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Registry No. I, 93895-59-1; II, 94348-89-7;  $(C_5H_5)_2YCl(THF)$ , 94348-90-0;  $(C_5H_5)_2YCl_2K(THF)$ , 94348-91-1;  $KC_5Me_5$ , 94348-

92-2;  $YCl_3$ , 10361-92-9;  $LiC_5Me_5$ , 51905-34-1.

**Supplementary Material Available:** Tables of thermal parameters and structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

## Photochemical Reaction of $\mu$ -Ethenylidene Complex $[(C_5H_5)(CO)Fe]_2(\mu-CO)(\mu-C=CH_2)$ with Acetylenes

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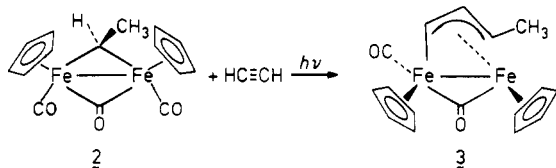
Photolysis of  $[(C_5H_5)(CO)Fe]_2(\mu-CO)(\mu-C=CH_2)$  and diphenylacetylene led to the formation of metallacyclopentenone  $[(C_5H_5)(CO)Fe]_2(\mu-\eta^2, \eta^2-COC(C_6H_5)C(C_6H_5)C=CH_2)$ , **5a**, in 43% yield. Photolysis of **5a** led to loss of CO and rearrangement to give the  $\sigma, \pi$ -allyl complex  $(C_5H_5)(CO)FeFe(C_5H_5)(\mu-CO)(\mu-\eta^1, \eta^3-C(C_6H_5)C(C_6H_5)C=CH_2)$ , **6**, in 49% yield. The structure of **5a** was determined by X-ray crystallography: monoclinic space group  $C2/c$ , with unit cell constants  $a = 26.183$  (6) Å,  $b = 11.163$  (2) Å,  $c = 22.931$  (3) Å,  $\beta = 106.90$  (1)°, and  $Z = 8$ .

The interest in the synthesis and reactivity of carbon-bridged bimetallic complexes has intensified in the last few years.<sup>1-4</sup> The study of bridging methylene and related complexes has been the result of their proposed involvement in carbon monoxide reduction chemistry (Fischer-Tropsch synthesis),<sup>5</sup> olefin metathesis,<sup>6</sup> alkyne polymerization,<sup>6-9</sup> and methylene transfer reactions.<sup>10</sup>

Both monometallic carbene complexes and bimetallic bridging carbene complexes have been proposed as intermediates in the metal-catalyzed polymerization of acetylenes.<sup>6</sup> The possible intermediacy of metal carbene complexes in alkyne polymerization prompted Katz<sup>11</sup> to use isolated metal carbene complexes as initiators. He found that metal carbene complexes  $(CO)_5W=C(C_6H_5)_2$  and  $(CO)_5W=C(C_6H_5)(OCH_3)$  initiated polymerization of several alkynes.

The reaction of alkynes with bimetallic bridging carbene complexes has recently been explored by several groups. Rudler<sup>7</sup> has found that  $\mu$ -alkylidene complex  $[(CO)_5W-W(CO)_4](\mu-\eta^1, \eta^3-CHCH=C(CH_3)_2)$ , **1**, initiates the polymerization of 2-butyne. In addition, he was able to isolate the product of the insertion of 2-butyne into the  $\mu$ -alkylidene bridge of **1**.

Knox<sup>8,12</sup> has studied the photochemical reaction of  $\mu$ -alkylidene complex  $[(C_5H_5)(CO)Fe]_2(\mu-CO)(\mu-CHCH_3)$ , **2**, with acetylene which gave  $(C_5H_5)(CO)FeFe(C_5H_5)(\mu-CO)(\mu-\eta^1, \eta^3-CHCHCHCH_3)$ , **3**. The analogous diruthenium complex  $(C_5H_5)(CO)RuRu(C_5H_5)(\mu-CO)(\mu-\eta^1, \eta^3-CHCHCHCH_3)$  was prepared in a similar manner.



Here we report the photochemical reaction of the bridging ethynylidene complex  $[(C_5H_5)(CO)Fe]_2(\mu-CO)(\mu-C=CH_2)$ ,<sup>13,14</sup> **4**, with alkynes. In contrast to the reactivity seen for **2** by Knox,<sup>12</sup> we observed that photolysis of

bridging ethynylidene complex **4** with diphenylacetylene and 2-butyne gave metallacyclopentenone complexes **5a** and **5b**, respectively. The X-ray crystal structure of **5a** is reported as well as the further photochemical rearrangement of **5a** to  $[(C_5H_5)(CO)FeFe(C_5H_5)](\mu-CO)(\mu-\eta^1, \eta^3-C(C_6H_5)C(C_6H_5)C=CH_2)$ , **6**.

