

# Reaction of Bis( $\eta$ -cyclopentadienyl)diiron Tetracarbonyl with Aryllithium Reagents. A Convenient Synthesis of Diiron Carbonyl Complexes with a Bridging Carbene Ligand. Crystal and Molecular Structures of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\mu\text{-CO})\{\mu\text{-C}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_5\}]$ and $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\mu\text{-CO})\{\mu\text{-C}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CF}_3\text{-}p\}]$

Jiabi Chen,<sup>\*,1a</sup> Desheng Li,<sup>1a</sup> Yong Yu,<sup>1a</sup> and Chenggang Chen<sup>1b</sup>

Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China, and Central Laboratory, Hangzhou University, Hangzhou 310028, China

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The reactions of  $[\eta\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$  (**1**) with aryllithium reagents ArLi (Ar = C<sub>6</sub>H<sub>5</sub>, *o*-, *m*-, *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, *p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>) at 0 °C in ether, after subsequent alkylation with Et<sub>3</sub>OBF<sub>4</sub> in aqueous solution at 0 °C, give the dimetal bridging alkoxycarbene complexes  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\mu\text{-CO})\{\mu\text{-C}(\text{OC}_2\text{H}_5)\text{Ar}\}]$  (**2**, Ar = C<sub>6</sub>H<sub>5</sub>; **3**, Ar = *o*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>; **4**, Ar = *m*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>; **5**, Ar = *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>; **6**, Ar = CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), among which the structures of complexes **2** and **6** have been determined by X-ray analyses. The X-ray crystal structures of **2** (orthorhombic, space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 9.839(3) Å, *b* = 17.787(7) Å, *c* = 11.212(2) Å, *V* = 1962.3(9) Å<sup>3</sup>, *Z* = 4, *D*<sub>calcd</sub> = 1.557 g/cm<sup>3</sup>, and *R* = 0.051, *R*<sub>w</sub> = 0.064 for 2575 independent reflections) and **6** (monoclinic, space group P2<sub>1</sub>/*n*, *a* = 14.435(2) Å, *b* = 9.534(5) Å, *c* = 18.207(2) Å,  $\beta$  = 92.58(2)°, *V* = 2503(1) Å<sup>3</sup>, *Z* = 4, *D*<sub>calcd</sub> = 1.524 g/cm<sup>3</sup>, and *R* = 0.065, *R*<sub>w</sub> = 0.071 for 2867 independent reflections) show that both crystallize as the *cis* isomer, and contain a symmetrically bridging carbene ligand and a bridging carbonyl ligand.

## Introduction

The increasing interest in the synthesis, structure, and chemistry of alkene–metal carbene complexes stems from the possible involvement of these species in various reactions of metal carbene complexes with alkenes.<sup>2–4</sup> In recent years, a series of novel olefin-coordinated transition metal carbene complexes and/or their isomerized products have been isolated and several novel isomerizations of olefin ligands have been observed by the reaction of olefin-ligated monometal carbonyls with nucleophiles, followed by alkylation with Et<sub>3</sub>OBF<sub>4</sub> in our laboratory.<sup>5–16</sup> As an extension of our

research on olefin-coordinating metal carbene complexes, we have studied the reaction of olefin-ligated dimetal carbonyl compounds with nucleophiles in order to investigate the effect of a binuclear metal on the isomerizations of olefin ligands. Recently, we discovered that pentacarbonyl(cyclooctatetraene)diiron reacted with aryllithium reagents at low temperatures and was subsequently alkylated with Et<sub>3</sub>OBF<sub>4</sub>, affording the cyclooctatetraene-coordinated dimetal complexes with a bridging carbene ligand, which is the first example of olefin-coordinated dimetal bridging carbene complexes. This is a new route to dimetal bridging carbene complexes<sup>17</sup> (eq 1).

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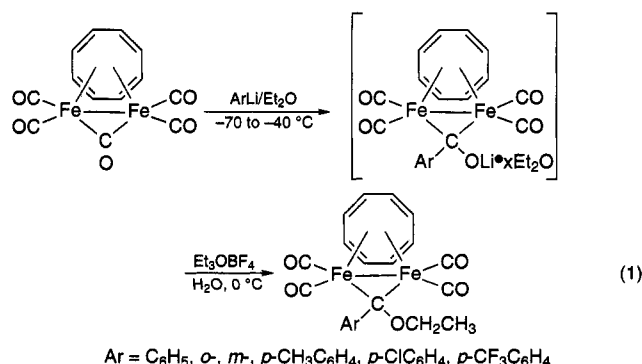
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We are now interested in examining the application range of the new synthesis method for bridging carbene complexes and the effect of bis( $\mu$ -carbonyl) ligands on the reaction products. Thus we chose bis( $\eta$ -cyclopentadienyl)diiron tetracarbonyl (**1**), which has two  $\mu$ -CO groups to the Fe-Fe bond, to react with aryllithium reagents. This paper describes a study of the reaction and the structural characterization of the resulting products.

### Experimental Section

All air-sensitive materials were manipulated under a prepurified  $N_2$  atmosphere by standard Schlenk techniques. All solvents employed were dried by reflux over appropriate drying agents and stored over 4-Å molecular sieves under an  $N_2$  atmosphere. Diethyl ether (Et<sub>2</sub>O) was distilled from a purple solution of sodium and benzophenone, petroleum ether (30–60 °C) from CaH<sub>2</sub>, and CH<sub>2</sub>Cl<sub>2</sub> from P<sub>2</sub>O<sub>5</sub>, while toluene was distilled from sodium. The neutral alumina (Al<sub>2</sub>O<sub>3</sub>) used for chromatography was deoxygenated at room temperature under a high vacuum for 16 h, deactivated with 5% w/w  $N_2$ -saturated water, and stored under  $N_2$ . Compound **1**,<sup>18</sup> Et<sub>3</sub>OBF<sub>4</sub>,<sup>19</sup> and aryllithium reagents<sup>20–23</sup> were prepared by literature methods.

The IR spectra were measured on a Zeiss Specord-75 spectrophotometer. The <sup>1</sup>H NMR spectra were normally obtained on a Varian-200 spectrometer at ambient temperature in acetone-*d*<sub>6</sub> solution with TMS as the internal reference. Electron ionization mass spectra (EIMS) were determined on a Finnigan 4021 GC/MS/DS spectrometer. The melting points were determined in sealed, nitrogen-filled capillaries and are not corrected.

