

Lewis Acid Promoted Intramolecular Cyclization of (η^4 -Diene)Fe(CO)₃ Complexes Bearing Functionalized Side Chains

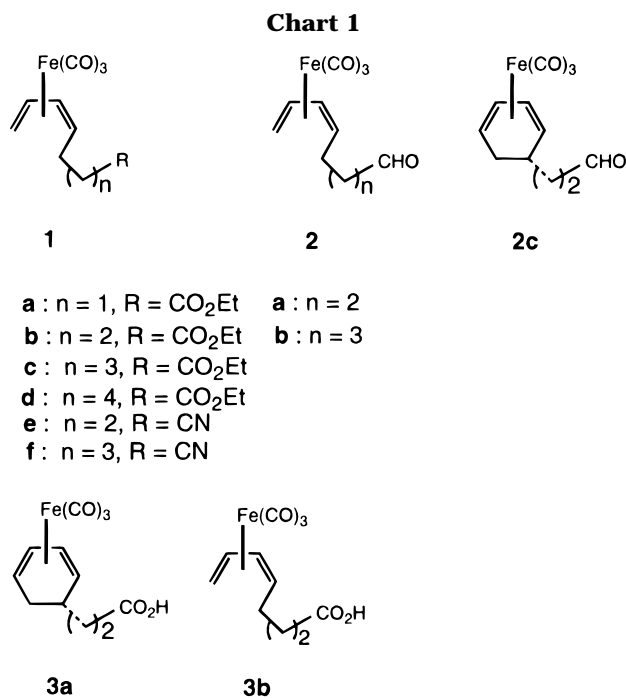
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Addition of aluminum chloride to the (η^4 -cyclohexadiene)Fe(CO)₃ complex bearing an acid chloride side chain at C-5 gives a cyclic keto complex, whereas Lewis acid assisted intramolecular cyclization of acyclic (η^4 -butadiene)Fe(CO)₃ complexes containing an aldehyde, an ester, or a nitrile functionality produces (σ,η^3 -allyl)tricarbonyliron complexes. Treatments of the (η^4 -butadiene)Fe(CO)₃ complexes bearing a chromium carbene moiety in refluxing toluene lead to formation of furan derivatives by intramolecular addition of the diene ligand to the chromium carbene carbon center.

The chemistry of (η^4 -1,3-diene)tricarbonyliron(0) complexes is a subject of continuing interest. The general applications of the complexes are (i) electrophilic reactions with reactive carbon nucleophiles;¹ (ii) hydride abstraction, followed by reaction with a number of different nucleophiles;² and (iii) Friedel–Crafts reactions with acid chlorides.³ Recently, we reported that sequential additions of nucleophiles to (η^5 -pentadienyl)tricarbonyliron(0) and (η^5 -cyclohexadienyl)tricarbonyliron(0) cations afforded fused and bridged bicyclic and tricyclic skeletons.⁴ Surprisingly, only limited examples of intramolecular nucleophilic reactions of the tricarbonylmyrceneiron(0) complex with carbon electrophiles have been reported.⁵ The reactions involved protonation or acylation of the pendant free double bond of the tricarbonylmyrceneiron(0) complex to generate the carbonium ion or the acyl chloride intermediate. Intramolecular nucleophilic additions of the diene ligand to the electron-deficient carbon centers gave cyclized products. In this paper, we report that Lewis acid promoted intramolecular cyclization of (η^4 -1,3-diene)tricarbonyliron(0) complexes bearing carbon electrophiles such as acid chlorides, aldehydes, esters, and nitriles generates cyclic ketones and (σ,η^3 -allyl)tricarbonyliron complexes, re-



spectively, whereas treatments of complexes containing a chromium carbene moiety provide furan derivatives.

Preparation of Starting Complexes. The starting complexes **1a–f** (Chart 1) were easily prepared by addition of the corresponding highly functionalized zinc–copper reagents RCu(CN)ZnI to the (η^5 -pentadienyl)tricarbonyliron cation salt.⁶ Aldehyde derivatives **2a–c** were obtained by reduction of the corresponding ester complexes with diisobutylaluminum hydride (DIBAL) at -78 °C in good yields. The acid complexes **3a,b** were synthesized by hydrolysis of the corresponding ester complexes^{4a} using KOH in MeOH–THF–H₂O at 23 °C in good yields (85 and 98% yields, respectively). Finally, (η^4 -diene)Fe(CO)₃ complexes bearing a Fischer carbene moiety were synthesized as follows. Treatment

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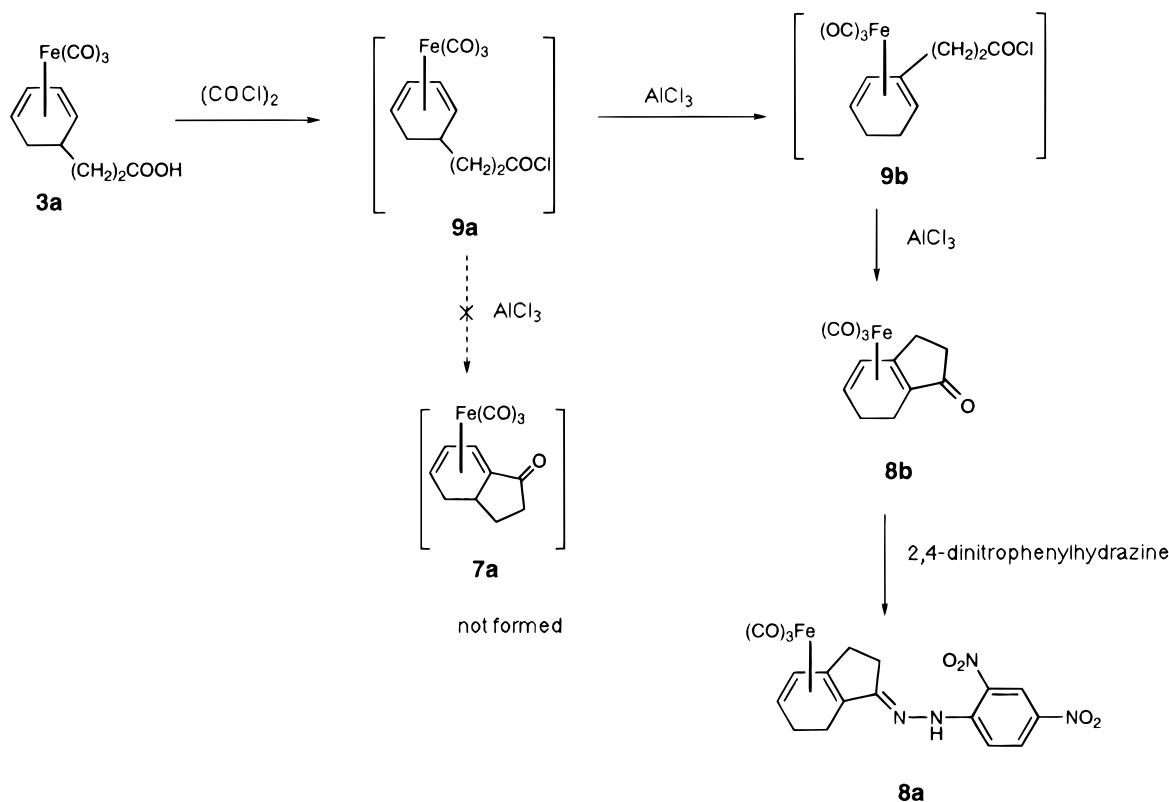
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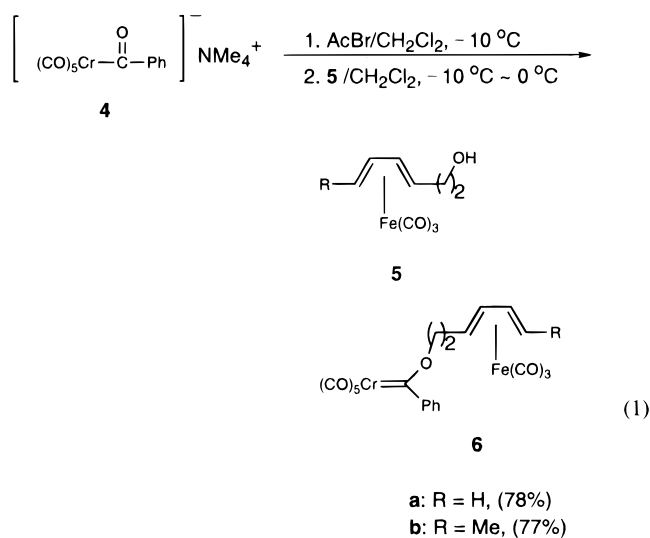
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Scheme 1



of 1.5 molar equiv of [tetramethylammonium(phenyl)-carbenyl oxide]pentacarbonylchromium (**4**) with 1.5



molar equiv of acetyl bromide at -10°C for 1 h followed by addition of 1.0 molar equiv of dienol complex **5** at -10°C for 2 h gave iron complex **6** with a chromium carbene moiety at the terminal position of the diene ligand.⁷

Intramolecular Electrophilic Addition Reactions. Our cyclization study began with complex **3a** (Scheme 1). Treatments of complex **3a** with oxalyl chloride (1.2 molar equiv) and triethylamine (1.2 molar equiv) in CH_2Cl_2 at 0°C for 45 min followed by addition of aluminum chloride (1.5 molar equiv) gave a crude iron–diene complex in 20% yield. The reaction is

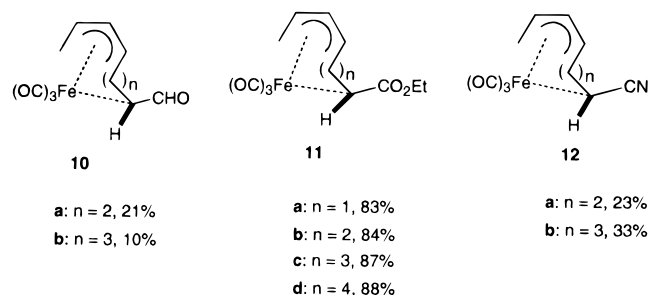
performed in the expectation that a fused bicyclic keto complex, such as **7a**, would be generated via Lewis acid assisted intramolecular Friedel–Crafts reaction. The infrared spectrum of the isolated complex shows a sharp ketone stretch at 1690 cm^{-1} and the usual iron CO bands at 2038 and 1972 cm^{-1} . The ^{13}C NMR spectrum of the complex has the usual ketone chemical shift at 204 ppm and the iron CO chemical shift at 210 ppm. However, the ^1H NMR spectrum of the complex shows only one vinyl proton at 5.57 ppm. Thus, the crude $(\eta^4\text{-diene})\text{Fe}(\text{CO})_3$ complex was treated with 2,4-dinitrophenylhydrazine to give the hydrazone derivative **8a**, which structure was confirmed by X-ray diffraction analysis and was consistent with the spectral data discussed above for the keto complex **8b**. The formation of the fused bicyclic skeleton of the keto complex **8b** may involve the initial formation of the acid chloride **9a** followed by Lewis acid promoted double bond migration to give **9b**. Intramolecular Friedel–Crafts reaction of **9b** lead to formation of **8b**. The Lewis acid promoted double bond migration of iron–diene complexes, presumably via a hydride abstraction/readdition process, had been reported in the literature.⁸ However, under the same reaction conditions, intramolecular Friedel–Crafts reaction of an acyclic acid complex, for example, **3b**, gave an unidentified crude oil. None of the desired keto complex was isolated.

