

## Scheme I

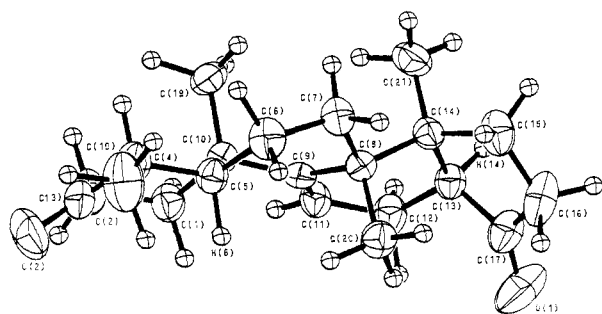
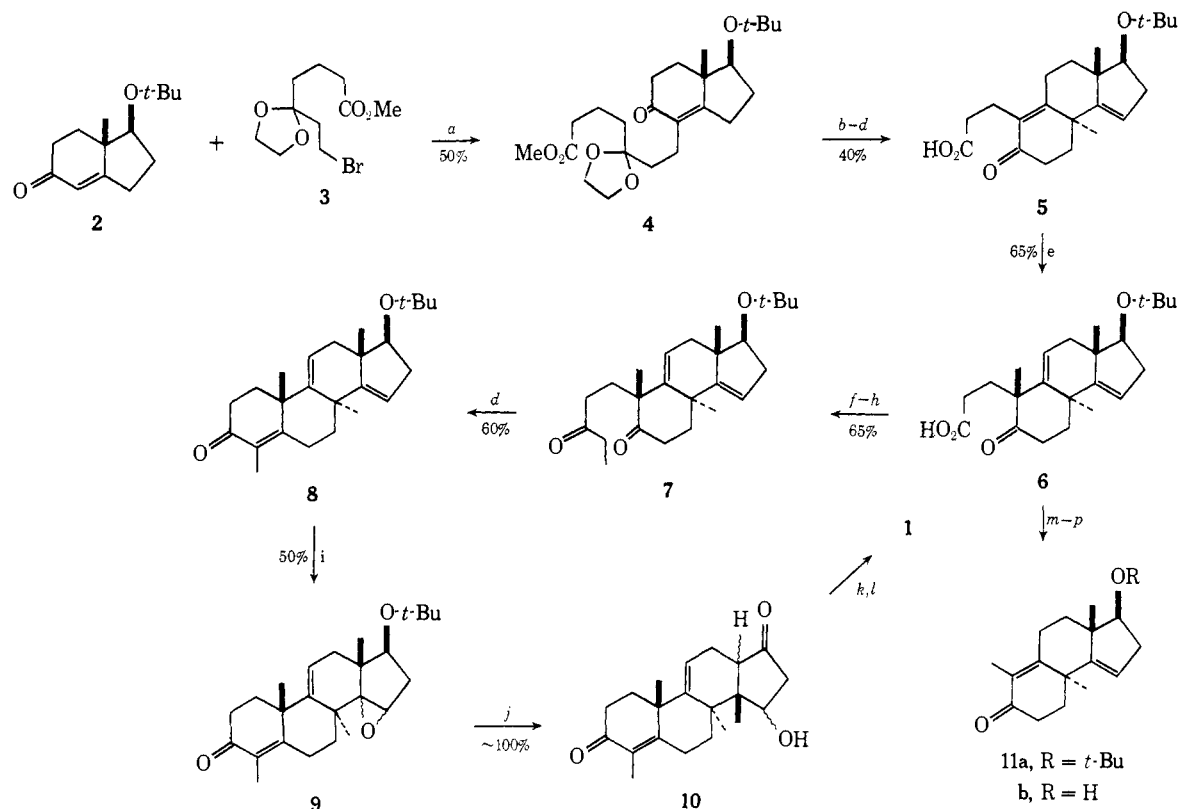


Figure 1. Projection drawing of **1**. The ring carbon atoms are numbered in the standard fashion.

with space group  $C2/c$  and  $a = 19.562(6)$ ,  $b = 11.915(4)$ , and  $c = 15.623(4)$  Å, and  $\beta = 107.84(4)^\circ$ . There are eight molecules in the unit cell and 1124 data where  $I > 3\sigma(I)$  were utilized. All C and O atoms were refined anisotropically and all H atoms refined isotropically. The final  $R$  value was 3.4%. Data were obtained with a Picker FACS-I automatic diffractometer with graphite monochromatized molybdenum  $K\alpha$  radiation.

