

**Reactions of *m*- and *p*-Divinylbenzene–Diiron
Hexacarbonyl with Aryllithium Reagents. Crystal
Structures of
[(CO)₃Fe(*m*-C₁₀H₁₀)(CO)₂FeC(OC₂H₅)C₆H₄CH₃-*o*)] and
[(CO)₃Fe(*p*-C₁₀H₁₀)(CO)₂FeC(OC₂H₅)C₆H₄CF₃-*p*)][†]**

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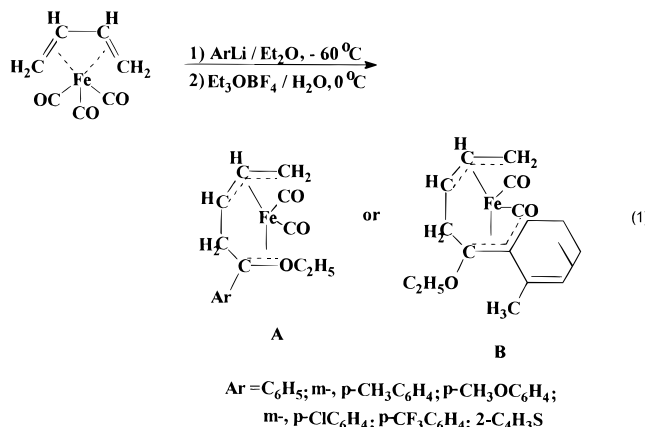
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The reactions of *m*-divinylbenzene–diiron hexacarbonyl (**1**) with aryllithium reagents, ArLi (Ar = C₆H₅, *o*-, *m*-, *p*-CH₃C₆H₄, *p*-CH₃OC₆H₄, *p*-CF₃C₆H₄, *m*-ClC₆H₄), in ether at low temperature gave acylmetalate intermediates followed by alkylation with Et₃OBF₄ in aqueous solution at 0 °C to afford the isomerized divinylbenzene-coordinated alkoxy-carbene complexes [(CO)₃Fe(*m*-C₁₀H₁₀)(CO)₂FeC(OC₂H₅)Ar] (**3**, Ar = C₆H₅; **4**, Ar = *o*-CH₃C₆H₄; **5**, Ar = *m*-CH₃C₆H₄; **6**, Ar = *p*-CH₃C₆H₄; **7**, Ar = *p*-CH₃OC₆H₄; **8**, Ar = *p*-CF₃C₆H₄; **9**, Ar = *m*-ClC₆H₄) with two types of structures. The *p*-divinylbenzene–diiron hexacarbonyl (**2**) also reacted with the aryllithium reagents under the same conditions to give the corresponding isomerized alkoxy-carbene complexes [(CO)₃Fe(*p*-C₁₀H₁₀)(CO)₂FeC(OC₂H₅)Ar] (**10**, Ar = C₆H₅; **11**, Ar = *o*-CH₃C₆H₄; **12**, Ar = *m*-CH₃C₆H₄; **13**, Ar = *p*-CH₃C₆H₄; **14**, Ar = *p*-CH₃OC₆H₄; **15**, Ar = *p*-CF₃C₆H₄; **16**, Ar = *m*-ClC₆H₄). The structures of complexes **4** and **15** have been determined by single-crystal X-ray diffraction studies.

Introduction

In view of the fact that alkene–metal carbene complexes are important intermediates in various reactions of metal carbene complexes with alkenes,^{1–3} the synthesis, structure, and chemistry of alkene–metal carbene complexes are one area of current interest. In previous studies of olefin-coordinated metal carbene and carbyne complexes, as part of a broader investigation of transition-metal carbene and carbyne complexes, we have shown^{4–14} that a series of novel olefin-coordinated transition-metal carbene complexes and/or their isomer-

ized products were isolated, and several novel isomerizations of olefin ligands have been observed by the reaction of olefin-ligated metallocarbonyls with nucleophiles, followed by alkylation with Et₃OBF₄. We have also shown that the isomerizations and resulting products depend not only on the olefin ligands but also on the central metals.^{5–10,15–17} For instance, the reaction of butadiene(tricarbonyl)iron with aryllithium reagents and subsequent alkylation with Et₃OBF₄ results in the formation of novel isomerized carbene complexes with two types of structures, A and B (eq 1).⁴ *o*-Chino-



[†] Dedicated to Professor Robert J. Angelici on the occasion of his 60th birthday and in recognition of his brilliant contributions to organometallic chemistry.

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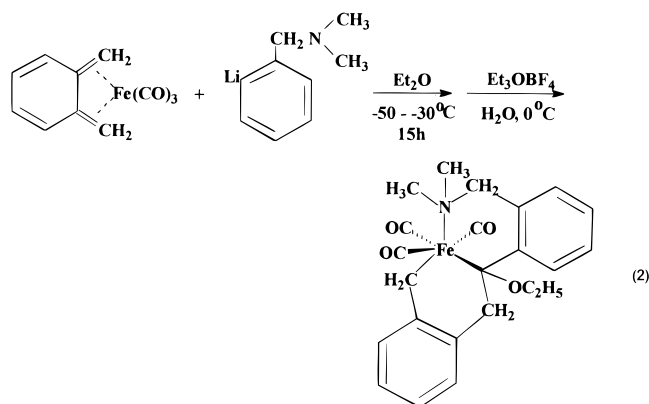
dimethaneiron tricarbonyl, where the Fe(CO)₃ is bonded to the butadiene-like residue of the *o*-chinomethane ligand, reacted with (*o*-lithiobenzyl)dimethylamine un-

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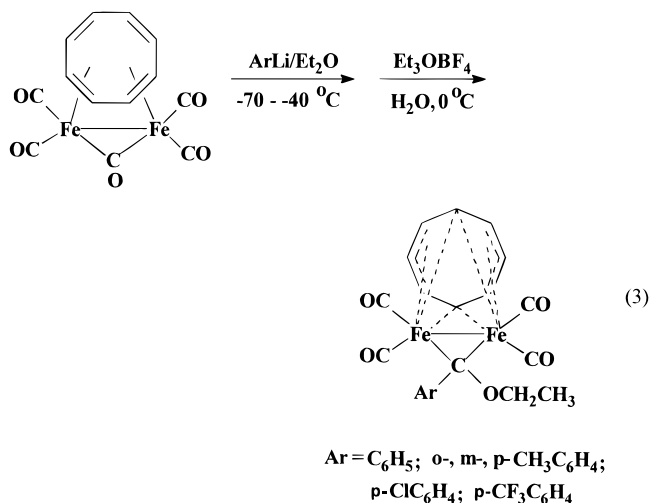
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der the analogous conditions to give a novel coupling product of the *o*-chinomethane ligand with CO and benzyldimethylamino groups¹⁸ (eq 2). In continuing our