### Results

**Synthesis of Metallacyclopentenone 5a.** Photolysis of a toluene solution of a 1.0:1.7 mixture of *cis*- and *trans*- $[(C_5H_5)(CO)Fe]_2(\mu-CO)(\mu-C=CH_2)$ ,<sup>13,14</sup> **4**, and diphenylacetylene under a nitrogen atmosphere for 1.75 h with a Hanovia medium-pressure lamp led to the formation of dark green crystalline metallacyclopentenone  $[(C_5H_5)(CO)Fe]_2(\mu-\eta^2, \eta^2-COC(C_6H_5)C(C_6H_5)C=CH_2)$ , **5a**, in 26% yield. Under these conditions, small amounts of starting material were recovered and about 16% of decarbonylated rearrangement product **6** was obtained. In a parallel experiment, the photolysis was run for 1.75 h while CO was bubbled through the solution. Under CO, the metallacyclopentenone **5a** was formed in higher yield (36%), starting material **4** was recovered in 44% yield and

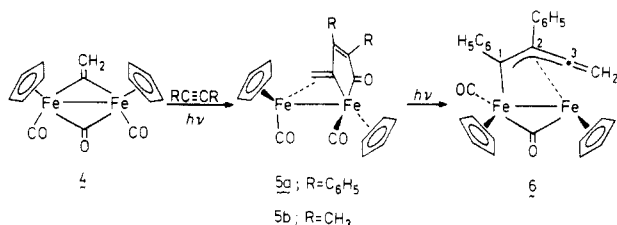
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<sup>†</sup> NSF Postdoctoral Fellow, 1981-1982.

Table I. Selected Interatomic Distances (Å) and Angles (deg)

Bond Distances					
Fe(1)-Fe(2)	2.616 (1)	Fe(2)-C(8)	2.096 (3)	C(15)-C(16)	1.482 (4)
Fe(1)-C(1)	1.752 (4)	Fe(2)-C(9)	2.097 (3)	C(15)-C(24)	1.483 (4)
Fe(1)-C(13)	1.984 (3)	Fe(2)-C(10)	2.104 (3)	C(16)-C(17)	1.411 (4)
Fe(1)-C(16)	1.950 (3)	Fe(2)-C(11)	2.107 (3)	C(3)-C(4)	1.406 (2)
Fe(1)-C(3)	2.097 (3)	Fe(2)-C(12)	2.103 (3)	C(8)-C(9)	1.396 (2)
Fe(1)-C(4)	2.090 (2)	Fe(1)-C(2)	3.017 (3)	C(18)-C(19)	1.388 (3)
Fe(1)-C(5)	2.126 (2)	C(1)-O(1)	1.156 (4)	C(19)-C(20)	1.386 (3)
Fe(1)-C(6)	2.156 (2)	C(2)-O(2)	1.153 (4)	C(20)-C(21)	1.373 (3)
Fe(1)-C(7)	2.139 (3)	C(13)-O(3)	1.218 (4)	C(24)-C(25)	1.388 (3)
Fe(2)-C(2)	1.748 (4)	C(13)-C(14)	1.495 (4)	C(25)-C(26)	1.388 (3)
Fe(2)-C(16)	2.018 (3)	C(14)-C(15)	1.348 (4)	C(26)-C(27)	1.366 (4)
Fe(2)-C(17)	2.093 (3)	C(14)-C(18)	1.494 (4)		
Bond Angles					
Fe(2)-Fe(1)-C(1)	68.9 (1)	Fe(1)-C(13)-O(3)	124.0 (2)	C(15)-C(16)-C(17)	123.4 (3)
Fe(2)-Fe(1)-C(13)	102.2 (1)	Fe(1)-C(13)-C(14)	114.3 (2)	Fe(2)-C(17)-C(16)	67.1 (2)
Fe(2)-Fe(1)-C(16)	49.9 (1)	O(3)-C(13)-C(14)	121.6 (3)	C(14)-C(18)-C(19)	122.0 (2)
C(1)-Fe(1)-C(13)	83.2 (2)	C(13)-C(14)-C(15)	113.4 (3)	C(14)-C(18)-C(23)	119.7 (2)
C(1)-Fe(1)-C(16)	110.8 (1)	C(13)-C(14)-C(18)	120.1 (2)	C(19)-C(18)-C(23)	118.4 (3)
C(13)-Fe(1)-C(16)	81.6 (1)	C(15)-C(14)-C(18)	126.5 (3)	C(18)-C(19)-C(20)	120.7 (3)
Fe(1)-Fe(2)-C(2)	85.0 (1)	C(14)-C(15)-C(16)	115.0 (3)	C(19)-C(20)-C(21)	120.1 (3)
Fe(1)-Fe(2)-C(16)	47.6 (1)	C(14)-C(15)-C(24)	123.8 (3)	C(20)-C(21)-C(22)	120.0 (4)
Fe(1)-Fe(2)-C(17)	76.4 (1)	C(16)-C(15)-C(24)	121.1 (2)	C(15)-C(24)-C(25)	119.9 (2)
C(2)-Fe(2)-C(16)	107.2 (1)	Fe(1)-C(16)-Fe(2)	82.5 (1)	C(15)-C(24)-C(29)	121.8 (2)
C(2)-Fe(2)-C(17)	85.4 (1)	Fe(1)-C(16)-C(15)	114.9 (2)	C(25)-C(24)-C(29)	118.3 (3)
C(16)-Fe(2)-C(17)	40.1 (1)	Fe(1)-C(16)-C(17)	121.4 (2)	C(24)-C(25)-C(26)	120.6 (3)
Fe(1)-C(1)-O(1)	166.6 (3)	Fe(2)-C(16)-C(15)	121.8 (2)	C(25)-C(26)-C(27)	120.0 (3)
Fe(2)-C(2)-O(2)	175.5 (3)	Fe(2)-C(16)-C(17)	72.8 (2)	C(26)-C(27)-C(28)	120.5 (4)

the decarbonylated rearrangement product **6** was not observed. The best yield of metallacyclopentenone **5a** (43%) was obtained when the photolysis was run for 9 h while CO was bubbled through the solution.