It is to be noted that earlier generalities<sup>15, 16</sup> with regard to the stereochemistry of the alkylation of enones upon which this present synthesis was planned were, indeed, followed in this group of compounds. The ultimate success of the synthesis relied upon the acid-catalyzed rearrangement of an angular methyl group

(15) F. H. Bottom and F. J. McQuillin, *Tetrahedron Lett.*, 1975 (1967); 459 (1968).

(16) R. E. Ireland, D. A. Evans, D. Glover, G. M. Rubottom, and H. Young, *J. Org. Chem.*, **34**, 3717 (1969).

upon the opening of an epoxide (the Westphalen rearrangement). It had been shown<sup>17</sup> that this rearrangement involved a nearly planar cationic reaction complex followed by the migration of the group which could achieve maximum coplanarity with the p orbital of the cationic center. Examination of a molecular model of the tetracyclic cation at C-14 formed from **9** clearly showed that only the C-13 angular methyl group met this criterion and, thus, the rearrangement would be expected to yield **10** as found.

**Acknowledgment.** The authors are indebted to the Hoffmann-La Roche Co. for kindly supplying the bicyclic enone starting material.

(17) J. M. Coxon, M. P. Hartshorn, and C. N. Muir, *Chem. Commun.*, 1591 (1970), and earlier papers.

W. G. Dauben,\* G. Ahlgren, T. J. Leitereg  
W. C. Schwarzel, M. Yoshioko  
Department of Chemistry, University of California  
Berkeley, California 94720  
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### Fluxional Nature of Benzo- and Naphthocyclooctatetraeneiron Carbonyl Complexes

Sir:

Contrary to statements in the literature,<sup>1</sup> shift isomerism of 3,4,5,6-tetrahydrobenzocyclooctatetraeneiron tricarbonyl (**1**) and its 2,3-naphtho analog **2** is sufficiently rapid to label them fluxional molecules.

(1) J. A. Elix and M. V. Sargent, *J. Amer. Chem. Soc.*, **91**, 4734 (1969).

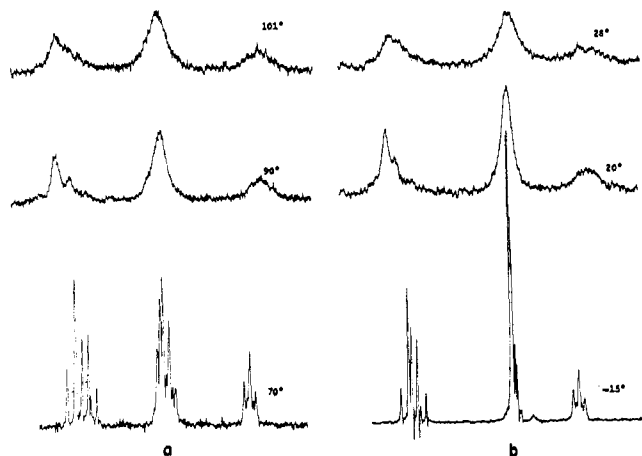
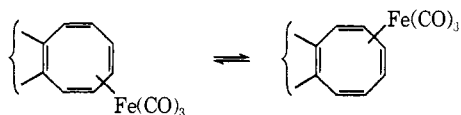


Figure 1. (a) 100-MHz variable-temperature spectra of the vinyl region of **2** in toluene- $d_8$ . From left to right the multiplets are centered at  $\delta$  6.27 (2 H), 4.80 (3 H), and 3.53 (1 H). (b) Spectra of **1** in toluene- $d_8$ . From left to right the multiplets are centered at  $\delta$  6.20 (2 H), 4.57 (3 H), and 3.58 (1 H).

The low-temperature limiting nmr spectrum of **1** is reached at  $-15^\circ$  (Figure 1b). The high-temperature spectrum ( $\delta$  4.10 (H-5, H-6, s), 5.40 (H-3, H-4, H-7, H-8, s)) is reached at  $93^\circ$ . A  $T_c$  of *ca.*  $55^\circ$  is observed. Simplification of the spectrum as a prelude to line-shape analysis<sup>2</sup> was achieved by synthesis of the 4,5,6,7-tetradeuterio derivative of **1** (**1-d<sub>4</sub>**, 93%  $d_4$ ) from 4,5,6,7-tetradeuteriobenzocyclooctatetraene<sup>3</sup> and iron pentacarbonyl. Spectra of **1-d<sub>4</sub>** are presented in Figure 2. One now has a simple equally populated interconverting uncoupled two-spin system. Simulation<sup>4</sup> of these spectra, using the standard<sup>5</sup> expression, afforded an  $E_a$  of 18.6 kcal/mol (correlation coefficient 0.977) for interconversion of the two nuclei.<sup>6</sup>

