

# Preparation and Structures of Methyl Phenylpropiolate-Iron Carbonyl Complexes. A New Dicarboxyl- $\pi$ -cyclopentadienyloxy- $\sigma$ -vinyliron Compound

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**Abstract:** The reaction of  $\text{Fe}_2(\text{CO})_9$  with methyl phenylpropiolate has yielded four organoiron carbonyl complexes. Three of these compounds have been characterized on the basis of infrared and nmr spectra—two as isomeric derivatives of tricarbonylcyclobutadieneiron and the third as tricarbonyl-2,4-dicarbomethoxy-3,5-diphenylcyclopentadieneiron. The fourth condensation product has required a three-dimensional single crystal X-ray investigation in order to identify it as dicarbonyl-1-carbomethoxy-2-phenyl-2- $[\pi$ -2',4'-dicarbomethoxy-3',5'-diphenyl-1'-cyclopentadienyloxy]- $\sigma$ -vinyliron. The structural features and properties of this new type complex are discussed.

Many structurally interesting compounds have been isolated as products of the reactions of alkynes with the three iron carbonyls.<sup>2-11</sup> In a number of these compounds, X-ray diffraction investigations have shown iron atoms bonded to organic ring systems formed by the condensation of two or more molecules of the substituted acetylene, often with a carbonyl group or an iron atom incorporated into the rings. Rings containing four, five, and seven atoms ascertained by X-ray work include the cyclobutadiene ring in  $(\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5)_2\text{Fe}(\text{CO})_3$ ;<sup>12</sup> five-membered organoiron rings in  $(\text{CH}_3\text{C}_2\text{OH})_2\text{Fe}_2(\text{CO})_6$ ,<sup>13</sup>  $\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5\text{Fe}_2(\text{CO})_6$ ,<sup>14</sup>  $(\text{C}_6\text{H}_5\text{C}_2\text{H})_3\text{COFe}_2(\text{CO})_3$ ,<sup>15</sup>  $(\text{C}_2\text{H}_5\text{C}_2\text{C}_6\text{H}_5)_3\text{COFe}_2(\text{CO})_3$ ,<sup>16</sup> and the black isomer of  $(\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5)_2\text{Fe}_3(\text{CO})_8$ ,<sup>17</sup> and seven-membered rings in the orange-red isomer of  $(\text{HC}_2\text{H})_3\text{Fe}_2(\text{CO})_6$ ;<sup>18</sup> and the tricarbonyltroponeiron complexes,  $(\text{C}_6\text{H}_5\text{C}_2\text{H})_3\text{COFe}(\text{CO})_3$ <sup>19</sup> and  $(\text{HC}_2\text{H})_3\text{COFe}(\text{CO})_3$ .<sup>20</sup> Surprisingly also the stable cyclopentadienyl ligand has been shown to be formed from acetylenes in the case of the dark red isomer of  $(\text{HC}_2\text{H})_3\text{Fe}_2(\text{CO})_6$ <sup>21</sup> and  $[(\text{HC}_2\text{H})_2\text{COFe}(\text{CO})_2]_2$ .<sup>22</sup>

The reaction of  $\text{Fe}_2(\text{CO})_9$  with methyl phenylpropiolate, reported in this paper, has yielded four new organoiron carbonyl complexes. On the basis of infrared and nmr spectra, three of these compounds have been postulated with reasonable certainty as structurally similar to previously reported metal-bonded ring compounds. The fourth product, of stoichiometry  $(\text{C}_6\text{H}_5\text{C}_2\text{CO}_2\text{CH}_3)_3\text{Fe}(\text{CO})_3$ , initially was thought from its infrared spectrum to be a substituted dicarbonyltroponeiron complex, in which the tropone ring functions as a six-electron donor with the iron bonded to all three double bonds of the ring rather than with only two double bonds such as occurs for the two structurally characterized tricarbonyltroponeiron complexes.<sup>19,20</sup> The stereochemical significance of the proposed configuration prompted a single crystal X-ray study which revealed an unexpected structure.

## Experimental Section

**Preparation of the Complexes.** Methyl phenylpropiolate (5.4 g, 33.8 mmoles),  $\text{Fe}_2(\text{CO})_9$  (8.2 g, 22.5 mmoles), and 30 ml of benzene were stirred *in vacuo* at 18° for 25 hr. After removal of 5.25 g (64%) of unreacted iron carbonyl, the filtrate was chromatographed on silica gel. Elution with benzene yielded a small amount of  $(\text{C}_6\text{H}_5\text{C}_2\text{CO}_2\text{CH}_3)_2\text{Fe}(\text{CO})_3$  (I) and 2.5 g of unreacted ester. The benzene-dichloromethane fraction contained 2.65 g (38% yield) of  $(\text{C}_6\text{H}_5\text{C}_2\text{CO}_2\text{CH}_3)_3\text{COFe}(\text{CO})_2$  (IV), whereas a 20% solution of ether in benzene eluted 0.77 g (9.4%) of  $(\text{C}_6\text{H}_5\text{C}_2\text{CO}_2\text{CH}_3)_2\text{COFe}(\text{CO})_3$  (III). Another compound (II) of identical composition as compound I, and presumably a geometrical isomer, generally was found in the fraction with IV and was separated by rechromatography. Extension of the reaction time to 72 hr increased the yield of III to about 30%, while the yield of IV remained about the same. More dilute reaction mixtures (150 ml of benzene) generally gave higher yields of III (40–60%) and lower yields of IV (5–12%). With the use of ethyl acetate as solvent, only III (38%) was obtained.

The reaction also could be carried out without the use of a solvent. A mixture of 6 g of  $\text{Fe}_2(\text{CO})_9$  and 15 ml of  $\text{C}_6\text{H}_5\text{C}_2\text{CO}_2\text{CH}_3$  was stirred under nitrogen at 25° for 24 hr. The unreacted  $\text{Fe}_2(\text{CO})_9$  (3.9 g) was removed by filtration, and the filtrate was chromatographed on silica gel. The ester was eluted with petroleum ether-benzene. The  $\text{CH}_2\text{Cl}_2$ -ether fraction contained 2.3 g of IV and a small amount of I, these being the only complexes formed under these conditions. However, when the reaction time was increased, III also was obtained.

