enhance ion intensities of $Fe(C_6H_4)_{1,2}^+$. Standard FT-ICR ion ejection techniques[28] and SWIFT excitation[29] were used to study ion−molecule reaction pathways and to isolate ions for CID experiments.[23]

Fe(benzyne)$^+$ (**1**) and Fe(biphenylene)$^+$ (**2**) were prepared *in situ* in the FT-ICR trapping cell via the well-characterized reactions 1 and 2.[30−32] These two ions react with background C_{60} to form $FeC_{60}C_6H_4^+$ and $FeC_{60}(C_6H_4)_2^+$, respectively, reaction 3. $FeC_6H_4^+$ also undergoes a charge transfer with C_{60}, reaction 4, to form C_{60}^+. The reaction is slow, however, suggesting that it is near thermoneutral or even slightly endothermic. $FeC_{60}C_6H_4^+$ and $FeC_{60}(C_6H_4)_2^+$ react to completion with C_6H_5Cl to form unmetalated $C_{60}C_6H_4^+$ and $C_{60}(C_6H_4)_2^+$, respectively, reaction 5. While $FeC_{60}(C_6H_4)_2^+$ is unreactive with background C_{60}, $FeC_{60}C_6H_4^+$ reacts to form $C_{60}FeC_{60}C_6H_4^+$, reaction 6.



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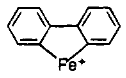

2

$$Fe^+ + C_6H_5Cl \longrightarrow FeC_6H_4^+ + HCl \tag{1}$$

$$FeC_6H_4^+ + C_6H_5Cl \longrightarrow Fe(C_6H_4)_2^+ + HCl \tag{2}$$

$$Fe(C_6H_4)_n^+ + C_{60} \xrightarrow{n = 1, 2} C_{60}Fe(C_6H_4)_n^+ \tag{3}$$

$$\xrightarrow{n = 1} C_{60}^+ + FeC_6H_4 \tag{4}$$

$$FeC_{60}(C_6H_4)_n^+ + C_6H_5Cl \xrightarrow{n = 1, 2} C_{60}(C_6H_4)_n^+ + C_6H_5FeCl \tag{5}$$

$$FeC_{60}C_6H_4^+ + C_{60} \longrightarrow C_{60}FeC_{60}C_6H_4^+ \tag{6}$$

Pseudo-first-order rate kinetics were observed for reaction 5 for both $FeC_{60}C_6H_4^+$ (see Figure 1) and $FeC_{60}(C_6H_4)_2^+$,[33] indicating, but not unequivocally, that each ion population is thermalized and consists of only one isomeric structure. The

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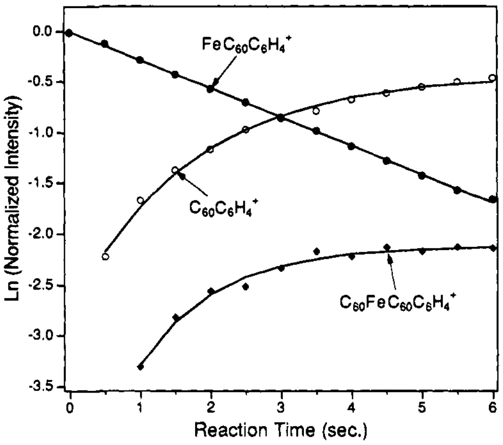


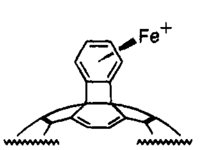
Figure 1. Intensity variation versus reaction time for $FeC_{60}C_6H_4^+$ reacting with C_6H_5Cl and C_{60}. Pressure of $C_6H_5Cl = 7.9 \pm 10^{-7}$ Torr; pressure of $C_{60} = \sim 1.0 \pm 10^{-8}$ Torr.

reactions were found to be relatively slow ($k \sim 10^{-11}$ cm^3 molecule^{-1} s^{-1}). Upon CID, $FeC_{60}C_6H_4^+$ yields both $C_{60}C_6H_4^+$ and $FeC_6H_4^+$, reactions 7 and 8, which seemingly rules out structures **3** and **4**. Reaction 8 implies that IP(FeC_6H_4) < IP(C_{60}) = 7.61 eV,[34] which supports the earlier proposition that reaction 4 proceeds slowly since it is somewhat endothermic. CID of **3** is expected to cleave the weak Fe^+–benzene bond to form $C_{60}C_6H_4^+$ or Fe^+. This structure could conceivably yield

$$FeC_{60}(C_6H_4)^+ \xrightarrow{\text{CID / Ar}} C_{60}(C_6H_4)^+ + Fe \qquad (7)$$

$$\longrightarrow Fe(C_6H_4)^+ + C_{60} \qquad (8)$$

$FeC_6H_4^+$, but it certainly would not be dominant. In addition, $C_{60}C_6H_4^+$ does not fragment under the same conditions. Similarly, upon CID, **4** is expected to lose only C_{60} since the bond energy $D°(Fe^+\text{–benzyne}) = 76 \pm 10$ kcal/mol[32] is far greater than $D°(Fe^+\text{–}C_{60}) < D°(Fe^+\text{–benzene}) = 51.1$ kcal/mol,[35] vide infra. Furthermore, reaction 6 of $FeC_{60}C_6H_4^+$ with C_{60} to form $C_{60}FeC_{60}C_6H_4^+$ also rules out structure **4** since the metal center is not accessible to attach another C_{60} ligand. Instead, structure **5** is the most likely structure of $FeC_{60}C_6H_4^+$ to yield both $FeC_6H_4^+$ and $C_{60}C_6H_4^+$ upon CID. Consistent with the demetalation reaction observed for **2** with C_6H_5Cl,[30–32] **5** has a similar structural moiety and undergoes the analogous demetalation reaction 5. Note that while a mixture of **3** and **4** could explain the CID results, it is very unlikely that each would exhibit the same rate constant for reaction 5.