The general structure of **5a** was deduced from spectral measurements and was fully confirmed by X-ray crystallography. In the IR spectrum of **5a**, two strong bands at 1953 and 1910  $\text{cm}^{-1}$  were observed for the terminal CO's and a weaker band at 1612  $\text{cm}^{-1}$  was seen for the acyl group of the metallacyclopentenone. In the  $^1\text{H}$  NMR, two resonances for the different cyclopentadienyl rings were seen at  $\delta$  4.55 and 4.52. Two doublets at  $\delta$  4.12 ( $J = 2.8$  Hz, 1 H) and 3.16 ( $J = 2.8$  Hz, 1 H) were observed for the bridging vinyl group. The appreciable upfield shift of the vinyl protons in complex **5a** is indicative of the coordination of the double bond.

In the  $^{13}\text{C}$  NMR of **5a**, the resonance at  $\delta$  258.7 was assigned to the iron acyl carbon and the resonances at  $\delta$  230.4 and 220.0 were assigned to the terminal carbonyl ligands. The metallacyclic carbon bridging the two iron atoms appeared at  $\delta$  197.7 and the methylene carbon of the bridging vinyl group appeared at  $\delta$  53.4. The resonances at  $\delta$  181.8 and 150.1 were assigned to the olefinic carbons derived from the acetylene.

**X-ray Structure of 5a.** The nearly planar metallacyclopentenone ring and the bridging vinyl unit of **5a** are clearly shown in Figure 1. Bond lengths and angles are presented in Table I. The largest deviation from the mean plane of the metallacyclopentenone is 0.06 Å for C(16). The exomethylene carbon, C(17), is 0.09 Å above the plane of the metallacycle. Both the exomethylene carbon and its attached ring carbon C(16) are bonded to Fe(2) which

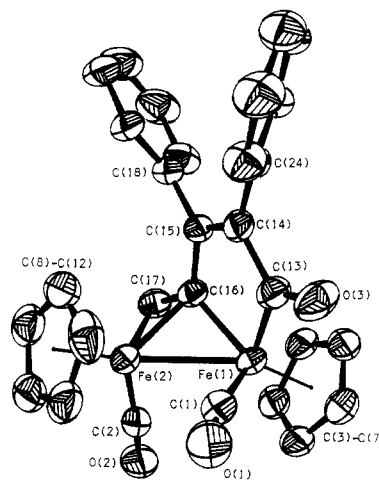


Figure 1. ORTEP diagram of  $[(\text{C}_5\text{H}_5)(\text{CO})\text{Fe}]_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-COC}(\text{C}_6\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{C}=\text{CH}_2)$ , **5a**, showing 50% probability thermal ellipsoids.

lies 1.84 Å above the metallacycle. The Fe(2) to exocyclic carbon distance (2.093 (3) Å) is slightly longer than the Fe(2) to endocyclic carbon distance (2.018 (3) Å). The endocyclic carbon to Fe(1) distance (1.950 (3) Å) is slightly shorter than the distance to Fe(2). The iron-iron distance of 2.616 (1) Å establishes the presence of a single bond. The cyclopentadienyl rings are in a transoid relationship; the torsional angle of Cp centroid-Fe(1)-Fe(2)-Cp' centroid is 162°.

In contrast to **5a**, bridging vinyl complexes of diiron systems normally possess a bridging carbonyl group.<sup>15,16</sup> Bridging vinyl complexes of other metals without supporting carbonyl bridges are also known.<sup>17-19</sup> The oxygen

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atom of the carbonyl group on Fe(1) is bent away from the cyclopentadienyl group on Fe(2) ( $\angle Fe(1)-C(1)-O(1) = 166.6(3)^\circ$ ). The long C(1)-Fe(2) distance of 3.017 (3) Å precludes a semibridging carbonyl.

**Photochemical Rearrangement of 5a.** In the photochemical synthesis of 5a from 4 and diphenylacetylene, a second product 6 was observed at longer times. When isolated 5a was photolyzed under nitrogen for 5 h, decarbonylation and rearrangement took place to produce the dark red complex  $(C_5H_5)(CO)FeFe(C_5H_5)(\mu-CO)(\mu-\eta^1, \eta^3-C(C_6H_5)C(C_6H_5)C=CH_2)$ , 6, in 49% isolated yield. The formation of 6 was strongly inhibited when the photolysis was carried out while CO was bubbled through the solution. While photolysis of 5a under  $N_2$  for 4 h led to complete consumption of starting material and formation of 6 in 80% crude yield, photolysis under CO for 4 h led to 80% recovery of starting material 5a and formation of 6 in only 10% yield.