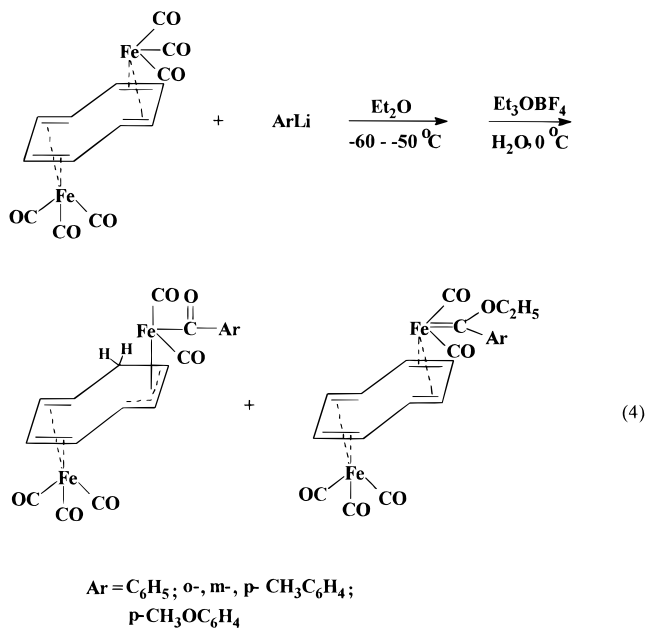


interest in olefin-coordinated metal carbene complexes, we have examined the reaction of olefin-ligated dimetal carbonyls, such as pentacarbonyl(cyclooctatetraene)-diiron, where the two iron atoms are directly bonded to each other, with aryllithium reagents, which gave the cyclooctatetraene-coordinated dimetal bridging carbene complexes⁹ (eq 3). While the reaction of the (cyclooct-



tetraene)diiron hexacarbonyl, C₈H₈[Fe(CO)₃]₂, where the two iron atoms are not directly bonded to each other and the two Fe(CO)₃ units are bonded to the two butadiene-like residues of cyclooctatetraene ligand, with aryllithium reagents under analogous conditions afforded the acyliron and (alkoxycarbene)iron complexes with only one acyl or carbene ligand (eq 4),¹⁹ instead of the expected diacyliron or (dialkoxycarbene)iron complexes.

In order to further investigate the effect of different olefin ligands and different binuclear central metals on the isomerization of the olefin ligand and reaction products, we chose *m*- and *p*-divinylbenzene–diiron hexacarbonyl, (*m*-C₁₀H₁₀)[Fe(CO)₃]₂ (**1**) and (*p*-C₁₀H₁₀)[Fe(CO)₃]₂ (**2**), where a vinyl double bond is used as one half of the butadiene residue and a double bond of the benzene ring can be used for the other half, the two iron atoms are not directly bonded to each other, and the



two Fe(CO)₃ units are, respectively, bonded to the two butadiene-like residues of the divinylbenzene ligands as the starting materials for the reaction with aryllithium reagents in a similar manner as previously described.^{9,19} These gave a series of chelated isomerized divinylbenzene-coordinated alkoxy carbene complexes with two types of structures, **A** and **B**, respectively (eqs 5 and 6). Herein we report the syntheses and structural characterizations of these new complexes.

Experimental Section

All procedures were performed under a dry, oxygen-free N₂ atmosphere by using standard Schlenk techniques. Solvents were reagent grade, dried by refluxing over appropriate drying agents, and stored over 4 Å molecular sieves under N₂ atmosphere. Diethyl ether (Et₂O) was distilled from sodium benzophenone ketyl, while petroleum ether (30–60 °C) was distilled from CaH₂ and CH₂Cl₂ from P₂O₅. The neutral alumina (Al₂O₃) used for chromatography was deoxygenated at room temperature under high vacuum for 16 h, deactivated with 5% w/w N₂-saturated water, and stored under N₂. Compounds **1**²⁰ and **2**,²⁰ Et₃OBF₄,²¹ and aryllithium reagents^{22–27} were prepared by literature methods.

The IR spectra were measured on a Zeiss Specord-75 spectrophotometer. All ¹H NMR spectra were recorded at ambient temperature in acetone-*d*₆ solution with TMS as the internal reference using a Varian 200 spectrometer. Electron ionization mass spectra (EIMS) were run on a Finnigan 4021 GC/MS/DS spectrometer. Melting points obtained on samples in sealed nitrogen-filled capillaries are uncorrected.

Preparation of [(CO)₃Fe(*m*-C₁₀H₁₀)(CO)₂Fe(CO)(OC₂H₅)-C₆H₅] (3**).** To a solution of 0.50 g (1.22 mmol) of **1** dissolved in 50 mL of ether at –90 °C was added dropwise 2.45 mmol of C₆H₅Li²² with stirring within 15 min. The reaction mixture

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was stirred at -90 to -70 °C for 1 h and then at -70 to -60 °C for 4 h, during which time the orange solution gradually turned bright red and then dark red. The resulting solution was evaporated under high vacuum at -40 to -50 °C to dryness. To the dark red solid residue obtained was added $\text{Et}_3\text{OBF}_4^{21}$ (ca. 5 g). This solid mixture was dissolved in 50 mL of N_2 -saturated water at 0 °C with vigorous stirring and the mixture covered with petroleum ether (30 – 60 °C). Immediately afterwards, Et_3OBF_4 (ca. 10 g) was added to the aqueous solution portionwise, with strong stirring, until it became acidic. The aqueous solution was extracted with petroleum ether. The combined extract was dried over anhydrous Na_2SO_4 . After removal of the solvent under vacuum, the residue was chromatographed on an alumina (neutral, 100 – 200 mesh) column (1.6×15 cm) at -25 °C with petroleum ether followed by petroleum ether/ CH_2Cl_2 ($15:1$) as the eluant. The orange-yellow band was eluted and collected. The solvent was removed under vacuum, and the residue was recrystallized from petroleum ether/ CH_2Cl_2 at -80 °C to give 0.49 g (78%, based on **1**) of orange-red crystals of **3**: mp 78 – 80 °C dec; IR (ν CO) (hexane) 2010 (s), 1998 (sh), 1990 (vs), 1940 (vs) cm^{-1} ; $^1\text{H NMR}$ δ 6.92 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 6.66 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 5.90 (m, 2H, $\text{C}_{10}\text{H}_{10}$), 3.86 (m, 2H, $\text{C}_{10}\text{H}_{10}$), 2.80 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 1.84 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 0.90 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 0.48 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 7.62–7.05 (m, 5H, C_6H_5), 1.36 (t, 3H, CH_2CH_3), 4.26 (q, 2H, CH_2CH_3); MS *m/e* 516 (M^+), 488 ($\text{M}^+ - \text{CO}$), 460 ($\text{M}^+ - 2\text{CO}$), 432 ($\text{M}^+ - 3\text{CO}$), 404 ($\text{M}^+ - 4\text{CO}$), 376 ($\text{M}^+ - 5\text{CO}$), 275 ($\text{M}^+ - 5\text{CO} - \text{Fe} - \text{OC}_2\text{H}_5$), 264 ($\text{M}^+ - 5\text{CO} - 2\text{Fe}$), 219 ($\text{M}^+ - 5\text{CO} - 2\text{Fe} - \text{OC}_2\text{H}_5$). Anal. Calcd for $\text{C}_{24}\text{H}_{20}\text{O}_6\text{Fe}_2$: C, 55.85; H, 3.91. Found: C, 55.69; H, 4.08.

