

Figure 1. Local ordered structure shown by the elementary units. The dots in the figures indicate the positions of particles, which were obtained from micrographs by computer treatment: (i) and (ii) were taken at an interval of 1/30 s at 24 h; (iii) and (iv) at 48 h after the onset of the deionization.

of metal from the molten state¹² and indicates the importance of an attractive interaction (in addition to short-range repulsion) between particles.

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The Formation of Substituted Ferrocenes in the Reaction between Iron Atoms, Cyclopentadiene, and Alkynes

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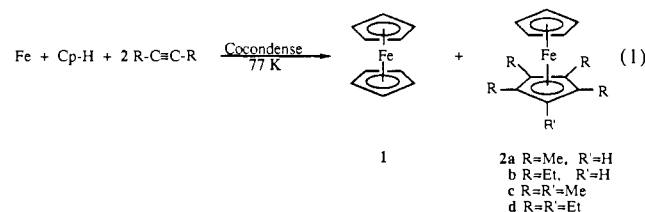
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An interesting route to cyclopentadienyl complexes involves the addition of alkynes to alkylidyne complexes and/or metalla-cyclobutadienes.^{1,2} We wish to report that cocondensation of iron atoms with cyclopentadiene and alkynes at 77 K also incorporates the alkyne skeleton into a cyclopentadienyl ring leading to ferrocenes substituted on one of the cyclopentadienyl rings as well

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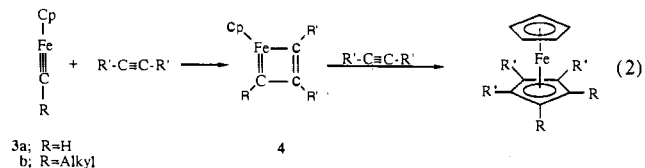
as the expected³ unsubstituted ferrocene, **1** (eq 1).⁴ For example,



cocondensation of approximately equimolar quantities of Cp-H, Fe, and 2-butyne leads to **1** and 1,2,3,4-tetramethylferrocene, **2a**, in a 2:1 ratio. The table demonstrates that condensation of Fe, Cp-H and an internal alkyne gives tetrasubstituted ferrocenes (for example, **2a** and **2b**), in which two R-C≡C-R's and a CH have been incorporated into one ferrocene ring, as major products and pentasubstituted ferrocenes (for example, **2c** and **2d**), containing two R-C≡C-R's and a C-R, as minor products.⁵ Internal alkynes undergo the reaction more efficiently than their terminal isomers. In a reaction related to that leading to the minor products **2c** and **2d**, Simmons and Lagowski⁸ have observed formation of decamethylferrocene and decaethylferrocene when Fe atoms are condensed with 2-butyne and 3-hexyne, respectively. In all of these reactions, a competing process is cyclization of the alkyne to the corresponding substituted benzene, a product known to be formed upon cocondensation of alkynes with iron in the absence of Cp-H.^{8,9}

Cocondensation of Fe, Cp-H, and 2-pentyne gives only two dimethyldiethylferrocenes each of which has equivalent methyl groups in the ¹H NMR leading us to conclude that these products are 1,4-dimethyl-2,3-diethylferrocene and 1,4-diethyl-2,3-dimethylferrocene. A mixture of 2-butyne and 3-hexyne gives only one dimethyldiethylferrocene which has nonequivalent methyl groups in the ¹H NMR. If we assume that the alkyne carbons remain bonded as indicated by the 2-pentyne result, this product is 1,2-dimethyl-3,4-diethylferrocene.

