Reaction of Ferrocene with Acetylene To Generate Methylferrocene. An Unusual Labeling Result

I-Wen Chuang and Philip B. Shevlin*

Department of Chemistry, Auburn University, Auburn, Alabama 36849-5312

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Summary: Heating a gaseous mixture of ferrocene and acetylene (1:6.3 mol ratio) at 450 °C results in the formation of methylferrocene. When $^{13}C_2H_2$ is the substrate, GC/MS analysis reveals that the methylferrocene fraction consists of predominately two compounds: methylferrocene-$^{13}C_1$ and methylferrocene-$^{13}C_6$ in a 1:2.5 ratio. A mechanism involving initial addition of the alkyne C–H bond across the Fe–Cp bond to generate an (ethynyl-η^4-cyclopentadiene)iron hydride is proposed to explain both products.

In addition to providing a practical route to alkyne oligomers[1] and polymers,[2] reaction of alkynes with metal compounds generates stable alkyne,[3] methylidyne,[4] vinylidene,[5] ethynyl,[5a] and cyclopentadienyl complexes,[6,7a,b] metallacyclobutadienes,[7] and metallacyclopentadienes.[8] We wish to report a high-temperature reaction of ferrocene (1) with acetylene which generates methylferrocene (2) with an unusual labeling pattern. Thus, when a gaseous mixture of 1 and acetylene (1:6.3 mol ratio) is heated in a Pyrex bulb for 1 h at 450 °C, the products in eq 1 result.[9]

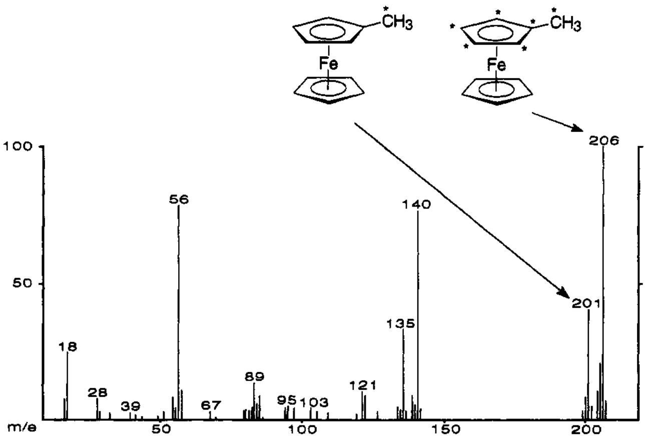
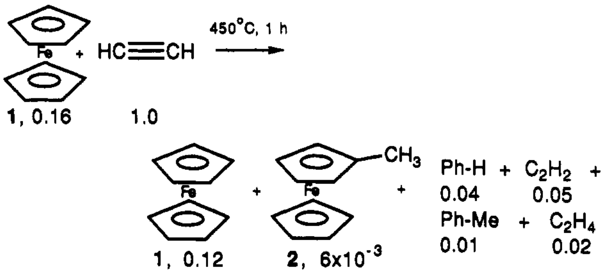


Figure 1. Mass spectrum of the methylferrocene fraction from the reaction of ferrocene with acetylene-$^{13}C_2$.



(1)

Although 1 is stable under these conditions in the absence of acetylene, the presence of the alkyne effects a 25% loss of 1, of which 15% is converted to methylferrocene (2). In an attempt to determine the extent of incorporation of the alkyne skeleton into 2, we have repeated the reaction with a 1:6.3 ratio of 1 to $^{13}C_2H_2$. A GC/MS analysis of the products, shown in Figure 1, reveals that the methylferrocene fraction consists of predominately two com-

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(9) Products were characterized by GC/MS, NMR, and IR spectroscopy. Quantities are in mmol.