*Anal.* I and II. Calcd for  $\text{C}_{23}\text{H}_{16}\text{O}_7\text{Fe}$ : C, 60.02; H, 3.51; O, 24.34; Fe, 12.14; mol wt, 460.2. Found for I: C, 60.31; H,

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3.43; O, 24.68. Found for II: C, 60.16; H, 3.59; O, 24.52. III. Calcd for  $C_{24}H_{16}O_8Fe$ : C, 59.04; H, 3.30; O, 26.22; Fe, 11.45; mol wt, 488.3. Found: C, 59.11; H, 3.14; O, 26.47; Fe, 11.45. IV. Calcd. for  $C_{33}H_{24}O_9Fe$ : C, 63.88; H, 3.90; O, 23.21;  $OCH_3$ , 15.0; Fe, 9.01; mol wt, 620.4. Found: C, 64.12; H, 3.89; O, 23.18;  $OCH_3$ , 14.6; Fe, 8.85; mol wt, 699.2 (vapor pressure osmometer in benzene).

Compound I was crystallized from petroleum ether as yellow needles which melt at 100–103°. Compound II was obtained from benzene–methanol as thick yellow blocks which melt at 140–144°. The infrared spectrum of I in  $CCl_4$  shows terminal CO bands at 2058, 2008, and 1992  $cm^{-1}$  and an ester CO band at 1718  $cm^{-1}$ . Compound II in  $CCl_4$  displays corresponding absorption bands at 2066, 2008, 1996, and 1709  $cm^{-1}$ . The nmr spectra of these two complexes also are similar. Signals for *para* and *meta* phenyl protons were observed at  $-7.2$  and  $-7.0$  ppm for I and II, respectively; *ortho* phenyl proton resonances for I and II were observed at  $-7.9$  and  $-7.6$  ppm, and methyl resonances at  $-3.27$  and  $-3.42$  ppm, respectively.

Thick yellow crystals of III with a melting point of 144–148° dec were obtained from benzene–methanol. Its infrared spectrum in KBr pellet form shows terminal CO bands at 2101, 2053, 2020  $cm^{-1}$ , ester CO bands at 1739 and 1721 (sh)  $cm^{-1}$ , and a ring CO band at 1667  $cm^{-1}$ . The nmr spectrum in carbon disulfide has resonances for aromatic protons at  $-6.6$  ppm and singlets at  $-3.68$  and  $-3.55$  ppm for methyl protons.

Compound IV was recrystallized from benzene–methanol as orange crystals which melt with decomposition at 170–173°. The infrared spectrum of IV in  $CH_2Cl_2$  contains terminal CO absorptions at 2049 and 2008  $cm^{-1}$  and ester CO bands at 1736 and 1695  $cm^{-1}$ . Its nmr spectrum in  $CDCl_3$  shows a multiplet for phenyl hydrogens at  $-7.35$  ppm and three singlets for methyl protons at  $-3.70$ ,  $-3.52$ , and  $-3.48$  ppm. No indication of isomerization was found when IV was heated in the nmr apparatus for 2 hr at 80°.

**Reactions of  $(C_6H_5C_2CO_2CH_3)_2COFe(CO)_3$  (III).** On heating 2 g of III in 20 ml of *dimethyl acetylenedicarboxylate* at 150°, an exothermic reaction occurred which raised the temperature to 230°. A workup of the reaction mixture, however, only gave oils.

Exposure of a solution of III (2 g in 200 ml of benzene) to bright sunlight for 3 days led, besides recovery of 0.55 g of unreacted material, only to oily and resin-like products.

A mixture of III (2.5 g) and *triphenylphosphine* (3.0 g) in 25 ml of benzene was heated in a sealed tube for 15 hr at 100°. The following products were isolated from chromatography of the reaction mixture on silica gel: 1.3 g of unreacted  $P(C_6H_5)_3$  (petroleum ether fraction) and 2.8 g (76%) of the complex  $(C_6H_5C_2CO_2CH_3)_2COFe(CO)_2P(C_6H_5)_3$  (eluted with benzene–ether). Crystallization from an ethanol–ether solution produced yellow blocks of mp 208–210° dec. Its infrared spectrum shows terminal carbonyl absorption bands at 2033 and 1976  $cm^{-1}$ , an ester carbonyl band at 1730  $cm^{-1}$ , and a ketonic band at 1634  $cm^{-1}$ .

*Anal.* Calcd for  $C_{41}H_{31}O_7FeP$ : C, 68.16; H, 4.32; O, 15.50; Fe, 7.73; P, 4.29; mol wt, 722.5. Found: C, 68.41; H, 4.34; Fe, 7.85; P, 4.38.

**Saponification** of an ester group of III was achieved by dissolving 2.0 g of III in 50 ml of acetic acid. After addition of 25 ml of 3 *N*  $H_2SO_4$ , the mixture was heated for 24 hr at 80°. After concentrating, 1.7 g (87%) of the saponified complex was filtered and crystallized from a benzene–petroleum ether solution as yellow plates of mp 151–157° dec. Its infrared spectrum shows terminal carbonyl bands at 2101 and 2045  $cm^{-1}$ ; ester and acid carbonyl groups at 1754 and 1736  $cm^{-1}$ ; and a ketonic group at 1587  $cm^{-1}$  (broad). In hexachlorobutadiene the compound shows a broad OH band at 2646  $cm^{-1}$ , presumably due to association. The analysis shows that only one of the two ester groups in III has been saponified, most probably the one *ortho* to the ketonic group.

*Anal.* Calcd for  $C_{23}H_{14}O_8Fe$ : C, 58.25; H, 2.96; O, 26.99;  $OCH_3$ , 6.55; Fe, 11.78; mol wt, 474.2. Found: C, 58.57; H, 3.02; O, 26.80;  $OCH_3$ , 6.22; Fe, 11.68.

Other reaction conditions (e.g., dioxane, 6 *N*  $H_2SO_4$ , 15 hr, 80°) also led to the same complex (63%) containing only one saponified ester group. Only oils were obtained under alkaline conditions (e.g., ethanol, 2 *N* KOH, 3-hr refluxing).

**Reactions of  $(C_6H_5C_2CO_2CH_3)_2COFe(CO)_2$  (IV).** Attempts to liberate the organic part of IV by reactions with *ferric chloride* (in dioxane–water solution at 90°) and *triphenylphosphine* (in boiling xylene) resulted only in the recovery of most of the unreacted starting materials and the formation of small amounts of oily products. Unsuccessful results also were obtained upon attempted

sublimation *in vacuo* up to 200° and upon refluxing in ethyl acetate or in xylene in the presence of a stream of air bubbled through the solution.