**1. Preparation of [Fe<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(CO)<sub>2</sub>( $\mu$ -CO){ $\mu$ -C(OC<sub>2</sub>H<sub>5</sub>)-C<sub>6</sub>H<sub>5</sub>}] (**2**).** To a solution of **1** (0.60 g, 1.70 mmol) in 70 mL of ether was added dropwise 2.54 mmol of C<sub>6</sub>H<sub>5</sub>Li<sup>20</sup> in 15 mL of ether at 0 °C within 25 min. The deep red solution turned dark red. The reaction mixture was stirred at 0 °C for an additional 45 min to 1 h. After the solution was evaporated under a high vacuum at –10 °C to dryness, the dark-red solid residue obtained was dissolved in 40 mL of  $N_2$ -saturated water at 0 °C and covered with petroleum ether (30–60 °C). Immediately afterward Et<sub>3</sub>OBF<sub>4</sub> was added portionwise with strong stirring to the aqueous solution until it became acidic. The aqueous solution was extracted with petroleum ether. The combined extract was evaporated in vacuo, and the residue was chromatographed on an alumina (neutral, 100–200 mesh) column (1.6 × 15 cm) at –10 °C with petroleum ether followed by petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> (15:1) as the eluant. The red band was eluted and collected. Removal of the solvent under vacuum and recrystallization of the crude product from petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> solution at –80 °C afforded 0.48 g (62%, based on **1**) of dark-red crystals of **2**, mp 117–120 °C dec. IR ( $\nu_{CO}$ ) (CH<sub>2</sub>Cl<sub>2</sub>): 1990 (vs), 1940 (w), 1774 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>):  $\delta$  5.05 (s, C<sub>5</sub>H<sub>5</sub>, 10 H), 7.84 (m, ph, 2 H), 7.32–7.07 (m, ph, 3 H), 3.44 (q, OEt, 2 H), 1.23 (t, OEt, 3 H). MS: *m/e* 432 (M<sup>+</sup> – CO), 404 (M<sup>+</sup> – 2CO), 376 (M<sup>+</sup> – 3CO), 255 (M<sup>+</sup> – 3CO – C<sub>5</sub>H<sub>5</sub>Fe), 134 (C<sub>6</sub>H<sub>5</sub>C(OC<sub>2</sub>H<sub>5</sub>)<sup>+</sup>), 105 (C<sub>6</sub>H<sub>5</sub>CO<sup>+</sup>), 121 (C<sub>5</sub>H<sub>5</sub>Fe<sup>+</sup>). Anal. Calcd for C<sub>22</sub>H<sub>20</sub>O<sub>4</sub>Fe<sub>2</sub>: C, 57.43; H, 4.38. Found: C, 57.51; H, 4.51.

**2. Preparation of [Fe<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(CO)<sub>2</sub>( $\mu$ -CO){ $\mu$ -C(OC<sub>2</sub>H<sub>5</sub>)-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-*o*}] (**3**).** Similar to the preparation of **2**, 0.60 g of **1**

(1.70 mmol) reacted with 2.37 mmol of *o*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>Li<sup>21</sup> at 0 °C for 0.5 h. The subsequent alkylation and further treatment gave 0.5 g (64%, based on **1**) of dark-red crystalline **3**, mp 135–136 °C dec. IR ( $\nu_{CO}$ ): (CH<sub>2</sub>Cl<sub>2</sub>) 1992 (vs), 1960 (m), 1775 (s) cm<sup>-1</sup>. MS: *m/e* 446 (M<sup>+</sup> – CO), 418 (M<sup>+</sup> – 2CO), 390 (M<sup>+</sup> – 3CO), 269 (M<sup>+</sup> – 3CO – C<sub>5</sub>H<sub>5</sub>Fe), 148 (CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>C(OC<sub>2</sub>H<sub>5</sub>)<sup>+</sup>), 119 (CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CO<sup>+</sup>), 121 (C<sub>5</sub>H<sub>5</sub>Fe<sup>+</sup>). <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>):  $\delta$  4.99 (s, C<sub>5</sub>H<sub>5</sub>, 10 H), 7.38–7.03 (m, ph, 4 H), 3.44 (q, OEt, 2 H), 0.92 (t, OEt, 3 H). Anal. Calcd for C<sub>23</sub>H<sub>22</sub>O<sub>4</sub>Fe<sub>2</sub>: C, 58.27; H, 4.68. Found: C, 58.21; H, 4.61.

**3. Preparation of [Fe<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(CO)<sub>2</sub>( $\mu$ -CO){ $\mu$ -C(OC<sub>2</sub>H<sub>5</sub>)-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-*m*}] (**4**).** The reaction of 0.60 g (1.70 mmol) of **1** with 2.34 mmol of *m*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>Li<sup>21</sup> was as described in (1) at 0 °C for 1 h. The subsequent alkylation and further treatment as described for the preparation of **2** yielded 0.55 g (69%, based on **1**) of **4** as dark-red crystals, mp 128–129 °C dec. IR ( $\nu_{CO}$ ): (CH<sub>2</sub>Cl<sub>2</sub>) 1982 (vs), 1941 (w), 1778 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>):  $\delta$  5.04 (s, C<sub>5</sub>H<sub>5</sub>, 10 H), 7.64 (m, ph, 2 H), 7.12 (m, ph, 2 H), 3.56 (q, OEt, 2 H), 1.22 (t, OEt, 3 H). MS: *m/e* 446 (M<sup>+</sup> – CO), 418 (M<sup>+</sup> – 2CO), 390 (M<sup>+</sup> – 3CO), 269 (M<sup>+</sup> – 3CO – C<sub>5</sub>H<sub>5</sub>Fe), 148 (CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>C(OC<sub>2</sub>H<sub>5</sub>)<sup>+</sup>), 119 (CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CO<sup>+</sup>), 121 (C<sub>5</sub>H<sub>5</sub>Fe<sup>+</sup>). Anal. Calcd for C<sub>23</sub>H<sub>22</sub>O<sub>4</sub>Fe<sub>2</sub>: C, 58.27; H, 4.68. Found: C, 58.31; H, 4.71.