The following complexes were similarly prepared. **[(CO)₃Fe(*m*-C₁₀H₁₀)(CO)₂FeC(OC₂H₅)C₆H₄CH₃-o] (4)**: orange-red crystals (82% yield); mp 75 – 77 °C dec; IR (ν CO) (hexane) 2005 (s), 1995 (sh), 1985 (vs), 1975 (sh), 1950 (s) cm^{-1} ; $^1\text{H NMR}$ δ 6.93 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 6.01 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 5.19 (m, 2H, $\text{C}_{10}\text{H}_{10}$), 3.15 (m, 2H, $\text{C}_{10}\text{H}_{10}$), 2.40 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 1.86 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 0.88 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 0.52 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 7.56 (m, 1H, $\text{C}_6\text{H}_4\text{CH}_3$), 7.36 (m, 1H, $\text{C}_6\text{H}_4\text{CH}_3$), 7.20 (m, 2H, $\text{C}_6\text{H}_4\text{CH}_3$), 2.46 (s, 3H, $\text{C}_6\text{H}_4\text{CH}_3$), 1.22 (t, 3H, CH_2CH_3), 4.56 (q, 2H, CH_2CH_3); MS *m/e* 530 (M^+), 502 ($\text{M}^+ - \text{CO}$), 474 ($\text{M}^+ - 2\text{CO}$), 446 ($\text{M}^+ - 3\text{CO}$), 418 ($\text{M}^+ - 4\text{CO}$), 390 ($\text{M}^+ - 5\text{CO}$), 289 ($\text{M}^+ - 5\text{CO} - \text{Fe} - \text{OC}_2\text{H}_5$), 278 ($\text{M}^+ - 5\text{CO} - 2\text{Fe}$), 233 ($\text{M}^+ - 5\text{CO} - 2\text{Fe} - \text{OC}_2\text{H}_5$). Anal. Calcd for $\text{C}_{25}\text{H}_{22}\text{O}_6\text{Fe}_2$: C, 56.64; H, 4.18. Found: C, 56.87; H, 4.41. **[(CO)₃Fe(*m*-C₁₀H₁₀)(CO)₂FeC(OC₂H₅)C₆H₄CH₃-m] (5)**: orange crystals (76% yield); mp 42 – 44 °C dec; IR (ν CO) (hexane) 2006 (s), 1997 (sh), 1988 (vs), 1945 (s) cm^{-1} ; $^1\text{H NMR}$ δ 6.68 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 6.32 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 5.80 (m, 2H, $\text{C}_{10}\text{H}_{10}$), 3.90 (m, 2H, $\text{C}_{10}\text{H}_{10}$), 2.80 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 1.74 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 0.89 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 0.50 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 7.56–6.82 (m, 4H, $\text{C}_6\text{H}_4\text{CH}_3$), 2.38 (s, 3H, $\text{C}_6\text{H}_4\text{CH}_3$), 1.40 (t, 3H, CH_2CH_3), 4.35 (q, 2H, CH_2CH_3); MS *m/e* 530 (M^+), 502 ($\text{M}^+ - \text{CO}$), 474 ($\text{M}^+ - 2\text{CO}$), 446 ($\text{M}^+ - 3\text{CO}$), 418 ($\text{M}^+ - 4\text{CO}$), 390 ($\text{M}^+ - 5\text{CO}$), 289 ($\text{M}^+ - 5\text{CO} - \text{Fe} - \text{OC}_2\text{H}_5$), 278 ($\text{M}^+ - 5\text{CO} - 2\text{Fe}$), 233 ($\text{M}^+ - 5\text{CO} - 2\text{Fe} - \text{OC}_2\text{H}_5$). Anal. Calcd for $\text{C}_{25}\text{H}_{22}\text{O}_6\text{Fe}_2$: C, 56.64; H, 4.18. Found: C, 56.98; H, 4.56. **[(CO)₃Fe(*m*-C₁₀H₁₀)(CO)₂FeC(OC₂H₅)C₆H₄CH₃-p] (6)**: orange-red crystals (80% yield); mp 73 – 74 °C dec; IR (ν CO) (hexane) 2008 (s), 1996 (sh), 1985 (vs), 1938 (s) cm^{-1} ; $^1\text{H NMR}$ δ 6.66 (m, 2H, $\text{C}_{10}\text{H}_{10}$), 5.82 (m, 2H, $\text{C}_{10}\text{H}_{10}$), 3.88 (m, 2H, $\text{C}_{10}\text{H}_{10}$), 2.78 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 1.82 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 0.86 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 0.45 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 7.24 (d, 2H, $\text{C}_6\text{H}_4\text{CH}_3$), 7.12 (d, 2H, $\text{C}_6\text{H}_4\text{CH}_3$), 2.24 (s, 3H, $\text{C}_6\text{H}_4\text{CH}_3$), 1.36 (t, 3H, CH_2CH_3), 4.30 (q, 2H, CH_2CH_3); MS *m/e* 530 (M^+), 502 ($\text{M}^+ - \text{CO}$), 474 ($\text{M}^+ - 2\text{CO}$), 446 ($\text{M}^+ - 3\text{CO}$), 418 ($\text{M}^+ - 4\text{CO}$), 390 ($\text{M}^+ - 5\text{CO}$), 289 ($\text{M}^+ - 5\text{CO} - \text{Fe} - \text{OC}_2\text{H}_5$), 278 ($\text{M}^+ - 5\text{CO} - 2\text{Fe}$), 233 ($\text{M}^+ - 5\text{CO} - 2\text{Fe} - \text{OC}_2\text{H}_5$). Anal. Calcd for $\text{C}_{25}\text{H}_{22}\text{O}_6\text{Fe}_2$: C, 56.64; H, 4.18. Found: C, 57.04; H, 3.89. **[(CO)₃Fe(*m*-C₁₀H₁₀)(CO)₂FeC(OC₂H₅)C₆H₄OCH₃-p] (7)**: orange-red crystals (76% yield); mp 60 – 62 °C dec; IR (ν CO) (hexane) 2000 (s), 1900 (sh), 1983 (vs), 1932 (s) cm^{-1} ; $^1\text{H NMR}$: δ 6.68 (m, 2H, $\text{C}_{10}\text{H}_{10}$), 5.84 (m, 2H, $\text{C}_{10}\text{H}_{10}$), 3.84 (m, 2H, $\text{C}_{10}\text{H}_{10}$), 2.76 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 1.84