An additional compound was formed when IV reacted with *bromine*. A cold solution of 0.32 g (2.0 mmoles) of bromine in benzene was added to a cold solution of 0.92 g (1.48 mmoles) of IV in benzene, and the resulting mixture was kept in the refrigerator for 3 hr. The reaction mixture then was washed with water and chromatographed on silica gel. Elution of a dark red band with benzene–petroleum ether yielded upon recrystallization from an ether–ethanol solution 0.12 g of brownish needles of the complex  $(C_6H_5C_2CO_2CH_3)_2BrCOFe(CO)_2Br$  (V). It melts at 110–112° with decomposition and shows in its infrared spectrum terminal carbonyl absorptions at 2066 and 2024  $cm^{-1}$ , an ester carbonyl absorption at 1730  $cm^{-1}$ , and a band at 1623  $cm^{-1}$ , tentatively assigned to the olefin stretching mode.

*Anal.* Calcd for  $C_{33}H_{24}Br_2O_9Fe$ : C, 50.80; H, 3.10; Br, 20.48; O, 18.46;  $OCH_3$ , 11.94; Fe, 7.16; mol wt, 780.2. Found: C, 50.55; H, 3.33; Br, 20.12; O, 18.75;  $OCH_3$ , 11.55; Fe, 6.98.

**Irradiation with sunlight** of IV in benzene for 4 days yielded only oils and unreacted IV. However, when 1 ml of 10 *N* HCl was added to a solution of 1 g of IV in 50 ml of benzene and 50 ml of ethanol or methanol, and the mixture exposed to ultraviolet light (125 w) for 1.5 hr with a slow stream of air bubbling through the mixture, an organic product was formed in yields of 73–90%. This compound (VI), separated from IV by chromatography on silica gel (*viz.*, IV was eluted with benzene and 15% of  $CH_2Cl_2$ , the organic product with  $CH_2Cl_2$ ), was crystallized as greenish fluorescent needles of mp 160–163°. The presence of the HCl avoided the precipitation of iron-containing insoluble material during irradiation. Without the use of air, IV was not decomposed. Chloroform was also used successfully as a solvent. When a methanol solution was irradiated with an immersion ultraviolet lamp (125 w), yields of 61–63% were obtained after 5 min.

Compound VI was readily soluble in benzene and dichloromethane and insoluble in petroleum ether or ether. It was not fluorescent in solution. Its nmr spectrum in  $CDCl_3$  is very similar to that of IV and indicates that VI is a mixture of two isomers in the ratio of 3:7 and that it has two more hydrogens than the organic part of IV. The resonance lines for the more prevalent isomer are: methyl protons at  $-3.65$ ,  $-3.50$ , and  $-3.43$  ppm and two additional hydrogens at  $-5.60$  and  $-5.10$  ppm. The other isomer has the following lines: methyl protons at  $-3.63$ ,  $-3.48$ , and  $-3.45$  ppm and two additional hydrogens at  $-5.43$  and  $-5.03$  ppm. The hydrogens of the phenyl groups show a complicated group of signals at *ca.*  $-7.4$  ppm.

*Anal.* Calcd for  $C_{31}H_{26}O_7$ : C, 72.93; H, 5.14; O, 21.94; mol wt, 510.5. Found: C, 72.67; H, 5.17; O, 21.83; mol wt, 485.2 (vapor pressure osmometer in benzene).

**Hydrogenation of VI** was achieved in methanol on palladium at 25°. The hydrogenated compound (VII) was obtained from benzene–cyclohexane as colorless needles of mp 151–159°. The infrared spectrum of VII has absorptions characteristic of ester carbonyl groups at 1730 and 1718  $cm^{-1}$  and an absorption in the ketonic carbonyl region at 1761  $cm^{-1}$ . The nmr spectrum in  $CDCl_3$  shows two singlets for methyl hydrogens at  $-3.75$  and  $-3.16$  ppm, a complex signal at  $-4.1$  to  $-3.7$  ppm, and two groups of phenyl hydrogen resonances at  $-7.28$  and  $-7.26$  ppm. The analysis and infrared spectrum indicate VII to be 2,4-dicarbomethoxy-3,5-diphenylcyclopentanone; yield, 41%.

*Anal.* Calcd for  $C_{21}H_{20}O_5$ : C, 71.57; H, 5.73; O, 22.71; mol wt, 352. Found: C, 72.0; H, 5.78; O, 22.42; mol wt, 345 (vapor pressure osmometer in benzene).

One ester group in VI was *saponified* by the refluxing of a solution of 0.5 g of the compound in 40 ml of ethanol with 20 ml of 2 *N* KOH for 2 hr. Acidification and recrystallization from benzene–ether led to a greenish yellow fluorescent product (VIII) which melted at 200–202°. The infrared spectrum of VIII has absorption bands for ester carbonyl groups at 1727  $cm^{-1}$  and for an olefinic double bond at 1626  $cm^{-1}$ ; yield, 65%.

*Anal.* Calcd for  $C_{30}H_{24}O_7$ : C, 72.57; H, 4.87; O, 22.56; mol wt, 496.5. Found: C, 72.25; H, 4.93; O, 22.84.

The nmr spectrum of VIII in  $CDCl_3$  indicates the presence of two isomers. Two resonances occur for methyl hydrogens at  $-3.66$  and  $-3.45$  ppm and two resonances for phenyl hydrogens at  $-7.4$  and  $-7.25$  ppm. Attempts to saponify additional ester groups by further reaction with potassium hydroxide were not successful.

**Reaction of Methyl Phenylpropiolate with  $Fe_2(CO)_9$ .** In the reaction of  $C_6H_5C_2CO_2CH_3$  with  $Fe_2(CO)_9$  in petroleum ether (2 hr at 75°) the complexes  $(C_6H_5C_2CO_2CH_3)_2Fe_2(CO)_6$  and  $(C_6H_5C_2-$

$\text{CO}_2\text{CH}_3)_2\text{COFe}_2(\text{CO})_6$  were isolated along with  $(\text{C}_6\text{H}_5\text{C}_2\text{CO}_2\text{CH}_3)_2\text{COFe}(\text{CO})_3$  (III) (7.5% yield). Crystals of  $(\text{C}_6\text{H}_5\text{C}_2\text{CO}_2\text{CH}_3)_2\text{Fe}_2(\text{CO})_6$  are yellow with mp 114–122° dec. The infrared spectrum of this compound in  $\text{CH}_2\text{Cl}_2$  shows absorption bands at 2083, 2045, 2020, 1992, and 1961  $\text{cm}^{-1}$  characteristic of terminal carbonyls and a band at 1712  $\text{cm}^{-1}$  assigned to the ester carbonyl group. The red complex,  $(\text{C}_6\text{H}_5\text{C}_2\text{CO}_2\text{CH}_3)_2\text{COFe}_2(\text{CO})_6$ , decomposes without melting at 170–180°. Its infrared spectrum in  $\text{CH}_2\text{Cl}_2$  shows terminal carbonyl bands at 2092, 2066, and 2033  $\text{cm}^{-1}$ , an ester carbonyl at 1718  $\text{cm}^{-1}$ , and a ketonic ring carbonyl at 1684  $\text{cm}^{-1}$ . These dinuclear iron carbonyl complexes are of the general type  $(\text{RC}_2\text{R}')_2\text{Fe}_2(\text{CO})_6$  and  $(\text{RC}_2\text{R}')_2\text{COFe}_2(\text{CO})_6$ .<sup>5,10</sup>

