

## The Diphenylacetylene Reaction with Tricarbonylbis( $\eta^2$ -*cis*-cyclooctene)iron in the Presence or Absence of Carbon Monoxide

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Known to be a facile irontricarbonyl transfer reagent, ( $\eta^2$ -*cis*-C<sub>8</sub>H<sub>14</sub>)<sub>2</sub>Fe(CO)<sub>3</sub> **1** transfers its Fe(CO)<sub>3</sub> unit to a variety of ligands at low temperature. Stirring a THF mixture of **1** and PhC≡CPh under N<sub>2</sub>(g) at -60 °C for 1 h then at room temperature overnight provides mainly a flyover-bridge product [-CPh=CPhC(O)-CPh=CPh-]Fe<sub>2</sub>(CO)<sub>6</sub> **2** with the organic bridge on diiron core in a complicated  $\mu$ -(1,2,5- $\eta^3$ :1,4,5- $\eta^3$ ) fashion. The keto fragment in **2** comes presumably from the decomposition of **1** that liberates CO. However, stirring a THF mixture of **1** and PhC≡CPh under CO(g) at -60 °C for 3 h then at room temperature overnight results in [-C(O)CPh=CPhC(O)-]Fe(CO)<sub>4</sub> **3**, a compound not isolated in the earlier thermal or photochemical reactions of PhC≡CPh with ironcarbonyl. The X-ray structure determinations for both **2** and **3** have been performed.

### INTRODUCTION

Acetylenes react with ironcarbonyls to give rise to a variety of organic and organometallic compounds. Although acetylenes may remain intact, for instance, as (*t*-BuC≡C*t*-Bu)Fe(CO)<sub>4</sub><sup>1</sup> and (*t*-BuC≡C*t*-Bu)Fe<sub>2</sub>(CO)<sub>6</sub><sup>1</sup> in the case of *t*-BuC≡C*t*-Bu and as (PhC≡CPh)Fe<sub>3</sub>(CO)<sub>9</sub><sup>2</sup> and (PhC≡CPh)Fe<sub>3</sub>(CO)<sub>8</sub><sup>3</sup> in the case of PhC≡CPh, these complexes are obtained only in low yields. The C-C bond formation, C-H activation, and CO insertion usually occur during an acetylene displacement for a coordinated ligand, resulting in interesting modes of organic chain to metallic framework.<sup>4,5,6</sup> A few examples are: [-C<sub>6</sub>H<sub>4</sub>CH=CPh-]Fe<sub>2</sub>(CO)<sub>6</sub>,<sup>7,8</sup> [-CPh=CPhCPh=CPh-]Fe<sub>2</sub>(CO)<sub>6</sub>,<sup>7,9,10</sup> and [-CPh=CPhC(O)CPh=CPh-]Fe<sub>2</sub>(CO)<sub>6</sub> **2**.<sup>7,11,12,13</sup> The nature and yield of an acetylene complex depend on the reaction condition, in particular the solvent used and the temperature. Similarly, the nature of the product varies considerably with changes from one acetylene to another or with changes of the stoichiometry of ironcarbonyl.

Reported in 1984, ( $\eta^2$ -*cis*-C<sub>8</sub>H<sub>14</sub>)<sub>2</sub>Fe(CO)<sub>3</sub> **1** was found to be a facile Fe(CO)<sub>3</sub> transfer reagent which is able to transfer its Fe(CO)<sub>3</sub> unit to a variety of ligands in common organic solvents.<sup>14</sup> The (*cis*-C<sub>8</sub>H<sub>14</sub>) displacement reaction occurs at temperatures lower than -35 °C. Successful preparation of (diene)Fe(CO)<sub>3</sub> complexes employing **1** followed in the literature, for instance, (2-stannylated butadiene)Fe(CO)<sub>3</sub><sup>15</sup> and (substituted cyclohexadiene)Fe(CO)<sub>3</sub>.<sup>16,17,18</sup> Since most of the reported acetylene reactions with ironcar-

bonyls, e.g., Fe(CO)<sub>5</sub>, Fe<sub>2</sub>(CO)<sub>9</sub>, or Fe<sub>3</sub>(CO)<sub>12</sub>, were under thermal or photochemical conditions, it would be interesting to know to what extent acetylene displacement for (*cis*-C<sub>8</sub>H<sub>14</sub>) in **1** would occur at a much lower temperature. Thus, we have attempted a study on the PhC≡CPh reaction with **1** under both N<sub>2</sub> and CO atmospheric conditions. The results are reported herein.

### EXPERIMENTAL SECTION

#### General

All manipulations were performed under an atmosphere of prepurified nitrogen with standard Schlenk techniques, and all solvents were distilled from an appropriate drying agent.<sup>19</sup> IR spectra were recorded in CH<sub>2</sub>Cl<sub>2</sub> using CaF<sub>2</sub> optics on a Perkin-Elmer 882 spectrophotometer. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained on Bruker AC200/AC300 spectrometers, with chemical shifts reported in  $\delta$  values relative to the residual solvent resonance of CDCl<sub>3</sub> (<sup>1</sup>H 7.24 ppm, <sup>13</sup>C 77.0 ppm). Mass spectra were obtained on a VG system, model 70-250S spectrometer. Microanalytical data were obtained with the use of a Perkin-Elmer 240C elemental analyzer, independently operated by the Institute of Chemistry, Academia Sinica. The melting points were measured on a Yanaco micro melting point apparatus. Compound **1** was prepared following a previous procedure.<sup>14</sup> All reagents were obtained from commercial sources (e.g. Aldrich, Merck) and used without further puri-

fication.