(m, 1H, $\text{C}_{10}\text{H}_{10}$), 0.90 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 0.46 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 7.55 (m, 1H, $\text{C}_6\text{H}_4\text{OCH}_3$), 7.30 (m, 1H, $\text{C}_6\text{H}_4\text{OCH}_3$), 7.14 (m, 2H, $\text{C}_6\text{H}_4\text{OCH}_3$), 2.36 (s, 3H, $\text{C}_6\text{H}_4\text{OCH}_3$), 1.38 (t, 3H, CH_2CH_3), 4.28 (q, 2H, CH_2CH_3); MS *m/e* 546 (M^+), 518 ($\text{M}^+ - \text{CO}$), 490 ($\text{M}^+ - 2\text{CO}$), 462 ($\text{M}^+ - 3\text{CO}$), 434 ($\text{M}^+ - 4\text{CO}$), 406 ($\text{M}^+ - 5\text{CO}$), 305 ($\text{M}^+ - 5\text{CO} - \text{Fe} - \text{OC}_2\text{H}_5$), 294 ($\text{M}^+ - 5\text{CO} - 2\text{Fe}$), 249 ($\text{M}^+ - 5\text{CO} - 2\text{Fe} - \text{OC}_2\text{H}_5$). Anal. Calcd for $\text{C}_{25}\text{H}_{22}\text{O}_7\text{Fe}_2$: C, 54.98; H, 4.06. Found: C, 54.67; H, 4.39. **[(CO)₃Fe(*m*-C₁₀H₁₀)(CO)₂FeC(OC₂H₅)C₆H₄CF₃-p] (8)**: orange-red crystals (79% yield); mp 78 – 80 °C dec; IR (ν CO) (hexane) 2003 (s), 1996 (sh), 1988 (vs), 1948 (s) cm^{-1} ; $^1\text{H NMR}$ δ 6.68 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 6.36 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 5.80 (m, 2H, $\text{C}_{10}\text{H}_{10}$), 3.82 (m, 2H, $\text{C}_{10}\text{H}_{10}$), 2.72 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 1.82 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 0.88 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 0.48 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 7.68 (d, 2H, $\text{C}_6\text{H}_4\text{CF}_3$), 7.54 (d, 2H, $\text{C}_6\text{H}_4\text{CF}_3$), 1.42 (t, 3H, CH_2CH_3), 4.38 (q, 2H, CH_2CH_3); MS *m/e* 584 (M^+), 556 ($\text{M}^+ - \text{CO}$), 528 ($\text{M}^+ - 2\text{CO}$), 500 ($\text{M}^+ - 3\text{CO}$), 472 ($\text{M}^+ - 4\text{CO}$), 444 ($\text{M}^+ - 5\text{CO}$), 343 ($\text{M}^+ - 5\text{CO} - \text{Fe} - \text{OC}_2\text{H}_5$), 332 ($\text{M}^+ - 5\text{CO} - 2\text{Fe}$), 287 ($\text{M}^+ - 5\text{CO} - 2\text{Fe} - \text{OC}_2\text{H}_5$). Anal. Calcd for $\text{C}_{25}\text{H}_{19}\text{O}_6\text{F}_3\text{Fe}_2$: C, 51.41; H, 3.28. Found: C, 50.95; H, 3.66. **[(CO)₃Fe(*m*-C₁₀H₁₀)(CO)₂FeC(OC₂H₅)C₆H₄Cl-m] (9)**: orange-red crystals (73% yield); mp 72 – 74 °C dec; IR (ν CO) (hexane) 2006 (s), 2000 (sh), 1992 (vs), 1982 (sh), 1949 (s) cm^{-1} ; $^1\text{H NMR}$ δ 6.58 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 6.34 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 5.76 (m, 2H, $\text{C}_{10}\text{H}_{10}$), 4.00 (m, 2H, $\text{C}_{10}\text{H}_{10}$), 2.86 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 1.80 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 0.86 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 0.45 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 7.70–7.06 (m, 4H, $\text{C}_6\text{H}_4\text{Cl}$), 1.45 (t, 3H, CH_2CH_3), 4.39 (q, 2H, CH_2CH_3); MS *m/e* 550 (M^+), 522 ($\text{M}^+ - \text{CO}$), 494 ($\text{M}^+ - 2\text{CO}$), 466 ($\text{M}^+ - 3\text{CO}$), 438 ($\text{M}^+ - 4\text{CO}$), 410 ($\text{M}^+ - 5\text{CO}$), 309 ($\text{M}^+ - 5\text{CO} - \text{Fe} - \text{OC}_2\text{H}_5$), 298 ($\text{M}^+ - 5\text{CO} - 2\text{Fe}$), 253 ($\text{M}^+ - 5\text{CO} - 2\text{Fe} - \text{OC}_2\text{H}_5$). Anal. Calcd for $\text{C}_{24}\text{H}_{19}\text{O}_6\text{ClFe}_2$: C, 52.36; H, 3.48. Found: C, 52.60; H, 3.69.

Preparation of [(CO)₃Fe(*p*-C₁₀H₁₀)(CO)₂FeC(OC₂H₅)C₆H₅] (10). Similar to the procedures described for the reaction of **1** with $\text{C}_6\text{H}_5\text{Li}$, compound **2** (0.40 g, 0.98 mmol) dissolved in 50 mL of ether was reacted with 2.00 mmol of $\text{C}_6\text{H}_5\text{Li}$ at -90 to -60 °C for 4 h, during which time the orange solution gradually turned bright red to dark red. Subsequent alkylation with Et_3OBF_4 and further treatment as described for the preparation of **3** gave 0.41 g (82%, based on **2**) of orange-red crystals of **10**: mp 50 – 52 °C dec; IR (ν CO) (hexane) 2006 (s), 1998 (sh), 1988 (vs), 1952 (w), 1940 (s) cm^{-1} ; $^1\text{H NMR}$ δ 6.80 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 6.62 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 5.88 (m, 2H, $\text{C}_{10}\text{H}_{10}$), 4.08 (m, 2H, $\text{C}_{10}\text{H}_{10}$), 2.72 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 1.74 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 0.87 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 0.45 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 7.60–7.10 (m, 5H, C_6H_5), 1.42 (t, 3H, CH_2CH_3), 4.30 (q, 2H, CH_2CH_3); MS *m/e* 516 (M^+), 488 ($\text{M}^+ - \text{CO}$), 460 ($\text{M}^+ - 2\text{CO}$), 432 ($\text{M}^+ - 3\text{CO}$), 404 ($\text{M}^+ - 4\text{CO}$), 376 ($\text{M}^+ - 5\text{CO}$), 275 ($\text{M}^+ - 5\text{CO} - \text{Fe} - \text{OC}_2\text{H}_5$), 264 ($\text{M}^+ - 5\text{CO} - 2\text{Fe}$), 219 ($\text{M}^+ - 5\text{CO} - 2\text{Fe} - \text{OC}_2\text{H}_5$). Anal. Calcd for $\text{C}_{24}\text{H}_{20}\text{O}_6\text{Fe}_2$: C, 55.85; H, 3.91. Found: C, 56.09; H, 4.25.

The following complexes were similarly prepared. **[(CO)₃Fe(*p*-C₁₀H₁₀)(CO)₂FeC(OC₂H₅)C₆H₄CH₃-o] (11)**: orange-red crystals (77% yield); mp 77 – 78 °C dec; IR (ν CO) (hexane) 2002 (s), 1988 (sh), 1978 (vs), 1940 (w) cm^{-1} ; $^1\text{H NMR}$ δ 6.70 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 6.40 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 5.90 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 5.22 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 3.25 (m, 2H, $\text{C}_{10}\text{H}_{10}$), 2.68 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 1.78 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 1.37 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 0.50 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 7.44 (m, 2H, $\text{C}_6\text{H}_4\text{CH}_3$), 7.20 (m, 1H, $\text{C}_6\text{H}_4\text{CH}_3$), 6.96 (m, 1H, $\text{C}_6\text{H}_4\text{CH}_3$), 2.44 (s, 3H, $\text{C}_6\text{H}_4\text{CH}_3$), 1.20 (t, 3H, CH_2CH_3), 4.50 (q, 2H, CH_2CH_3); MS *m/e* 530 (M^+), 502 ($\text{M}^+ - \text{CO}$), 474 ($\text{M}^+ - 2\text{CO}$), 446 ($\text{M}^+ - 3\text{CO}$), 418 ($\text{M}^+ - 4\text{CO}$), 390 ($\text{M}^+ - 5\text{CO}$), 289 ($\text{M}^+ - 5\text{CO} - \text{Fe} - \text{OC}_2\text{H}_5$), 278 ($\text{M}^+ - 5\text{CO} - 2\text{Fe}$), 233 ($\text{M}^+ - 5\text{CO} - 2\text{Fe} - \text{OC}_2\text{H}_5$). Anal. Calcd for $\text{C}_{25}\text{H}_{22}\text{O}_6\text{Fe}_2$: C, 56.64; H, 4.18. Found: C, 57.00; H, 4.46. **[(CO)₃Fe(*p*-C₁₀H₁₀)(CO)₂FeC(OC₂H₅)C₆H₄CH₃-m] (12)**: orange-red crystals (73% yield); mp 39 – 41 °C dec; IR (ν CO) (hexane) 2004 (s), 1996 (sh), 1986 (vs), 1948 (s), 1939 (w) cm^{-1} ; $^1\text{H NMR}$ δ 6.82 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 5.98 (m, 2H, $\text{C}_{10}\text{H}_{10}$), 5.55 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 3.80 (m, 2H, $\text{C}_{10}\text{H}_{10}$), 2.69 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 1.78 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 1.20 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 0.54 (m, 1H, $\text{C}_{10}\text{H}_{10}$), 7.62–6.90 (m, 4H, $\text{C}_6\text{H}_4\text{CH}_3$), 2.17 (s, 3H, $\text{C}_6\text{H}_4\text{CH}_3$), 1.43 (t, 3H, CH_2CH_3), 4.21 (q, 2H, CH_2CH_3); MS *m/e* 530 (M^+), 502 ($\text{M}^+ - \text{CO}$), 474 (M^+