Formation of $(\sigma,\eta^3\text{-Allyl})\text{tricarbonyliron}$ Complexes. Interestingly, aluminum chloride promoted intramolecular cyclization of the acyclic complexes with an aldehyde moiety, for example, **2a**, generated $(\sigma,\eta^3\text{-allyl})\text{tricarbonyliron}$ complex **10a** (Chart 2), as the only diastereomeric isomer isolated. None of the cyclized product derived from addition of the diene ligand at the

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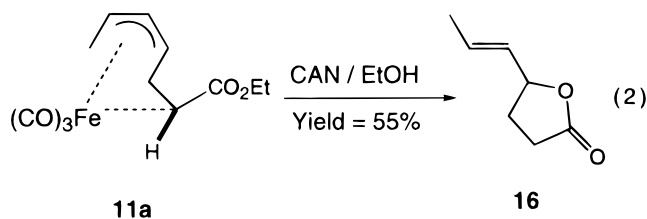
Chart 2



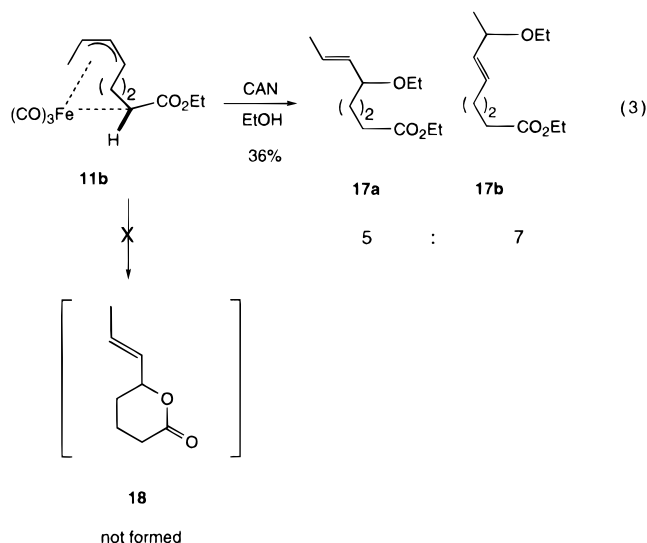
carbonyl carbon of the aldehyde functionality was found. Thus, treatment of **2a** with 3.0 molar equiv of aluminum chloride at 25 °C under nitrogen for 3 h in dichloromethane followed by quenching the reaction mixture with aqueous ammonium chloride produced a major product in 21% yield, identified as (σ,η^3 -allyl)tricarbonyliron complex **10a** after purification by flash column chromatography. The stereochemistry of the allyl ligand is assigned as shown on the basis of the coupling pattern for the internal vinyl protons of the allyl ligand. The ¹H NMR exhibited a triplet at δ 4.93, assigned to the proton at the internal allyl carbon. The coupling constant of 12.2 Hz for the triplet indicated a cis-cis relationship between allyl protons. Complexes of the (σ,η^3 -allyl)tricarbonyliron type were previously made by reaction of iron pentacarbonyl with vinylcyclopropane,⁹ addition of lithium reagents to the (η^5 -pentadienyl)Fe(CO)₃ cation,¹⁰ or intramolecular nucleophilic addition of (η^4 -diene)Fe(CO)₃ complexes bearing functionalized side chains at the C-2 position of the diene ligand.¹¹ Similarly, intramolecular cyclization of complexes **2b** using aluminum chloride afforded (σ,η^3 -allyl)tricarbonyliron derivative **10b** in 10% yield. Furthermore, complexes with an ester or nitrile functional group also produced (σ,η^3 -allyl)tricarbonyliron complexes **11a–d** and **12a,b**, respectively, in the presence of Lewis acid. It is important to mention that only ester functionalized complexes **1a–d** produced (σ,η^3 -allyl)tricarbonyliron complexes in good yields (83–88%) and titanium chloride is the best Lewis acid for the intramolecular cyclizations.

The formation of (σ,η^3 -allyl)tricarbonyliron complexes was suggested in Scheme 2. Because of the coordination of titanium chloride with the carbonyl and hydroxy of the ester enol, the ethoxy group will point away from the metal center in the transition state conformation. Addition of the α -face of ester enolate **13** at the carbonyl of the Fe(CO)₃ moiety would generate the acyl-hydride intermediate with the relative stereochemistry depicted in **14**. Rearrangement of **14** might produce (σ,η^2 -alkene)tricarbonyliron complex **15**. Hydride addition to the alkene ligand would generate (σ,η^3 -allyl)tricarbonyliron complex **11a**. It is important to note that two new stereogenic centers of (σ,η^3 -allyl)tricarbonyliron

complexes **10** and **11** are created; however, only the single diastereomer shown was isolated. Due to their apparent instability, further manipulation of some (σ,η^3 -allyl)tricarbonyliron complexes was demonstrated as follows. Oxidative cleavage of complex **11a** with an



excess of ethanolic ceric ammonium nitrate (CAN) under nitrogen provided γ -lactone **16** in 55% yield after evaporation and flash column chromatography of the crude residue.¹² None of vinylcyclopropane derivatives is isolated.¹³ The stereochemistry of the double bond of **16** was assigned as trans on the basis of ¹H NMR studies. The proton at δ 5.81 as a dq, $J = 16.0, 6.4$ Hz, was assigned to H_a. The coupling constant of H_a–H_b (J_{ab}) of 16.0 Hz agrees with 14–17 Hz coupling constant for most trans hydrogens of olefins. However, oxidation of the complex with one more carbon unit, for example, **11b**, with CAN-generated olefins **17a** and **17b** in a ratio



of 5:7 in 36% yield. None of the desired δ -lactones was isolated. The reaction may involve addition of methanol at the terminal position of the allyl ligand to provide olefins **17a** and **17b**. Both olefins were assigned as trans on the basis of their coupling constants (15.1 and 15.6 Hz, respectively) of the vinyl protons. The formation of *trans*-lactone **16** and olefins **17a** and **17b** may be derived from syn/anti isomerization via π -allyl/ σ -allyl interconversion of the allyl ligand during the oxidation process at 25 °C.¹⁴ The formation of olefins by oxidative

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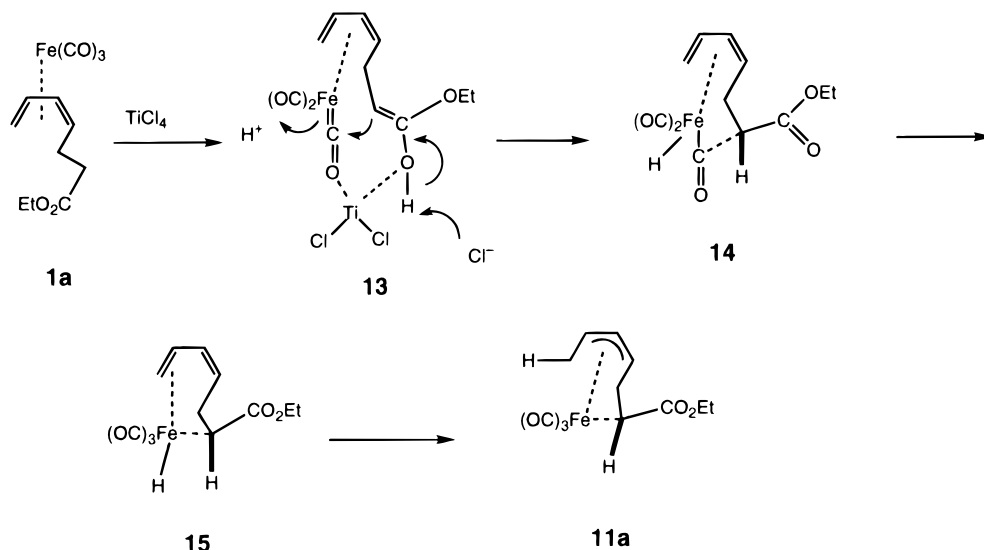
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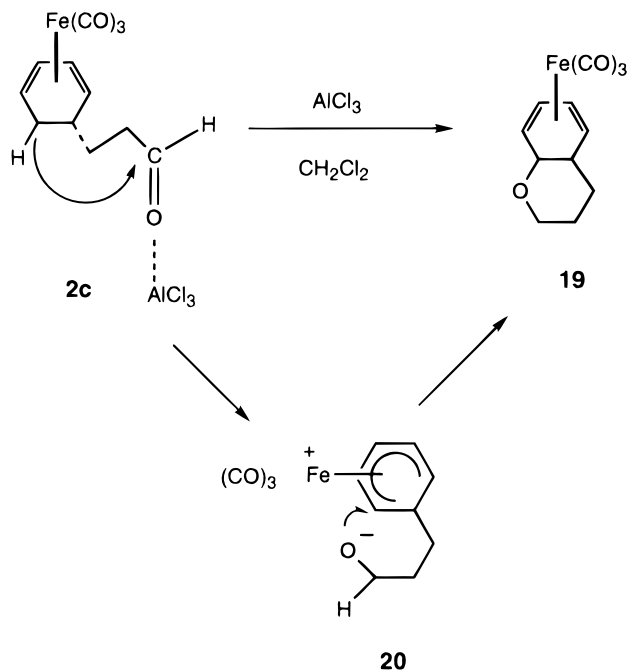
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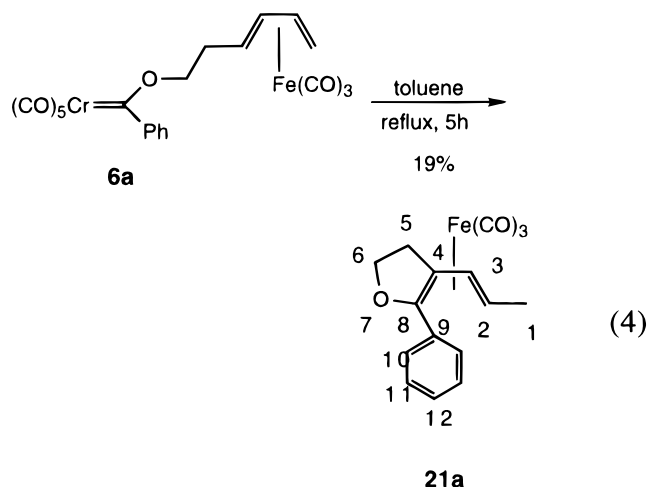
Scheme 2