**X-Ray Data for  $(\text{C}_6\text{H}_5\text{C}_2\text{CO}_2\text{CH}_3)_2\text{COFe}(\text{CO})_2$  (IV).** The density of  $(\text{C}_6\text{H}_5\text{C}_2\text{CO}_2\text{CH}_3)_2\text{COFe}(\text{CO})_2$  was determined by the flotation method. The crystal used for gathering intensity data was an orange rod-shaped fragment of approximate dimensions  $0.45 \times 0.25 \times 0.15$  mm mounted about the  $a$  axis, which corresponded to the 0.45-mm direction. Multiple-film, equi-inclination Weissenberg data were collected for layers  $0kl$  through  $16kl$ . Timed-exposure precession data were taken for the  $h0l$ ,  $h1l$ , and  $h2l$  levels. A total of 1352 independent diffraction maxima were observed, of which 1196 reflections were obtained from Weissenberg photographs and an additional 156 reflections from precession photographs. The only precession data used in the refinement were those for which no corresponding Weissenberg data had been observed. All photographs were taken with Zr-filtered Mo  $K\alpha$  radiation. The intensities were measured by comparison with a calibrated set of intensities taken from the same crystal. Lattice constants were determined from  $h0l$  and  $hk0$  precession photographs which were calibrated by superimposing a zero-level NaCl exposure on the same film. Corrections for Lorentz-polarization effects and spot extension<sup>23</sup> were applied to the data, but absorption corrections were neglected because of the small absorption coefficient ( $\mu_{\text{max}} = 0.075$ ). The atomic scattering factors were taken from the "International Tables."<sup>24</sup> The standard deviations of the individual reflections were estimated as follows: if  $I(hkl)_0 < \sqrt{10}I_{\text{min}}$ ,  $\sigma(F(hkl)_0) = [I(hkl)_0/20][\sqrt{10}I_{\text{min}}/I(hkl)_0]^2$ ; if  $I(hkl)_0 \geq \sqrt{10}I_{\text{min}}$ ,  $\sigma(F(hkl)_0) = |F(hkl)_0|/20$ . Prior to the refinement of the structure, the precession and Weissenberg data were placed on a common scale by a least-squares method.

**Crystal Data.** Crystals of  $(\text{C}_6\text{H}_5\text{C}_2\text{CO}_2\text{CH}_3)_2\text{COFe}(\text{CO})_2$  are monoclinic, with lattice parameters  $a = 19.29 \pm 0.05$ ,  $b = 9.88 \pm 0.025$ ,  $c = 15.47 \pm 0.04$  Å, and  $\beta = 103^\circ 50' \pm 10'$ . The observed density of 1.45  $\text{g cm}^{-3}$  agrees well with the value of 1.44  $\text{g cm}^{-3}$  calculated on the basis of four formula species per unit cell. The probable space group  $P2_1/a$ , uniquely determined by the systematic absences of  $h = 2n + 1$  for  $\{h0l\}$  and  $k = 2n + 1$  for  $\{0k0\}$ , was verified by the satisfactory refinement of the structure. All atoms occupy the general fourfold set of positions (4e):  $\pm(x, y, z; 1/2 + x, 1/2 - y, z)$ .<sup>25</sup>

**Determination of the Structure.** The structural analysis of  $(\text{C}_6\text{H}_5\text{C}_2\text{CO}_2\text{CH}_3)_2\text{COFe}(\text{CO})_2$  required the location of the coordinates of 1 iron, 33 carbon, and 9 oxygen atoms (and ideally 24 hydrogen atoms) which correspond to one molecule. Initial coordinates were found for the independent iron atom from an interpretation of the Harker peaks of the Patterson function computed with corrected intensity data. The calculation of structure factors based only on the iron parameters (with an assumed thermal parameter of 2.0 Å<sup>2</sup>) yielded discrepancy factors of  $R_1 = [\sum |F_o| - F_c] / \sum |F_o| \times 100 = 41\%$  and  $R_2 = [\sum w|F_o| - |F_c|^2 / \sum w|F_o|^2]^{1/2} \times 100 = 51\%$ . A first approximation to an electron density map phased on the iron atom was calculated. Fourteen of the peaks found were in positions which could be interpreted as atoms on the basis of the presumed conformations of the carbonyl groups, phenyl rings, and methyl carboxylate groups. These fourteen atoms together with the iron atom were used in the calculation of a second approximation to the electron density map. This map yielded fourteen additional probable atomic positions. At this point, it became clear that the iron atom was bonded to a five-membered ring rather than to a seven-membered ring. The positions of the remaining atoms were found from a third Fourier synthesis. Structure factors calculated on the basis of the atomic positions from this map (together with assumed thermal parameters) gave decreased values of  $R_1 = 25\%$  and  $R_2 = 27\%$  thereby indicating

the correctness of the over-all structure. A fourth Fourier map based on these structure factors produced only slightly different atomic coordinates which were used as input for the first cycle of an isotropic least-squares refinement. A total of nine cycles was performed with a modified version of the Busing–Martin–Levy full-matrix least-squares program.<sup>26</sup> The singly-scaled data were used for the first five cycles, but the scale factors for individual reciprocal lattice layers were allowed to vary in the last four cycles. In the last cycle discrepancy factors of  $R_1 = 13.9\%$  and  $R_2 = 12.8\%$  were obtained, and no positional or thermal parameter shifted by more than one-third of its corresponding standard deviation. The resulting parameters were utilized as input data for a rigid-body, least-squares refinement<sup>27</sup> in which the three independent phenyl rings were confined to their known geometry and individual isotropic thermal parameters were utilized for all atoms including the phenyl carbon atoms. The particular rigid-body program utilized is an extensive modification of the local version of the normal Busing–Martin–Levy least-squares program<sup>26</sup> written in FORTRAN 63 for the CDC 1604 and 3600 computers.<sup>28</sup> Since the discrepancy factors of  $R_1 = 14.1\%$  and  $R_2 = 13.3\%$  obtained from this refinement were slightly higher than those from the normal least-squares