**4. Preparation of [Fe<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(CO)<sub>2</sub>( $\mu$ -CO){ $\mu$ -C(OC<sub>2</sub>H<sub>5</sub>)-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-*p*}] (**5**).** Similarly, compound **1** (0.60 g, 1.70 mmol) dissolved in 60 mL of ether was treated with 2.37 mmol of *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>Li<sup>21</sup> at 0 °C for 1 h, followed by alkylation; further treatment as described above gave 0.47 g (59%, based on **1**) of dark-red crystals of **5**, mp 122–124 °C dec. IR ( $\nu_{CO}$ ): (CH<sub>2</sub>Cl<sub>2</sub>) 1980 (vs), 1960 (s), 1780 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>):  $\delta$  5.03 (s, C<sub>5</sub>H<sub>5</sub>, 10 H), 7.70 (m, ph, 2 H), 7.06 (m, ph, 2H), 3.44 (q, OEt, 2 H), 1.20 (t, OEt, 3 H). MS: the same as compound **4**. Anal. Calcd for C<sub>23</sub>H<sub>22</sub>O<sub>4</sub>Fe<sub>2</sub>: C, 58.27; H, 4.68. Found: C, 58.39; H, 4.59.

**5. Preparation of [Fe<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(CO)<sub>2</sub>( $\mu$ -CO){ $\mu$ -C(OC<sub>2</sub>H<sub>5</sub>)-C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>-*p*}] (**6**).** A solution of 2.62 mmol of *n*-C<sub>4</sub>H<sub>9</sub>Li<sup>22</sup> in 20 mL of ether was added dropwise to a solution of 0.59 g (2.62 mmol) of *p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>Br in 20 mL of ether. After 30 min of stirring at room temperature, the resulting ether solution of *p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>Li<sup>23</sup> was reacted, in a manner similar to that described in (1), with 0.60 g (1.70 mmol) of **1** in 60 mL of ether at 0 °C for 1 h. Subsequent alkylation and further treatment similar to the procedures described in (1) gave 0.64 g (71%, based on **1**) of dark-red crystals of **6**, mp 126–127 °C dec. IR ( $\nu_{CO}$ ): (CH<sub>2</sub>Cl<sub>2</sub>) 1980 (vs), 1940 (m), 1770 (s) cm<sup>-1</sup>. MS: *m/e* 500 (M<sup>+</sup> – CO), 472 (M<sup>+</sup> – 2CO), 444 (M<sup>+</sup> – 3CO), 323 (M<sup>+</sup> – 3CO – C<sub>5</sub>H<sub>5</sub>Fe), 202 (CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>C(OC<sub>2</sub>H<sub>5</sub>)<sup>+</sup>), 173 (CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CO<sup>+</sup>), 121 (C<sub>5</sub>H<sub>5</sub>Fe<sup>+</sup>). <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>):  $\delta$  5.07 (s, C<sub>5</sub>H<sub>5</sub>, 10 H), 8.06 (m, ph, 2 H), 7.58 (m, ph, 2 H), 3.56 (q, OEt, 2 H), 1.24 (t, OEt, 3 H). Anal. Calcd for C<sub>23</sub>H<sub>19</sub>O<sub>4</sub>F<sub>3</sub>Fe<sub>2</sub>: C, 52.31; H, 3.63. Found: C, 52.20; H, 3.65.

**X-ray Crystal Structure Determinations of Complexes **2** and **6**.** The single crystals of **2** and **6** suitable for X-ray diffraction study were obtained by recrystallization from petroleum ether/toluene and petroleum ether/toluene/EtOH solution at –80 °C. Single crystals of approximate dimensions 0.20 × 0.20 × 0.30 mm for **2** and 0.25 × 0.30 × 0.30 mm for **6** were sealed in capillaries under an  $N_2$  atmosphere. The X-ray diffraction intensity data for 3140 and 4044 independent reflections, of which 2575 and 2867 with  $F_o^2 > 3\sigma(F_o^2)$  were observable, were collected with an Enraf-Nonius CAD4 diffractometer at room temperature using Mo K $\alpha$  radiation with a  $\theta/2\theta$  scan mode within the ranges  $0^\circ \leq 2\theta \leq 50^\circ$  and  $2^\circ \leq 2\theta \leq 48^\circ$  for **2** and **6**, respectively. The intensity data were corrected for Lorentz and polarization factors. An empirical absorption correction based on a series of  $\psi$ -scans was applied to the data for **6**, but not for **2**. A secondary extinction correction was also applied (coefficients of  $2.5494 \times 10^{-7}$  and  $2.095 \times 10^{-3}$  for **2** and **6**, respectively).

The crystal structures of **2** and **6** were solved by the heavy-atom method. After the two iron atom positions were determined, the successive Fourier synthesis showed all the non-

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Table 1. Crystal Data and Experimental Details for Complexes 2 and 6

	2	6
formula	C <sub>22</sub> H <sub>20</sub> O <sub>4</sub> Fe <sub>2</sub>	C <sub>23</sub> H <sub>19</sub> O <sub>4</sub> F <sub>3</sub> Fe <sub>2</sub>
fw	460.10	574.16
space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	P2 <sub>1</sub> /n
a, Å	9.839(3)	14.435(2)
b, Å	17.787(7)	9.534(5)
c, Å	11.212(2)	18.207(4)
β, deg	90	92.58(2)
V, Å <sup>3</sup>	1962.3(9)	2503(1)
Z	4	4
d <sub>calcd</sub> , g/cm <sup>3</sup>	1.557	1.524
cryst size, mm	0.20 × 0.20 × 0.30	0.25 × 0.30 × 0.30
μ(Mo Kα), cm <sup>-1</sup>	15.021	12.121
radiation (monochromated in incident beam) (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
orientation reflections: no.; range (2θ), deg	25; 20–30	25; 20–30
temp, °C	20	20
scan method	θ–2θ	θ–2θ
data coll range, 2θ, deg	0–50	2–48
no. of unique data, total with F <sub>o</sub> <sup>2</sup> > 3σ(F <sub>o</sub> <sup>2</sup> )	3140	4044
no. of params refined	2575	2867
trans factors: max, min (ψ-acans)	no	0.9992, 0.8432
correction factors: max, min (numerical)	no	0.9996, 0.9183
R <sup>a</sup>	0.051	0.065
R <sub>w</sub> <sup>b</sup>	0.064	0.071
quality-of-fit indicator <sup>c</sup>	2.19	2.526
largest shift/esd, final cycle	0.03	0.69
largest peak, e/Å <sup>3</sup>	0.712	1.08