Scheme 3



Formation of Furan Derivatives via Intramolecular Nucleophilic Addition of (Diene)iron Tricarbonyl Complexes to the Chromium Carbene Carbon Center. Complex **6a** was dissolved in toluene, and the solution was refluxed under nitrogen for 5 h to produce a major product in 19% yield, identified as $(\eta^4\text{-diene})\text{iron}$ complex **21a** (eq 4). Spectroscopic studies



cleavage of $(\sigma,\eta^3\text{-allyl})\text{tricarbonyliron}$ complexes using CAN in methanol was reported in the literature.¹⁵

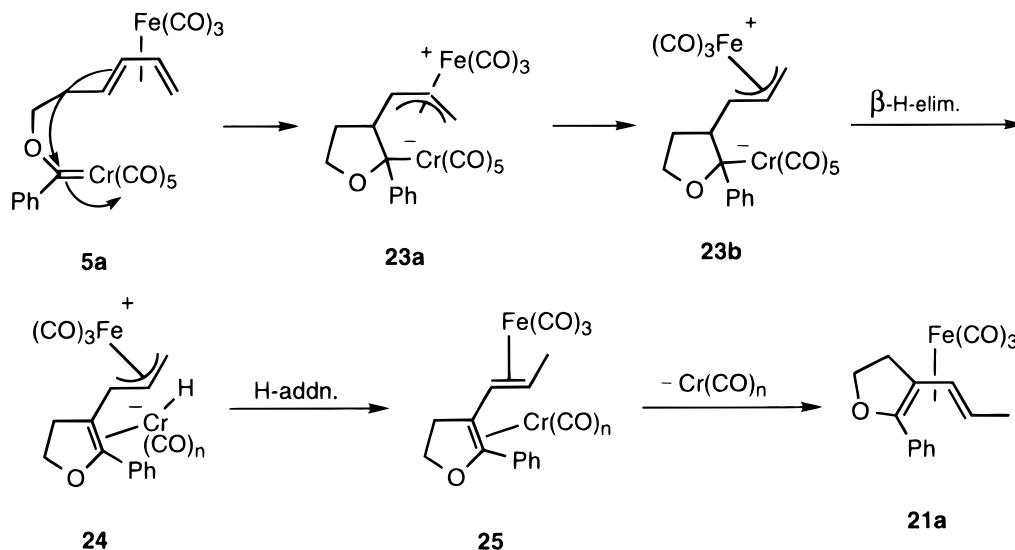
Interestingly, Lewis acid assisted intramolecular cyclization of the cyclic complex containing an aldehyde functionality, for example, complex **2c**, produced tetrahydrobenzopyran-iron complex **19** in 56% yield as the sole product isolated (Scheme 3). However, our approach to the synthesis of the heterobicyclic complex **19** is different from that developed in Pearson's group.¹⁶ In the previous method, tetrahydrobenzofuran-iron complexes were obtained by oxidative cyclization of $(\eta^4\text{-cyclohexadiene})\text{Fe}(\text{CO})_3$ complexes bearing an primary alcohol. The formation of **19** was presumably derived from Lewis acid assisted hydride migration of **2c** to generate zwitterion **20**. Addition of the oxygen anion at the terminal position of the $(\eta^5\text{-cyclohexadienyl})\text{Fe}(\text{CO})_3$ cation led to formation of complex **19**.

provided the initial evidence for support of the structural assignments of **21a**. The infrared spectrum of **21a** showed the usual iron CO bands at 2031 and 1962 cm^{-1} . The ^1H NMR spectrum of complex **21a** exhibited the following: a multiplet, centered at δ 7.21, assigned to the phenyl protons at C-11 and -12; a triplet, centered at δ 7.16, assigned to the proton at C-10; a doublet, centered at δ 5.49, assigned to the vinyl proton at C-3; a multiplet, centered at δ 4.21, assigned to the protons at C-6; a triplet of doublets, centered at δ 3.45, assigned to one of the two diastereotopic methylene protons at C-5; a multiplet, centered at δ 2.88, assigned to the other diastereotopic methylene protons at C-5; a doublet, centered at δ 1.38, assigned to the methyl group at C-1; a doublet of quartets centered at δ 1.10, assigned to the terminal proton at C-2. The chemical shift of 1.10 for the terminal proton agrees with that of an endo proton of most diene-iron complexes bearing an endo substituent at the other terminal position of the diene ligand. The ^{13}C NMR spectrum of complex **21a** exhibited the

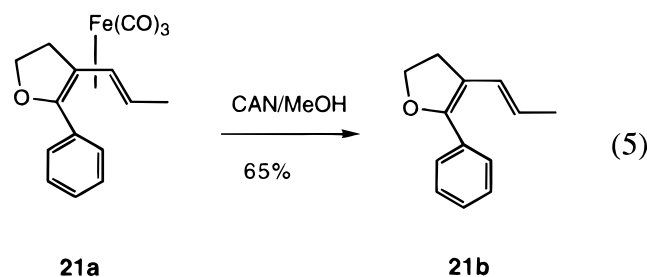
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Scheme 4

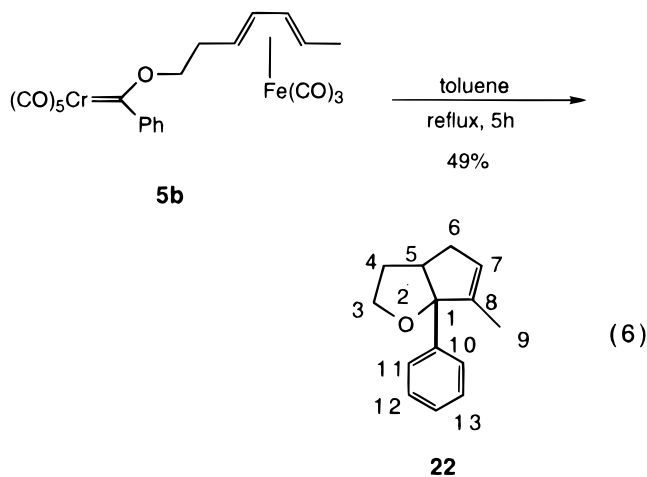


following: a signal at δ 212.5 assigned to the carbonyl of the tricarbonyliron moiety; four signals at δ 136.1, 128.2, 127.8, and 127.5 assigned to C-9, -10, -11, and -12 (carbons of the phenyl group); a signal at δ 117.8 assigned to C-8; a signal at δ 89.9 assigned to C-4; a signal at δ 82.3 assigned to C-3; a signal at δ 65.3 assigned to C-6; a signal at δ 55.8 assigned to C-2; a signal at δ 34.4 assigned to C-5; a signal at δ 19.8 assigned to C-1. Furthermore, treatment of complex **21a** with methanolic CAN provided dihydrofuran derivative **21b** in 65% yield after purification by flash column chromatograph and distillation under reduced pressure (eq 5). However, under the same reaction conditions,



cyclization of the complex with an additional methyl group at the terminal position of the diene ligand, for example, **6b**, afforded a colorless liquid. The compound does not possess the carbonyl functionality of Fe(CO)₃ or Cr(CO)₅ on both infrared and ¹³C NMR spectroscopies. The compound was assigned as fused furan derivative **22** (49% yield, eq 6) on the basis of its ¹H NMR and COSY spectrum. The ¹H NMR spectrum of complex **22** exhibited the following: a multiplet, centered at δ 7.32, assigned to the phenyl proton at C-11, -12, -14, and -15; a multiplet, centered at δ 7.22, assigned to the phenyl proton at C-13; a doublet, centered at δ 5.60, assigned to the vinyl proton at C-7; a doublet of doublets of doublets, centered at δ 4.01, assigned to one of the two diastereotopic methylene protons at C-3; a triplet of doublets, centered at δ 3.77, assigned to the other diastereotopic methylene protons at C-3; a multiplet, centered at δ 2.71, assigned to the protons at C-6 and C-5; a multiplet centered at δ 2.17 assigned to the protons at C-4 and C-6; a multiplet at δ 1.63, assigned to the proton at C-4; a doublet at δ 1.50,