The structure of 6 is assigned solely on the basis of spectroscopic data. The IR spectrum established the presence of a terminal carbonyl ligand with a band at 1972  $cm^{-1}$  and a bridging carbonyl ligand with a band at 1777  $cm^{-1}$ . In the  $^1H$  NMR, the observation of two doublets at  $\delta$  5.44 ( $J = 2.3$  Hz) and 5.19 ( $J = 2.3$  Hz) established the presence of an uncomplexed  $C=CH_2$  group in 6. In the  $^{13}C$  NMR, resonances at  $\delta$  189.0, 171.0 ( $C_1$  and  $C_3$ ), and 73.2 ( $C_2$ ) are assigned to the  $\eta^1, \eta^3$  three-carbon unit of 6. Other  $^{13}C$  resonances were seen at  $\delta$  266.0 for the bridging CO, at  $\delta$  213.4 for the terminal CO, and at  $\delta$  103.5 (t,  $J = 162$  Hz) for the uncomplexed methylene carbon.

The phenyl region of the  $^1H$  NMR spectrum of 6 was more complex than expected and required the postulation of hindered rotation of one of the phenyl rings. In addition to complex multiplets, two one proton resonances were seen at  $\delta$  8.36 (d,  $J = 7.6$  Hz, one ortho H) and at 7.50 (m). As expected for one freely rotating phenyl ring and for one ring with nonequivalent ortho and meta sites, the  $^{13}C$  NMR of 6 has two resonances at  $\delta$  130.3 and 126.9 for two carbons each and eight resonances between  $\delta$  156.2 and 124.6 for one carbon each.

**Reactions of 4 with Other Acetylenes.** Photolysis of a solution of bridging ethynylidene complex 4 and 2-butyne for 1 h led to the formation of metallacyclopentenone 5b in 22% yield. The spectral properties of 5a and 5b are similar and established the close relationship between the structures of the compounds. In the IR spectrum of 5b, the bands for the terminal CO ligands appear at 1951 and 1909  $cm^{-1}$  and the band for the acyl group of the metallacyclopentenone appears at 1592  $cm^{-1}$ . In the  $^1H$  NMR, the complexed bridging vinyl group gave rise to two doublets ( $J = 2.8$  Hz) at  $\delta$  4.26 and 2.80. In the  $^{13}C$  NMR, the carbons of the bridging vinyl group appear at  $\delta$  200.6 ( $C=CH_2$ ) and 49.5 ( $C=CH_2$ ).

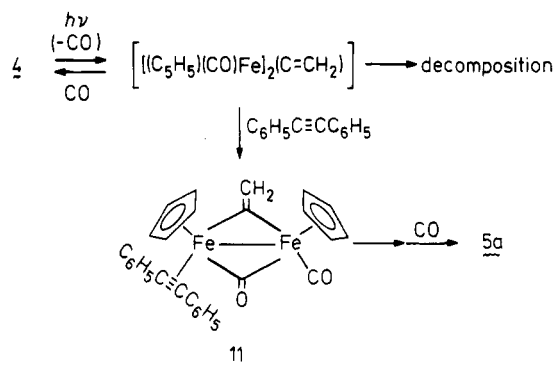
In contrast to the photolysis of 5a, extended photolysis of 5b did not lead to a decarbonylated rearrangement product similar to 6. Only slow decomposition (75%) was seen after prolonged photolysis of 5b for 17 h.

Attempts to prepare other metallacyclopentenones by photolysis of vinylidene complex 4 in the presence of  $(CH_3)_3SiC\equiv CSi(CH_3)_3$  or acetylene failed.

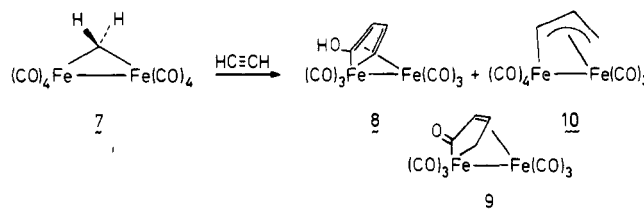
### Discussion

The photochemical formation of metallacyclopentenone 5a from the photolysis of ethynylidene complex 4 and diphenylacetylene provides an interesting and unprecedented synthesis of a new kind of metallacyclic complex.

### Scheme I



The only reaction which resembles the formation of 5a is the thermal reaction of diiron methylene complex 7 with acetylene studied by Sumner, Collier, and Pettit.<sup>20</sup> They observed formation of five-membered metallacycle 8 that incorporated the elements of CO, a bridging carbene ligand, and an acetylene. Complex 8 can be thought of as the enol tautomer of a metallacyclopentenone 9.



The effect of CO on the photochemical formation of 5a provides some limited insight into its mechanism of formation. The major effects of CO were to inhibit decomposition of starting material 4 and to inhibit further photochemical conversion of 5a to 6. The extent of formation of 5a was changed significantly by CO. We suggest that the effect of CO can be understood in terms of Scheme I. Photolysis of 4 leads to loss of CO and formation of a reactive intermediate which can decompose, react with CO to regenerate 4, or react with diphenylacetylene to give intermediate 11 which rearranges and adds CO to eventually produce 5a.