#### Reaction of 1 and PhC≡CPh under N<sub>2</sub> in THF

Under N<sub>2</sub>, compound 1 (360 mg, 1.00 mmol) was dissolved in pre-cooled THF (30 mL) in a round-bottomed flask and maintained at -60 °C. PhC≡CPh (360 mg, 2.00 mmol) in THF (10 mL) was then added dropwise *via* a pressure-equalizing dropping funnel. The mixture was stirred for 1 h before being slowly warmed to room temperature and stirred overnight. The solvent was then evaporated to dryness under vacuum. The resulting residue was extracted with ether. The ether-soluble fraction was purified by SiO<sub>2</sub> column chromatography, eluting with 1:8 CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane eventually adjusted to 2:1 CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane, to give recovered PhC≡CPh (252 mg, 1.41 mmol), two minor unidentified byproducts, and a major, red powdery product [-CPh=CPhC(O)CPh=CPh-]Fe<sub>2</sub>(CO)<sub>6</sub> 2 (101 mg, 0.15 mmol, 50% yield based on the consumed PhC≡CPh). The crystals suitable for X-ray diffraction were grown from CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane by a slow evaporation method.

2: m.p. 154 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{\text{CO}}$  2075 (m), 2051 (s), 2018 (s), 1661 (w) cm<sup>-1</sup> [lit.<sup>13</sup> (MeC<sub>6</sub>H<sub>11</sub>) 2065, 2043, 2010, 1662 cm<sup>-1</sup>]; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.54-7.07 (m, Ph); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  210.0, 207.1 (br, C≡O), 195.6 (s, C=O), 192.6 (s, C=C $\alpha$ -Fe), 149.1, 137.8, 129.2, 128.4, 128.1, 127.8, 127.5, 127.1 (Ph), 94.3 (s, C $\beta$ =C-Fe) [lit.<sup>12</sup>  $\delta$  209.0, 205.8, 205.4, 195.0, 192.3, 93.8, Ph omitted]; MS (*m/z*) 665 (M<sup>+</sup> + 1).

#### Reaction of 1 and PhC≡CPh under N<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>

Under N<sub>2</sub>, compound 1 (500 mg, 1.40 mmol) was dissolved in pre-cooled CH<sub>2</sub>Cl<sub>2</sub> (75 mL) in a round-bottomed flask and maintained at -60 °C, then PhC≡CPh (500 mg, 2.80 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (25 mL) was added dropwise *via* a pressure-equalizing dropping funnel. The mixture was stirred for 3 h before being slowly warmed to room temperature and stirred overnight. The solvent was then evaporated to dryness under vacuum. The resulting residue was extracted with ether. The ether-soluble fraction was purified by SiO<sub>2</sub> column chromatography, eluting with 1:100 ethylacetate/*n*-hexane eventually adjusted to 1:5 ethylacetate/*n*-hexane, to give recovered PhC≡CPh (287 mg, 1.60 mmol) and 2 (199 mg, 0.30 mmol, 50% yield based on the consumed PhC≡CPh).

#### Reaction of 1 and PhC≡CPh under CO in THF

Compound 1 (500 mg, 1.40 mmol) was dissolved in pre-cooled THF (50 mL) in a round-bottomed flask and maintained at -60 °C. Throughout the reaction a stream of CO (1 atm) was purged through a needle that was immersed

under the surface of THF solution. PhC≡CPh (500 mg, 2.80 mmol) in THF (200 mL) was added dropwise to the solution *via* a pressure-equalizing dropping funnel. The mixture was stirred for 3 h before being slowly warmed to room temperature and stirred overnight. The solvent was then evaporated to dryness. The resulting residue was extracted with ether. The ether-soluble fraction was purified by SiO<sub>2</sub> column chromatography, eluting with 1:8 CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane slowly adjusted to 2:1 CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane, to give recovered PhC≡CPh (400 mg, 2.25 mmol) and one major, orange solid [-C(O)CPh=CPhC(O)-]Fe(CO)<sub>3</sub> 3 (114 mg, 0.28 mmol, yield 50% based on the unrecovered PhC≡CPh). The crystals suitable for X-ray diffraction were grown from CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane by a slow evaporation method.

3: m.p. 116-118 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{\text{CO}}$  2117 (s), 2054 (s), 2033 (vs), 1655 (m) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.23-7.03 (m, Ph); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  241.9 (s, 2C=O), 202.2 (s, C≡O), 198.9 (s, C=O), 169.2 (s, C=C), 131.6, 129.4, 128.8, 128.1 (Ph); Anal. Calcd. for C<sub>20</sub>H<sub>10</sub>FeO<sub>6</sub>: C, 59.73; H, 2.51; Found: C, 59.73; H, 2.71.

#### Reaction of 1 and PhC≡CPh under CO in CH<sub>2</sub>Cl<sub>2</sub>

Compound 1 (440 mg, 1.22 mmol) was dissolved in pre-cooled CH<sub>2</sub>Cl<sub>2</sub> (70 mL) in a round-bottomed flask and maintained at -60 °C. Throughout the reaction a stream of CO (1 atm) was purged through a needle that was immersed under the surface of CH<sub>2</sub>Cl<sub>2</sub> solution. PhC≡CPh (444 mg, 2.49 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added dropwise to the solution *via* a pressure-equalizing dropping funnel. The mixture was stirred for 3 h before being slowly warmed to room temperature and stirred overnight. The solvent was then evaporated to dryness. The resulting residue was extracted with ether. The ether-soluble fraction was purified by SiO<sub>2</sub> column chromatography, eluting with pure *n*-hexane slowly adjusted to 1:100 ethylacetate/*n*-hexane, to give recovered PhC≡CPh (298 mg, 1.67 mmol) and 3 (250 mg, 0.62 mmol, yield 76%, based on the unrecovered PhC≡CPh).