<sup>a</sup> R = Σ|F<sub>o</sub> - |F<sub>c</sub>||/Σ|F<sub>o</sub>|. <sup>b</sup> R<sub>w</sub> = [Σw(|F<sub>o</sub> - |F<sub>c</sub>||)<sup>2</sup>/Σw|F<sub>o</sub>|<sup>2</sup>]<sup>1/2</sup>; w = 1/σ<sup>2</sup>(|F<sub>o</sub>|). <sup>c</sup> Quality-of-fit = [Σw(|F<sub>o</sub> - |F<sub>c</sub>||)<sup>2</sup>/(N<sub>obs</sub> - N<sub>params</sub>)]<sup>1/2</sup>.

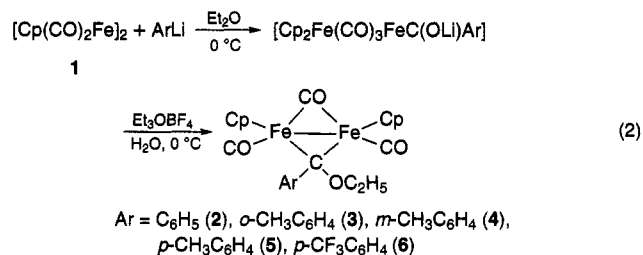
hydrogen atom coordinates. For **2**, the structure was refined by full-matrix least-squares refinement. Final refinement converged to R = 0.051 and R<sub>w</sub> = 0.064, (Δ/ρ)<sub>max</sub> = 0.712 e/Å<sup>3</sup>, (Δ/σ)<sub>max</sub> = 0.03. For **6**, after several cycles of full-matrix least-squares refinement, R = 0.093 and the following difference Fourier synthesis showed that there exists an ethanol solvent molecule. Final refinement, with anisotropic temperature factors for the non-hydrogen atoms in compound **6** and isotropic temperature factors for the atoms of ethanol, converged to R = 0.065 and R<sub>w</sub> = 0.071, (Δ/ρ)<sub>max</sub> = 1.08 e/Å<sup>3</sup>, (Δ/σ)<sub>max</sub> = 0.69. All the calculations were performed on a MicroVAXII computer using SDP/VAX.

The details of the crystallographic data and the procedures used for data collection and reduction information for **2** and **6** are given in Table 1. The positional parameters and temperature factors of non-hydrogen atoms for **2** and **6** are presented in Table 2. The bond lengths and selected bond angles for **2** and **6** are listed in Tables 3 and 4, respectively.

## Results and Discussion

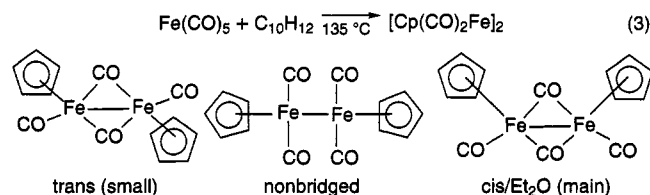
Similar to the reaction of pentacarbonyl(cyclooctatetraene)diiron<sup>17</sup> with aryllithium reagents, bis(η-cyclopentadienyl)diiron tetracarbonyl (**1**) was treated with a 40–50% molar excess of aryllithium reagents, ArLi (Ar = C<sub>6</sub>H<sub>5</sub>, o-, m-, p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, p-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), in ether at 0 °C for 0.5–1 h, and the acyl metalate intermediates formed were subsequently alkylated with Et<sub>3</sub>OBF<sub>4</sub> in aqueous solution at 0 °C. After removal of the solvents under a high vacuum at a low temperature, the residue was chromatographed on an alumina column at -20 °C, and the crude product was recrystallized from petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> solution at -80 °C to afford dark-red crystalline complexes **2–6** with the compositions

[Fe<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(CO)<sub>2</sub>(μ-CO){μ-C(OC<sub>2</sub>H<sub>5</sub>)Ar}] (eq 2) in 59–71% yields.



Complexes **2–6** are formulated as bis(η-cyclopentadienyl)-coordinated dimetal monobridging alkoxy-carbene complexes on the basis of their elemental analyses and IR, <sup>1</sup>H NMR, and mass spectra, as well as the single-crystal X-ray diffraction studies of complexes **2** and **6**. However, no dibridging alkoxy-carbene complexes were obtained from the reaction even though 2 or 3 M of the aryllithium reagents was used for the reactions.

On the other hand, starting material **1**, prepared by heating the cyclopentadiene dimer with Fe(CO)<sub>5</sub> at 135 °C, exists as cis, trans, and nonbridged isomers in solution as shown in eq 3.<sup>24,25</sup> Among these isomers, the



amounts of the nonbridged isomer are negligibly small, and the contents of the cis and trans isomers depend on the employed solvents. In general, the greater is the polarity of the solvent, the higher are the contents of the cis isomer; therefore, there should exist cis and trans isomers in the resulting products produced by the reaction of **1** with aryllithium reagents. In contrast, only the cis isomer product was isolated, which may be reasonably explained from the fact that the cis structure of the intermediate and product formed is more stable than the trans structure.

Complexes **2–6** are soluble in polar organic solvents, but slightly soluble in nonpolar solvents. They are very sensitive to air and temperature in solution, but stable for a short period on exposure to air at room temperature in the crystalline state. The IR spectra, the solution <sup>1</sup>H NMR spectra, and mass spectra are consistent with the proposed structure. The IR spectra (Experimental Section) of complexes **2–6** showed two CO absorption bands at 1900–2100 cm<sup>-1</sup> and one CO absorption band at 1770–1850 cm<sup>-1</sup> in the (CO) region, which signified a (CO)<sub>2</sub>Fe<sub>2</sub>(μ-CO) moiety in these complexes and suggested that only one μ-CO was attacked by the aryllithium nucleophiles and converted into a bridging carbene ligand upon subsequent treatment with the alkylation reagent in the four-carbonyl compound **1**. In the <sup>1</sup>H NMR spectra of **2–6**, a triplet (about 1.22 ppm) and a quartet (about 3.44 ppm) resonance were observed from each of the complexes, which

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(25) Bryan, R. F.; Greene, P. T. *J. Chem. Soc. A* **1970**, 3064.