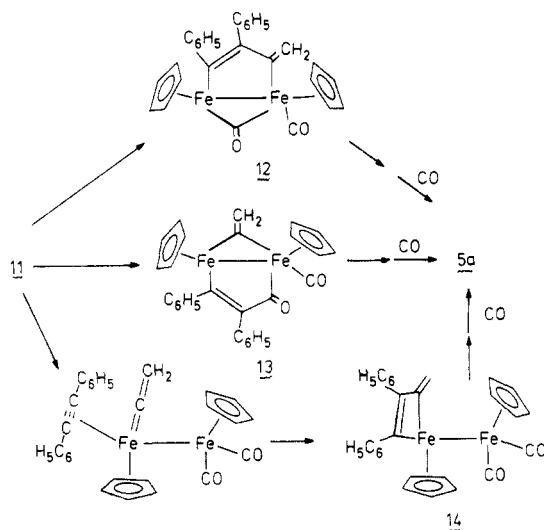
A number of different pathways are possible for conversion of the proposed acetylene complex 11 to 5a. Insertion of the acetylene into the bridging ethynylidene-iron bond could lead to 12 and then on to 5a; this route appears unattractive since 12 might be expected to rearrange directly with 6. Insertion of the acetylene into the bridging CO-iron bond, by analogy with Knox's results from photolysis of  $[(C_5H_5)Fe(CO)]_2$  and diphenylacetylene,<sup>21</sup> would lead to 13, which might then couple with the ethynylidene ligand and eventually lead to 5a. A third alternative would involve unbridging the ethynylidene ligand and forming an intermediate metallacyclobutene 14 which could insert CO and eventually give 5a.

The photochemical conversion of 5a to 6 provides an interesting example of an interconversion of metallacyclic complexes. The observed CO inhibition of the conversion to 6 suggests that photolysis generates a reactive intermediate that either reads CO or rearranges to 6. The detailed mechanism of the conversion of 5a to 6 must be very complex since loss of CO, deinsertion of CO, carbonyl bridging, and decomplexation of the  $C=CH_2$  unit all must occur at some stage.

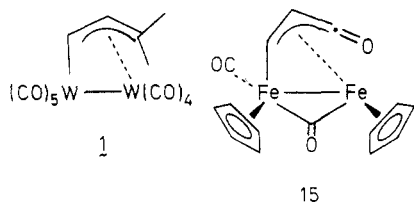
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The  $\sigma, \pi$  allyl unit of **6** is similar to that of **1**, **7**, **3**, **8**, and **15**.<sup>21</sup> The exo methylene unit attached to the  $\sigma$ - $\pi$  allyl system is unique to **6**.



### Experimental Section

**General Data.** All reactions were carried out under an atmosphere of dry nitrogen using degassed solvents. <sup>1</sup>H NMR spectra were recorded on a Bruker WH-270 spectrometer; <sup>13</sup>C NMR spectra were recorded on a JEOL FX-200 spectrometer. Infrared spectra were recorded on a Beckman 4230 infrared spectrometer. Mass spectra were recorded on a AEI-MS-902 spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Labs (Woodside, NY).

**[(C<sub>5</sub>H<sub>5</sub>)(CO)Fe]<sub>2</sub>( $\mu$ - $\eta^2$ ,  $\eta^2$ -COC(C<sub>6</sub>H<sub>5</sub>)C(C<sub>6</sub>H<sub>5</sub>)C=CH<sub>2</sub>) (**5a**).** Bridging vinylidene complex **4**<sup>13,14</sup> (0.50 g, 1.40 mmol; cis:trans, 1.0:1.7) and diphenylacetylene (0.25 g, 1.40 mmol) in toluene (25 mL) were photolyzed with a Hanovia 450-W medium-pressure mercury lamp for 9 h while CO was bubbled through the solution. The reaction mixture was chromatographed on activity III alumina, eluting first with toluene to give a small amount of **6** and unreacted **4** and then with 1:1 ether/toluene to give the dark green product **5a**. Metallacyclopentenone **5a** was further purified by dissolving in methylene chloride (10 mL), adding hexane (25 mL), and slowly evaporating about half the solvent under a stream of nitrogen. The supernatant was decanted, and the black-green, crystalline **5a** (0.32 g, 43%) was washed with additional hexane; mp >250 °C. For **5a**: <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 270 MHz)  $\delta$  7.2 (m, 10 H), 4.55 (s, 5 H), 4.52 (s, 5 H), 4.12 (d,  $J$  = 2.8 Hz, 1 H), 3.16 (d,  $J$  = 2.8 Hz, 1 H); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 0.07 M Cr(acac)<sub>3</sub>, 50.1 MHz)  $\delta$  258.7 (FeCOC), 230.4 (CO), 222.0 (CO), 197.0 (FeCFe), 181.8 and 150.1 (=C=C<sub>6</sub>H<sub>5</sub>), 136.9, 135.6, 130.1, 129.6, 127.9, 127.6, 127.2, 126.2 (aromatic), 89.1 (C<sub>5</sub>H<sub>5</sub>), 85.5 (C<sub>5</sub>H<sub>5</sub>), 53.4 (CH<sub>2</sub>); IR (CH<sub>2</sub>Cl<sub>2</sub>) 1953 (s), 1910 (s), 1612 (m) cm<sup>-1</sup>; exact mass (30 eV) 530.0267, calcd for C<sub>29</sub>H<sub>22</sub>Fe<sub>2</sub>O<sub>3</sub> 530.0267. Anal. Calcd for C<sub>29</sub>H<sub>22</sub>Fe<sub>2</sub>O<sub>3</sub>: C, 65.70; H, 4.10; Fe, 21.07. Found: C, 65.43; H, 4.38; Fe, 21.40.