#### X-ray Structure Analysis

A summary of crystal data and refinement details for 2 and 3 is given in Table 1. Diffraction intensities were measured with background counts made for half the total scan time on each side of peak. Three standard reflections, re-measured after every hour, showed no significant decrease in intensity during data collection. Data were corrected for Lorentz-polarization and absorption (empirical  $\psi$  corrections). The structure were solved by direct methods MULTAN.<sup>20</sup> Calculations and full-matrix least-squares refine-

Table 1. Crystal Data and Structure Refinement Details for [-CPh=CPhC(O)CPh=CPh-] $\text{Fe}_2(\text{CO})_6$  **2c** and [-C(O)CPh=CPhC(O)-] $\text{Fe}(\text{CO})_4$  **3**

	<b>2c</b>	<b>3</b>
crystal system	monoclinic	monoclinic
space group	P2 <sub>1</sub> /n	P2 <sub>1</sub> /c
cell dimensions		
a, Å	11.922(2)	10.6226(6)
b, Å	10.590(3)	13.2557(9)
c, Å	23.876(3)	13.0265(8)
a, deg.	90	90
b, deg.	103.91(1)	89.980(5)
g, deg.	90	90
volume, Å <sup>3</sup>	2926.(1)	1834.9(2)
reflins. for cell params.	25	25
2 $\theta$ range, deg.	15.85-30.76	14.68-30.54
crystal dimensions, mm	0.34 × 0.25 × 0.16	0.63 × 0.34 × 0.44
empirical formula	C <sub>35</sub> H <sub>20</sub> Fe <sub>2</sub> O	C <sub>20</sub> H <sub>10</sub> FeO <sub>6</sub>
formula weight	664.23	402.14
F(000)	1351.79	815.88
Z	4	4
D <sub>calc</sub> , g/cm <sup>3</sup>	1.508	1.456
$\mu$ , (mm <sup>-1</sup> )	1.04	0.85
radiation	MoK $\alpha$	MoK $\alpha$
$\lambda$ , Å	0.7107	0.7107
diffractometer	Nonius CAD4	Nonius CAD4
scan mode	$\theta/2\theta$	$\theta/2\theta$
2 $\theta$ (max)	45.0	45.0
h,k,l ranges	-12 < h < 12 0 < k < 11 0 < l < 25	-11 < h < 11 0 < k < 14 0 < l < 14
no. reflins. measd	7623	2536
no. unique reflins.	3825	2388
no. observations	2656[I <sub>o</sub> > 2.5 $\sigma$ (I <sub>o</sub> )]	1937[I <sub>o</sub> > 2.5 $\sigma$ (I <sub>o</sub> )]
absorption corr.	$\psi$ scans	$\psi$ scans
min. - max. trans. factors	0.930-1.000	0.955-1.000
no. atoms	64	37
no. parameters	397	244
weights	counting statistics	counting statistics
R <sup>a</sup>	0.059	0.028
R <sub>w</sub> <sup>b</sup>	0.067	0.033
GOF <sup>c</sup>	2.72	1.84
max. $\Delta$ /s	0.0285	0.0031
D-map highest peak, e Å <sup>-3</sup>	0.460	0.140
deepest hole, e Å <sup>-3</sup>	-0.380	-0.230

<sup>a</sup>  $R = \sum |F_o - F_c| / \sum F_o$ . <sup>b</sup>  $R_w = \{\sum w(|F_o - F_c|)^2 / \sum w F_o^2\}^{1/2}$ .

<sup>c</sup>  $GOF = \{\sum w(|F_o - F_c|)^2 / (n - v)\}^{1/2}$ , n = no. of observations, v = no. of parameters.

ments were performed utilizing the NRCVAX program package.<sup>21</sup> All non-H atoms were refined with anisotropic thermal parameters and all hydrogen atoms fixed (C-H = 1.00 Å) at the anisotropic convergence stage. Scattering factor curves of Fe, O, C, and H were taken from the International Tables.<sup>22</sup> Final fractional coordinates of **2** and **3** are given in Tables 2 and 3, respectively. Relevant bond lengths and angles of **2** and **3** are listed in the captions of Figs. 1 and

2, showing respectively the molecular plots for **2** and **3**.

## RESULTS AND DISCUSSION

### Reaction

Stirring **1** with 2 equiv. PhC $\equiv$ CPh under N<sub>2</sub>(g) in THF at -60 °C for 1 h then at ambient temperature overnight gave

Table 2. Final Fractional Coordinates for  $[-\text{CPh}=\text{CPhC}(\text{O})\text{CPh}=\text{CPh}]_2\text{Fe}_2(\text{CO})_6$ , **2c**