**Table I.** Atomic Parameters and Standard Deviations

Atom	$x$ ( $10^4\sigma_x$ )	$y$ ( $10^4\sigma_y$ )	$z$ ( $10^4\sigma_z$ )	$B$ ( $\sigma_B$ )
Fe	0.3713 (2)	0.6596 (4)	0.2350 (3)	1.11 (0.12)
C(1)	0.3033 (15)	0.6684 (33)	0.1402 (19)	3.71 (0.68)
O(1)	0.2576 (10)	0.6617 (23)	0.0765 (14)	5.23 (0.51)
C(2)	0.3759 (17)	0.8291 (44)	0.2411 (23)	5.85 (1.36)
O(2)	0.3901 (9)	0.9388 (23)	0.2573 (11)	3.46 (0.51)
C(3)	0.4369 (13)	0.5120 (30)	0.3017 (18)	2.90 (0.64)
C(4)	0.4283 (13)	0.6118 (26)	0.3713 (17)	2.31 (0.64)
C(5)	0.3507 (10)	0.6052 (23)	0.3573 (14)	0.29 (0.53)
C(6)	0.3154 (12)	0.5124 (27)	0.2948 (16)	1.39 (0.58)
C(7)	0.3700 (14)	0.4526 (32)	0.2585 (18)	3.23 (0.69)
O(3)	0.5052 (8)	0.5016 (17)	0.2823 (11)	1.90 (0.38)
C(8)	0.5035 (13)	0.5831 (29)	0.2023 (17)	1.94 (0.60)
C(9)	0.4499 (11)	0.6565 (30)	0.1723 (16)	1.52 (0.54)
C(10)	0.4825 (14)	0.7007 (31)	0.4353 (21)	3.82 (0.71)
C(11)	0.5329 (18)	0.7644 (34)	0.3942 (22)	5.35 (0.82)
C(12)	0.5808 (19)	0.8390 (46)	0.4582 (26)	8.43 (1.04)
C(13)	0.5768 (17)	0.8508 (38)	0.5549 (22)	6.42 (0.87)
C(14)	0.5261 (15)	0.7758 (32)	0.5775 (19)	4.09 (0.75)
C(15)	0.4754 (15)	0.7004 (34)	0.5154 (22)	5.11 (0.79)
C(16)	0.3175 (14)	0.6852 (43)	0.4184 (20)	4.16 (0.77)
O(4)	0.2907 (11)	0.6230 (23)	0.4728 (15)	6.28 (0.59)
O(5)	0.3112 (9)	0.8060 (25)	0.4071 (12)	3.78 (0.47)
C(17)	0.2757 (13)	0.8934 (29)	0.4699 (18)	3.19 (0.72)
C(18)	0.2434 (12)	0.4754 (30)	0.2770 (15)	1.40 (0.57)
C(19)	0.1930 (15)	0.5697 (32)	0.2562 (17)	2.78 (0.67)
C(20)	0.1192 (15)	0.5385 (32)	0.2485 (18)	4.16 (0.76)
C(21)	0.0967 (14)	0.4036 (32)	0.2630 (16)	2.85 (0.67)
C(22)	0.1503 (16)	0.3021 (35)	0.2863 (20)	5.23 (0.83)
C(23)	0.2233 (12)	0.3461 (35)	0.2933 (16)	3.25 (0.65)
C(24)	0.3618 (16)	0.3557 (34)	0.1806 (19)	3.90 (0.71)
O(6)	0.3037 (10)	0.3234 (23)	0.1397 (12)	5.45 (0.51)
O(7)	0.4197 (9)	0.3034 (21)	0.1719 (12)	4.39 (0.48)
C(25)	0.4107 (14)	0.2060 (32)	0.0927 (19)	4.62 (0.75)
C(26)	0.5745 (13)	0.5513 (28)	0.1829 (20)	2.27 (0.62)
C(27)	0.5721 (17)	0.5060 (37)	0.1004 (24)	6.65 (0.94)
C(28)	0.6449 (19)	0.4883 (36)	0.0806 (22)	6.25 (0.89)
C(29)	0.7071 (15)	0.4950 (32)	0.1404 (22)	4.28 (0.76)
C(30)	0.7038 (14)	0.5295 (31)	0.2250 (20)	3.65 (0.71)
C(31)	0.6382 (16)	0.5598 (32)	0.2456 (19)	4.10 (0.77)
C(32)	0.4585 (17)	0.7506 (33)	0.1058 (20)	4.25 (0.74)
O(8)	0.5067 (12)	0.7829 (25)	0.0750 (16)	7.98 (0.67)
O(9)	0.3913 (10)	0.7918 (22)	0.0558 (13)	5.25 (0.52)
C(33)	0.3891 (16)	0.8922 (35)	-0.0234 (22)	5.91 (0.88)

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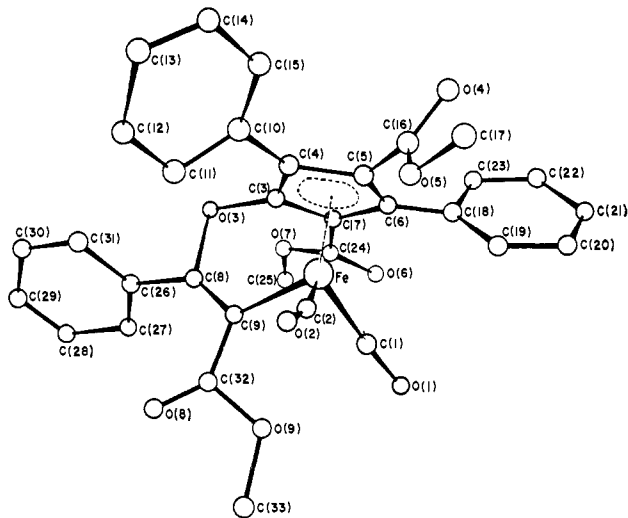


Figure 1. Molecular configuration of  $(C_6H_5C_2CO_2CH_3)_3COFe(CO)_2$  (IV).

3,5-diphenylcyclopentadienoneiron. Attempts to isolate the free cyclopentadienone ligand of III failed; its reaction with triphenylphosphine yielded  $(C_6H_5C_2CO_2CH_3)_2COFe(CO)_2P(C_6H_5)_3$ . Under acidic conditions one of the ester groups of III could be saponified, most probably the one in the 2 position.