– 2CO), 446 ($M^+ - 3CO$), 418 ($M^+ - 4CO$), 390 ($M^+ - 5CO$), 289 ($M^+ - 5CO - Fe - OC_2H_5$), 278 ($M^+ - 5CO - 2Fe$), 233 ($M^+ - 5CO - 2Fe - OC_2H_5$). Anal. Calcd for $C_{25}H_{22}O_6Fe_2$: C, 56.64; H, 4.18. Found: C, 56.99; H, 4.24. [(CO)₃Fe(*p*-C₁₀H₁₀)(CO)₂FeC(OC₂H₅)C₆H₄CH₃-*p*)] (**13**): orange-red crystals (75% yield); mp 63–64 °C dec; IR (ν CO) (hexane) 2010 (s), 1998 (sh), 1988 (vs), 1980 (sh), 1940 (s) cm⁻¹; ¹H NMR δ 6.78 (m, 1H, C₁₀H₁₀), 6.60 (m, 1H, C₁₀H₁₀), 5.84 (m, 2H, C₁₀H₁₀), 4.00 (m, 2H, C₁₀H₁₀), 2.68 (m, 1H, C₁₀H₁₀), 1.70 (m, 1H, C₁₀H₁₀), 0.88 (m, 1H, C₁₀H₁₀), 0.40 (m, 1H, C₁₀H₁₀), 7.38–7.04 (m, 4H, C₆H₄CH₃), 2.26 (s, 3H, C₆H₄CH₃), 1.38 (t, 3H, CH₂CH₃), 4.28 (q, 2H, CH₂CH₃); MS *m/e* 530 (M^+), 502 ($M^+ - CO$), 474 ($M^+ - 2CO$), 446 ($M^+ - 3CO$), 418 ($M^+ - 4CO$), 390 ($M^+ - 5CO$), 289 ($M^+ - 5CO - Fe - OC_2H_5$), 278 ($M^+ - 5CO - 2Fe$), 233 ($M^+ - 5CO - 2Fe - OC_2H_5$). Anal. Calcd for $C_{25}H_{22}O_6Fe_2$: C, 56.64; H, 4.18. Found: C, 56.76; H, 4.53. [(CO)₃Fe(*p*-C₁₀H₁₀)(CO)₂FeC(OC₂H₅)C₆H₄OCH₃-*p*)] (**14**): orange-red crystals (77% yield); mp 57–58 °C dec; IR (ν CO) (hexane) 2004 (s), 1992 (sh), 1983 (vs), 1978 (sh), 1943 (s) cm⁻¹; ¹H NMR δ 6.76 (m, 1H, C₁₀H₁₀), 6.58 (m, 1H, C₁₀H₁₀), 5.72 (m, 2H, C₁₀H₁₀), 3.84 (m, 2H, C₁₀H₁₀), 2.66 (m, 1H, C₁₀H₁₀), 1.74 (m, 1H, C₁₀H₁₀), 0.90 (m, 1H, C₁₀H₁₀), 0.42 (m, 1H, C₁₀H₁₀), 7.54 (m, 1H, C₆H₄OCH₃), 7.30 (m, 1H, C₆H₄OCH₃), 7.14 (m, 2H, C₆H₄OCH₃), 3.80 (s, 3H, C₆H₄OCH₃), 1.40 (t, 3H, CH₂CH₃), 4.20 (q, 2H, CH₂CH₃); MS *m/e* 546 (M^+), 518 ($M^+ - CO$), 490 ($M^+ - 2CO$), 462 ($M^+ - 3CO$), 434 ($M^+ - 4CO$), 406 ($M^+ - 5CO$), 305 ($M^+ - 5CO - Fe - OC_2H_5$), 294 ($M^+ - 5CO - 2Fe$), 249 ($M^+ - 5CO - 2Fe - OC_2H_5$). Anal. Calcd for $C_{25}H_{22}O_7Fe_2$: C, 54.98; H, 4.06. Found: C, 54.54; H, 4.29. [(CO)₃Fe(*p*-C₁₀H₁₀)(CO)₂FeC(OC₂H₅)C₆H₄CF₃-*p*)] (**15**): orange-red crystals (75% yield); mp 63–65 °C dec; IR (ν CO) (hexane) 2003 (s), 1997 (sh), 1987 (vs), 1979 (sh), 1942 (s) cm⁻¹; ¹H NMR δ 6.84 (m, 1H, C₁₀H₁₀), 6.64 (m, 1H, C₁₀H₁₀), 5.78 (m, 2H, C₁₀H₁₀), 4.10 (m, 2H, C₁₀H₁₀), 2.78 (m, 1H, C₁₀H₁₀), 1.72 (m, 1H, C₁₀H₁₀), 0.89 (m, 1H, C₁₀H₁₀), 0.49 (m, 1H, C₁₀H₁₀), 7.64 (d, 2H, C₆H₄CF₃), 7.56 (d, 2H, C₆H₄CF₃), 1.42 (t, 3H, CH₂CH₃), 4.38 (q, 2H, CH₂CH₃); MS *m/e* 584 (M^+), 556 ($M^+ - CO$), 528 ($M^+ - 2CO$), 500 ($M^+ - 3CO$), 472 ($M^+ - 4CO$), 444 ($M^+ - 5CO$), 343 ($M^+ - 5CO - Fe - OC_2H_5$), 332 ($M^+ - 5CO - 2Fe$), 287 ($M^+ - 5CO - 2Fe - OC_2H_5$). Anal. Calcd for $C_{25}H_{19}O_6F_3Fe_2$: C, 51.41; H, 3.28. Found: C, 51.36; H, 3.69. [(CO)₃Fe(*p*-C₁₀H₁₀)(CO)₂FeC(OC₂H₅)C₆H₄Cl-*m*)] (**16**): orange crystals (70% yield); mp 65–67 °C dec; IR (ν CO) (hexane) 2007 (s), 1999 (sh), 1990 (vs), 1955 (w), 1943 (w) cm⁻¹; ¹H NMR δ 6.85 (m, 1H, C₁₀H₁₀), 6.61 (m, 1H, C₁₀H₁₀), 5.88 (m, 2H, C₁₀H₁₀), 4.12 (m, 2H, C₁₀H₁₀), 2.74 (m, 1H, C₁₀H₁₀), 1.76 (m, 1H, C₁₀H₁₀), 0.87 (m, 1H, C₁₀H₁₀), 0.48 (m, 1H, C₁₀H₁₀), 7.75–7.20 (m, 4H, C₆H₄Cl), 1.42 (t, 3H, CH₂CH₃), 4.35 (q, 2H, CH₂CH₃); MS *m/e* 550 (M^+), 522 ($M^+ - CO$), 494 ($M^+ - 2CO$), 466 ($M^+ - 3CO$), 438 ($M^+ - 4CO$), 410 ($M^+ - 5CO$), 309 ($M^+ - 5CO - Fe - OC_2H_5$), 298 ($M^+ - 5CO - 2Fe$), 253 ($M^+ - 5CO - 2Fe - OC_2H_5$). Anal. Calcd for $C_{24}H_{19}O_6ClFe_2$: C, 52.36; H, 3.48. Found: C, 51.93; H, 3.22.