Atom	x	y	z	Biso
Fe1	0.03272(10)	0.19000(11)	0.18551(5)	3.71(6)
Fe2	-0.05290(12)	0.25466(11)	0.08131(5)	4.17(6)
O1	0.1366(7)	-0.0451(7)	0.1576(4)	8.4(5)
O2	-0.0604(6)	0.1054(7)	0.2823(3)	6.8(4)
O3	0.2716(6)	0.2378(7)	0.2532(3)	6.4(4)
O4	0.1598(8)	0.2107(7)	0.0430(3)	8.5(5)
O5	-0.1405(7)	0.4909(7)	0.0233(3)	7.7(5)
O6	-0.1563(8)	0.0946(6)	-0.0181(3)	8.6(5)
O7	-0.2318(5)	0.3875(6)	0.1985(2)	5.2(3)
C1	0.0905(8)	0.0451(10)	0.1666(4)	5.3(5)
C2	-0.0210(8)	0.1360(9)	0.2457(4)	4.8(5)
C3	0.1782(9)	0.2242(8)	0.2262(4)	4.5(5)
C4	0.0790(10)	0.2295(9)	0.0594(4)	5.5(6)
C5	-0.1062(8)	0.3977(10)	0.0447(4)	5.1(5)
C6	-0.1232(10)	0.1533(9)	0.0216(4)	6.1(6)
C7	-0.1619(8)	0.3485(7)	0.1735(3)	3.7(4)
C8	-0.0343(7)	0.3800(7)	0.1906(3)	3.6(4)
C9	0.0239(7)	0.3640(7)	0.1472(3)	3.7(4)
C10	-0.1959(7)	0.2566(7)	0.1230(3)	3.8(4)
C11	-0.1248(7)	0.1475(8)	0.1352(3)	3.7(4)
C21	-0.0039(7)	0.4676(8)	0.2411(3)	3.7(4)
C22	-0.0550(8)	0.5871(8)	0.2356(3)	4.6(5)
C23	-0.0323(9)	0.6730(9)	0.2815(5)	6.0(6)
C24	0.0428(9)	0.6378(11)	0.3332(4)	5.8(6)
C25	0.0914(8)	0.5224(11)	0.3387(4)	5.7(6)
C26	0.0717(7)	0.4351(9)	0.2940(3)	4.5(5)
C31	0.1190(8)	0.4535(8)	0.1410(3)	3.9(4)
C32	0.2301(9)	0.4138(9)	0.1413(4)	5.1(5)
C33	0.3101(9)	0.4992(12)	0.1307(4)	6.0(6)
C34	0.2820(11)	0.6218(12)	0.1178(4)	6.2(6)
C35	0.1677(12)	0.6636(9)	0.1157(4)	6.4(7)
C36	0.0925(8)	0.5789(8)	0.1292(3)	4.3(5)
C41	-0.3169(7)	0.2652(8)	0.0859(3)	3.9(4)
C42	-0.3788(8)	0.3760(9)	0.0840(4)	4.6(5)
C43	-0.4897(9)	0.3888(10)	0.0492(4)	5.7(6)
C44	-0.5383(10)	0.2911(13)	0.0159(5)	7.5(7)
C45	-0.4790(11)	0.1792(11)	0.0146(5)	8.4(7)
C46	-0.3659(9)	0.1677(9)	0.0497(4)	6.6(6)
C51	-0.1698(7)	0.0166(7)	0.1302(3)	3.8(4)
C52	-0.1341(7)	-0.0781(8)	0.0983(3)	4.2(5)
C53	-0.1797(8)	-0.1979(9)	0.0972(4)	4.8(5)
C54	-0.2611(8)	-0.2262(8)	0.1274(4)	5.0(5)
C55	-0.2963(8)	-0.1339(10)	0.1605(4)	5.2(5)
C56	-0.2503(8)	-0.0123(8)	0.1613(3)	4.3(5)

**2** (18% yield if based on  $(\eta^2\text{-cis-C}_8\text{H}_{14})_2\text{Fe}(\text{CO})_3$ ; 55% yield if based on unrecovered  $\text{PhC}\equiv\text{CPh}$ ). Very similar results were also obtained in  $\text{CH}_2\text{Cl}_2$ . The raise of temperature should be very slow to maximize the yield of **2**. The large amount of unreacted  $\text{PhC}\equiv\text{CPh}$  (252 mg recovered out of initial 360 mg) suggested that at low temperature the  $\text{PhC}\equiv\text{CPh}$  replacement for  $(\text{cis-C}_8\text{H}_{14})$  was not facile enough

as would be expected. The originally envisaged products were  $(\text{PhC}\equiv\text{CPh})_2\text{Fe}(\text{CO})_3$  if  $\text{PhC}\equiv\text{CPh}$  to Fe ratio is 2:1 or  $[(\text{PhC}\equiv\text{CPh})\text{Fe}(\text{CO})_3]_n$  if  $\text{PhC}\equiv\text{CPh}$  to Fe ratio is 1:1. But neither one was realized in the mixture. The two minor, unidentified byproducts were believed to be the cyclopentadienone- or quinone-iron derivatives. Cotton *et al.* reported that the preparation of **2** was achieved by stirring 1:1  $\text{PhC}\equiv\text{CPh}$  and  $\text{Fe}_2(\text{CO})_9$  under  $\text{N}_2(\text{g})$  in THF at 23 °C for 4 h (80% yield based on  $\text{PhC}\equiv\text{CPh}$ ).<sup>13</sup> Hickey *et al.* reported that the preparation of **2** was made by stirring 2:1  $\text{PhC}\equiv\text{CPh}$  and  $\text{Fe}_2(\text{CO})_9$  under  $\text{N}_2(\text{g})$  in petroleum ether for 24 h [60% yield based on  $\text{Fe}_2(\text{CO})_9$ ].<sup>12</sup> The preparation of **2** with the current means is comparable in yield to Hickey's method. Yet the reaction with **1** is performed at a much lower temperature. The keto fragment of **2** comes presumably from the decomposition of **1**. In the literature, compound **2** is an already known molecule, whose properties have been studied in a number of experiments, for instance, <sup>13</sup>C NMR. If the keto fragment of **2** was derived from the decomposition of **1**, then the keto fragment of **2** might possibly be supplied by the externally bubbled  $\text{CO}(\text{g})$ . For comparison, the reac-