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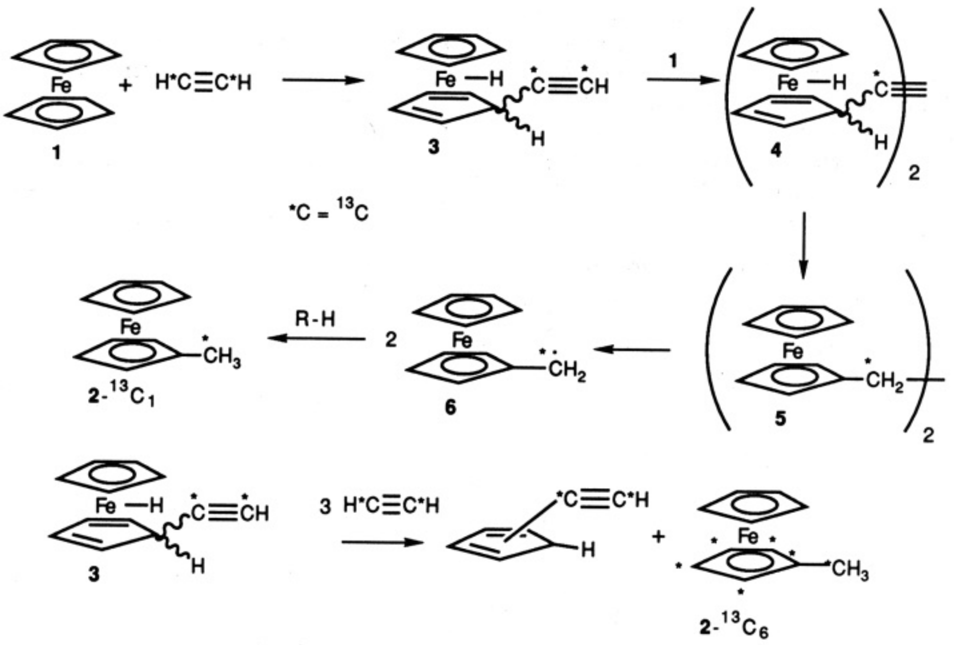
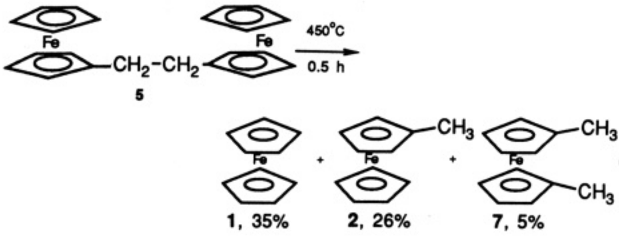
Scheme 1



pounds: **2**-$^{13}C_1$ and **2**-$^{13}C_6$ in a 1:2.5 ratio. The observation of only a FeC_5H_5-$^{13}C_0$ (*m/e* 121) fragment and peaks at *m/e* 135 (FeC_6H_6-$^{13}C_1$) and 140 (FeC_6H_6-$^{13}C_6$)[10] demonstrates that **2**-$^{13}C_6$ has all of its labeled carbons on the methylated ring. In order to explain this unusual labeling result, we propose the mechanisms in Scheme 1, in which initial coordination of acetylene to iron is followed by an addition of the alkyne C–H bond across the Fe–Cp bond to generate the (ethynyl-η^4-cyclopentadiene)iron hydride **3**. Addition of a second ferrocene across the remaining alkyne C–H bond in **3** gives the alkyne-linked dimer **4**. Tautomerization of **4** forms 1,2-diferrocenylethane (**5**). Subsequent cleavage of **5** under the high-temperature reaction conditions gives a pair of monolabeled ferrocenylmethyl radicals (**6**), which abstract hydrogen to produce **2**-$^{13}C_1$. A competing reaction of **3** is postulated to be addition of excess acetylene, displacing the cyclopentadienylacetylene and forming both **2**-$^{13}C_6$ and hexalabeled benzene by trimerization reactions.[1,6]

That **5** will cleave to **6** under the reaction conditions is indicated by the fact that heating it at 450 °C for 0.5 h results in a 26% yield of **2** along with **1** and 1,1′-dimethylferrocene (**7**) (eq 2). Both **1** and **7** in eq 2 are most probably the result of a high-temperature disproportionation of **2**. Evidence for this disproportionation has been obtained by heating either **2** or a mixture of **1** and **7** and observing mixtures of the three ferrocenes.