**2**, mp  $164$ – $165^\circ$ , was prepared from 2,3-naphthocyclooctatetraene<sup>7</sup> and  $\text{Fe}(\text{CO})_5$  in refluxing toluene. The nmr spectrum of the vinyl region of **2** (Figure 1a) at  $70^\circ$  is virtually superimposable on that of **1** at  $-15^\circ$ . An estimation of the rate of shift isomerism of **2** was arrived at by assuming that at temperatures wherein the appearance of the spectra of **1** and **2** are the same the rates of rearrangement are the same. This affords an  $E_a$  of 31 kcal/mol<sup>8</sup> for rearrangement of **2**.

The rate processes observed certainly involve interconversion of two shift isomeric iron tricarbonyl complexes



Comparison of activation energies for this process in cyclooctatetraeneiron tricarbonyl (7.2 kcal/mol<sup>9</sup>), **1** (18.6 kcal/mol), and **2** (31 kcal/mol) suggests that the

(2) M. Cooke, R. J. Goodfellow, M. Green, and J. P. Maher, *Chem. Commun.*, 565 (1970).

(3) L. A. Paquette, J. R. Malpass, and G. R. Krow, *J. Amer. Chem. Soc.*, **92**, 1980 (1970).

(4) A Wang 720B calculator was used.

(5) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

(6) At  $333^\circ\text{K}$ ,  $k = 735 \text{ sec}^{-1}$  ( $\Delta F^\ddagger = 15.2 \text{ kcal/mol}$ ).

(7) A. Krebs and D. Byrd, *Justus Liebigs Ann. Chem.*, **707**, 66 (1967).

(8) This is not very accurate. At worst, however, an error of *ca.* 35% (probably substantially smaller) is expected.

(9)  $\Delta F^\ddagger$ : C. G. Kreiter, A. Maasbol, F. A. L. Anet, H. D. Kaesz, and S. Winstein, *J. Amer. Chem. Soc.*, **88**, 3444 (1966).

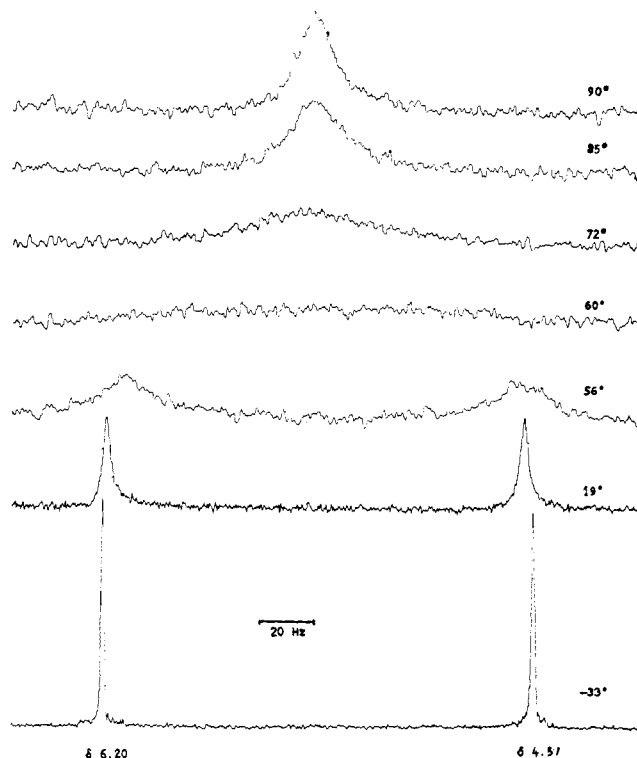
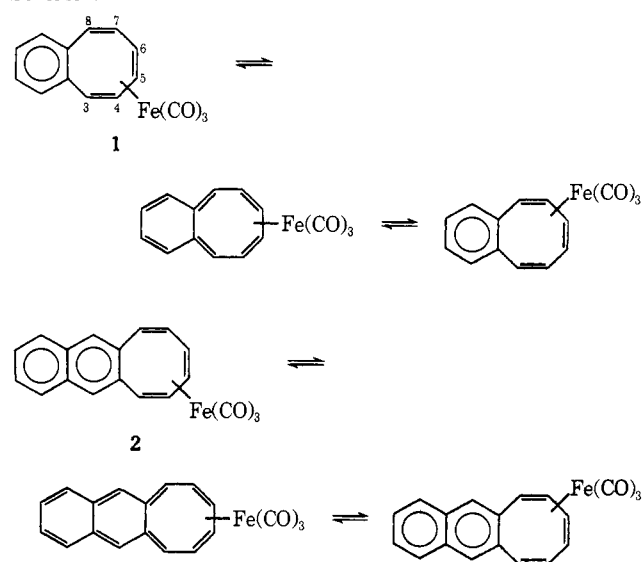


Figure 2. 100-MHz variable-temperature deuterium noise decoupled spectra of **1-d<sub>4</sub>** in toluene- $d_8$ .