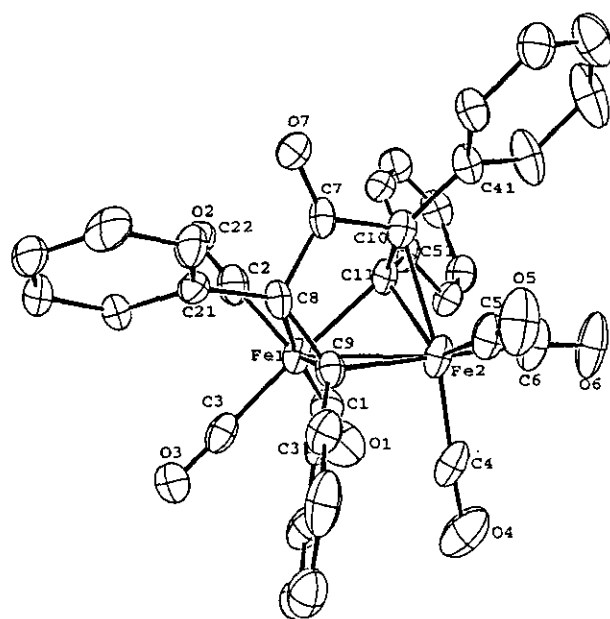


Fig. 1. Molecular plot of **2c**. The thermal ellipsoids for non-H atoms are plotted at the 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Fe1-Fe2 2.5456(16), Fe1-C11 2.201(8), Fe2-C9 1.990(8), C8-C9 1.387(11), C10-C11 1.422(12), C8-C7 1.515(12), C10-C7 1.527(11), C7-O7 1.208(11); Selected bond angles (deg.): Fe2-C9-C8 116.3(6), Fe1-C11-C10 111.4(6), C9-C8-C7 115.0(7), C11-C10-C7 108.9(6), C8-C7-C10 114.3(7).

tion under CO(g) instead of N<sub>2</sub>(g) was performed and gave a completely different result. Stirring **1** with 2 equiv. PhC≡CPh under CO(g) in THF at -60 °C for 3 h then at ambient temperature overnight resulted in, not **2**, but mainly an orange solid **3** (20% yield if based on ( $\eta^2$ -*cis*-C<sub>8</sub>H<sub>14</sub>)<sub>2</sub>-

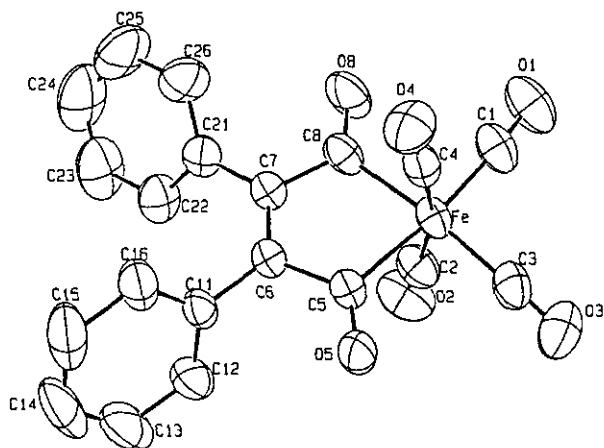


Fig. 2. ORTEP plot of **3**. The thermal ellipsoids for non-H atoms are plotted at the 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Fe-C1 1.851(3), Fe-C2 1.808(3), Fe-C3 1.857(3), Fe-C4 1.810(3), Fe-C5 2.0151(24), Fe-C8 2.021(3), C7-C8 1.515(4), C5-C6 1.509(3), C6-C7 1.340(4), C8-O8 1.202(3), C5-O5 1.202(3); Selected bond angles (deg.): C1-Fe-C5 171.52(12), C2-Fe-C4 164.67(12), C3-Fe-C8 172.78(11), C2-Fe-C8 85.98(12), C4-Fe-C8 83.25(11), C5-Fe-C8 81.91(11), Fe-C5-C6 113.22(17), Fe-C8-C7 113.45(18), C5-C6-C7 116.25(21), C8-C7-C6 114.90(22).

Fe(CO)<sub>3</sub>; 50% yield if based on consumed PhC≡CPh). The reaction gave even better yield in CH<sub>2</sub>Cl<sub>2</sub> (76%, based on consumed PhC≡CPh). The overall reactions are shown in Scheme 1.

Surprisingly, complex **3** could not be obtained directly from reactions of PhC≡CPh with ironcarbonyl. In the literature, complexes of the tetracarbonyl-ferra-cyclopent-3-en-2,5-dione skeleton were prepared only independently. Korerer von Gustorf *et al.* photochemically converted ( $\eta^2$ -CHBr=CHBr)Fe(CO)<sub>4</sub> to Fe(CO)<sub>3</sub>[ $\mu$ -(1- $\eta^1$ :1,2- $\eta^2$ )-*trans*-CHBr=CH]( $\mu$ -Br)Fe(CO)<sub>3</sub> which when heated in concentrated acetic acid gave the parent [-C(O)CH=CHC(O)-]Fe(CO)<sub>4</sub> in 15% yield.<sup>23</sup> Bird *et al.* found that the reaction of diphenylcyclopropane with Fe<sub>2</sub>(CO)<sub>9</sub> in benzene at room temperature in the dark yielded **3** as an additional product apart from isolation of PhC≡CPh, [ $\eta^4$ -C<sub>3</sub>Ph<sub>4</sub>(=O)]Fe(CO)<sub>3</sub>, [-CPh=CPhCPh=CPh-]Fe<sub>2</sub>(CO)<sub>6</sub>, and **2**. Presumably the formation of **3** with the diphenylcyclopropane route was *via* a CO insertion in the intermediate [-CPh=CPhC(O)-]Fe(CO)<sub>4</sub>.<sup>24</sup> Whiting *et al.* obtained **3** in the oxidation of [-C(OH)=CPhCPh=C(OH)-]Fe<sub>2</sub>(CO)<sub>6</sub> by FeCl<sub>3</sub>.<sup>25</sup> Thus the reaction of PhC≡CPh with **1** under CO likely affords a new strategy for the preparation of complexes of tetracarbonyl-ferra-cyclopent-3-en-2,5-dione skeleton.