Table III. Bond Lengths with Standard Deviations (Å)

Fe-C(1)	1.72 ± 0.03	C(12)-C(13)	1.52 ± 0.04
Fe-C(2)	1.68 ± 0.04	C(13)-C(14)	1.34 ± 0.04
Fe-C(3)	2.04 ± 0.03	C(14)-C(15)	1.41 ± 0.03
Fe-C(4)	2.18 ± 0.03	C(15)-C(10)	1.28 ± 0.03
Fe-C(5)	2.09 ± 0.02	C(16)-N(4)	1.25 ± 0.03
Fe-C(6)	2.15 ± 0.02	C(16)-O(5)	1.21 ± 0.03
Fe-C(7)	2.08 ± 0.03	O(5)-C(17)	1.57 ± 0.03
Fe-C(9)	1.99 ± 0.02	C(18)-C(19)	1.33 ± 0.03
C(1)-O(1)	1.16 ± 0.03	C(19)-C(20)	1.43 ± 0.03
C(2)-O(2)	1.13 ± 0.04	C(20)-C(21)	1.44 ± 0.03
C(3)-C(4)	1.50 ± 0.03	C(21)-C(22)	1.42 ± 0.03
C(4)-C(5)	1.46 ± 0.03	C(22)-C(23)	1.45 ± 0.03
C(5)-C(6)	1.39 ± 0.03	C(23)-C(18)	1.38 ± 0.03
C(6)-C(7)	1.44 ± 0.03	C(24)-O(6)	1.19 ± 0.03
C(7)-C(3)	1.43 ± 0.03	C(24)-O(7)	1.27 ± 0.03
C(3)-O(3)	1.42 ± 0.03	O(7)-C(25)	1.54 ± 0.03
O(3)-C(8)	1.47 ± 0.03	C(26)-C(27)	1.34 ± 0.04
C(8)-C(9)	1.26 ± 0.03	C(27)-C(28)	1.52 ± 0.04
C(4)-C(10)	1.53 ± 0.03	C(28)-C(29)	1.33 ± 0.04
C(5)-C(16)	1.49 ± 0.03	C(29)-C(30)	1.37 ± 0.03
C(6)-C(18)	1.40 ± 0.03	C(30)-C(31)	1.41 ± 0.03
C(7)-C(24)	1.52 ± 0.04	C(31)-C(26)	1.37 ± 0.03
C(8)-C(26)	1.50 ± 0.03	C(32)-O(8)	1.18 ± 0.03
C(9)-C(32)	1.43 ± 0.03	C(32)-O(9)	1.40 ± 0.03
C(10)-C(11)	1.43 ± 0.04	O(9)-C(33)	1.57 ± 0.03
C(11)-C(12)	1.39 ± 0.04		

**Description and Discussion of the Structure of IV.** The molecular structure of  $(C_6H_5C_2CO_2CH_3)_3COFe(CO)_2$  is shown in Figure 1. The iron atom is coordinated to a  $\pi$ -cyclopentadienyl ring, two carbonyl groups, and a  $\sigma$ -bonding olefinic carbon atom. The completely substituted cyclopentadienyl ring is formed by the condensation of two of the  $C_6H_5C_2CO_2CH_3$  molecules with a carbonyl carbon atom. The third  $C_6H_5C_2CO_2CH_3$  molecule is incorporated into the complex as a vinyl group in which one of the olefinic carbons is coordinated to the ether-like oxygen, and the other is

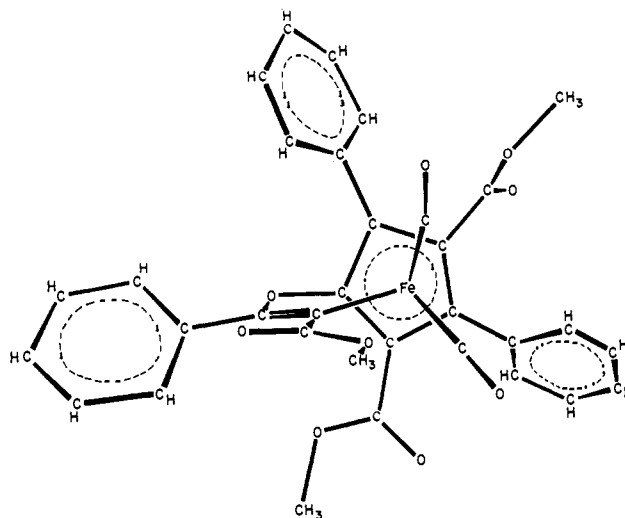


Figure 2. View of  $(C_6H_5C_2CO_2CH_3)_3COFe(CO)_2$  (IV) normal to the plane of the cyclopentadienyl carbon atoms.

$\sigma$ -bonded to the iron atom. The over-all configuration is consistent with the complex being named as dicarbonyl-1-carbomethoxy-2-phenyl-2- $[\pi$ -2',4'-dicarbomethoxy-3',5'-diphenyl-1'-cyclopentadienyloxy]- $\sigma$ -vinyliron. The iron atom thus attains a closed-shell electronic configuration similar to those of other  $C_5H_5Fe(CO)_2X$  compounds where X represents a  $\sigma$ -bonding, one-electron donor (e.g., X = H,<sup>31</sup> Cl,<sup>32</sup> Br,<sup>33</sup> I,<sup>33,34</sup> CN,<sup>32</sup> alkyl and aryl derivatives including unsaturated hydrocarbons and perfluoro analogs,<sup>35-39</sup> acyl derivatives<sup>37,40-42</sup> Si(CH<sub>3</sub>)<sub>3</sub>,<sup>43</sup> CH<sub>3</sub>S,<sup>44</sup> C<sub>6</sub>H<sub>5</sub>C(O)S,<sup>41</sup> SO<sub>2</sub>R,<sup>45</sup> and Mn(CO)<sub>5</sub>.<sup>46</sup> The  $(C_6H_5C_2CO_2CH_3)_3COFe(CO)_2$  molecules of point group symmetry C<sub>1</sub>-1 should exist as optical isomers, but the centrosymmetric space group demands that the crystal contain the racemate.

The side-chain linking the  $\pi$ -cyclopentadienyl ring with the metal-bonded olefinic carbon atom, C(9), presumably accounts for a small tilt of the ring relative to the other three ligands. The angle between the mean plane of the cyclopentadienyl carbons and the plane defined by the two carbonyl carbon atoms, C(1) and C(2), and a point 1.70 Å (the average of the Fe-C(1) and Fe-C(2) distances) along the Fe-C(9) bond is 13°.