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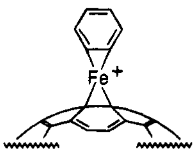

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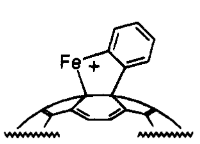
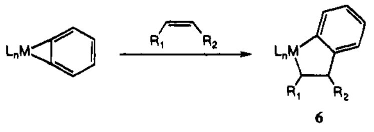


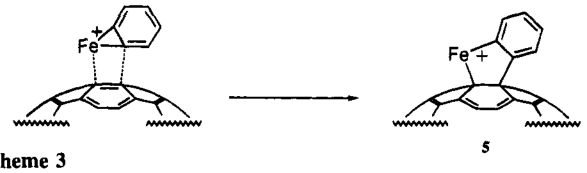
5

It has been established that there is substantial double-bond localization in the C_{60} molecule.[36,37] As a result of this, C_{60} in many cases behaves like an alkene rather than an aromatic hydrocarbon. The 6,6 ring junction is the reaction site in many addition reactions.[4–6,38,39] This is also true for many characterized organometallic complexes in which C_{60} acts like an η^2 ligand.[6] Likewise, a study of the reaction of C_{60}^+ with $Fe(CO)_5$ revealed that C_{60} acts as a two-electron donor in gas-phase organometallic ions.[40] Furthermore, ligand displacement reactions indicate that $D°(M^+\text{–alkene}) < D°(M^+\text{–}C_{60}) < D°(M^+\text{–benzene})$ for M = Fe, Co.[22] This is consistent with either of two interpretations: C_{60} behaves like a highly polarizable alkene, and C_{60} behaves like an electron-deficient arene.[8] Formation of **5**, however, is consistent with the alkene property of C_{60}. As shown in Scheme 1, a commonly observed reaction of metallobenzynes in condensed phases is olefin coupling to form metallacyclic complexes, **6**.[41–43] Similarly, in the gas phase the 6,6 junction double bond couples with one of the Fe–C bonds in $FeC_6H_4^+$ to form **5**, Scheme 2.

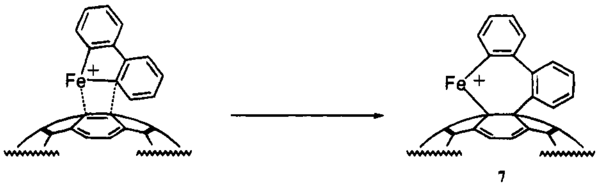
Scheme 1



Scheme 2



Scheme 3



Upon CID, $FeC_{60}(C_6H_4)_2^+$ yields $Fe(C_6H_4)_2^+$, predominantly, with a minor amount of $C_{60}(C_6H_4)_2^+$. In analogy to **5** and $Fe(C_6H_4)_3^+$ in the Fe^+/C_6H_5Cl system,[30–32] $FeC_{60}(C_6H_4)_2^+$ is proposed to have structure **7**, which undergoes demetalation (reaction 5) with chlorobenzene, as do **5** and $Fe(C_6H_4)_3^+$. These results, together with the pseudo-first-order decay kinetics observed for reaction 5, reasonably eliminate the presence of other isomers. Again, the formation of **7** is consistent with the alkene-like property of C_{60} resulting in coupling to $Fe(C_6H_4)_2^+$, Scheme 3.

In addition, as stated above, $FeC_{60}C_6H_4^+$ undergoes a second addition of a C_{60} molecule (reaction 6), but $FeC_{60}(C_6H_4)_2^+$ does not, even though the Fe centers presumably have similar coordination in both structures. We propose that this is due to the steric differences in the two structures, which is consistent with **5** and **7**.

Metal complexes of benzynes, cycloalkynes, and acyclic alkynes have the common property that they can couple with π bonds such as C=C, C≡C, C=O in CO_2, CO, and $R_1(CO)R_2$, C≡N, and N≡N.[41–43] They have been used extensively in the condensed phase for the preparation of various organometallic complexes. C_{60} acts like an alkene, but, to our knowledge, its reactivity toward metal–benzynes has not yet been studied. This gas-phase example, in which we have demonstrated that a reactive metal–benzyne structure can couple with C_{60} to form metallacyclic C_{60} C–C-bound complexes, suggests that it will be possible to produce this, as yet unknown, class of metallo-C_{60} derivatives in condensed-phase syntheses.

Acknowledgment is made to the Division of Chemical Sciences in the United States Department of Energy (DE-FG02-87ER13766) for supporting this work.

JA942800D

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