In the presence of CO(g), the carbonyl insertion was enhanced such that **3** was preferred to **2** in the PhC≡CPh reaction with **1** at low temperature. When the reaction vessel was filled partially with N<sub>2</sub> and partially with CO, the product distribution varied between **2** and **3**. Qualitatively, the greater the partial pressure of CO, the higher the yield of **3**.

### Scheme 1

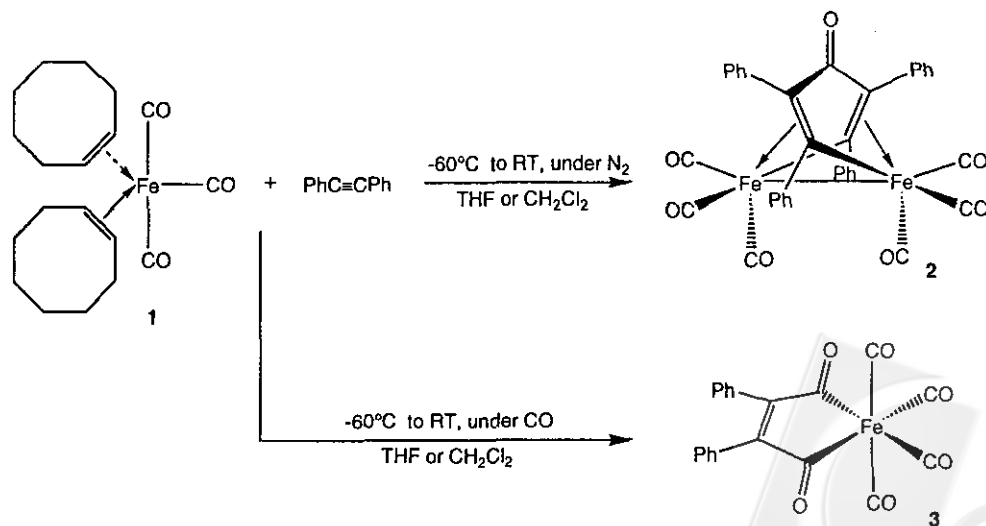


Table 3. Final Fractional Coordinates for  $[-C(O)CPh=CPhC(O)-]Fe(CO)_4$ , **3**

Atom	x	y	z	Biso
Fe	0.54965(3)	0.33572(3)	0.15133(3)	3.73(2)
O1	0.7790(2)	0.2305(2)	0.2265(2)	7.7(1)
O2	0.4185(2)	0.3450(2)	0.3499(2)	7.4(1)
O3	0.6418(2)	0.5484(2)	0.1576(2)	6.3(1)
O4	0.6048(2)	0.3042(1)	-0.0674(2)	5.4(1)
O5	0.3530(2)	0.4695(1)	0.0827(2)	5.0(1)
O8	0.5182(2)	0.1195(2)	0.1483(2)	6.4(1)
C1	0.6943(3)	0.2732(2)	0.1985(2)	5.2(2)
C2	0.4725(3)	0.3417(2)	0.2749(2)	4.9(1)
C3	0.6085(3)	0.4675(3)	0.1565(2)	4.5(1)
C4	0.5859(2)	0.3183(2)	0.0167(2)	3.9(1)
C5	0.3805(2)	0.3833(2)	0.1008(2)	3.5(1)
C6	0.2868(2)	0.2988(2)	0.0873(2)	3.3(1)
C7	0.3292(2)	0.2055(2)	0.1061(2)	3.5(1)
C8	0.4668(2)	0.1993(2)	0.1360(2)	4.1(1)
C11	0.1582(2)	0.3255(2)	0.0526(2)	3.7(1)
C12	0.0783(2)	0.3794(2)	0.1161(2)	5.3(2)
C13	-0.0417(3)	0.4034(3)	0.0835(4)	7.2(2)
C14	-0.0819(3)	0.3767(3)	-0.0114(4)	7.9(2)
C15	-0.0035(3)	0.3238(3)	-0.0758(3)	6.9(2)
C16	0.1176(3)	0.2973(2)	-0.0445(2)	5.0(1)
C21	0.2525(2)	0.1126(2)	0.1021(2)	4.1(1)
C22	0.1365(3)	0.1105(2)	0.1513(2)	5.4(1)
C23	0.0627(4)	0.0252(3)	0.1477(3)	8.0(2)
C24	0.1019(5)	-0.0572(3)	0.0956(4)	9.7(3)
C25	0.2152(5)	-0.0573(3)	0.0471(4)	8.8(3)
C26	0.2922(3)	0.0270(2)	0.0501(2)	5.9(2)

The yield of **3** increased at the expense of **2**.

