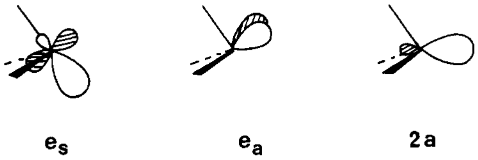
orbital to match $\pi_\perp$ and thus constrains the acetylene to two-electron donation. The pyramidal $IrP_3^+$ fragment (leading to $T_d$ or $C_s$) has the requisite three orbitals in the form of the 2e and 2a of a regular $C_{3v}$ $IrP_3^+$ pyramid:[9] $e_s$ (one of the 2e set) matches $\pi_\perp$, 2a matches $\pi_\parallel$, and $e_a$ (from the 2e pair) is close in energy to $\pi_\parallel^*$. The acetylene is thus a formal four-electron donor. Optimizing this last interaction significantly increases the metal/acetylene bonding, and this is accomplished by pointing the two lobes of the $e_a$ more toward the acetylene carbons. In terms of nuclear motions, this is achieved by bending the two Ir–P bonds toward the $IrC_2$ plane, which converts the $T_d$ to the $C_s$ structure.



Reaction of $Ir(MeC_2Me)P_3^+$ with $H_2$ (1 atm) at 25 °C in $CD_2Cl_2$ yields butane (no butenes) and $IrH_4P_3^+$, which closes the cycle of Scheme I. Further mechanistic details of the steps in this scheme, together with a broader survey of the reactivity of $Ir(MeC_2Me)P_3^+$, are currently under investigation.

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**Supplementary Material Available:** Tables of positional and thermal parameters for $[Ir(MeC_2Me)(PMe_2Ph)_3]BF_4$ and a figure showing thermal ellipsoids (5 pages). Ordering information is given on any current masthead page.

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## Life Span of a Local Structure in Colloidal Suspensions

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The existence of local ordered structures in colloidal suspensions has been confirmed by various techniques,[1-7] but only the static aspect of the structure has been described except in a few papers, as was reviewed recently,[8] In the present paper, we describe the life span of the local ordered structure which has not been discussed before but is of great significance to the complete understanding of the colloidal phenomena.

Polystyrene latex, purchased from the Sekisui Chemical Company (N300, diameter: 0.32 × $10^{-6}$ m, charge density: 1.8 × $10^{-6}$ C/cm$^2$), was thoroughly purified as described earlier[8,9] before use. The micrographs showing particle distributions were taken at a fixed position of the suspensions (0.5%) at room temperature by the ultramicroscope (AXIOMAT IAC, Carl Zeiss, Oberkochen, FRG) and digitized by the image processing system (IBAS) of the same company. The particle positions were determined at an interval of 1/30 s (at every video frame) and fed into a personal computer (PC9801, NEC). The interparticle distance ($2D_{exp}$) was estimated to be 1.16 × $10^{-6}$ m by Fourier patterns of the particle distribution.[10] The $2D_{exp}$ was smaller than the average interparticle spacing ($2D_0$, 1.69 × $10^{-6}$ m) and practically constant with time through the growing process. A regular triangle with a side of $2D_{exp}$ was defined as an elementary unit of the ordered structure, because the (111) plane of the face-centered cubic lattice was observed in the present experiments. An uncertainty of 15% in the length of the side was taken into consideration, which seems reasonable in light of thermal vibration of the particles and distortion of the lattice in the ordered structure.[8] After NaCl was added to a purified suspension up to 1.0 × $10^{-4}$ M, the crystallization was allowed to take place by putting ion-exchange resin beads into the suspension. During the first 2 h, the electric conductivity decreased with time and thereafter became nearly constant, which indicates the almost complete removal of added NaCl.

**Table I.** Distribution of Life Span of Core Particles

| time (×1/30 s) | 24 h (%) | 48 h (%) |
|---|---|---|
| 1 | 69.3 | 58.0 |
| 2 | 20.0 | 13.9 |
| 3 | 6.7 | 8.3 |
| 4 | 2.7 | 8.3 |
| 5 | 1.3 | 5.2 |
| 6 | | 2.4 |
| 7 | | 1.0 |
| 8 | | 0.7 |
| 9 | | 0.7 |
| 10 | | 1.4 |