Table 2. Positional Parameters and Their Estimated Standard Deviations<sup>a</sup> for 2 and 6

atom	2				6			
	x	y	z	B (Å <sup>2</sup> )	x	y	z	B (Å <sup>2</sup> )
Fe(1)	0.0694(1)	0.23562(6)	0.7547(1)	3.19(2)	0.48454(8)	-0.0250(1)	0.69534(6)	4.52(3)
Fe(2)	0.0553(1)	0.11260(7)	0.6453(1)	3.08(2)	0.59987(8)	0.1581(1)	0.65946(6)	4.08(2)
O(1)	-0.1875(5)	0.1617(4)	0.7665(6)	3.9(1)	0.4682(4)	0.2371(7)	0.7645(3)	5.6(1)
O(2)	0.2905(8)	0.2040(5)	0.5953(7)	6.0(2)	0.5841(4)	-0.0825(7)	0.5641(3)	5.8(1)
O(3)	0.2683(7)	0.1944(5)	0.9339(7)	5.6(2)	0.6084(5)	-0.2313(8)	0.7603(4)	7.8(2)
O(4)	0.2538(8)	0.0279(5)	0.7769(7)	6.9(2)	0.7676(4)	0.0135(7)	0.7059(3)	5.8(1)
F(1)					0.7059(7)	0.134(1)	1.0844(3)	15.9(3)
F(2)					0.7290(6)	-0.0663(9)	1.0629(3)	12.6(2)
F(3)					0.8240(5)	0.072(1)	1.0342(4)	15.5(3)
C(1)	-0.052(1)	0.1458(4)	0.7895(6)	3.2(2)	0.5369(5)	0.1359(9)	0.7546(4)	4.4(2)
C(2)	-0.0363(8)	0.1083(5)	0.9111(7)	3.0(2)	0.5925(5)	0.1132(9)	0.8270(4)	4.2(2)
C(3)	-0.044(1)	0.1528(5)	1.0126(7)	4.1(2)	0.5566(6)	0.024(1)	0.8803(4)	5.3(2)
C(4)	-0.034(1)	0.1221(6)	1.1241(8)	4.8(2)	0.6055(6)	0.006(1)	0.9480(4)	5.4(2)
C(5)	-0.015(1)	0.0444(7)	1.1398(9)	5.1(2)	0.6881(6)	0.076(1)	0.9612(4)	5.0(2)
C(6)	-0.011(1)	0.0009(6)	1.038(1)	5.3(3)	0.7239(6)	0.163(1)	0.9098(4)	5.2(2)
C(7)	-0.021(1)	0.0322(5)	0.9257(8)	4.0(2)	0.6765(5)	0.1816(9)	0.8415(4)	4.7(2)
C(8)	-0.293(1)	0.1226(9)	0.820(1)	6.6(3)	0.4659(8)	0.325(1)	0.8267(6)	9.1(3)
C(9)	-0.420(1)	0.1550(8)	0.784(1)	7.0(3)	0.3890(9)	0.431(2)	0.8081(7)	12.8(4)
C(10)	0.188(1)	0.1906(6)	0.6416(9)	4.0(2)	0.5643(6)	-0.013(1)	0.6153(4)	4.9(2)
C(11)	0.1888(9)	0.2089(5)	0.8628(8)	3.7(2)	0.5612(6)	-0.146(1)	0.7353(5)	5.3(2)
C(12)	0.1744(9)	0.0615(6)	0.7279(8)	4.2(2)	0.7000(5)	0.0725(9)	0.6898(4)	4.4(2)
C(13)	0.061(2)	0.3431(6)	0.826(1)	9.1(4)	0.3702(6)	-0.144(1)	0.7270(6)	7.0(3)
C(14)	-0.094(1)	0.3161(5)	0.796(1)	5.8(3)	0.3494(6)	-0.001(1)	0.7380(5)	6.6(3)
C(15)	-0.086(1)	0.3023(5)	0.6736(8)	5.1(2)	0.3518(6)	0.067(1)	0.6689(5)	6.4(2)
C(16)	0.042(2)	0.3252(5)	0.632(1)	6.5(3)	0.3735(6)	-0.034(1)	0.6139(5)	6.3(2)
C(17)	0.130(1)	0.3475(6)	0.719(1)	6.8(3)	0.3846(7)	-0.165(1)	0.6491(6)	7.4(3)
C(18)	-0.011(2)	0.1410(6)	0.4718(9)	10.1(5)	0.5530(7)	0.258(1)	0.5592(4)	6.0(2)
C(19)	-0.127(1)	0.1172(9)	0.5340(9)	6.8(3)	0.5181(7)	0.332(1)	0.6196(5)	5.9(2)
C(20)	-0.107(2)	0.0435(8)	0.568(1)	7.7(4)	0.5967(7)	0.3820(9)	0.6639(5)	6.0(2)
C(21)	0.037(2)	0.0212(6)	0.530(1)	6.4(3)	0.6780(6)	0.333(1)	0.6305(5)	5.7(2)
C(22)	0.103(2)	0.0823(8)	0.4692(9)	7.9(4)	0.6521(7)	0.255(1)	0.5651(5)	5.9(2)
C(23)					0.7381(7)	0.058(1)	1.0340(5)	7.2(3)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as  $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$ .