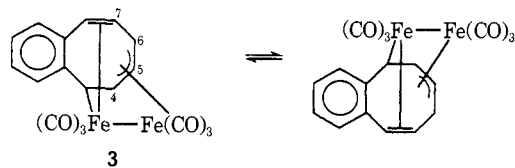
differentiating factor among these complexes is the energy of mandatory ortho quinoidal intermediates (Scheme I). A similar explanation has been advanced by Cotton, *et al.*,<sup>10</sup> for the fluxional nature of some  $\sigma$ -cyclopentadienyl (but not  $\sigma$ -indenyl) metal complexes.

#### Scheme I

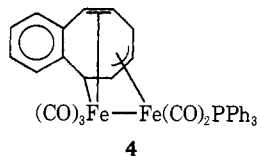


The above results are to be contrasted with the much more facile shift isomerism of 3,4,8-*trihapto*-5,6,7-*trihapto*benzocyclooctatetraenediiron hexacarbonyl (**3**). Variable temperature spectra of 4,5,6,7-tetradeuterio **3** (**3-d<sub>4</sub>**) in fluorotrichloromethane affords a  $T_c$  of  $-108^\circ$ , above which appears a singlet at  $\delta$  2.81 ( $\nu_{1/2} = 1 \text{ Hz}$  at  $0^\circ$ ) and below which appears two singlets ultimately

(10) F. A. Cotton, A. Musco, and G. Yagupsky, *ibid.*, **89**, 6136 (1967).



centered at  $\delta$  3.93 and 1.69 ( $\nu_{1/2} = 8$  Hz at  $-125^\circ$ ). An  $E_a$  of 8.1 kcal/mol may be calculated from these data. A "twitch" mechanism involving neither valence isomerism of the polyene ligand nor interconversion of the iron tricarbonyl groups is compatible with these data. The *mono*-triphenylphosphine derivative **4**, prepared



from **3** and triphenylphosphine in cyclohexane at  $100^\circ$ , possesses a time-averaged plane of symmetry<sup>11</sup> (nmr equivalence of H-3 and H-8) with the phosphine residing on the iron furthest from the aromatic ring (P-H coupling<sup>12</sup> of H-5-H-6 but not of H-3-H-8). Of two alternative mechanisms considered<sup>13</sup> for dimetal hexacarbonyl isomerizations of this type, only the above twitch process is possible for **4**. By inference this is true of **3** also.<sup>14, 15</sup>

- (11) The insolubility of **4** precluded low-temperature spectra.  
 (12) H. Brunner and E. Schmidt, *Angew. Chem.*, **87**, 570 (1969).  
 (13) F. A. Cotton, D. G. DeBoer, and T. J. Marks, *J. Amer. Chem. Soc.*, **93**, 5069 (1971).  
 (14) The question of any intermediates involved is of course open.  
 (15) Partial support by the National Science Foundation.  
 (16) National Institutes of Health Predoctoral Fellow, 1968-1971.

H. W. Whitlock, Jr.,\* H. Stucki<sup>16</sup>

Department of Chemistry, University of Wisconsin  
 Madison, Wisconsin 53706

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## Organic Chemistry of Transition Metal Ligands.

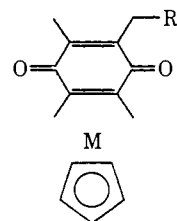
### I. Duroquinone

Sir:

$\pi$  ligands which undergo electrophilic substitution are well known, the cyclopentadienyl rings of ferrocene and cymantrene being prime examples. Likewise, a number of unstable or unreactive  $\pi$  ligands have been found to undergo substitution reactions when complexed by a transition metal. Electrophilic substitution of  $\pi$ -cyclobutadieneiron tricarbonyl<sup>1</sup> and  $\pi$ -cyclooctatetraeneiron tricarbonyl<sup>2</sup> serves as an example of a process whereby derivatives of unstable organic molecules as ligands are prepared, while electrophilic substitution of a cobalt cluster complex of tolan<sup>3</sup> and a two-step sequence, which amounts to nucleophilic substitution of an allylic position of a series of cyclopentadienyl(cycloocta-1,5-diene)metal complexes (metal = Co, Rh, Ir),<sup>4</sup> serve as examples of transformations of unreactive organic molecules as ligands. How-