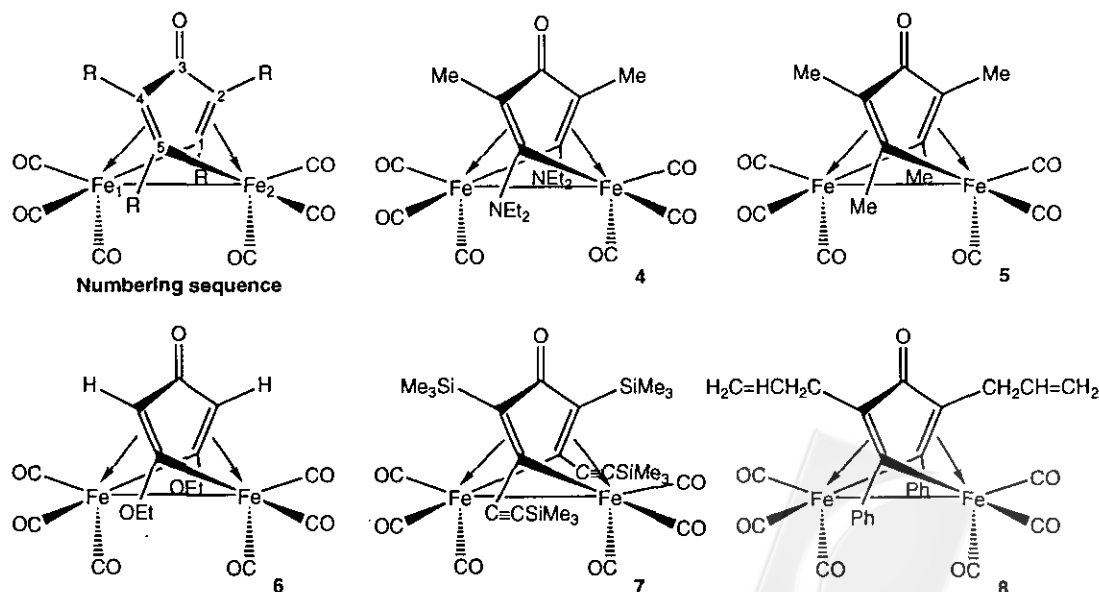
### Spectroscopy

The IR  $\nu_{CO}$  absorptions of **3** (2117, 2054, 2033  $cm^{-1}$ ) are much higher in wave numbers than those of **2** (2075, 2051, 2018  $cm^{-1}$ ). Compound **3** has the band shape of a tetracarbonyliron moiety. The high IR  $\nu_{CO}$  absorptions indicate that the  $Fe(CO)_4$  fragment in **3** is attached to strongly electron-withdrawing group(s). The intense ketonic absorption of **3** at 1655  $cm^{-1}$  is a sharp contrast to the weak absorption of **2** at 1661  $cm^{-1}$  -- 2 ketonic groups in **3** vs. only 1 in **2**. In the  $^{13}C$  NMR spectrum of **2**, there are apparently two phenyl types whereas in the  $^{13}C$  NMR spectrum of **3**, there is only one phenyl type. The  $^{13}C$  peak assignments for **3** are  $\delta$  241.9 to the ketonic carbons attached to the Fe metal center,  $\delta$  169.1 to the olefinic carbons, and  $\delta$  202.2 and 198.9 to the equatorial and axial CO, respectively, parallel to the  $^{13}C$  assignments in the parent tetracarbonyl-ferra-cyclopent-3-en-2,5-dione.<sup>23</sup>

### X-ray Structure

In the literature, there are six X-ray structures with a flyover-bridge diiron core -- **2**, **4**,<sup>26</sup> **5**,<sup>27</sup> **6**,<sup>28</sup> **7**,<sup>29</sup> and **8**<sup>30</sup> (Scheme II). Among them, **2** has already been reported to crystallize in Pcab (**2a**)<sup>13</sup> and in P2<sub>1</sub>/n (**2b**).<sup>31</sup> During purification of **2** in this study, a third crystalline form has been found (**2c**) whose space group is also P2<sub>1</sub>/n yet with much

Scheme II



smaller cell parameters, cell volume of **2b** being 3295.9(9) Å<sup>3</sup> and that of **2c** being 2926.0(11) Å<sup>3</sup>. Accordingly, a structure determination of **2c** has been performed to compliment the earlier studies. The difference in packing is apparent as there are no solvate molecules involved in the structure of **2c** whereas it is 1:0.5 **2**/C<sub>6</sub>H<sub>6</sub> composition in the structure of **2b**. The molecular structure of **2c** is displayed with complete structure in Fig. 1. With phenyl groups omitted, Fig. 3 shows in two side views the conformation of a five-carbon chain which links two iron atoms with direct metal-metal bonding, each olefin function employing the  $\eta^1$ : $\eta^2$  mode to

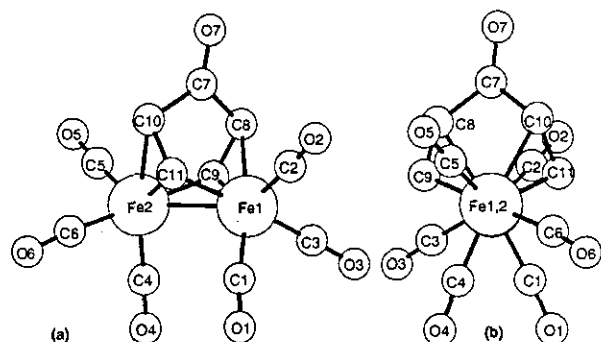


Fig. 3. Two side views of **2c** to show the conformation of five-carbon chain linking two iron centers: (a) and (b) being perpendicular to and along the Fe<sub>1</sub>-Fe<sub>2</sub> axis. The phenyl groups are omitted for clarity.

coordinate the diiron core. Overall the organic chain is in a complicated [ $\mu$ -(1,2,5- $\eta^3$ :1,4,5- $\eta^3$ )] bonding pattern. Although not constrained crystallographically, compound **2c** comes very close to having a C<sub>2</sub> axis passing through the keto group and bisecting the Fe-Fe bond. The symmetry-related structural parameters are consistent with each other. The torsion angle of the  $\eta^1$ : $\eta^2$  olefin groups clearly give differentiation to the  $\sigma$  Fe-C bond and  $\pi$  Fe-C bond at the terminal C atoms, e.g., the torsion angles Fe1-C11-C10-C7 = 30.3(3)° and Fe2-C9-C8-C7 = 18.8(3)° for  $\sigma$  bond (Fe1-C11 and Fe-C9) and Fe1-C9-C8-C7 = 87.7(6)° and Fe2-C11-C10-C7 = 99.8(6)° for  $\pi$  bond (Fe1-C9 and Fe2-C11). If a plane is considered to pass through the keto group and perpendicular to the Fe-Fe bond, the displacements of the atoms of the five-carbon chain conform to a C<sub>2</sub> symmetry e.g., for C9, C8, C7, C10, and C11. The displacements are found to be 0.049(10), 0.627(11), 0.030(12), -0.816(11), and -0.050(10) Å from the plane, respectively.