Table 3. Bond Distances (Å)<sup>a</sup> for Complexes 2 and 6

	2	6	2	6	
Fe(1)—Fe(2)	2.512(1)	2.519(2)	C(1)—C(2)	1.525(7)	1.527(6)
Fe(1)—C(1)	2.032(7)	2.004(5)	C(2)—C(3)	1.388(8)	1.405(7)
Fe(1)—C(10)	1.899(7)	1.901(6)	C(2)—C(7)	1.371(9)	1.391(7)
Fe(1)—C(11)	1.754(7)	1.733(6)	C(3)—C(4)	1.369(9)	1.403(7)
Fe(1)—C(13)	2.073(8)	2.013(6)	C(4)—C(5)	1.40(1)	1.380(8)
Fe(1)—C(14)	2.198(8)	2.144(6)	C(5)—C(6)	1.38(1)	1.369(8)
Fe(1)—C(15)	2.135(7)	2.143(6)	C(6)—C(7)	1.38(1)	1.403(7)
Fe(1)—C(16)	2.120(7)	2.136(5)	C(8)—C(9)	1.43(1)	1.53(1)
Fe(1)—C(17)	2.113(9)	2.111(6)	C(13)—C(14)	1.63(2)	1.41(1)
Fe(2)—C(1)	2.019(6)	2.003(5)	C(13)—C(17)	1.37(2)	1.457(9)
Fe(2)—C(10)	1.903(8)	1.882(6)	C(14)—C(15)	1.40(1)	1.418(9)
Fe(2)—C(12)	1.748(7)	1.729(6)	C(15)—C(16)	1.40(1)	1.438(9)
Fe(2)—C(18)	2.112(8)	2.140(5)	C(16)—C(17)	1.36(1)	1.405(9)
Fe(2)—C(19)	2.184(9)	2.146(6)	C(18)—C(19)	1.40(2)	1.421(8)
Fe(2)—C(20)	2.197(9)	2.137(6)	C(18)—C(22)	1.53(1)	1.430(9)
Fe(2)—C(21)	2.086(8)	2.093(6)	C(19)—C(20)	1.38(1)	1.441(8)
Fe(2)—C(22)	2.100(7)	2.119(6)	C(20)—C(21)	1.54(1)	1.426(9)
O(1)—C(1)	1.387(8)	1.401(6)	C(21)—C(22)	1.44(1)	1.439(8)
O(1)—C(8)	1.390(9)	1.412(7)	C(5)—C(23)		1.492(7)
O(2)—C(10)	1.162(8)	1.187(6)	F(1)—C(23)		1.277(8)
O(3)—C(11)	1.146(8)	1.145(7)	F(2)—C(23)		1.304(9)
O(4)—C(12)	1.126(8)	1.153(6)	F(3)—C(23)		1.247(8)

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

showed characteristically the presence of the ethoxy group. From the <sup>1</sup>H NMR spectra, it is also noted that the proton signal attributed to the cyclopentadienyl protons at about 5.00 ppm showed only a single resonance. However, for a complex of a  $\mu$ -carbene with different substituents, the cis form displays one C<sub>5</sub>H<sub>5</sub> resonance and the trans form two, as shown in complexes [Ru<sub>2</sub>(CO)<sub>2</sub>( $\mu$ -CO){ $\mu$ -C(H)COOEt}( $\eta$ -C<sub>5</sub>H<sub>5</sub>)]<sup>26</sup> and [Ru<sub>2</sub>(CO)<sub>2</sub>( $\mu$ -CO){ $\mu$ -C(R)CH<sub>2</sub>R}( $\eta$ -C<sub>5</sub>H<sub>5</sub>)].<sup>27</sup> Hence, we

consider that complexes 2–6 were the single resonance cis form products.

The mass spectra of complexes 2–6, given in the Experimental Section, showed no molecular ion peaks owing to its difficulty to be vaporized and easy thermolysis, but showed the principal fragments produced by successive loss of CO ligands and the featured ion peaks from the fragmentation generated by further cleavage of these principal fragments.

The structures of complexes 2 and 6 were established by their single-crystal X-ray structural determinations. The molecular structures of 2 and 6 are shown in Figures 1 and 2, respectively. The crystal structure studies show that the two complexes have similar structures. Both are diiron systems with Fe–Fe bond lengths of 2.512(1) and 2.519(2) Å, respectively; the ethoxy and aryl groups are attached to the one with the bridged CO group, and the two cyclopentadienyl rings are in a cis, almost totally eclipsed configuration, as anticipated from the IR and <sup>1</sup>H NMR spectra. The distance between the Fe atom and the Cp ring plane is approximately 1.741 Å. In the two complexes, there exist two different coordinated CO groups, and the bond lengths of Fe–C are also different: Fe–CO (bridged, sp<sup>2</sup>) is 1.90 Å, while Fe–CO (nonbridged, sp) is 1.75 Å. The least-squares plane calculations show that the carbon atoms in the Cp ring are coplanar and the two CO groups coordinated on the same Fe atom are not coplanar, which is caused by bridging.

(26) Davies, D. L.; Dyke, A. F.; Knox, S. A. R.; Morris, M. J. *J. Organomet. Chem.* **1981**, *215*, C30.

(27) Dyke, A. F.; Knox, S. A. R.; Morris, M. J.; Naish, P. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1417.