X-ray Crystal Structure Determinations of Complexes 4 and 15. The single crystals of **4** and **15** suitable for X-ray diffraction study were obtained by recrystallization from petroleum ether/CH₂Cl₂ solution at –80 °C. Single crystals of approximate dimensions 0.20 × 0.10 × 0.30 mm for **4** and 0.20 × 0.20 × 0.30 mm for **15** were sealed in capillaries under an N₂ atmosphere. The X-ray diffraction intensity data for 3102 and 3170 independent reflections, of which 1750 and 1342 with $I > 3.00\sigma(I)$ were observable, were collected with a Rigaku AFC7R diffractometer at 20 °C using Mo K α irradiation with an $\omega - 2\theta$ scan mode within the ranges $5^\circ \leq 2\theta \leq 45^\circ$ for **4** and **15**, respectively. The intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction based on azimuthal scans of several reflections was applied, which resulted in transmission factors ranging from 0.80 to 1.00 for **4**, and an empirical absorption correction using the program DIFABS was applied, which resulted in transmission factors ranging from 0.88 to 1.03 for **15**.

The structures of **4** and **15** were solved by the direct methods and expanded using Fourier techniques. For **4**, the non-

Table 1. Crystal Data and Experimental Details for Complexes 4 and 15

	4	15
formula	C ₂₅ H ₂₂ O ₆ Fe ₂	C ₂₅ H ₁₉ O ₆ F ₃ Fe ₂
fw	530.14	584.11
space group	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> $\bar{1}$ (No. 2)
<i>a</i> (Å)	12.032(3)	12.060(3)
<i>b</i> (Å)	14.568(4)	13.535(3)
<i>c</i> (Å)	7.686(2)	9.293(2)
α (deg)	97.45(2)	93.27(2)
β (deg)	104.95(2)	110.17(2)
γ (deg)	109.92(2)	87.11(2)
<i>V</i> (Å ³)	1188.1(6)	1420.8(6)
<i>Z</i>	2	2
<i>d</i> _{calcd} (g/cm ³)	1.482	1.365
cryst size (mm)	0.20 × 0.10 × 0.30	0.20 × 0.20 × 0.30
μ (Mo K α) (cm ⁻¹)	12.57	10.73
radiation (monochromated in incident beam)	Mo K α (λ = 0.710 69 Å)	Mo K α (λ = 0.710 69 Å)
diffractometer	Rigaku AFC7R	Rigaku AFC7R
<i>T</i> (°C)	20	20
orientation reflns: no.; range 2θ (deg)	20; 18.5–21.5	19; 18.4–24.7
scan method	$\omega - 2\theta$	$\omega - 2\theta$
data coll. range, 2θ (deg)	5–45	5–45
no. of unique data, total with $I > 3.00\sigma(I)$	3102 1750	3170 1319
no. of params refined	298	259
correction factors, max, min (DIFABS)	1.0000, 0.7979	1.0000, 0.9457
<i>R</i> ^a	0.049	0.073
<i>R</i> _w ^b	0.050	0.078
quality-of-fit indicator ^c	1.63	3.23
largest shift/esd final cycle	0.00	0.05
largest peak, e/Å ³	0.41	1.33
minimum peak, e/Å ³	–0.39	–0.70

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^c Quality-of-fit = $[\sum w(|F_o| - |F_c|)^2 / (N_{obs} - N_{parameters})]^{1/2}$.

hydrogen atoms were refined anisotropically. The hydrogen atoms were included but not refined, the final cycle of full-matrix least-squares refinement was based on 1750 observed reflections ($I > 3.00\sigma(I)$), and 298 variable parameters and converged (largest parameter was 0.00 times its esd) with unweighted and weighted agreement factors of $R = 0.049$ and $R_w = 0.050$. For **15**, some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. The hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 1319 observed reflections ($I > 3.00\sigma(I)$) and 296 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.073$ and $R_w = 0.078$. All the calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.

The details of the crystallographic data and the procedures used for data collection and reduction information for **4** and **15** are given in Table 1. The positional parameters and temperature factors of the non-hydrogen atoms and the bond lengths and angles for **4** and **15** are given in the Supporting Information.

Results and Discussion

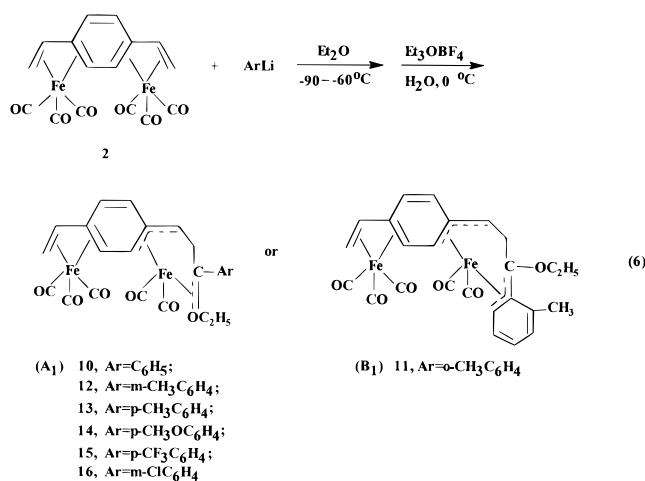
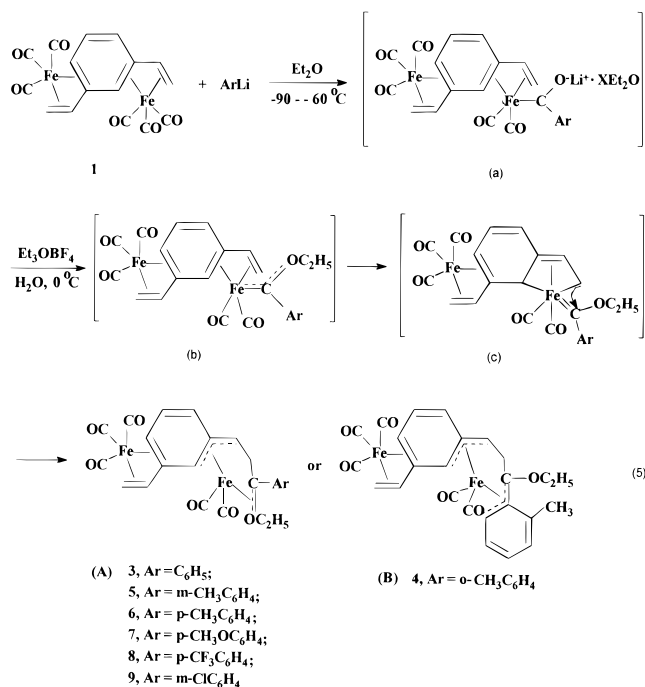
The *m*-divinylbenzene–diiron hexacarbonyl, (*m*-C₁₀H₁₀)[Fe(CO)₃]₂ (**1**), was treated with 2 molar equiv of aryllithium reagents, ArLi (ArLi = C₆H₅, *o*-, *m*-, *p*-CH₃C₆H₄, *p*-CH₃OC₆H₄, *p*-CF₃C₆H₄, *m*-ClC₆H₄), in ether at –90 to –60 °C for 4 h. The acylmetalate intermediates formed were subsequently alkylated with Et₃OBf₄ in aqueous solution at 0 °C. After removal of the solvent under high vacuum at low temperature, the solid residue was chromatographed on an alumina column at –20 °C, and the crude product was recrystal-