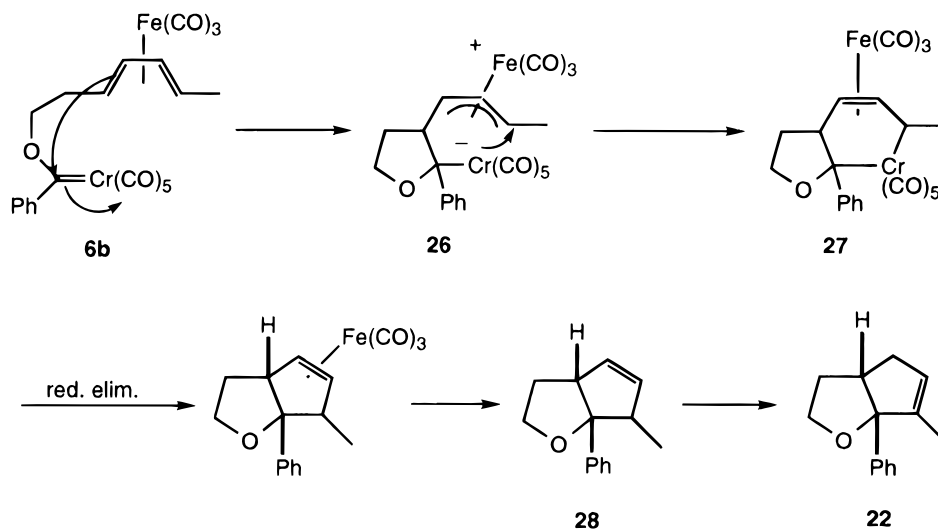
assigned to the methyl group at C-9. The ¹³C NMR spectrum of **22** exhibited the following: a signal at δ



144.7 assigned to the vinyl carbon at C-8; four signals at δ 141.6, 128.1, 127.3, and 124.9 assigned to phenyl carbons; a signal at δ 126.5 assigned to the vinyl carbon at C-7; a signal at δ 99.7 assigned to C-1; a signal at δ 67.0 assigned to C-3; a signal at δ 49.3 assigned to C-6; a signal at δ 37.9 assigned to C-4; a signal at δ 35.9 assigned to C-5; a signal at δ 12.1 assigned to C-9.

The formation of **21a** may start with nucleophilic addition of the diene ligand of **6a** at the carbene carbon center to give the cyclic intermediate **23a**, which underwent (π -allyl) *syn/anti* isomerization (to produce **23b**), followed by β -hydride elimination to generate zwitterion **24**. Hydride addition at the terminal position of the ally ligand produced **25**. Detachment of the chromiumcarbonyl moiety followed by reattachment of the alkene ligand to the iron center gave complex **21**. However, cyclization of **6b** underwent a different reaction pathway (Scheme 5). Due to the steric reason, the *syn/anti* isomerization of the disubstituted π -allyl anionic intermediate **26** may be slow. Thus, addition of the anionic chromium atom at the terminal position of the ally ligand may occur to give the metalcyclohexene intermediate **27**, which underwent reductive elimination followed by the detachment of the Fe(CO)₃ moiety

Scheme 5



produced the bicyclic skeleton **28**. Double bond migration of **28** furnished **22**.¹⁷

The reactions described herein demonstrate that Lewis acid promoted intramolecular cyclization of acyclic (η^4 -diene)Fe(CO)₃ complexes containing an aldehyde, an ester, or a nitrile functionality provides (σ, η^3 -allyl)tricarbonyliron complexes. Intramolecular nucleophilic addition of (η^4 -diene)Fe(CO)₃ complexes to the chromiumcarbene carbon center leads to formation of furan derivatives.

Experimental Section

All reactions were run under a nitrogen atmosphere in oven-dried glassware unless otherwise indicated. Anhydrous solvents or reaction mixtures were transferred via an oven-dried syringe or cannula. Diethyl ether (ether) and tetrahydrofuran (THF) were distilled under nitrogen from a deep blue sodium benzophenone ketyl solution. Methylene chloride was distilled from calcium hydride before used. Complexes **1a–f** were synthesized according to the literature procedures.^{4a} Flash column chromatography, following the method of Still,¹⁸ was carried out with E. Merck silica gel (Kieselgel 60, 230–400 mesh) using the indicated solvents. Analytical thin-layer chromatography was performed with silica gel 60 F₂₅₄ plastic plates of 0.2-mm thickness from E. Merck. The term “concentration” refers to the removal of solvent with an aspirator pump (Yamato Instrument Co. Model WP-15) with a Buchi Rotovapor-R. The term “under nitrogen” implies that the apparatus was evacuated (oil pump) and then filled with nitrogen three times. The term “flash distillation” refers to a vacuum distillation at 25 °C with a receiver at –78 °C. Melting points were determined in open capillaries with a Thomas-Hoover apparatus and are uncorrected. ¹H nuclear magnetic resonance (NMR) spectra were obtained with a JEOL EX 400 instrument (400 MHz). Chemical shifts are reported in parts per million with either tetramethylsilane (0.00 ppm) or CHCl₃ (7.26 ppm) as internal standard. ¹³C NMR spectra were recorded with a JEOL EX 400 spectrometer (100.4 MHz) with CDCl₃ (77.0 ppm) as the internal standard. Infrared (IR) spectra were recorded with a Jasco IR-700 spectrometer. Mass spectra were acquired on a JEOL JMS-D 100 spectrometer at an ionization potential of 70 eV and are reported as mass/charge (*m/e*) with percent relative abundance. High-resolution

mass spectra were obtained with an AEI MS-9 double-focusing mass spectrometer and a JEOL JMS-HX 110 spectrometer at the Department of Chemistry, Central Instrument Center, Taichung, ROC.

General Procedure for Hydrolysis of Ester **1 to Acid **3**.** A solution of potassium hydroxide (0.33 g) in water (5 mL) at 25 °C was added to ester complexes **1a,b** (1.0 mmol) in 1:1 methanol/THF (10 mL). The reaction mixture was stirred for 4 h at 25 °C, and then it was added to 100 mL of 10% aqueous hydrochloric acid at 0 °C. The aqueous solution was extracted two times with 50 mL of 50% ethyl acetate/hexanes. The resultant solution was washed with water (100 mL × 3) and brine (100 mL × 3), dried over anhydrous magnesium sulfate (10 g), and concentrated to give the crude mixture.

[*exo*-3-(η^4 -Cyclohexa-1,3-diene-5-yl)propionic acid]tricarbonyliron (3a**).** The crude mixture obtained from the hydrolysis of the corresponding ester^{4a} (0.97 g, 3.0 mmol) was purified via flash column chromatography (silica gel, 20% ethyl acetate/hexanes) to give **3a** (0.75 g, 2.6 mmol, 85%) as a yellow solid mp: 79–80 °C; IR(CH₂Cl₂) 3500–2800 (br), 2042, 1972, 1708, 1606, 1437, 1418, 1286, 1041, 940 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.38 (dd, *J* = 6.3, 4.6 Hz, 1 H), 5.29 (td, *J* = 4.9, 1.5 Hz, 1 H), 3.07 (dd, *J* = 6.4, 4.3 Hz, 1 H), 3.04 (dd, *J* = 4.2, 2.0 Hz, 1 H), 2.29 (t, *J* = 7.3 Hz, 2 H), 2.06 (m, 2 H), 1.58 (m, 2 H), 1.23 (br doublet, *J* = 14.2 Hz, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 211.9, 180.0, 85.7, 84.3, 65.3, 59.4, 37.2, 34.2, 32.6, 30.4; MS (30 eV) *m/e* (relative intensity) 292 (M⁺, 4), 264 (19), 236 (57), 208 (75), 160 (100); HRMS (EI) *m/e* calcd for C₁₂H₁₂FeO₅ (M⁺) 292.0034, found 292.0022.

[5-*8*- η -*cis*-5,7-Octadienoic acid]tricarbonyliron (3b**).** The crude mixture obtained from the hydrolysis of **1b**^{4a} (0.53 g, 1.70 mmol) was purified via flash column chromatography (silica gel, 20% ethyl acetate/hexanes) to give **3b** (0.46 g, 1.6 mmol, 98%) as a yellow oil: IR (CH₂Cl₂) 3500–2700 (br), 2047, 1973, 1711, 1453, 1362, 1275, 1223, 1128 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.44 (m, 1 H), 5.30 (t, *J* = 7.4 Hz, 1 H), 2.52 (m, 1 H), 2.30 (m, 2 H), 1.86 (d, *J* = 7.8 Hz, 1 H), 1.73 (m, 1 H), 1.58 (m, 2 H), 1.43 (d, *J* = 9.8 Hz, 1 H), 1.07 (m, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 211.1, 179.5, 90.9, 86.8, 59.0, 40.9, 28.1, 27.6; MS (30 eV) *m/e* (relative intensity) 252 (M⁺ – CO, 6), 224 (34), 196 (100), 178 (7), 154 (11), 150 (16), 148 (23), 140 (50), 136 (10), 134 (18), 122 (29), 112 (8), 84 (15), 81 (27), 79 (26), 73 (15), 67 (18), 56 (33), 53 (13); HRMS (EI) *m/e* calcd for C₁₁H₁₂FeO₅ (M⁺) 280.0034, found 280.0036.

Intramolecular Friedel–Crafts Reaction of Complex **3a. Formation of Complex **8a**.** To a solution of 1.0 mmol (0.29 g) of complex **3a** in 30 mL of methylene chloride was added a solution of 0.1 mL (1.2 mmol) of oxallyl chloride in 0.17 mL (1.2 mmol) of triethylamine at 0 °C under nitrogen.

(17) Alternatively, intramolecular cyclopropanation followed by iron-mediated rearrangement of **6a** and **6b** would produce **21a** and **22**, respectively.