Table 4. Selected Bond Angles (deg)<sup>a</sup> for 2 and 6

	2	6		2	6
Fe(2)—Fe(1)—C(1)	51.4(2)	51.0(2)	Fe(1)—Fe(2)—C(18)	105.0(2)	110.0(2)
Fe(2)—Fe(1)—C(10)	48.7(2)	47.9(2)	Fe(1)—Fe(2)—C(19)	107.0(3)	105.3(2)
Fe(2)—Fe(1)—C(11)	98.0(2)	98.7(2)	Fe(1)—Fe(2)—C(20)	136.1(4)	131.8(2)
Fe(2)—Fe(1)—C(13)	171.4(3)	168.5(2)	Fe(1)—Fe(2)—C(21)	170.6(3)	170.8(2)
Fe(2)—Fe(1)—C(14)	129.1(3)	129.9(2)	Fe(1)—Fe(2)—C(22)	132.1(3)	140.9(2)
Fe(2)—Fe(1)—C(15)	103.7(2)	104.6(2)	C(1)—Fe(2)—C(10)	99.3(3)	98.8(2)
Fe(2)—Fe(1)—C(16)	109.3(3)	109.5(2)	C(1)—Fe(2)—C(12)	94.5(3)	94.5(2)
Fe(2)—Fe(1)—C(17)	138.1(3)	141.4(2)	C(1)—Fe(2)—C(18)	120.5(5)	130.2(2)
C(1)—Fe(1)—C(10)	99.0(3)	98.1(2)	C(1)—Fe(2)—C(19)	91.0(3)	96.3(2)
C(1)—Fe(1)—C(11)	92.8(3)	93.6(2)	C(1)—Fe(2)—C(20)	95.7(4)	93.5(3)
C(1)—Fe(1)—C(13)	128.9(5)	123.1(3)	C(1)—Fe(2)—C(21)	132.9(4)	124.9(2)
C(1)—Fe(1)—C(14)	92.4(3)	92.9(2)	C(1)—Fe(2)—C(22)	160.9(4)	159.9(2)
C(1)—Fe(1)—C(15)	95.7(3)	96.8(2)	C(10)—Fe(2)—C(12)	86.1(3)	86.3(2)
C(1)—Fe(1)—C(16)	129.9(4)	131.2(3)	C(10)—Fe(2)—C(18)	90.9(5)	87.2(2)
C(1)—Fe(1)—C(17)	160.1(4)	158.8(3)	C(10)—Fe(2)—C(19)	121.4(4)	113.1(2)
C(10)—Fe(1)—C(11)	86.4(3)	87.9(3)	C(10)—Fe(2)—C(20)	153.8(4)	151.3(2)
C(10)—Fe(1)—C(13)	132.1(5)	138.7(3)	C(10)—Fe(2)—C(21)	127.7(4)	136.3(3)
C(10)—Fe(1)—C(14)	149.7(3)	149.7(2)	C(10)—Fe(2)—C(22)	90.8(4)	97.6(2)
C(10)—Fe(1)—C(15)	112.8(3)	111.7(2)	C(12)—Fe(2)—C(18)	144.9(5)	135.2(3)
C(10)—Fe(1)—C(16)	87.8(4)	86.1(2)	C(12)—Fe(2)—C(19)	150.6(4)	155.9(2)
C(10)—Fe(1)—C(17)	95.8(4)	99.1(3)	C(12)—Fe(2)—C(20)	114.0(4)	118.6(2)
C(11)—Fe(1)—C(13)	90.7(4)	91.3(3)	C(12)—Fe(2)—C(21)	88.8(4)	90.2(2)
C(11)—Fe(1)—C(14)	121.2(3)	119.5(3)	C(12)—Fe(2)—C(22)	102.4(4)	98.2(3)
C(11)—Fe(1)—C(15)	157.4(3)	156.1(3)	Fe(1)—C(1)—Fe(2)	76.7(2)	77.9(2)
C(11)—Fe(1)—C(16)	137.4(4)	135.2(3)	Fe(1)—C(1)—O(1)	111.6(4)	110.1(3)
C(11)—Fe(1)—C(17)	101.4(4)	99.2(3)	Fe(1)—C(1)—C(2)	122.3(4)	121.8(4)
Fe(1)—Fe(2)—C(1)	51.9(2)	51.1(2)	Fe(2)—C(1)—O(1)	114.4(4)	112.9(3)
Fe(1)—Fe(2)—C(10)	48.6(2)	48.6(2)	Fe(2)—C(1)—C(2)	122.3(4)	121.3(3)
Fe(1)—Fe(2)—C(12)	99.1(3)	98.2(2)	Fe(1)—C(11)—O(3)	177.3(6)	176.0(5)
Fe(2)—C(12)—O(4)	177.2(7)	176.0(5)	O(1)—C(1)—C(2)	110.7(5)	109.5(4)
Fe(1)—C(10)—Fe(2)	82.7(3)	83.5(2)	C(1)—C(2)—C(3)	118.6(6)	119.1(5)
Fe(1)—C(10)—O(2)	138.2(7)	138.1(5)	C(1)—C(2)—C(7)	123.3(5)	121.1(5)
Fe(2)—C(10)—O(2)	139.1(7)	138.4(5)	O(1)—C(8)—C(9)	109.4(8)	105.0(5)
C(1)—O(1)—C(8)	122.6(6)	123.7(4)			

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

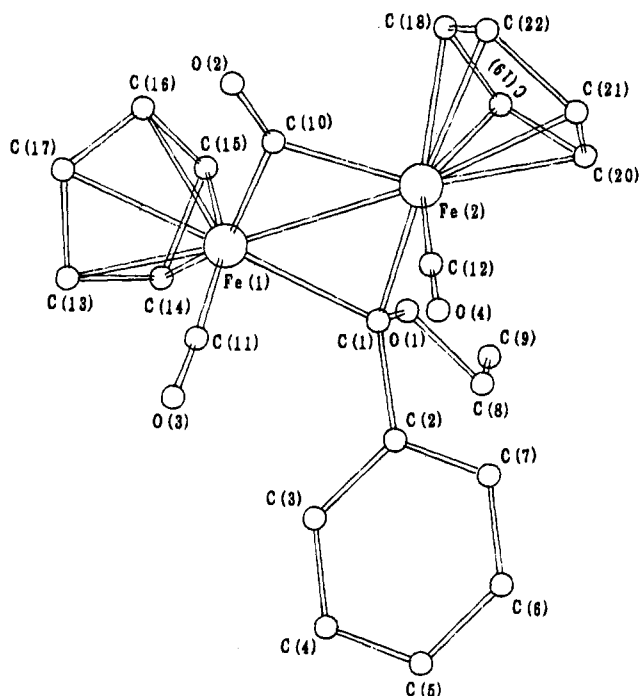


Figure 1. Molecular structure of 2 showing the atom labeling scheme.

The distance of the Fe—Fe bond bridged by the  $\mu$ -carbene ligand in 2 and 6 is somewhat shorter than that (2.531(2) Å) found in 1,<sup>28</sup> but significantly shorter than that found (2.686(1) Å) in the cyclooctatetraene-