**[(C<sub>5</sub>H<sub>5</sub>)(CO)Fe]<sub>2</sub>( $\mu$ - $\eta^2$ ,  $\eta^2$ -COC(CH<sub>3</sub>)C(CH<sub>3</sub>)C=CH<sub>2</sub>) (**5b**).** Bridging vinylidene complex **4**<sup>13,14</sup> (1.40 g, 4.00 mmol) and 2-butyne (1.0 mL, 12 mmol) in toluene (75 mL) were photolyzed with a 450-W medium-pressure mercury lamp for 1 h in an apparatus fitted with a dry ice-acetone condenser. The reaction mixture was filtered and chromatographed (100 g of activity III alumina), eluting first with toluene to collect the unreacted starting material and then with 3:1 toluene/diethyl ether to elute the dark green metallacycle **5b**. The crude product was purified by dissolving

Table II. Summary of Crystal Data and Intensity Collection

empirical formula	Fe <sub>2</sub> C <sub>29</sub> H <sub>22</sub> O <sub>3</sub> ·2C <sub>7</sub> H <sub>8</sub>
fw	714.4
cryst dimens, mm	0.35 × 0.4 × 0.5
temp, K	293 ± 1
cell parameters	
<i>a</i> , Å	26.183 (6)
<i>b</i> , Å	11.163 (2)
<i>c</i> , Å	22.931 (3)
$\beta$ , deg	106.90 (1)
space group	C2/c
<i>Z</i>	8
<i>D</i> (calcd), g/cm <sup>3</sup>	1.48
abs coeff $\mu$ , cm <sup>-1</sup>	8.85
scan range	
deg below $2\theta_{K\alpha_1}$	0.65
deg above $2\theta_{K\alpha_1}$	0.65
scan speed, deg/min	2.0–24
scan type	$\theta$ - $2\theta$
$2\theta$ limits, deg	3.5–54.9
( $\sin\theta$ )/ $\lambda_{\max}$ , (Å <sup>-1</sup> )	0.649
unique data, measd	7329
unique data, $F_o > 3\sigma(F_o)$	4803
discrepancy indices, $R_1$	0.045
$R_2$	0.057
goodness of fit	1.76

in methylene chloride (10 mL) and slowly adding hexane (30 mL) and evaporating about half the solvent under a stream of nitrogen. The supernatant was decanted, and the residue was washed with hexane (25 mL) to give crystalline, black-green metallacyclopentenone **5b** (0.35 g, 22%), mp >250 °C. For **5b**: <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 270 MHz)  $\delta$  4.43 (s, 5 H), 4.35 (s, 5 H), 4.26 (d,  $J$  = 2.8 Hz, 1 H), 2.80 (d,  $J$  = 2.8 Hz, 1 H), 2.24 (s, 3 H), 1.58 (s, 3 H); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 0.07 M Cr(acac)<sub>3</sub>, 50.1 MHz)  $\delta$  259.4 (FeCOC), 230.2 (CO), 222.9 (CO), 200.6 (FeCFe), 177.2 (=CCH<sub>3</sub>), 145.7 (=CCH<sub>3</sub>), 88.8 (C<sub>5</sub>H<sub>5</sub>), 85.2 (C<sub>5</sub>H<sub>5</sub>), 49.5 (CH<sub>2</sub>), 15.3 (CH<sub>3</sub>), 11.2 (CH<sub>3</sub>); IR (CH<sub>2</sub>Cl<sub>2</sub>) 1951 (s), 1909 (s), 1623 (w), 1592 (m) cm<sup>-1</sup>; exact mass (30 eV) 405.9953, calcd for C<sub>15</sub>H<sub>18</sub>Fe<sub>2</sub>O<sub>3</sub> 405.9954. Anal. Calcd for C<sub>15</sub>H<sub>18</sub>Fe<sub>2</sub>O<sub>3</sub>: C, 56.20; H, 4.47; Fe, 27.51. Found: C, 55.92; H, 4.55; Fe, 27.38.