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Table IV. Bond Angles with Standard Deviations (deg)

C(1)-Fe-C(2)	90.0 ± 1.6	C(12)-C(13)-C(14)	115.2 ± 3.3
C(1)-Fe-C(9)	95.7 ± 1.1	C(13)-C(14)-C(15)	123.0 ± 3.0
C(2)-Fe-C(9)	90.4 ± 1.4	C(14)-C(15)-C(10)	116.3 ± 3.0
Fe-C(1)-O(1)	173.8 ± 3.2	C(5)-C(16)-O(4)	118.4 ± 3.5
Fe-C(2)-O(2)	167.1 ± 3.3	C(5)-C(16)-O(5)	118.5 ± 3.1
C(4)-C(3)-O(3)	117.8 ± 2.3	O(4)-C(16)-O(5)	122.6 ± 3.3
C(4)-C(3)-C(7)	111.4 ± 2.4	C(16)-O(5)-C(17)	119.8 ± 2.4
C(7)-C(3)-O(3)	130.4 ± 2.6	C(6)-C(18)-C(19)	119.9 ± 2.8
C(3)-C(4)-C(5)	98.6 ± 2.1	C(6)-C(18)-C(21)	173.2 ± 1.8
C(3)-C(4)-C(10)	131.7 ± 2.3	C(6)-C(18)-C(23)	121.2 ± 2.5
C(5)-C(4)-C(10)	129.6 ± 2.3	C(19)-C(18)-C(23)	118.2 ± 2.5
C(4)-C(5)-C(6)	116.5 ± 2.0	C(18)-C(19)-C(20)	121.6 ± 2.9
C(4)-C(5)-C(16)	117.6 ± 2.2	C(19)-C(20)-C(21)	121.2 ± 2.6
C(6)-C(5)-C(16)	125.5 ± 2.0	C(20)-C(21)-C(22)	117.8 ± 2.5
		C(21)-C(22)-C(23)	116.1 ± 2.9
C(5)-C(6)-C(7)	105.0 ± 2.0	C(22)-C(23)-C(18)	125.1 ± 2.8
C(5)-C(6)-C(18)	127.4 ± 2.3	C(7)-C(24)-O(6)	119.9 ± 2.7
C(7)-C(6)-C(18)	127.2 ± 2.6	C(7)-C(24)-O(7)	114.4 ± 2.7
C(3)-C(7)-C(24)	122.9 ± 2.5	O(6)-C(24)-O(7)	125.2 ± 3.3
C(6)-C(7)-C(3)	108.3 ± 2.6	C(24)-O(7)-C(25)	114.0 ± 2.3
C(6)-C(7)-C(24)	128.4 ± 2.5	C(8)-C(26)-C(27)	115.8 ± 2.6
C(3)-O(3)-C(8)	107.6 ± 1.8	C(8)-C(26)-C(29)	178.1 ± 2.0
O(3)-C(8)-C(9)	118.5 ± 2.3	C(8)-C(26)-C(31)	123.4 ± 2.6
O(3)-C(8)-C(26)	102.5 ± 2.1	C(27)-C(26)-C(31)	120.8 ± 2.7
C(8)-C(9)-Fe	119.0 ± 2.2	C(26)-C(27)-C(28)	114.1 ± 2.9
C(8)-C(9)-C(32)	114.5 ± 2.5	C(27)-C(28)-C(29)	125.3 ± 3.2
C(32)-C(9)-Fe	125.3 ± 2.2	C(28)-C(29)-C(30)	115.9 ± 2.8
C(4)-C(10)-C(11)	113.4 ± 2.7	C(29)-C(30)-C(31)	121.2 ± 2.7
C(4)-C(10)-C(13)	177.2 ± 2.2	C(30)-C(31)-C(26)	121.9 ± 2.7
C(4)-C(10)-C(15)	114.2 ± 2.9	C(9)-C(32)-O(8)	134.8 ± 3.2
C(11)-C(10)-C(15)	132.3 ± 3.3	C(9)-C(32)-O(9)	109.6 ± 2.6
C(10)-C(11)-C(12)	108.8 ± 3.0	O(8)-C(32)-O(9)	114.2 ± 3.0
C(11)-C(12)-C(13)	124.0 ± 3.4	C(32)-O(9)-C(33)	117.6 ± 2.2

A view normal to the plane of the cyclopentadienyl carbon atoms is shown in Figure 2. The C-C bond lengths of the cyclopentadienyl ring are equal within their standard deviations. There is no evidence in these bond lengths of a cyclopentadienyl distortion proposed<sup>47</sup> for this type of compound. The perpendicular distance of 1.71 Å from the iron atom to the mean plane of the cyclopentadienyl carbon atoms (which are coplanar within 0.02 Å) agrees well with the corresponding distance of 1.74 Å calculated from the coordinates of Mills<sup>48</sup> for  $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$  but is considerably longer than the 1.66 Å calculated from the coordinates of Dunitz, *et al.*,<sup>49</sup> for ferrocene. These results indicate that the bond energies of the cyclopentadienyliron interactions in the former two complexes containing carbonyl groups are similar, but are weaker than that in bis( $\pi$ -cyclopentadienyl)iron. A similar lengthening of metal-ring distances for other organometal carbonyl complexes has been noted in tricarbonylbenzenechromium<sup>50</sup> and tricarbonylhexamethylbenzenechromium<sup>51</sup> relative to the metal-ring distances in dibenzenechromium.<sup>52</sup> Except for the bending of O(3) toward the iron atom, no apparent pattern is exhibited in the deviations of the atoms bonded to the cyclopentadienyl ring from the mean cyclopentadienyl carbon plane. These deviations are (with a + sign denoting displacement on the side of the ring plane

toward the iron atom): O(3), +0.21; C(10), -0.02; C(16), -0.09; C(18), -0.14; and C(24), +0.13 Å. The maximum deviation of any of the carbon atoms in the cyclopentadienyl ring from the plane determined by the three atoms to which it is bonded is 0.06 Å.

The angle of 108° at the ether-like oxygen atom, O(3), which is coordinated to two trigonal carbon atoms, is of the magnitude expected for an aliphatic ether, as opposed to the angle of approximately 120° commonly found in aromatic and unsaturated ethers.<sup>53</sup> The two olefinic carbon atoms (*viz.*, C(8) and C(9)) and the four atoms to which they are bonded (*viz.*, Fe, O(3), C(26), and C(32)) form a reasonably good plane, with the maximum deviation from the "best" least-squares plane of the six atoms being 0.1 Å. The two olefinic carbons, O(3), and C(26) form a "best" plane within 0.01 Å, with the iron atom and C(32) deviating from this plane by 0.1 and 0.3 Å, respectively. This latter mean plane makes an angle of 99° with the mean plane of the cyclopentadienyl carbon atoms. Hence, essentially no electron delocalization occurs through the ether-like oxygen, O(3).