(2)

The mechanisms in Scheme 1 require that a 1:1 mixture of $^{12}C_2H_2$ and $^{13}C_2H_2$ produce **2**-$^{13}C_0$, **2**-$^{13}C_1$, **2**-$^{13}C_2$, **2**-$^{13}C_4$, and **2**-$^{13}C_6$ (with the last three in a 3:3:1 ratio) and no **2**-$^{13}C_3$ or **2**-$^{13}C_5$. Figure 2 shows the ratios of labeled **2** from this experiment ($^{12}C_2H_2$:$^{13}C_2H_2$:**1** = 4.7:4.7:1) along with ratios calculated by assuming that the mechanism in Scheme 1 is valid and that 75% of **2** arises by acetylene trimerization. The excellent agreement between calculated and observed label distributions provides additional evidence for the mechanisms in Scheme 1.

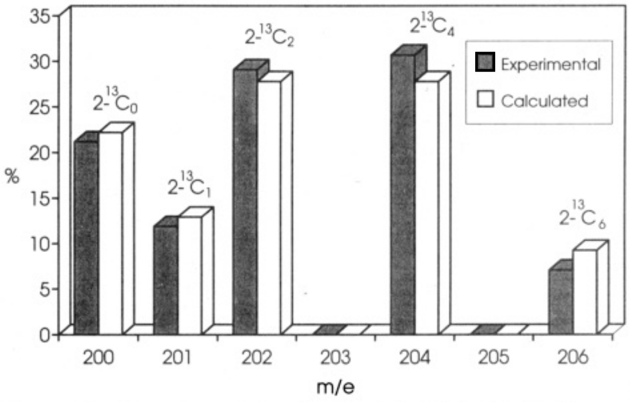


Figure 2. Experimental and calculated ^{13}C distribution in methylferrocene from the reaction of a 1:1 C_2H_2 and $^{13}C_2H_2$ mixture with ferrocene.

Although the mechanism of the initial reaction of **1** with the C–H bond in acetylene is unknown, it is tempting to propose a simple acid–base reaction with the weakly acidic terminal alkyne protonating the ferrocene. Reaction of **1** with deuterated acids is known to lead to deuterium exchange,[11] and we have observed that acetylene-d_2 will exchange its deuteriums with those of **1** under the reaction conditions. Thus, heating a 1:6.3 ratio of **1**:C_2D_2 leads not only to deuterated **2**, as expected, but also to extensive deuteration of recovered **1** (d_0:d_1:d_2:d_3 = 1:0.50:0.11:0.02).

Reactions of Fe-containing intermediates with alkynes to generate substituted-cyclopentadienyl complexes are known to occur under the energetic conditions of Fe atom

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(10) (a) A major fragmentation peak in the mass spectrum of **2** has *m/e* 134 from the loss of C_6H_6.[10b] (b) Zagorevskii, D. V.; Nekrasov, Yu. S.; Lemenovskii, D. A. *J. Organomet. Chem.* **1978**, *146*, 279.

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chemistry. Thus, cocondensation of Fe atoms with alkynes generates substituted ferrocenes,[12] while cocondensation of Fe, Cp–H, and alkynes yields ferrocenes substituted on one Cp ring.[13] These reactions and those in the present investigation are facilitated by the thermodynamic driving force to form the ferrocenyl moiety and the energetic reaction conditions. Although 1 and its derivatives exhibit rich solution and gas-phase ion chemistry, there have been relatively few studies of the neutral molecules in the gas phase. The high stability of 1 ($D_{\mathrm{Fe-Cp}}$ = 91 kcal/mol)[14] in the absence of added reactants facilitates gas-phase studies at rather high temperatures. Such studies have the potential of uncovering new mechanistic pathways for the activation of organic molecules by ferrocene and its derivatives.

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