- (1) R. G. Amiet and R. Pettit, *J. Amer. Chem. Soc.*, **90**, 1059 (1968).  
 (2) B. F. G. Johnson, J. Lewis, and G. L. P. Randall, *J. Chem. Soc. A*, 422 (1971).  
 (3) D. Seyferth and A. T. Wehman, *J. Amer. Chem. Soc.*, **92**, 5520 (1970).  
 (4) (a) J. Lewis and A. W. Parkins, *J. Chem. Soc. A*, 1150 (1967);  
 (b) J. Lewis and A. W. Parkins, *ibid.*, 953 (1969).

ever, no example of a relatively general activation of the ability of a saturated carbon atom in a  $\pi$  complex to undergo both acid- and base-catalyzed substitutions and condensations has ever been reported. We now describe a series of such molecules, namely, cyclopentadienylduroquinone cobalt, rhodium, and iridium (**1a-c**).<sup>5</sup>



**1a**, M = Co; R = H

**b**, M = Rh; R = H

**c**, M = Ir; R = H

**2a**, M = Co; R = CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>

**b**, M = Rh; R = CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>

**c**, M = Ir; R = CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>

**3a**, M = Co; R = CH<sub>2</sub>N(CH<sub>3</sub>)<sub>3</sub><sup>+</sup>I<sup>-</sup>

**b**, M = Rh; R = CH<sub>2</sub>N(CH<sub>3</sub>)<sub>3</sub><sup>+</sup>I<sup>-</sup>

**4a**, M = Co; R = CH<sub>2</sub>OCH<sub>3</sub>

**b**, M = Rh; R = CH<sub>2</sub>OCH<sub>3</sub>

Complexes **1a-c** were demonstrated to undergo a variety of substitution reactions. Dimethylamino-methylation (Mannich conditions) of **1a-c** produced the derivatives **2a-c** in which substitution of a methyl hydrogen had occurred in yields of 90, 42, and 38%, respectively.<sup>6,7</sup> These dimethylaminomethyl derivatives were converted to their respective methiodides **3a-c**, each in *ca.* 98% yield. Methiodides **3a** and **3b** were also converted into the ethers **4a** and **4b** with sodium methoxide in benzene in each case with yields of 95%.<sup>6</sup>

Support for the structures proposed for these complexes rests primarily on their 100-MHz spectra and their mass spectra. For example, the nmr spectrum of dimethylaminomethyl derivative **2a** presented overlapping peaks at  $\tau$  7.95, 7.92, and 7.88 (nine protons) which were assigned to the three ring methyls. Signals at  $\tau$  7.74-7.21 (total ten protons) and a singlet at 5.23 (five protons) were assigned to the two methylene groups, the *N*-methyls and the unsubstituted cyclopentadienyl ring, respectively. Spectra of **2b** and **2c** were very similar to that of **2a**. Similarly, the mass spectrum of complex **2a** provided distinct evidence as to the assigned structure. Positive fragments characteristic of C<sub>5</sub>H<sub>5</sub> (*m/e* 65), C<sub>5</sub>H<sub>5</sub>Co (*m/e* 124), C<sub>11</sub>H<sub>12</sub>O<sub>2</sub> (*m/e* 176), and the molecular ion, C<sub>5</sub>H<sub>5</sub>CoC<sub>13</sub>H<sub>19</sub>NO<sub>2</sub> (*m/e* 345), were found in high abundances. The spectrum of **2b** was more complex, notably in exhibit-

(5) G. N. Schrauzer and H. Thyret, *Angew. Chem.*, **75**, 641 (1963); G. N. Schrauzer and K. C. Dewhirst, *J. Amer. Chem. Soc.*, **86**, 3265 (1964).

(6) Elemental analyses of complexes **3a**, **2b**, **3a**, **3b**, and **4b** revealed the presence of varying amounts of water of hydration, but were otherwise acceptable.

(7) A thorough search of the literature has revealed no example of an organic reaction which allows derivatization of duroquinone at a methyl group. Furthermore, R. Marchal of these laboratories has duplicated the Mannich conditions used for complex **1a** on duroquinone itself. A crude product was obtained after chromatographic removal of duroquinone (*ca.* 30%) that by nmr analysis obviously no longer contained a quinoid structure.