**(C<sub>5</sub>H<sub>5</sub>)(CO)FeFe(C<sub>5</sub>H<sub>5</sub>)( $\mu$ -CO)( $\mu$ - $\eta^1$ ,  $\eta^3$ -C(C<sub>6</sub>H<sub>5</sub>)C(C<sub>6</sub>H<sub>5</sub>)C=CH<sub>2</sub>) (**6**).** Metallacycle **5a** (0.50 g, 0.94 mmol) in toluene (50 mL) was photolyzed with a 450-W medium-pressure mercury lamp for 5 h. The crude product was chromatographed (activity III alumina, toluene) to give an oily, dark red residue which was purified by dissolving in methylene chloride (5 mL) and adding hexane (30 mL) and evaporating about half the solvent under a stream of nitrogen until dark red **6** was precipitated as a powder. The resulting red powder was washed with hexane to give **6** (0.23 g, 49%): mp 195 °C dec; For **6**: <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 270 MHz)  $\delta$  8.37 (d,  $J$  = 7.6 Hz, 1 H), 7.50 (m, 1 H), 7.10 (m, 8 H), 5.44 (d,  $J$  = 2.3 Hz, 1 H), 5.19 (d,  $J$  = 2.3 Hz, 1 H), 4.79 (s, 5 H), 4.61 (s, 5 H); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 0.07 M Cr(acac)<sub>3</sub>, 50.1 MHz)  $\delta$  266.0 ( $\mu$ -CO), 213.4 (CO), 189.0, 171.0 (FeCFe, C=CH<sub>2</sub>), 156.2 (ipso), 138.8 (ipso'), 130.3 (2 C), 128.6 (2 overlapping resonances), 127.9, 127.7, 126.9 (2 C), 126.1, 124.6 (aromatic), 103.5 (C=CH<sub>2</sub>,  $J$  = 162 Hz), 89.0 (C<sub>5</sub>H<sub>5</sub>,  $J$  = 176 Hz), 85.6 (C<sub>5</sub>H<sub>5</sub>,  $J$  = 176 Hz), 73.2 (C(C<sub>6</sub>H<sub>5</sub>)); IR (CH<sub>2</sub>Cl<sub>2</sub>) 1972 (s), 1777 (s) cm<sup>-1</sup>; exact mass (30 eV) 502.0319, calcd for C<sub>28</sub>H<sub>22</sub>Fe<sub>2</sub>O<sub>2</sub> 502.0319. Anal. Calcd for C<sub>28</sub>H<sub>22</sub>Fe<sub>2</sub>O<sub>2</sub>: C, 66.97; H, 4.42; Fe, 22.24. Found: C, 66.14; H, 4.40; Fe, 21.91.

**X-ray Structural Determination.** A single crystal of Fe<sub>2</sub>-C<sub>29</sub>H<sub>22</sub>O<sub>3</sub>, **5a**, obtained as the toluene disolvate by slow cooling of a saturated toluene solution was mounted in a thin walled glass capillary for the X-ray study. Preliminary examination of the crystal and collection of the diffraction data were carried out by a Syntex-Nicolet P1 diffractometer equipped with a graphite-monochromated Mo K $\alpha$  X-radiation source ( $\lambda$  = 0.710 73 Å). Unit cell dimensions were determined from 30 accurately centered high-angle reflections ( $32^\circ < 2\theta < 38^\circ$ ) each collected at plus and minus  $2\theta$ . The systematic absence ( $hkl$ ,  $h + k = 2n + 1$ , and  $h0l$ ,  $l = 2n + 1$ ) do not distinguish between C2/c and Cc. The space group was subsequently assumed to be the centrosymmetric choice. Successful solution and refinement of the structure indicate the appropriateness of this choice. Structure amplitudes

Table III. Fractional Monoclinic Coordinates for the Non-Hydrogen Atoms

atom	x	y	z
Fe(1)	0.11229 (2)	0.10044 (4)	0.50153 (2)
Fe(2)	0.17827 (2)	0.03569 (4)	0.44082 (2)
C(1)	0.17875 (16)	0.1233 (3)	0.54464 (17)
O(1)	0.21806 (12)	0.1496 (3)	0.58076 (13)
C(2)	0.16686 (13)	0.1788 (3)	0.40871 (16)
O(2)	0.16142 (11)	0.27120 (22)	0.38519 (13)
C(13)	0.11690 (14)	-0.03635 (28)	0.55805 (15)
O(3)	0.12270 (13)	-0.02552 (22)	0.61246 (11)
C(14)	0.10897 (12)	-0.15632 (27)	0.52778 (14)
C(15)	0.10170 (11)	-0.15082 (25)	0.46719 (13)
C(16)	0.10703 (12)	-0.02953 (24)	0.44328 (13)
C(17)	0.10313 (14)	-0.0064 (3)	0.38166 (15)
C(3)	0.03930 (10)	0.13687 (21)	0.51843 (12)
C(4)	0.07731 (10)	0.22360 (22)	0.54690 (11)
C(5)	0.09268 (10)	0.28531 (21)	0.50127 (12)
C(6)	0.06418 (10)	0.23672 (21)	0.44460 (12)
C(7)	0.03119 (10)	0.14498 (21)	0.45520 (12)
C(8)	0.26067 (11)	0.03653 (25)	0.48403 (13)
C(9)	0.25154 (11)	0.03208 (23)	0.42098 (13)
C(10)	0.22350 (11)	-0.07309 (26)	0.39952 (13)
C(11)	0.21530 (11)	-0.13364 (24)	0.44932 (16)
C(12)	0.23827 (12)	-0.06589 (29)	0.50155 (13)
C(18)	0.10775 (8)	-0.26669 (25)	0.56420 (12)
C(19)	0.06487 (12)	-0.34541 (24)	0.54903 (13)
C(20)	0.06512 (15)	-0.44792 (24)	0.58322 (16)
C(21)	0.10804 (11)	-0.4727 (3)	0.63269 (14)
C(22)	0.15081 (16)	-0.39586 (28)	0.64838 (14)
C(23)	0.15078 (12)	-0.29323 (24)	0.61436 (13)
C(24)	0.08556 (9)	-0.25475 (24)	0.42560 (12)
C(25)	0.03885 (12)	-0.24960 (27)	0.37760 (12)
C(26)	0.02171 (15)	-0.3482 (3)	0.34017 (14)
C(27)	0.05087 (13)	-0.4516 (3)	0.35039 (16)
C(28)	0.09696 (17)	-0.45892 (25)	0.39732 (17)
C(29)	0.11447 (13)	-0.36085 (23)	0.43503 (14)
C(S1)	0.25458 (26)	0.1618 (4)	0.24820 (15)
C(S2)	0.27129 (27)	0.0932 (4)	0.20818 (18)
C(S3)	0.3209 (3)	0.1208 (6)	0.20062 (24)
C(S4)	0.3422 (3)	0.2063 (6)	0.22868 (27)
C(S5)	0.33473 (29)	0.2695 (5)	0.26648 (28)
C(S6)	0.2861 (3)	0.2522 (5)	0.27858 (18)
C(S7)	0.2039 (3)	0.1386 (8)	0.25835 (29)
C(SS1)	0.0194 (3)	0.1873 (8)	0.2407 (3)
C(SS2)	0.0209 (3)	0.0658 (9)	0.2363 (4)
C(SS3)	-0.0138 (4)	0.0009 (7)	0.2601 (5)
C(SS4)	-0.0473 (3)	0.0471 (9)	0.2860 (3)
C(SS5)	-0.0475 (3)	0.1633 (10)	0.2892 (3)
C(SS6)	-0.0150 (4)	0.2395 (6)	0.2674 (4)
C(SS7)	0.0542 (5)	0.2601 (13)	0.2171 (5)