(18) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

The reaction mixture was stirred for 45 min followed by addition of 0.2 g (1.5 mmol) of aluminum chloride in 10 mL of methylene chloride. The reaction was stirred at 0 °C for 1 h and was quenched with 50 mL of water. The reaction mixture was diluted with 200 mL of methylene chloride. The resultant solution was washed with water (300 mL \times 3) and brine (300 mL \times 3), dried over anhydrous magnesium sulfate, and finally concentrated on a rotary evaporator to give the crude mixture (55 mg, 20%). The above crude mixture in 3 mL of ethanol was added to a solution of 0.33 g of 2,4-dinitrophenylhydrazine in 9 mL of phosphoric acid (85% in H₂O) and 9 mL of ethanol (95%) following the literature procedure.¹⁹ The reaction mixture was stirred at 25 °C for 20 min and diluted with 50 mL of ethyl acetate. The resultant solution was washed with water (100 mL \times 3) and brine (100 mL \times 3), dried over anhydrous magnesium sulfate (10 g), and concentrated to give the crude mixture. The crude mixture was purified via flash column chromatography (silica gel, 20% ethyl acetate/hexanes) and recrystallization (ethanol) to give **7** (0.03 g, 0.06 mmol, 6%) as a yellow solid: mp 118 °C (dec); IR (CH₂Cl₂) 3053, 2988, 2045, 1981, 1616, 1460, 1421, 1337, 1314, 1275, 1267, 1251, 1092 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 11.0 (s, 1 H), 9.13 (d, J = 2.5 Hz, 1 H), 8.31 (dd, J = 9.7, 2.5 Hz, 1 H), 7.97 (d, J = 9.7 Hz, 1 H), 5.60 (d, dd, J = 6.5 Hz, 1 H), 3.30 (t, J = 4.3 Hz, 1 H), 3.18 (m, 1 H), 2.90 (m, 2 H), 2.70 (m, 1 H), 2.39 (td, J = 11.3, 3.9 Hz, 1 H), 1.91 (m, 1 H), 1.71 (dd, 143.7, 3.4 Hz, 2 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 210.7, 167.6, 144.6, 137.8, 130.0, 128.9, 123.6, 116.6, 113.8, 82.4, 78.8, 59.0, 29.0, 26.1, 23.9, 22.8; MS (EI) m/e (relative intensity) 454 (22), 426 (36), 398 (60), 370 (16), 354 (76), 322 (100).

General Procedure for Reduction of Ester 1 to Aldehyde 2 Using Diisobutylaluminum Hydride. To a solution of 5.0 mmol of an ester complex in 50 mL of methylene chloride was added a solution of 6.0 mL (6.0 mmol) of DIBAL (1.0 M in toluene) at -78 °C. The reaction was stirred at -78 °C for 15 min and was decomposed with 30 mL of 50% toluene/methanol followed by addition of 30 mL of 10% aqueous hydrochloric acid. The reaction mixture was diluted with 200 mL of ether. The ethereal solution was washed with water (300 mL \times 3) and brine (300 mL \times 3), dried over anhydrous magnesium sulfate, and concentrated to give the crude mixture.

[(5- η)-*cis*-5,7-Octadienyl]tricarbonyliron (2a**).** The crude mixture obtained from reduction of the corresponding ester **1b**^{4a} (0.30 g, 1.0 mmol) was purified via flash column chromatography (silica gel, 10% ethyl acetate/hexanes) to give **2a** (0.19 g, 0.72 mmol, 72%) as a yellow oil: ¹H NMR (400 MHz, CDCl₃) δ 9.72 (t, J = 1.5 Hz, 1 H), 5.46 (dt, J = 8.3, 4.9 Hz, 1 H), 5.30 (dd, J = 7.8, 4.9 Hz, 1 H), 2.42 (m, 1 H), 2.39 (dd, J = 9.8, 6.4 Hz, 2 H), 1.87 (dd, J = 7.4, 2.0 Hz, 1 H), 1.72 (m, 1 H), 1.69-1.49 (m, 2 H), 1.43 (dd, J = 8.3, 1.9 Hz, 1 H), 1.07 (m, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 211.1, 201.9, 90.8, 86.8, 59.0, 43.1, 40.9, 28.2, 25.1.

[(6- η)-*cis*-6,8-Nonadienyl]tricarbonyliron (2b**).** The crude mixture obtained from reduction of the corresponding ester **1c**^{4a} (0.32 g, 1.0 mmol) was purified via flash column chromatography (silica gel, 10% ethyl acetate/hexanes) to give **2b** (0.2 g, 0.70 mmol, 70%) as a yellow oil: ¹H NMR (400 MHz, CDCl₃) δ 9.74 (t, J = 1.5 Hz, 1 H), 5.42 (m, 1 H), 5.29 (dd, J = 7.8, 4.9 Hz, 1 H), 2.54 (dd, J = 13.2, 8.3 Hz, 1 H), 2.38 (td, J = 7.3, 1.3 Hz, 2 H), 1.86 (dd, J = 7.8, 1.9 Hz, 1 H), 1.62-1.52 (m, 3 H), 1.46-1.40 (m, 2 H), 1.26 (m, 1 H), 1.06 (m, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 211.3, 201.7, 90.7, 86.9, 59.7, 43.6, 40.8, 32.3, 28.4, 21.4; MS (70 eV) m/e (relative intensity) 278 (M⁺, 12), 250 (12), 222 (38), 194 (100), 150 (14), 134 (12), 126 (37), 121 (8), 84 (6), 56 (10); HRMS (EI) m/e calcd for C₁₁H₁₄FeO₃ (M⁺ - CO) 250.0292, found 250.0299.

[*exo*-3-(η^4 -Cyclohexa-1,3-diene-5-yl)propanyl]tricarbonyliron (2c**).** The crude mixture obtained from reduction of

the corresponding ester complex^{4a} (0.97 g, 3.04 mmol) was purified via flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give **2c** (0.64 g, 2.3 mmol, 76%) as a yellow oil: IR (CH₂Cl₂) 3007, 2936, 2847, 2044, 1970, 1723, 1609, 1424, 1362, 1289, 1094, 918, 654 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 9.73 (s, 1 H), 5.37 (m, 1 H), 5.29 (dd, J = 5.3, 2.7 Hz, 1 H), 3.04 (m, 2 H), 2.38 (t, J = 7.3 Hz, 2 H), 2.08-1.98 (m, 2 H), 1.59-1.45 (m, 2 H), 1.21 (d, J = 14.2 Hz, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 211.9, 201.9, 85.7, 84.5, 65.4, 59.4, 42.4, 37.4, 31.5, 30.6; MS (EI) m/z (relative intensity): 276 (M⁺, 2), 248 (12), 220 (52), 192 (52), 190 (62), 134 (100); HRMS (EI) m/e calcd for C₁₂H₁₂FeO₄ 276.0085, found 276.0092.

General Procedure for Intramolecular Nucleophilic Addition of (η^4 -diene)Fe(CO)₃ Complexes to Aldehyde, Ester, or Nitrile Functional Groups in the Presence of a Lewis Acid. Formation of (σ,η^3 -Allyl)tricarbonyliron Complexes. To a stirred suspension of 3.0 mmol of Lewis acid (AlCl₃ or TiCl₄) in 2 mL was added a solution of 1.0 mmol of a complex in 5.0 mL of methylene chloride at 0 °C under nitrogen. The reaction temperature was raised to 25 °C. The reaction was monitored by TLC until no starting iron complexes was detected. The reaction mixture was then diluted with 200 mL of methylene chloride. The resultant solution was washed with water (300 mL \times 3) and brine (300 mL \times 3), dried over anhydrous magnesium sulfate, and finally concentrated to give the crude mixture.

Formation of (σ,η^3 -Allyl)tricarbonyliron Complex 10a. The crude mixture obtained from intramolecular cyclization of complex **2a** (0.22 g, 0.83 mmol) and AlCl₃ was purified via flash column chromatography (silica gel, 15% ethyl acetate/hexanes) to give **10a** (0.05 g, 0.21 mmol, 21%) as a yellow oil: IR (CH₂Cl₂) 3061, 2988, 2948, 2087, 2035, 2006, 1725, 1424, 1269, 1250, 1117, 909 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 9.84 (s, 1 H), 4.93 (t, J = 12.2 Hz, 1 H), 4.00 (m, 1 H), 3.89 (m, 1 H), 2.64 (m, 2 H), 2.65 (t, J = 6.9 Hz, 1 H), 2.05 (d, J = 5.8 Hz, 3 H), 2.03 (m, 2 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 207.4, 205.1, 204.9, 201.3, 104.9, 87.5, 84.6, 43.0, 34.2, 24.1, 20.1; MS (70 eV) m/e (relative intensity) 264 (M⁺, 2), 236 (6), 208 (6), 180 (19), 149 (11), 141 (28), 140 (13), 125 (49), 124 (42), 123 (14), 109 (20), 97 (42), 95 (38), 81 (75), 68 (100), 55 (80); HRMS (EI) m/e calcd for C₈H₁₂FeO (M⁺ - 3CO) 180.0237, found 180.0238.

Formation of (σ,η^3 -Allyl)tricarbonyliron Complex 10b. The crude mixture obtained from intramolecular cyclization of complex **2b** (0.10 g, 0.35 mmol) and AlCl₃ was purified via flash column chromatography (silica gel, 15% ethyl acetate/hexanes) to give **10b** (0.01 g, 0.02 mmol, 10%) as a yellow oil: IR (CH₂Cl₂) 3067, 3046, 2992, 2982, 2085, 2035, 2006, 1713, 1607, 1424, 1273, 1248, 1105, 914 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 9.81 (s, 1 H), 4.91 (t, J = 12.2 Hz, 1 H), 4.01-3.92 (m, 2 H), 2.53 (t, J = 7.3 Hz, 2 H), 2.52 (m, 1H), 2.04 (d, J = 6.4 Hz, 3 H), 1.82-1.58 (m, 4 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 207.6, 205.2, 205.0, 201.9, 104.8, 88.4, 84.3, 43.6, 34.9, 31.3, 21.6, 20.1; MS (70 eV) m/e (relative intensity) 278 (M⁺, 1), 250 (10), 222 (64), 195 (30), 194 (100), 192 (19), 166 (8), 152 (13), 150 (27), 148 (11), 140 (18), 138 (28), 136 (13), 134 (31), 127 (11), 126 (85), 110 (18), 99 (14), 98 (18), 96 (23), 84 (15), 82 (20), 67 (12), 57 (15), 56 (47); HRMS (EI) m/e calcd for C₁₂H₁₄FeO₄ (M⁺) 278.0241, found 278.0239.