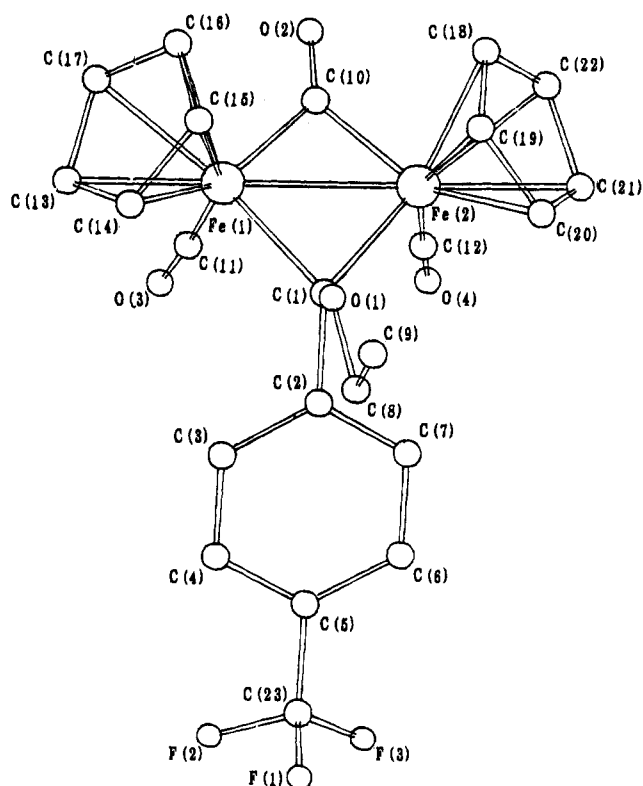


Figure 2. Molecular structure of 6, showing the atom labeling scheme.

coordinated diiron bridging carbene complex C<sub>8</sub>H<sub>8</sub>-(CO)<sub>2</sub>Fe{ $\mu$ -C(OC<sub>2</sub>H<sub>5</sub>)C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>-*p*}Fe(CO)<sub>2</sub>.<sup>17</sup> The alkylidene carbon almost symmetrically bridges the Fe—Fe

(28) Bryan, R. F.; Greene, P. T.; Newlands, M. J.; Field, D. S. *J. Chem. Soc. A* 1970, 3068.

bond with C(1)–Fe(1) 2.032(7) Å and C(1)–Fe(2) 2.019(6) Å for **2** and C(1)–Fe(1) 2.004(5) Å and C(1)–Fe(2) 2.003(5) Å for **6**. The  $\mu$ -C–Fe distances in **2** and **6** are much longer than the  $\mu$ -Fe–CO bond (C(10)–Fe(1) 1.899(7) Å, C(10)–Fe(2) 1.903(8) Å for **2**, C(10)–Fe(1) 1.901(6) Å, C(10)–Fe(2) 1.882(6) Å for **6**) but similar to

that found in  $C_8H_8(CO)_2Fe\{\mu-C(OC_2H_5)C_6H_4CF_3-p\}Fe(CO)_2$  (C–Fe(1) 2.063(3) Å, C–Fe(2) 2.010(3) Å)<sup>17</sup> and  $[Fe_2Cp_2(CO)_2(\mu-CO)\{\mu-C(CN)NPh\}]$  (C(4)–Fe(1) 2.004(2) Å, C(4)–Fe(2) 2.028(2) Å).<sup>29</sup>

The bridging carbon atom, C(1), in **2** and **6** lies essentially in the plane of the benzene ring ( $\pm 0.009$  Å). The benzene ring lies in the trans position of the cyclopentadienyl rings. The angles between the benzene ring C(2)C(3)C(4)C(5)C(6)C(7) and the cyclopentadienyl ring C(13)C(14)C(15)C(16)C(17) planes and the benzene ring C(2)C(3)C(4)C(5)C(6)C(7) and the cyclopentadienyl ring C(18)C(19)C(20)C(21)C(22) planes are 100.87 and 111.91°, respectively, for **2**, and the benzene ring plane is at angles of 106.56 and 114.90° to the planes of the two cyclopentadienyl rings, respectively, for **6**. Thus, complexes **2** and **6** exist in a cis structure that could avoid the steric repelling action between the aryl six-membered ring and the cyclopentadienyl ring.

In fact, the reaction of the compound having two forms of coordinated carbonyl groups (terminal and bridging CO) with a nucleophilic reagent is very complicated. Specifically, it is uncertain whether the nucleophilic attack in the initial step occurs actually on the bridging CO or the terminal CO. The results of the studies by Brown et al.<sup>30</sup> and Koelle et al.<sup>31</sup> suggested that the nucleophilic attack on the coordinated carbonyls relates to the electron density at CO. In general, the CO having a lower electron density is easily attacked by nucleophiles. In a supposition for the reaction mechanism of compound **1** with  $LiAlH_4$ , Atwood et al.,<sup>32</sup> according to their experimental results and the viewpoint of Brown and Koelle et al. mentioned above, presumed that in the initial step of the reaction process, the nucleophilic (hydride) addition to coordinated carbonyl occurred on the terminal CO having a lower electron density but not on the bridging CO having a higher electron density.<sup>33</sup>

We consider that the reaction courses of the metal carbonyl compounds with nucleophiles depend not only on the structure of the metal carbonyls themselves but also on the nucleophilic ability of the nucleophiles and

the stability of the acyl metalate intermediates formed by the reaction of metal carbonyl compounds with nucleophiles, as well as the experimental conditions and others. Under a different experimental system, the reaction mechanism could be different. However, as for the reaction of bis( $\eta$ -cyclopentadienyl)diiron tetracarbonyl with aryllithium reagents, either aryllithium first attacked the bridging CO or the aryllithium first attacked the terminal CO, though of the acyl metalate intermediate which might have isomers that can convert to each other in the solution, only the more stable cis product was obtained.

A number of dimetal bridging carbene complexes has been prepared by Stone et al. by the reactions<sup>34–36</sup> of carbene complexes with low-valent metal species or by reactions<sup>37,38</sup> of neutral carbyne complexes with metal hydrides. We recently also showed an unusual reaction of a cationic rhenium carbyne complex with the carbonyliron dianion that afforded a bridging complex.<sup>39</sup> However, we recently found that the reaction of olefinligated carbonyl metal compounds, such as pentacarbonyl(cyclooctatetraene)diiron, with aryllithium reagents followed by alkylation with  $Et_3OBF_4$  in a one-pot reaction gave a series of olefin-coordinated bridging carbene complexes in high yields, which is a convenient, high-yield synthesis to dimetal bridging carbene complexes.<sup>17</sup> Complexes **2–6**, as dimetal complexes with a bridging carbene ligand, were synthesized by the reaction of a bis( $\mu$ -carbonyl)metal compound with nucleophiles under analogous conditions. The titled reaction further shows that it is a most direct, simple, and convenient method for the preparation of dimetal bridging carbene complexes.

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**Supplementary Material Available:** Tables of additional bond angles, general displacement parameter expressions, and least-squares planes for **2** and **6** (12 pages). Ordering information is given on any current masthead page.

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