In order to rationalize the incorporation of alkynes into cyclopentadienyl rings, it is tempting to postulate the intermediacy of coordinatively unsaturated alkylidyne complexes, **3** (eq 2). If



a complex such as **3a** were involved, it could add two alkyne molecules, perhaps via the ferracyclobutadienes **4**, to give the tetrasubstituted ferrocenes.^{1,2} Methylidyne complex **3a** could then generate the substituted complexes **3b**, precursors to the pentasubstituted ferrocenes, by a conventional metathesis mechanism.¹⁰ Although there is little analogy for the formation of **3** and **4** in mononuclear organometallic iron chemistry,^{11,12} the driving force

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(5) In all experiments roughly equimolar amounts of iron atoms and substrate(s) were cocondensed on a surface of methylcyclohexane at 77 K in a reactor based on that designed by Timms⁶ which has been described.⁷ Reaction products were identified by GC/MS, in many cases (see table) separated by prep GC and their structures confirmed by NMR spectroscopy.

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(9) Under the conditions of our reactions, cocondensation of Fe with 2-butyne gives a 73% yield of hexamethylbenzene.

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(12) Casey et al. (Casey, C. P.; Woo, L. K.; Fagan, P. J.; Palermo, R. E.; Adams, B. R. *Organometallics* **1987**, *6*, 447) have investigated the reactions of a cationic diiron bridging methylidyne complex with alkynes.

Table I. Yields of Ferrocenes in the Cocondensation of Fe Atoms, Cyclopentadiene, and Alkynes

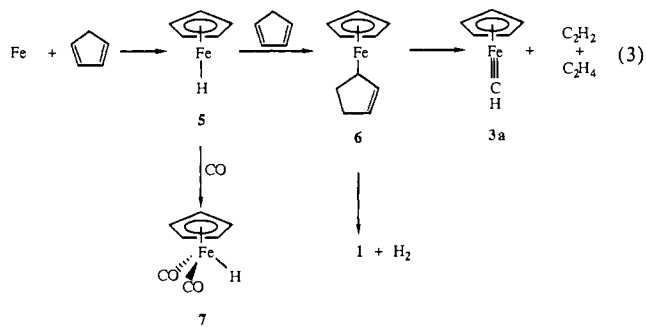
alkyne reactant(s) (mmol) [mmol Fe] ^a	product yields (mmol)
CH ₃ C≡CCH ₃ (18.3) [15.4]	1 (0.43), 2a (0.223), ^b 2c (0.049) ^b
CH ₃ CH ₂ C≡CCH ₂ CH ₃ (17.6) [34.0]	1 (0.31), 2b (0.23), ^b 2d (0.012)
CH ₃ CH ₂ C≡CCH ₃ (17.5) [30.0]	1 (0.25), 1,4-dimethyl-2,3-diethyl-1 (0.42), ^b 1,4-diethyl-2,3-dimethyl-1 (0.027) ^b
CH ₃ C≡CCH ₃ (13.0), EtC≡CEt (8.8) [37.0]	1 (0.12), 2a (0.042), ^b 1,2-diethyl-3,4-dimethyl-1 (0.027), ^b 2b (0.013) ^b
CH ₃ C≡CCH ₃ (12.3), C ₂ D ₂ (17.4) ^c [25.0]	1 (0.12), 1,2-dimethyl-1 (0.014), trimethyl-1 (0.009), 2a (0.012), 2c (0.005)
EtC≡CEt (10.6), C ₂ D ₂ (15.0) ^c [28.0]	1 (0.09), 1,2-diethyl-1 (0.008), diethyl methyl-1 (0.003), 2b (0.012), 2d (trace)
CH ₃ C≡CH (11.4) [17.6]	1 (0.349), 1,2-dimethyl-1 (0.018), 1,3-dimethyl-1 (0.012), trimethyl-1 (0.009)
CH ₃ C≡CH (13.4), C ₂ H ₂ (13.4) [25.0]	1 (0.247), 1,2-dimethyl-1 (0.017), 1,3-dimethyl-1 (0.013), trimethyl-1 (0.011)
HC≡CCH ₂ CH ₃ (19.0) [22.5]	1 (0.713), 1,2-diethyl-1 (0.11), 1,3-diethyl-1 (0.076), trimethyl-1 (trace)
C ₂ H ₂ (21.8) [16.6]	1 (0.513), methyl-1 (0.034), dimethyl-1 (trace)