lized from petroleum ether/ CH_2Cl_2 solution at -80°C to afford orange-red crystalline complexes (**3–9**) with the compositions $[(\text{CO})_3\text{Fe}(m\text{-C}_{10}\text{H}_{10})(\text{CO})_2\text{FeCO}(\text{OC}_2\text{H}_5)\text{Ar}]$ (eq 5) in 73–82% yields. The *p*-divinylbenzene–diiron hexacarbonyl, $(p\text{-C}_{10}\text{H}_{10})[\text{Fe}(\text{CO})_3]_2$ (**2**), also reacted with the same aryllithium reagents under the same conditions to give the orange-red complexes (**10–16**) with the compositions $[(\text{CO})_3\text{Fe}(p\text{-C}_{10}\text{H}_{10})(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{Ar}]$ (eq 6) in nearly same (70–82%) yields.

When only 1 molar equiv, instead of 2, of aryllithium reagents was used for the reactions under the same conditions, the same products (**3–9**) (65–76%) and (**10–16**) (62–75%) were obtained in somewhat lower yields. On the basis of the elemental analyses, spectral analyses, and the single-crystal X-ray diffraction studies of complexes of **4** and **15**, complexes **3–9** and **10–16** are formulated as isomerized (*m*-divinylbenzene)- and (*p*-divinylbenzene)tricarbonyliron dicarbonyl[ethoxy(aryl)carbene]iron complexes with two types of structures, **A** or **A**₁ and **B** or **B**₁, respectively, among which complexes **4** and **11** exist in the form of structure **B** or **B**₁, while the others exist in the form of structure **A** or **A**₁. Complex **11** is assigned similar structure since its spectral data are similar to those of **4**. Likely, complexes **10** and **12–16** are assigned similar structures since their spectral data are similar to those of **15**. There are two $\text{Fe}(\text{CO})_3$ units in starting materials **1** and **2**, and there should exist isomerized divinylbenzene-coordinated (dialkoxycarbene)iron complexes in the resulting products when treating **1** and **2** with aryllithium reagents. However, no expected isomerized dialkoxycarbene complexes were obtained from the reactions even though more than 2 molar equiv of the aryllithium reagents was used for the reactions.

A possible mechanism for the formation (eq 5) of complexes **3–9** might involve the acylmetalate intermediates (a) formed by attack of aryllithium nucleophiles on one of the two $\text{Fe}(\text{CO})_3$ units. As soon as the ethoxycarbene complexes (b) were formed by alkylation of (a) with Et_3OBF_4 , rearrangement of π -bonding of the double bonds of the butadiene-like residue in divinylbenzene ligand to give an intermediate, metallacycle (c), which converted then to the stable isomerized alkoxy-carbene complexes **3–9**, as that of the isomerized butadiene(dicarbonyl)[ethoxy(aryl)carbene]iron complexes.⁴ The mechanism for the formation (eq 6) of complexes **10–16** is similar to that of **3–9**. The formations of complexes **3–9** and **10–16** in eqs 5 and 6 are not surprising since the analogous reaction of butadiene-(tricarbonyl)iron with aryllithium reagents gave the analogous isomerized carbene complexes with two types of structures, **A** and **B**, as mentioned above in the Introduction.

Complexes **3–9** and **10–16** 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 ^1H NMR spectra, and mass spectra are consistent with the proposed structure shown in eqs 5 and 6. The IR spectra of complexes **3–9** and **10–16** in the $\nu(\text{CO})$ region showed four to five CO absorption bands at ca. $2010\text{--}1932\text{ cm}^{-1}$. The data given in the Experimental Section showed that the different olefin ligands and different aryl substituents



exerted variant influence on the $\nu(\text{CO})$ frequency in these complexes.

The ^1H NMR spectra of complexes **3–9** and **10–16**, given in the Experimental Section, showed complex proton signals attributed to the olefin ligand arising from a $\sigma\text{-}\pi$ rearrangement of the divinylbenzene ligand. As a result of rearrangement, the structure of the olefin ligand consists of a η^3 -allyl and a terminal carbon atom of vinyl moiety of the divinylbenzene ligand bonding to the "carbene" carbon. Thus, the proton signals of the original olefin ligand shifted accordingly. In the ^1H NMR spectra of complexes **3–9** and **10–16**, a triplet (ca. 1.20–1.45 ppm) and a quartet (ca. 4.20–4.56 ppm), and a set of multiplet (ca. 6.90–7.75 ppm) bands were observed from each of the complexes, which showed characteristic presence of the ethoxy and aryl groups.

The mass spectra of complexes **3–9** and **10–16**, given in the Experimental Section, showed expected molecular ion peaks and the principal fragments produced by successive loss of CO ligands as well as the featured ions bearing useful structure information from the fragments generated by further cleavage of these principal fragments.

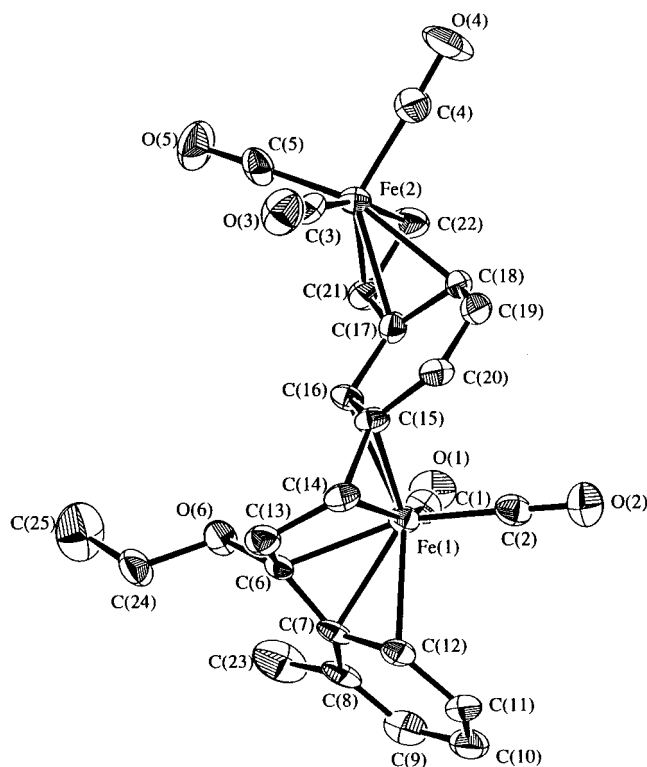


Figure 1. Molecular structure of **4** showing the atom-labeling scheme.