Based on common molecular features, Table 4 is a summary of relevant geometrical parameters for seven flyover-bridge diiron structures, all being approximately in C<sub>2</sub> molecular symmetry. The Fe-Fe distances average 2.542 Å. For a  $\sigma$  Fe-C bonding, the average torsion angle Fe1-1-2-3 = 27.5° and for a  $\pi$  Fe-C bonding, Fe2-1-2-3 = 95.3°. The average length of  $\sigma$  Fe-C bonds is 1.991 Å and that of the terminal  $\pi$  Fe-C bonds is 2.081 Å.

Table 4. Selected Structural Parameters of Flyover-Bridge Complexes **2**, **4**, **5**, **6**, **7**, and **8**.<sup>a</sup> The Numbering System Used is Shown in Scheme II

	2a	2b	2c	4	5	6 <sup>b</sup>	7	8	Ave.	
Distances										
Fe <sub>1</sub> -Fe <sub>2</sub> , Å	2.537	2.536	2.546	2.586	2.506	2.554	2.557	2.527	2.535	2.542
Fe <sub>1</sub> -1, Å	1.999	2.018	2.021	2.072	1.937	1.918	1.912	2.009	2.004	1.991
Fe <sub>2</sub> -5, Å	2.014	2.050	1.990	2.078	1.941	1.919	1.915	2.009	2.004	1.991
1-2, Å	1.408	1.414	1.422	1.478	1.400	1.403	1.386	1.423	1.424	1.417
4-5, Å	1.397	1.410	1.387	1.440	1.434	1.395	1.386	1.423	1.424	1.414
Fe <sub>1</sub> -5, Å	2.031	2.034	2.048	2.058	2.082	2.178	2.136	2.087	2.034	2.080
Fe <sub>2</sub> -1, Å	2.082	2.072	2.052	2.064	2.056	2.135	2.134	2.087	2.034	2.083
Angles										
∠1-Fe <sub>1</sub> -Fe <sub>2</sub> , °	53.05	52.63	51.86	51.16	53.27	54.83	54.77	53.31	51.65	53.08
∠Fe <sub>1</sub> -Fe <sub>2</sub> -5, °	51.46	51.32	51.94	50.94	54.04	56.15	54.81	53.31	51.65	52.96
∠5-Fe <sub>1</sub> -Fe <sub>2</sub> , °	50.84	51.89	49.92	51.64	48.98	47.03	47.11	50.54	50.58	49.83
∠Fe <sub>1</sub> -Fe <sub>2</sub> -1, °	50.09	50.73	50.78	51.43	49.04	47.26	47.03	50.54	50.58	49.59
Torsion angles										
Fe <sub>1</sub> -1-2-3, °	18.61	22.21	30.3	25.11	27.28	32.31	31.52	29.13	23.40	26.2
Fe <sub>2</sub> -5-4-3, °	30.50	31.95	18.8	24.99	23.98	31.91	29.23	29.13	23.40	28.1
Fe <sub>1</sub> -5-4-3, °	100.5	100.9	87.7	94.63	92.03	96.49	94.99	95.84	93.37	96.1
Fe <sub>2</sub> -1-2-3, °	86.80	89.60	99.8	94.70	94.94	98.34	98.41	95.84	93.37	94.6

<sup>a</sup> This table was compiled with the Cambridge Structural Database system.<sup>33</sup>

<sup>b</sup> Two crystallographically independent molecules were present in structure **6**.

The structure of **3** has been determined by a single crystal X-ray diffraction study, too. As depicted in Fig. 2, the coordination geometry around Fe is octahedral with the ferra-cyclopenta-3-en-2,5-dione ring roughly planar (deviations  $\pm 0.11$  Å for equatorial atoms except phenyl groups) and  $\angle C5-Fe-C8 = 81.9(1)^\circ$ . The axial CO ligands are leaning towards the ring with  $\angle C2-Fe-C4$  of  $164.7(1)^\circ$ . The phenyl substituents show dihedral angles with the ferra-cyclopenta-3-en-2,5-dione ring of *ca*  $67^\circ$  for C11-C16 and of *ca*  $48^\circ$  for C21-C26, respectively, the two phenyl groups being in conrotatory directions. Unconstrained in the solid state, compound **3** also reveals in its structural parameters an approximate  $C_2$  molecular symmetry with the axis passing through Fe and the midpoint of olefin. The equatorial Fe-CO lengths [average  $1.854(3)$  Å] are much longer than the axial Fe-C(CO) length [average  $1.809(3)$  Å], suggesting that the dione competes favorably for the  $\pi$ -back bonding from Fe center. Such an elongation of the equatorial Fe-C(CO) bond has also been reported in the X-ray structure of the parent tetracarbonyl-ferra-cyclopenta-3-en-2,5-dione.<sup>32</sup>

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#### SUPPLEMENTARY MATERIAL

Tables of crystal data and refinement details, atomic coordinates, anisotropic thermal parameters, bond distances, angles, torsion angles, and plane calculations for **2c** and **3** (17 pages) are available from L.-K. L.

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#### Key Words

Diphenylacetylene; Ironcarbonyl; *cis*-Cyclooctene.

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