The Fe-C  $\sigma$ -bond length of 1.99 Å is in the range of previously reported values of 1.94 and 1.95 Å in  $(\text{CH}_3\text{-C}_2\text{OH})_2\text{Fe}_2(\text{CO})_6$ ;<sup>13</sup> 2.09 Å in  $\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5\text{Fe}_2(\text{CO})_6$ ;<sup>14</sup> 2.01, 2.09, and 2.10 Å in  $(\text{C}_6\text{H}_5\text{C}_2\text{H})_3\text{COFe}_2(\text{CO})_5$ ;<sup>15</sup> and 2.00-2.06 Å in the two isomers of  $(\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5)_2\text{Fe}_3(\text{CO})_8$ .<sup>17</sup> The Fe-CO and carbonyl C-O bond lengths likewise are normal. The average of the C-C bond lengths in the phenyl rings is 1.40 Å; the deviations from this average are somewhat greater than would be expected on the basis of the standard devia-

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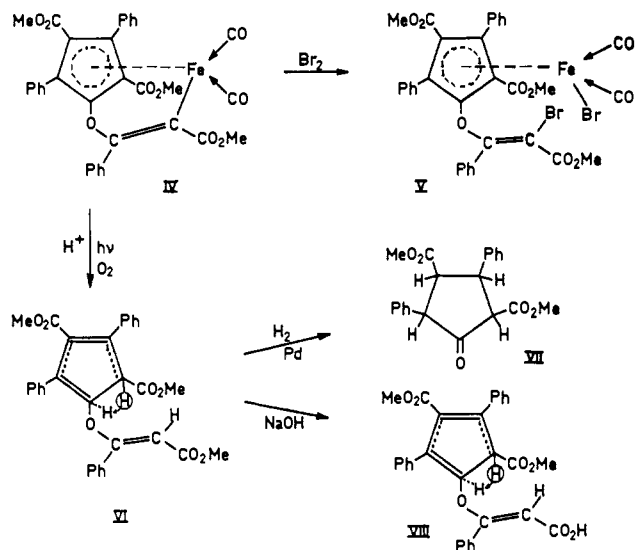


Figure 3. Reactions of  $(C_6H_5C_2CO_2CH_3)_3COFe(CO)_2$  (IV).

tions of the individual bond lengths. Considerable differences exist in the bond lengths in the three methyl carboxylate groups, but any attempt to attach significance to these deviations is not justified in view of the variations among the presumably equal bond lengths in the phenyl rings.

The methyl carboxylate and phenyl substituents bonded to the cyclopentadienyl ring are twisted in varying amounts out of the plane of the ring. The mean planes of these groups make the following angles with the mean plane of the cyclopentadienyl carbon ring: C(4),  $46^\circ$ ; C(5),  $69^\circ$ ; C(6),  $58^\circ$ ; C(7),  $11^\circ$ . These twists are all in the clockwise sense, referred to an axis directed from the cyclopentadienyl ring toward the substituent group. The magnitudes of the twistings are presumably dictated both by intermolecular and intramolecular packing interactions.

The intermolecular contacts are all greater than 3.35 Å, with the exception of  $CO \cdots CH_3$  distances of 2.85 Å which are somewhat longer than the intramolecular  $CO \cdots CH_3$  distances of 2.69, 2.62, and 2.64 Å found in the three methyl carboxylate groups.

In view of the structure found for  $(C_6H_5C_2CO_2CH_3)_3COFe(CO)_2$  (IV) and the characterization of  $(C_6H_5C_2CO_2CH_3)_2COFe(CO)_3$  (III), the other principal product in the reaction of methyl phenylpropiolate with  $Fe_2(CO)_9$  in benzene at room temperature, as tricarbonyl-2,4-dicarbomethoxy-3,5-diphenylcyclopentadienone-iron, one might expect that III is the precursor of IV. However, the decrease of the yield of IV when the reaction time is prolonged, as well as the failure of III to give an analogous complex when treated with the more reactive dimethyl acetylenedicarboxylate, contradicts this reaction mechanism.

The structural analysis of  $(C_6H_5C_2CO_2CH_3)_3COFe(CO)_2$  (IV) also has established the identities of its reaction products (Figure 3). Thus, the reaction of IV with bromine undoubtedly results in the cleavage of the  $\sigma$ -vinyl-iron bond,  $Fe-C(9)$ , with attachment of one bromine atom to the iron and the other bromine to C(9), to give a dicarbonylcyclopentadienyliron bromide derivative (V). The fluorescent organic product VI of formula  $C_{31}H_{26}O_7$ , which resulted from ultraviolet irradiation of IV in an acidic, aerated solution, is therefore a cyclopentadiene derivative formed by addition of hydrogen to the organic part of IV, at C(9) and at either C(3) or C(7) (Figure 1). This would also explain the two isomers indicated by the nmr spectrum of VI, since alkyl-substituted cyclopentadienes have been shown<sup>54</sup> to exist in a thermodynamic equilibrium mixture of endocyclic double bond isomers. From a consideration of the conjugation in the five-membered ring of VI, the predominant isomer would be expected to be that with the hydrogen attached on C(7). This formulation of VI is furthermore supported by the hydrogenation of VI to give 2,4-dicarbomethoxy-3,5-diphenylcyclopentanone (VII), a reaction which also proves VI to contain a cyclopentadiene ring. The reaction of VI with NaOH results in saponification of one ester group, most probably the one located on the vinyl group. According to its nmr spectrum the saponification product VIII also exists in two isomeric forms.

Although the formation of  $\pi$ -cyclopentadienyl metal systems from acetylene-metal carbonyl condensation reactions is somewhat unusual, other examples are known. In addition to the previously mentioned cyclopentadienyliron complexes,  $(HC_2H)_3Fe_2(CO)_6$ <sup>21</sup> and  $[(HC_2H)_2COFe(CO)_2]_2$ ,<sup>22</sup> the reaction of diphenylacetylene with (diglyme)Mo(CO)<sub>3</sub> has produced pentaphenylcyclopentadienyl rings as ligands in  $[(C_6H_5)_3C_3]_2Mo$ .<sup>55</sup> Also, reactions of  $\pi$ - $C_5H_5Fe(CO)_2CH_3$  with various acetylenes have been reported to give ferrocene complexes.<sup>56</sup>

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