Formation of (σ,η^3 -Allyl)tricarbonyliron Complex 11a. The crude mixture obtained from intramolecular cyclization of the corresponding ester complex^{4a} (0.60 g, 2.26 mmol) and TiCl₄ was purified via flash column chromatography (silica gel, 10% ethyl acetate/hexanes) to give **11a** (0.55 g, 1.88 mmol, 83%) as a yellow oil: IR (CH₂Cl₂) 3005, 2967, 2087, 2037, 2006, 1730, 1628, 1564, 1433, 1416, 1375, 1292, 1109, 924 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.02 (t, J = 12.2 Hz, 1 H), 4.19 (q, J = 7.3 Hz, 2 H), 4.00 (m, 1 H), 3.84 (m, 1 H), 2.79-2.65 (m, 2 H), 2.36 (m, 1 H), 2.03 (d, J = 6.8 Hz, 3 H), 1.30 (t, J = 7.3 Hz, 3 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 207.2, 205.5, 205.2, 172.2, 105.2, 86.2, 84.8, 60.8, 35.7, 30.1, 20.1,

(19) The hydrazone **8a** was formed in the usual way: Pavia, D. L.; Lampman, G. M.; Kriz, G. S., Jr. *Introduction to Organic Laboratory Techniques*; W. B. Saunders Co.: Philadelphia, PA, 1975; p 668.

14.2; MS (EI) m/e (relative intensity) 294 (M^+ , 8), 266 (4), 246 (100), 210 (90), 182 (18), 155 (84).

Formation of (σ,η^3 -Allyl)tricarbonyliron Complex 11b.

The crude mixture obtained from intramolecular cyclization of the corresponding ester complex^{4a} (0.50 g, 1.70 mmol) and $TiCl_4$ was purified via flash column chromatography (silica gel, 10% ethyl acetate/hexanes) to give **11b** (0.46 g, 1.50 mmol, 84%) as a yellow oil: IR (CH_2Cl_2) 3067, 3046, 2992, 2982, 2087, 2035, 2006, 1728, 1424, 1256, 1155, 929 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 4.94 (t, $J = 12.2$ Hz, 1 H), 4.16 (q, $J = 7.3$ Hz, 2 H), 4.01 (m, 1 H), 3.95 (m, 1 H), 2.57 (m, 1 H), 2.47 (t, $J = 6.8$ Hz, 1 H), 2.04 (d, $J = 6.4$ Hz, 3 H), 2.03–1.98 (m, 3 H), 1.28 (t, $J = 7.3$ Hz, 3 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 207.5, 205.3, 205.0, 172.9, 104.9, 87.7, 84.5, 60.5, 34.3, 33.5, 26.9, 20.1, 14.2; MS (70 eV) m/e (relative intensity) 168 [$M^+ - Fe(CO)_3$], 140 (6), 139 (37), 138 (22), 123 (6), 111 (23), 110 (28), 99 (10), 97 (66), 96 (54), 95 (32), 81 (19), 71 (22), 69 (100), 55 (21). HRMS (EI) m/e calcd for $C_{10}H_{16}O_2$ [$M^+ - Fe(CO)_3$] 168.1150, found 168.1146.

Formation of (σ,η^3 -Allyl)tricarbonyliron Complex 11c.

The crude mixture obtained from intramolecular cyclization of the corresponding ester complex^{4a} (0.50 g, 1.70 mmol) and $TiCl_4$ was purified via flash column chromatography (silica gel, 10% ethyl acetate/hexanes) to give **11c** (0.48 g, 1.48 mmol, 87%) as a yellow oil: IR (CH_2Cl_2) 3383, 3067, 2992, 2982, 2085, 2035, 2004, 1728, 1427, 1419, 1289, 1242, 1182, 1153 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 4.91 (t, $J = 12.7$ Hz, 1 H), 4.15 (q, $J = 6.8$ Hz, 2 H), 3.99–3.96 (m, 2 H), 2.54 (m, 1 H), 2.37 (t, $J = 7.4$ Hz, 2 H), 2.17 (m, 1 H), 2.04 (d, $J = 6.3$ Hz, 3 H), 1.78–1.64 (m, 3 H), 1.27 (t, $J = 6.8$ Hz, 3 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 207.6, 205.2, 205.1, 173.3, 104.8, 88.7, 84.3, 60.4, 34.9, 34.0, 31.4, 24.5, 20.1, 14.3; MS (70 eV) m/e (relative intensity) 266 ($M^+ - 2CO$, 1), 238 (2), 199 (4), 198 (26), 183 (3), 182 (9), 156 (3), 155 (7), 154 (5), 153 (18), 152 (18), 137 (14), 125 (39), 124 (11), 111 (24), 110 (55), 101 (20), 97 (48), 94 (36), 84 (34), 81 (40), 71 (26), 69 (100), 67 (39), 55 (40); HRMS (EI) m/e calcd for $C_{11}H_{18}FeO_2$ ($M^+ - 3CO$) 238.0656, found 238.0655.

Formation of (σ,η^3 -Allyl)tricarbonyliron Complex 11d.

The crude mixture obtained from intramolecular cyclization of the corresponding complex^{4a} (0.54 g, 1.62 mmol) and $TiCl_4$ was purified via flash column chromatography (silica gel, 12% ethyl acetate/hexanes) to give **11d** (0.48 g, 1.43 mmol, 88%) as a yellow oil: IR (CH_2Cl_2) 3084, 3029, 2938, 2085, 2033, 2004, 1728, 1566, 1437, 1414, 1302, 1103 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 4.91 (t, $J = 12.2$ Hz, 1 H), 4.13 (q, $J = 7.4$ Hz, 2 H), 3.95 (m, 2 H), 2.52 (m, 1 H), 2.33 (t, $J = 7.3$ Hz, 2 H), 2.03 (d, $J = 6.3$ Hz, 3 H), 1.97 (m, 2 H), 1.78–1.42 (m, 4 H), 1.27 (t, $J = 6.9$ Hz, 3 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 207.7, 205.2, 205.0, 173.6, 104.8, 89.2, 84.1, 60.3, 34.9, 34.1, 31.6, 28.7, 24.7, 20.1, 14.2; MS (EI) m/e (relative intensity) 336 (M^+ , 2), 288 (100), 252 (70), 206 (18), 197 (40), 184(72), 149(41), 123(23), 91(25); HRMS (EI) m/e calcd for $C_{12}H_{20}FeO_2$ ($M^+ - 3CO$) 252.0805, found 2252.0812.

Formation of (σ,η^3 -Allyl)tricarbonyliron Complex 12a.

The crude mixture obtained from intramolecular cyclization of the corresponding cyano complex^{4a} (0.08 g, 0.22 mmol) and $AlCl_3$ was purified via flash column chromatography (silica gel, 12% ethyl acetate/hexanes) to give **12a** (0.02 g, 0.05 mmol, 23%) as a yellow oil: IR (CH_2Cl_2) 3065, 3052, 2988, 2249, 2087, 2037, 2008, 1424, 1281, 1262, 1248, 914 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 4.96 (t, $J = 12.2$ Hz, 1 H), 4.03 (m, 1 H), 3.81 (m, 1 H), 2.66 (m, 1 H), 2.54 (t, $J = 6.4$ Hz, 2 H), 2.13–2.05 (m, 2 H), 2.05 (d, $J = 6.3$ Hz, 3 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 207.0, 204.7, 203.3, 118.9, 105.0, 85.2, 85.1, 33.7, 27.2, 20.1, 16.8; MS (70 eV) m/e (relative intensity) 233 ($M^+ - CO$, 10), 213 (46), 205 (42), 178 (50), 177 (41), 176 (100), 150 (32), 134 (29), 122 (39), 110 (10), 94 (39), 83 (67), 81 (43), 55 (25); HRMS (EI) m/e calcd for $C_8H_{11}FeN$ ($M^+ - 3CO$) 177.0241, found 177.0246.

Formation of (σ,η^3 -Allyl)tricarbonyliron Complex 12b.

The crude mixture obtained from intramolecular cyclization

of the corresponding cyano complex^{4a} (0.08 g, 0.30 mmol) and $AlCl_3$ was purified via flash column chromatography (silica gel, 12% ethyl acetate/hexanes) to give **12b** (0.03 g, 0.1 mmol, 33%) as a yellow oil: IR (CH_2Cl_2) 3065, 3046, 2992, 2961, 2930, 2239, 2087, 2035, 2006, 1462, 1424, 1379, 1278, 1098 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 4.93 (t, $J = 12.2$ Hz, 1 H), 4.01 (m, 1 H), 3.89 (m, 1 H), 2.57 (m, 1 H), 2.44 (m, 2 H), 2.32 (t, $J = 6.5$ Hz, 1 H), 2.05 (d, $J = 5.8$ Hz, 3 H), 1.83–1.66 (m, 3 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 207.4, 205.1, 204.9, 119.2, 104.9, 87.3, 84.7, 34.3, 30.9, 24.9, 20.1, 17.1; MS (30 eV) m/e (relative intensity) 191 ($M^+ - 3CO$, 56), 152 (14), 122 (33), 108 (34), 97 (21), 81 (27), 71 (37), 69 (100), 55 (27); HRMS (EI) m/e calcd for $C_9H_{13}FeN$ ($M^+ - 3CO$) 191.0397, found 191.0392.

Formation of γ -trans-1-Propenyl- γ -butyrolactone (16).

To a solution of ceric ammonium nitrate (5.92 g, 10.8 mmol) in 25 mL of ethanol was added a solution of complex **11a** (0.55 g, 1.88 mmol) in 5.0 mL of ethanol. The reaction was stirred at room temperature under nitrogen for 18 h. The solvent was removed under reduced pressure, and the residue was diluted with water (100 mL). The aqueous solution was extracted with methylene chloride (50 mL \times 3). The resultant solution was washed with water (200 mL \times 3) and brine (200 mL \times 3), dried over anhydrous magnesium sulfate (20 g), and concentrated to give the crude mixture. The crude mixture was purified via flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give **16** (0.13 g, 1.03 mmol, 55%): IR (CH_2Cl_2) 3013, 2928, 2856, 1773, 1676, 1578, 1456, 1377, 1325, 1215, 1176, 1120, 1011, 972, 848 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 5.81 (dq, $J = 16.0, 6.4$ Hz, 1 H), 5.53 (ddd, $J = 16.0, 7.0, 1.4$ Hz, 1 H), 4.89 (q, $J = 7.3$ Hz, 1 H), 2.54 (m, 1 H), 2.38 (m, 1 H), 1.98 (m, 2 H), 1.75 (dd, $J = 6.4, 1.4$ Hz, 3 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 177.0, 130.4, 128.7, 81.1, 28.7, 17.6; MS (EI) m/e (relative intensity) 126 (M^+ , 78), 111 (100), 85 (30), 67 (28), 56 (22); HRMS (EI) m/e calcd for $C_7H_{10}O_2$ 126.0681, found 126.0676.