<sup>a</sup> The estimated standard deviations of the least significant digits are given in parentheses.

and their standard deviations were calculated from the intensity data by procedures similar to those described previously.<sup>22</sup> Absorption corrections were calculated by using an empirical spherical harmonic model.<sup>23</sup> Crystal data and details of the intensity data collection are given in Table II.

The structure was solved from the Patterson map which revealed the positions of both iron atoms. A series of difference electron density maps revealed the other non-hydrogen atoms in the complex and one toluene of solvation. Constrained least-squares refinement was carried out by using the program RAELS.<sup>24</sup> Standard values for the atomic scattering factors including corrections for anomalous dispersion were employed in the structure analysis.<sup>25</sup> The cyclopentadienyl rings were modeled as groups

possessing  $D_{5h}$  symmetry and a single reorientable relocatable thermal libration axial system (TLX model).<sup>26</sup> Each of the phenyl rings in the molecule was modeled as a group having  $mm2$  symmetry and a reorientable thermal libration axial system (TL model) centered on the carbon atom to which the group is attached. The toluene molecule was modeled as a group having  $mm2$  symmetry and TLX thermal motion. Each of the five groups had refineable local atomic coordinates which were constrained to be planar relative to the groups refineable local axial system and which were constrained to obey symmetry requirements imposed by the use of equal change, equal but opposite change, and equal percentage change instructions. The refineable parameters for each cyclopentadienyl ring included a "breathing motion" coordinate for each ring. Hydrogen atoms were included in idealized positions ( $d[C-H] = 0.95 \text{ \AA}$ ) with thermal parameters defined by the rigid-body thermal models.

Least-squares refinement of this model using both strict<sup>26</sup> and slack<sup>27</sup> constraints converged with discrepancy indices  $R_1 = \sum |F_o| - |F_c| / \sum |F_o| = 0.084$  and  $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2} = 0.152$ . The conventional  $R$  factor for the 20 data with  $(\sin \theta) / \lambda < 0.1$  was 0.401, indicating some serious inadequacy in the model. Examination of the difference electron density map revealed four low intensity peaks in the vicinity of the twofold axis  $(0, y, 1/4)$ . The peak positions did not appear to define any reasonable solvent molecule (based on solvents used in both the preparation and the recrystallization of the complex). The difference electron density map was printed and contoured for the undescribed region. From the contoured map it was possible to assign positions for a second toluene of solvation. This second toluene was disordered about the twofold axis such that several of the individual atoms were overlapping. It was included in the model as an idealized group with half occupancy (the other half occupancy is generated by the twofold symmetry operator). The position of the group was established by overlaying the idealized group on positions taken from the contoured map. The geometry of the second toluene molecule was constrained to be identical with the ordered toluene molecule by use of the same refineable local coordinates. The group origin coordinates and the group orientation angles were included as variables in the least squares refinement as were the variables associated with the TLX thermal model assumed for it.

The final discrepancy indices for this model were  $R_1 = 0.045$  and  $R_2 = 0.057$ . The value of the conventional  $R$  factor for the data with  $(\sin \theta) / \lambda < 0.1$  is 0.036. The estimated standard deviation of an observation of unit weight was 1.76, and the final data/variable ratio was 20.7. There were no significant peaks on the final electron density difference map. Atomic coordinates are given in Table III. Anisotropic thermal parameters, positional parameters for the hydrogen atoms, and a list of  $10|F_o|$  and  $10|F_c|$  are given as supplementary material.

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**Registry No.** *cis*-4, 86420-26-0; *trans*-4, 86420-25-9; **5a**, 94369-88-7; **5a**-2C<sub>7</sub>H<sub>8</sub>, 94369-89-8; **5b**, 94369-90-1; **6**, 94348-93-3; diphenylacetylene, 501-65-5; 2-butyne, 503-17-3.

**Supplementary Material Available:** Tables listing anisotropic thermal parameters, positional parameters for the hydrogen atoms, and structure factors (20 pages). Ordering information is given on any current masthead page.

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