The elementary units appeared even at 1 h after the addition of the ion-exchange beads. The units (triangles) were found on the micrograph sporadically, and the appearance and disappearance of the units were observed at every video frame. The same situation was also observed at 6 h. Clusters of elementary units were observed at 24 h, and a halo pattern was obtained by the 2-D Fourier transformation therefrom. The clusters grew further at 48 h and became large lattices at 72 h. Figure 1 shows the elementary units defined above at 24 and 48 h. The isolated dots in each figure represent the particles which were not involved in the clusters. The average numbers of the elementary units per cluster were about 12 at 24 h and 30 at 48 h. Most clusters assumed different shapes at every video frame. While the clusters are large, their central part was left unchanged whereas surrounding parts disappeared. Rather small clusters became smaller and finally disappeared. The number of bonds of one particle varied accordingly. To measure this number, we adopted tentatively the following procedure. The particles having six bonds were defined as core particles. The number of bonds of each core particle was followed up to 10 consecutive video frames (for 1/3 s). The period in which the core particles maintained six bonds was measured as the life span of the clusters. Table I shows the life span measured at 24 and 48 h. About 69% of the core particles lost at least one bond in 1/30 s at 24 h, and the longest life span was 5/30 s. At 48 h, 58% of the core particles also lost the bonds in 1/30 s. The number of particles with a longer life span (longer than 3/30 s) was larger at 48 h than at 24 h. At 48 h, 1.4% of the core particles lived longer than 1/3 s. That is, at 24 h, the clusters disappeared before 5/30 s, although at 48 h some of the clusters did not disappear but seemed to grow further.

In the present conditions, the so-called Kossel mechanism[11] of crystal growth was not observed. Instead, the life span of the clusters depended mainly on the size of the clusters. This tendency coincides, at least qualitatively, with the mode of crystallization

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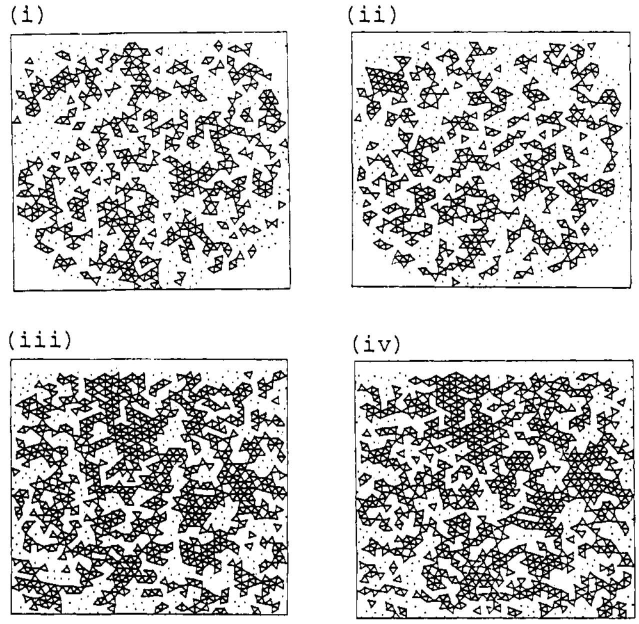

**Figure 1.** Local ordered structure shown by the elementary units. The dots in the figures indicate the positions of particles, which were obtained from micrographs by computer treatment: (i) and (ii) were taken at an interval of 1/30 s at 24 h; (iii) and (iv) at 48 h after the onset of the deionization.

of metal from the molten state[12] 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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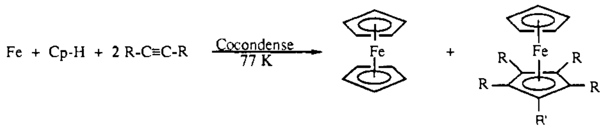
An interesting route to cyclopentadienyl complexes involves the addition of alkynes to alkylidyne complexes and/or metallacyclobutadienes.[1,2] We wish to report that cocondensation of iron atoms with cyclopentadiene and alkynes at 77 K also incorporates the alkyne skeleton into a cyclopentadienyl ring leading to ferrocenes substituted on one of the cyclopentadienyl rings as well as the expected[3] 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 Lagowski[8] 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]



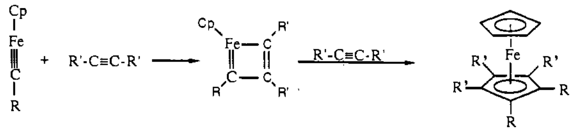
(1)

**1**

**2a** R=Me, R'=H
**b** R=Et, R'=H
**c** R=R'=Me
**d** R=R'=Et

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



(2)

**3a**; R=H
**b**; R=Alkyl

**4**

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(5) In all experiments roughly equimolar amounts of iron atoms and substrate(s) were concodensed on a surface of methylcyclohexane at 77 K in a reactor based on that designed by Timms[6] 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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