Ethyl trans-2-Ethoxy-6-octenoate (17a). To a solution of ceric ammonium nitrate (7.50 g, 13.8 mmol) in 45 mL of ethanol was added a solution of complex **11b** (0.20 g, 0.70 mmol) in 5.0 mL of ethanol. The reaction was stirred at 25 °C under nitrogen for 18 h. The solvent was concentrated under reduced pressure, and the residue was diluted with water (100 mL). The aqueous solution was extracted with methylene chloride (50 mL \times 3). The resultant solution was washed with water (200 mL \times 3) and brine (200 mL \times 3), dried over anhydrous magnesium sulfate (25 g), and concentrated to give the crude mixture. Flash column chromatography of the crude mixture (silica gel, 5% ethylacetate/hexanes) gave **17a** (0.03 g, 0.14 mmol, 11%) and **17b** (0.04, 0.19 mmol, 16%) as colorless liquid.

Ethyl cis-2-Ethoxy-4-octenoate (17a): 1H NMR (400 MHz, $CDCl_3$) δ 5.58 (dq, $J = 15.6, 6.8$ Hz, 1 H), 5.30 (dd, $J = 15.6, 8.3$ Hz, 1 H), 4.13 (q, $J = 6.8$ Hz, 2 H), 3.55 (m, 2 H), 3.28 (m, 1 H), 2.29 (t, $J = 7.3$ Hz, 2 H), 1.69 (dd, $J = 6.3, 1.4$ Hz, 3 H), 1.68 (m, 2 H), 1.46 (m, 2 H), 1.25 (t, $J = 6.8$ Hz, 3 H), 1.16 (t, $J = 6.8$ Hz, 3 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 173.7, 132.1, 128.2, 80.2, 63.2, 60.2, 35.1, 34.2, 21.1, 17.6, 15.3, 14.2; MS (30 eV) m/e (relative intensity) 214 (M^+ , 0.1), 185 (3), 169 (7), 139 (7), 123 (15), 111 (5), 100 (8), 99 (100), 95 (9), 81 (21), 79 (5), 71 (75), 69 (5), 67 (6), 55 (13); HRMS (EI) m/e calcd for $C_{12}H_{22}O_3$ (M^+) 214.1569 found 214.1568.

Ethyl trans-2-Ethoxy-4-octenoate (17b): 1H NMR (400 MHz, $CDCl_3$) δ 5.56 (dt, $J = 15.6, 6.8$ Hz, 1 H), 5.37 (dd, $J = 15.6, 7.9$ Hz, 1 H), 4.13 (q, $J = 6.8$ Hz, 2 H), 3.78 (pentet, $J = 7.3$ Hz, 1 H), 3.49 (dq, $J = 13.7, 6.8$ Hz, 1 H), 3.33 (dq, $J = 13.7, 7.3$ Hz, 1 H), 2.30 (t, $J = 7.3$ Hz, 2 H), 2.08 (q, $J = 6.8$ Hz, 2 H), 1.72 (m, 2 H), 1.24 (m, 2 H), 1.20 (m, 7 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 173.5, 133.4, 130.9, 76.1, 63.2, 60.2, 33.6, 31.5, 24.4, 21.7, 15.4, 14.2; MS (30 eV) m/e (relative intensity) 214 (M^+ , 1), 199 (10), 185 (3), 169 (18), 168 (38), 141 (10), 139 (9), 125 (14), 123 (54), 111 (62), 99 (100), 97 (32), 95 (46), 94 (78), 86 (18), 83 (29), 71 (78), 67 (25), 55 (35); HRMS (EI) m/e calcd for $C_{12}H_{22}O_3$ (M^+) 214.1569 found 214.1566.

Intramolecular Cyclization of Complex 2c. Formation of Complex 19. A solution of complex **2c** (0.64 g, 2.31 mmol) in 10.0 mL of methylene chloride at 0 °C under nitrogen was added to a stirred suspension of 0.92 g (6.93 mmol) of AlCl₃ in 2 mL of methylene chloride. The reaction temperature was raised to 25 °C. The reaction was monitored by TLC until no starting iron complex was detected. The reaction mixture was diluted with 200 mL of methylene chloride. The resultant solution was washed with water (300 mL \times 3) and brine (300 mL \times 3), dried over anhydrous magnesium sulfate, and finally concentrated to give the crude mixture. Flash column chromatography (silica gel, 25% ethyl acetate/hexanes) gave complex **19** (0.36 g, 1.29 mmol, 56%) as a yellow oil: IR (CH₂Cl₂) 3057, 2984, 2049, 1975, 1624, 1582, 1451, 1400, 1072 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.45 (dd, J = 5.4, 4.9 Hz, 1 H), 5.39 (dd, J = 5.8, 4.8 Hz, 1 H), 3.73 (m, 2 H), 3.40 (m, 1 H), 3.07 (t, J = 4.4 Hz, 1 H), 3.03 (dd, J = 5.4, 4.4 Hz, 1 H), 1.97 (m, 1 H), 1.64 (m, 2 H), 1.30 (m, 1 H), 0.97 (m, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 211.3, 85.9, 84.9, 73.8, 63.4, 62.9, 58.9, 37.1, 28.9, 21.5; MS (EI) m/e (relative intensity): 248 (63), 218 (36), 190 (100), 162 (17); HRMS (EI) m/e calcd for C₁₂H₁₂FeO₄ 276.0084, found 276.0087.

Synthesis of [(3-6- η)-*trans*-3,5-Hexadienol]tricarbonyliron Complex (5a). Ethyl *trans*-3,5-hexadienoate (2.9 g, 20.7 mmol, 87%) was synthesized starting from ethyl sorbate (3.3 g, 23.7 mmol) according to the literature procedure.²⁰ Complexation of ethyl *trans*-3,5-hexadienoate with 7.9 g (0.022 mol) of Fe₂(CO)₉ gave the corresponding [(3-6- η)-ethyl *trans*-3,5-hexadienoate]tricarbonyliron complex (3.14 g, 0.011 mol, 57%). Reduction of the complex with Diisobutylaluminum hydride (20 mL, 1.0 M in toluene) at 0 °C according to the procedure described above produced the desired complex **5a** (1.2 g, 5.0 mmol, 93%) as a yellow oil after workup and purification by flash column chromatography (silica gel, 20% ethyl acetate/hexanes): IR (CH₂Cl₂) 3615, 3065, 3046, 2984, 2938, 2882, 2047, 1977, 1607, 1474, 1424, 1383, 1281, 1263, 1246, 1042, 907, 841, 785, 633 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.24 (m, 2 H), 3.73 (m, 1 H), 3.63 (dt, J = 10.2, 7.3 Hz, 1 H), 1.98 (m, 1 H), 1.79 (m, 1 H), 1.72 (d, J = 5.4 Hz, 1 H), 1.04 (q, J = 7.3 Hz, 1 H), 0.31 (dd, J = 8.3, 2.4 Hz, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 211.8, 88.3, 81.6, 63.8, 59.5, 39.9, 36.9; MS (EI, 70 eV) m/e (relative intensity) 238 (M⁺, 9), 210 (63), 182 (88), 154 (100), 134 (100), 108 (62), 56 (71)-HRMS (EI) m/e calcd for C₉H₁₀FeO₄ (M⁺) 237.9928, found 237.9936.

Synthesis of [(3-6- η)-*trans*-3-*trans*-5-Heptadienol]tricarbonyliron Complex (5b). To a stirred suspension of 0.32 g (1.04 mmol) of (η^3 -*trans*-1-methylpentadienyl)Fe(CO)₃ cation^{4a} in 7.0 mL of CH₂Cl₂ was added a solution of 0.33 g (1.25 mmol) of triphenylphosphine in 5 mL of methylene chloride under nitrogen at 25 °C. The reaction mixture was allowed to stir at 25 °C for 12 h, and the solvent was concentrated under reduced pressure. The residue was diluted with 5.0 mL of THF and cooled to -78 °C. To the above solution was added slowly *n*-butyllithium (0.8 mL, 1.2 mmol, 1.5 M in hexanes) via syringe. The reaction mixture was allowed to stir at -78 °C for 1 h followed by addition of 0.095 g (3.1 mmol) of paraformaldehyde. The reaction was stirred at 0 °C for 6 h. The mixture was diluted with 200 mL of hexane, and the hexane solution was washed with water (200 mL \times 3) and brine (200 mL \times 3), dried over anhydrous magnesium sulfate, and concentrated to give the crude mixture. Flash column chromatography of the crude mixture on the silica gel (hexanes) gave [(3-6- η)-*trans*-3-*trans*-5-1,3,5-heptatriene]tricarbonyliron complex (0.15 g, 0.65 mmol, 63%). To a solution of 0.26 g (1.1 mmol) of [(3-6- η)-*trans*-3-*trans*-5-1,3,5-heptatriene]tricarbonyliron complex in 20 mL of THF was added a solution of 1.0 M BH₃·THF (2.2 mL) under nitrogen at 0 °C. After 30 min at 0 °C, the mixture is stirred at 25 °C for an additional

3 h. To the reaction mixture at 0 °C, a solution of aqueous sodium hydroxide (3.0 mL, 3.0 N) was added followed by addition of aqueous hydrogen peroxide (35%, 2.0 mL). The reaction was allowed to stir at 0 °C for 1 h and was quenched with 5.0 mL of 10% aqueous hydrochloric acid solution. The reaction mixture was diluted with 200 mL of ether. The ethereal solution was washed with water (200 mL \times 3) and brine (200 mL \times 3), dried over magnesium sulfate (10 g), and concentrated to give the crude mixture. Flash column chromatography of the crude mixture on the silica gel (20% ethyl acetate/hexanes) gave 0.21 g (0.84 mmol, 74%) of complex **5b** as a yellow oil: IR (CH₂Cl₂) 3684, 3605, 3056, 3025, 2988, 2926, 2039, 1961, 1607, 1445, 1381, 1279, 1258, 1044, 847, 793, 741, 712, 691 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.04 (m, 2 H), 3.68 (m, 1 H), 3.61 (m, 1 H), 1.95 (m, 1 H), 1.72 (m, 1 H), 1.39 (d, J = 6.4 Hz, 3 H), 1.15 (m, 1 H), 1.00 (q, J = 7.3 Hz, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 212.5, 85.4, 83.9, 63.8, 58.2, 36.9, 19.1; MS (EI, 70 eV) m/e (relative intensity) 252 (M⁺, 17), 224 (49), 196 (56), 168 (100), 140 (76), 122 (47), 84 (59), 56 (38); HRMS (EI) m/e calcd for C₁₀H₁₂FeO₄ (M⁺) 252.0085, found 252.0076.