^aThis value is the mmol of Fe vaporized. In all condensations 12.2 mmol of Cp-H was used. ^bThese products were isolated by preparative GC and characterized by their NMR spectra. These and all other products were characterized by GC-MS and NMR spectra of product mixtures. See Supplementary Material tables. ^cSome products contained deuterium, see text.

in the present case may be a combination of the energetic reaction conditions¹³ and the coordinative unsaturation about Fe which mandates the sharing of as many electrons as possible with the metal and renders these reactive intermediates kinetically accessible.

In order to gain information regarding possible high-energy gas-phase modes of reaction of Cp-H in the presence of Fe, we have carried out the reaction under conditions in which a gas-phase encounter between Cp-H and Fe is likely. Thus, when Fe is vaporized in the presence of Cp-H and the products are not condensed on the walls of the reactor but pumped directly into a trap at 77 K, C₂H₂ and C₂H₄ (in a 1.2:1 ratio) and **1** are isolated. Ball, Kafafi, Hauge, and Margrave¹⁴ have demonstrated the formation of cyclopentadienyliron hydride, **5**, in the cocondensation of Fe atoms with Cp-H in an Ar matrix at 14 K. If we assume that **5** is an intermediate in the reaction between Cp-H and Fe under our conditions, we may postulate its reaction with Cp-H to give the η¹-cyclopentenyl complex **6** which could either go on to **1** or, under more energetic conditions,¹³ cleave to C₂H₂, C₂H₄, and **3a**. That **5** is formed and has appreciable lifetime at 77 K is demonstrated by the fact that addition of CO after cocondensation of Fe and Cp-H gives cyclopentadienyldicarbonyliron hydride, **7**¹⁵ (eq 3).

Further evidence that gas-phase metal-atom reactions occur in this system is provided by the fact that cocondensation of Fe on preformed surface of Cp-H and 2-butyne at 77 K (no hydrocarbons in the gas phase) gives only **1** and hexamethylbenzene (1:0.38 ratio) with no detectable **2a**. However, cocondensation of Fe and Cp-H onto a matrix of 2-butyne (Fe + Cp-H but no



2-butyne in gas phase) gives **1**, hexamethylbenzene, and **2a** in a 1:0.024:0.020 ratio.

The possible involvement of the acetylene, generated by the reaction in eq 3, was probed through the use of C₂D₂. When Fe, Cp-H, 2-butyne, and C₂D₂ are cocondensed, one of the products is 1,2-dimethylferrocene containing deuterium (*d*₀:*d*₁:*d*₂:*d*₃ = 0.3:15.3:43.6:40.9). Interestingly, the **2a** formed in this reaction is also labeled (*d*₀:*d*₁:*d*₂ = 72.7:25.6:1.6). The formation of **2a-d**₁ and dimethylferrocene-*d*₃ in this reaction implies that some Cp-Fe≡CD, formed by a metathesis between **3a** and C₂D₂, is present.¹⁸

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Supplementary Material Available: Tables of NMR and mass spectral data for substituted ferrocenes (3 pages). Ordering information is given on any current masthead page.

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A Direct Mechanism for S_N2 Nucleophilic Substitution Enhanced by Mode Selective Vibrational Excitation

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An important problem in gas-phase reaction dynamics is understanding the manner in which vibrational excitation of reactants may affect chemical reactions. This problem is of concern for both unimolecular¹⁻³ and bimolecular⁴⁻¹¹ reactions. It is well known that vibrational excitation of a diatomic reactant can enhance the reaction for A + BC → AB + C displacement with a late barrier so that the BC bond is extended at the saddlepoint.⁴ For bimolecular reactions with polyatomic reactants, mode selective vibrational excitation is expected to enhance reaction if

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