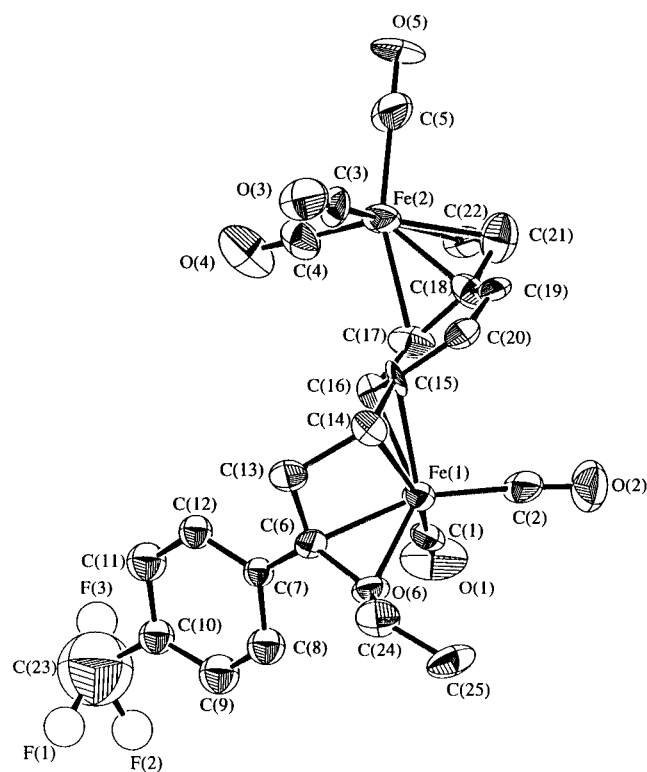


Figure 2. Molecular structure of **15** showing the atom-labeling scheme.

The molecular structures of complexes **4** and **15** established by the X-ray diffraction studies are shown in Figures 1 and 2, respectively. Both complexes have approximate steric configuration. The $\text{Fe}(\text{CO})_3$ unit and the $(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-}o$ in **4** and $(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CF}_3\text{-}p$ moiety in **15** are on the opposite side of the benzene ring of the divinylbenzene ligand, as can

be visualized in the ORTEP diagrams of **4** and **15** represented in Figures 1 and 2.

The molecular structure of **4** confirmed the assigned structure and has many common features of previously determined analogous complex structure of $\text{C}_4\text{H}_6(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-}o$.⁴ The “carbene” carbon atom (C(6)) is now bonded to a terminal carbon (C(13)) of the vinyl moiety of the divinylbenzene ligand besides bonding to the ethoxy and aryl groups and has become four-coordinate. That the sum of the bond angles around C(6) atom is 358° , only deviated slightly from 360° , means that the “carbene” carbon atom forms three σ bonds with three adjacent (C(13), C(7), and O(6)) by using its sp^2 -hybridized orbitals and a π -bond with Fe(1) atom using its approximate pure p_z orbital. The Fe(1)–C(6) bond length of 2.114(9) Å is much longer than the $\text{Fe}=\text{C}_{\text{carbene}}$ bond in carbeneiron complexes $\text{C}_{10}\text{H}_{16}(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-}o$ (1.915(15) Å)¹³ and $\text{C}_6\text{H}_8(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_5\text{-}o$ (1.89(2) Å)²⁸ and is the same within experimental error as that of the Fe–C(3) bond (2.110(7) Å) in analogous complexes $\text{C}_4\text{H}_6(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-}o$ ⁴ and Fe–C(7) bond (2.127(6) Å) in $\text{C}_8\text{H}_8(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_5$.⁵ It is noteworthy that in order to form an allyl-type η^3 -bonding to the Fe atom, the benzene ring has resumed the Kekule structural character to a certain extent, which is demonstrated by the alternate change of the bond lengths in the benzene ring.

The structure of **15** has many common features of previously determined analogous complex structures of $\text{C}_4\text{H}_6(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-}p$.⁴ Analogous to **4**, the sum of the bond angles around C(6) atom is 354° (slightly deviating from 360°), and the “carbene” carbon C(6) forms three σ -bonds to C(13), C(7), and O(6) with sp^2 -hybridized orbitals and provides an approximately pure p_z atomic orbital to interact with the Fe(1) atom. Because the p_z orbital of C(6) is almost parallel to that of O(6), a ligand analogous to π -allyl is able to be formed with one electron in the p_z orbital of C(6) and two electrons in the p_z orbital of O(6). The Fe(1)–C(6) bond length of 2.00(2) Å in **15** is slightly shorter than that found in **4** and analogous complexes $\text{C}_4\text{H}_6(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-}o$ and $\text{C}_8\text{H}_8(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_5$ but is comparable with the $\text{Fe}-\text{C}_{\text{carbene}}$ bond found in carbeneiron complexes $\text{C}_{10}\text{H}_{16}(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-}o$ and $\text{C}_6\text{H}_8(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-}o$.

The dihedral angle between the plane defined by C(14), C(15), and C(16) and the plane comprised of C(17) through C(22) is 169.05° in **4** and 176.43° in **15**, while the angles between the C(15)C(16)C(17)C(18)C(19)C(20) and C(14)C(15)C(16) planes and the C(15)C(16)C(17)C(18)C(19)C(20) and C(17)C(18)C(21)C(22) planes, respectively, are 169.10 and 6.84° in **4** and 171.59 and 7.66° in **15**. The benzene ring plane defined by C(7) through C(12) is, respectively, oriented at an 102.29 , 88.40 , and 85.11° in **4** and 113.23 , 74.55 , and 66.90° in **15** with respect to the C(14)C(15)C(16) plane, the C(15)C(16)C(17)C(18)C(19)C(20) plane, and the C(17)C(18)C(21)C(22) plane. The $\text{Fe}(\text{CO})_3$ unit is located (1.640 Å in **4** and 1.679 Å in **15**) above the C(17)C(18)C(21)C(22) plane, and the $(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{Ar}$ moiety is located (1.636 Å in **4** and 1.685 Å in **15**) below the

(28) Chen, J.-B.; Yu, Y.; Hu, L.-H.; Jin, Z.-S. *J. Organomet. Chem.* **1993**, *447*, 113.

C(14)C(15)C(16) plane. The average distances of the Fe(1) atom to carbon atoms C(14), C(15), and C(16) in **4** and **15** are 2.12 and 2.14 Å, respectively, which is very close to that of the Fe(2) atom to carbon atoms C(17), C(18), C(21), and C(22) (2.11 Å in **4** and 2.13 Å in **15**).

Owing to the variation of the bond type of Fe–C_{carbene} in both complexes **3–9** and **10–16** caused by the bonding of the terminal carbon atom of the vinyl moiety to the “carbene” carbon atom, the resulting products **3–9** and **10–16** may also be regarded as isomerized carbene complexes as described in isomerized butadiene alkoxy-carbeneiron complexes C₄H₆(CO)₂FeC(OC₂H₅)-Ar.⁴

Acknowledgment. Financial support for the National Natural Science Foundation of China and the Science Foundation of the Chinese Academy of Sciences is gratefully acknowledged.

Supporting Information Available: Text giving detailed procedures for the preparations of complexes **3–9** and **10–16** and tables of the positional parameters and temperature factors, H atom coordinates, anisotropic displacement parameters, bond lengths and angles, and least-squares planes for **4** and **15** (29 pages). Ordering information is given on any current masthead page.

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