Synthesis of Chromium Carbene Complex 6a. To a solution of [tetramethylammonium(phenyl)carbenyl oxide]pentacarbonylchromium (**4**) (1.89 g, 5.1 mmol) in 60 mL of CH₂Cl₂ was added acetyl bromide (0.38 mL, 5.1 mmol) at -10 °C under nitrogen.⁷ The reaction mixture turned red immediately. A solution of complex **5a** (0.81 g, 3.4 mmol) in 3.0 mL of CH₂Cl₂ was added slowly to the reaction at -10 °C. The reaction mixture was stirred at 0 °C for 2 h before being filtered through a bed of Celite. The resultant solution was concentrated to give a crude mixture. Flash column chromatography of the crude mixture (silica gel, 5% ethyl acetate/hexanes) produced complex **6a** (1.37 g, 2.6 mmol, 78%) as a red oil: IR (CH₂Cl₂) 3030, 2980, 2062, 2048, 1946, 1605, 1437, 1418, 1292, 1157 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.42 (m, 3 H), 7.18 (d, J = 6.8 Hz, 2 H), 5.29 (m, 2 H), 4.76 (m, 1 H), 4.66 (m, 1 H), 2.45 (m, 1 H), 2.11 (m, 1 H), 1.79 (m, 1 H), 1.07 (d, J = 7.3 Hz, 1 H), 0.36 (d, J = 8.3 Hz, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 350.8, 224.3, 216.1, 211.3, 153.4, 129.8, 128.3, 122.0, 88.1, 82.3, 80.8, 56.9, 40.5, 33.9; MS (EI, 70 eV) m/e (relative intensity): 518 (M⁺, 5), 462 (8), 434 (10), 378 (59), 322 (49), 294 (100), 264 (32), 210 (14), 134 (17), 129 (27), 108 (20), 52 (41); HRMS (EI) m/e calcd for C₂₁H₁₄CrFeO₉ (M⁺) 517.9392, found 517.9396.

Synthesis of Chromium Carbene Complex 6b. To a solution of **4**⁷ (0.31 g, 0.83 mmol) in 12 mL of methylene chloride was added acetyl bromide (0.062 mL, 0.83 mmol) at -10 °C under nitrogen. The reaction mixture turned red immediately. To the reaction mixture was added slowly a solution of complex **5b** (0.066 g, 0.26 mmol) in 3.0 mL of CH₂Cl₂ at -10 °C. The reaction mixture was stirred at 0 °C for 2 h before being filtered through a bed of Celite. The resultant solution was concentrated to give a crude mixture. Flash column chromatography of the crude mixture (5% ethyl acetate/hexanes) produced complex **6b** (0.11 g, 0.20 mmol, 77%) as a red oil: IR (CH₂Cl₂) 3073, 3042, 2996, 2976, 2411, 2305, 2062, 2043, 1946, 1715, 1607, 1453, 1428, 1381, 1316, 1242, 1159, 1103, 929 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.37-7.44 (m, 3 H), 7.18 (d, J = 6.8 Hz, 2 H), 5.09 (m, 2 H), 4.76 (m, 1 H), 4.65 (m, 1 H), 2.43 (m, 1 H), 2.07 (m, 1 H), 1.40 (d, J = 6.4 Hz, 3 H), 1.19 (m, 1 H), 1.03 (q, J = 7.3 Hz, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 350.5, 224.2, 216.1, 212.1, 153.5, 129.8, 128.3, 122.1, 85.9, 83.7, 81.0, 58.3, 55.8, 33.9, 19.1; MS (EI, 70 eV) m/e (relative intensity): 532 (M⁺, 3), 476 (8), 392 (30), 364 (8), 336 (60), 308 (74), 278 (20), 256 (41), 226 (17), 198 (28), 174 (19), 129 (90), 80 (50), 52 (100); HRMS (EI) m/e calcd for C₂₂H₁₆CrFeO₉ (M⁺) 531.9549, found 531.9546.

Formation of Dihydrofuran Iron Complex 21a. A solution of complex **6a** (0.32 g, 0.62 mmol) in 50 mL of toluene was heated at reflux for 5 h. The reaction mixture was filtered through a bed of Celite, and the solvent was concentrated. Flash column chromatography of the residue (silica gel, 3%

(20) Stevens, R. V.; Cherpeck, R. E.; Harrison, B. L.; Lai, J.; Lapalme, R. *J. Am. Chem. Soc.* **1976**, *98*, 6317.

ethyl acetate/hexanes) gave complex **21a** (0.039 g, 0.12 mmol, 19%) as a yellow oil: IR (CH₂Cl₂) 3067, 3057, 3049, 2992, 2982, 2031, 1962, 1601, 1481, 1453, 1422, 1399, 1368, 1277, 1262, 1252, 1188, 1103, 1044, 856, 828, 812, 787, 748, 721, 691, 629 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.21–7.08 (m, 5 H), 5.49 (d, *J* = 8.8 Hz, 1 H), 4.21 (m, 2 H), 3.45 (td, *J* = 10.7, 6.2 Hz, 1 H), 2.88 (m, 1 H), 1.38 (d, *J* = 6.3 Hz, 3 H), 1.10 (dq, *J* = 8.8, 6.3 Hz, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 212.5, 136.1, 128.2, 127.8 and 127.5, 117.8, 89.9, 82.3, 65.3, 55.8, 34.4, 19.8; MS (EI, 70 eV) *m/e* (relative intensity) 326 (M⁺, 3), 298 (24), 270 (22), 242 (100), 212 (13), 105 (9), 77 (14); HRMS (EI) *m/e* calcd for C₁₆H₁₄FeO₄ (M⁺) 326.0241, found 326.0240.

Formation of Dihydrofuran Derivative 21b. To a solution of CAN (1.0 g, 2.0 mmol) in 6 mL of ethanol was added a solution of complex **21a** (32 mg, 0.10 mmol) in 5.0 mL of ethanol. The reaction was stirred at 25 °C under nitrogen for 18 h. The solvent was concentrated under reduced pressure, and the residue was diluted with water (50 mL). The aqueous solution was extracted with methylene chloride (30 mL × 3). The resultant solution was washed with water (100 mL × 3) and brine (100 mL × 3), dried over anhydrous magnesium sulfate (15 g), and concentrated to give the crude mixture. Flash column chromatography of the crude mixture (silica gel, 3% ethylacetate/hexanes) gave **21b** (12 mg, 0.65 mmol, 65%) as a colorless oil. IR (CH₂Cl₂) 3067, 3050, 2984, 2930, 2305, 2047, 1975, 1603, 1493, 1424, 1376, 1316, 1262, 1069, 1028, 909, 868, 795, 758, 698, 639 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, *J* = 6.8 Hz, 2 H), 7.38 (dd, *J* = 7.3, 6.8 Hz, 2 H), 7.31 (t, *J* = 7.3 Hz, 1 H, H at C-12), 6.53 (d, *J* = 15.6 Hz, 1 H), 5.46 (dq, *J* = 15.6, 6.8 Hz, 1 H), 4.44 (t, *J* = 9.3 Hz, 2 H), 2.93 (t, *J* = 9.3 Hz, 2 H), 1.82 (d, *J* = 6.8 Hz, 3 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 150.8, 131.7, 129.7, 128.2, 127.7, 124.4, 123.5, 111.0, 68.4, 32.3, 18.6; MS (EI, 70 eV) *m/e* (relative intensity)

186 (M⁺, 100), 171 (26), 157 (5), 128 (4), 105 (13), 94 (2), 77 (7). HRMS (EI) *m/z*: calcd for C₁₃H₁₄O (M⁺) 186.1045, found 186.1051.

Formation of Furan Derivative 22. A solution of complex **6b** (0.27 g, 0.51 mmol) in 50 mL of toluene was heated at reflux for 5 h. The reaction mixture was filtered through a bed of Celite, and the solvent was concentrated. Flash column chromatography of the residue (silica gel, 3% ethyl acetate/hexanes) gave complex **22** (0.050 g, 0.25 mmol, 49%) as a colorless oil: IR (CH₂Cl₂) 3059, 2986, 2062, 1970, 1605, 1491, 1447, 1424, 1316, 1281, 1269, 1086, 1059, 1026, 903, 872, 822, 752, 723, 666, 615 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.31–7.33 (m, 4 H), 7.22 (m, 1 H), 5.60 (d, *J* = 1.5 Hz, 1 H), 4.01 (ddd, *J* = 8.3, 6.8, 4.4 Hz, 1 H), 3.77 (td, *J* = 8.3, 6.4 Hz, 1 H), 2.71 (m, 2 H), 2.17 (m, 2 H), 1.63 (m, 1 H), 1.50 (d, *J* = 1.5 Hz, 3 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 144.7, 141.6, 128.1, 127.3, 126.5, 124.9, 99.7, 67.0, 49.3, 37.9, 35.9, 12.1; MS (EI, 70 eV) *m/e* (relative intensity) 200 (M⁺, 100), 185 (35), 171 (23), 156 (59), 128 (11), 123 (50), 105 (18), 95 (4), 77 (2); HRMS (EI) *m/e* calcd for C₁₄H₁₆O (M⁺) 200.1201, found 200.1195.

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Supporting Information Available: ORTEP diagram showing the atom-numbering scheme and tables of crystallographic data and bond lengths and angles for **8a** (5 pages). Ordering information is given on any current masthead page.

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