Intramolecular Addition of Nucleophiles to (η⁴-Diene)Fe(CO)₃ Complexes Bearing Functionalized Side Chains at C-2

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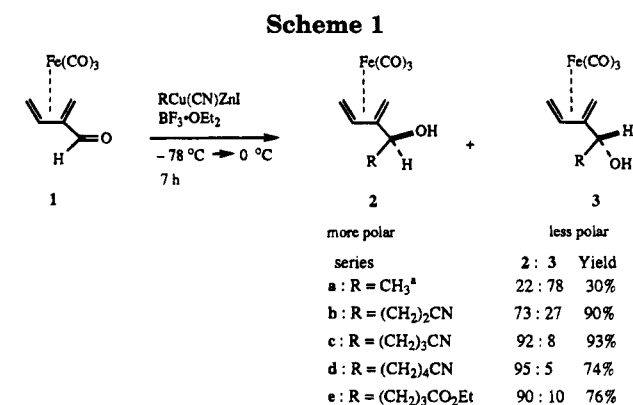88 Section 4, Ding-Jou Road, Taipei, Taiwan, 117 ROC*

The addition of a variety of highly functionalized zinc-copper reagents RCu(CN)ZnI to (η⁴-2-formylbuta-1,3-diene)Fe(CO)₃ complex in the presence of an excess of boron trifluoride etherate proceeds in a highly diastereoselective fashion to afford dienol complexes in good yields. Intramolecular cyclization of a cyano-substituted dienol complex containing a three-carbon side chain using lithium diisopropylamide (LDA) produces (σ,η³-allyl)tricarbonyliron complexes, whereas treatments of the cyano-substituted dienol complex containing a four-carbon side chain with LDA furnishes fused tetracarbonylbicyclo[4.3.0]ferranonanones at −78 °C and complexes of the trimethylenemethane type at 25 °C.

We have recently reported that intramolecular addition of nucleophiles to acyclic (η⁴-diene)Fe(CO)₃ complexes bearing functionalized side chains at the terminal position of the diene ligand under an atmosphere of CO generated fused bicyclo[4.3.0]nonanone and bicyclo[3.3.0]octanone derivatives.[1] We now report that intramolecular cyclization of complexes with functionalized side chains at the internal position (C-2) of the diene ligand gives (σ,η³-allyl)tricarbonyliron complexes or fused tetracarbonylbicyclo[4.3.0]ferranonanone derivatives depending on the length of the side chains and the experimental conditions.

Results and Discussion

Preparation of Starting Complexes. The starting complexes are easily prepared by the addition of highly functionalized zinc–copper reagents RCu(CN)ZnI to (η⁴-2-formylbuta-1,3-diene)tricarbonyliron complex (1). In our preliminary result, the addition of dimethylcuprate to 1 at 0 °C gives the less polar diastereomer 3a as the major product and the more polar diastereomer 2a as the minor product in 78:22 ratio in 30% total yield (Scheme 1), and this result was consistent with reports found in the literature.[2] However, under the same reaction conditions, the functionalized zinc–copper reagents failed to react with complex 1. Nevertheless, with an excess of boron trifluoride etherate,[3] we have successfully performed the addition reaction under mild reaction conditions. Thus, treatment of 1 with 4.0 molar equiv of the functionalized zinc–copper reagents RCu-(CN)ZnI in the presence of 3.0 molar equiv of boron trifluoride etherate under nitrogen at −78 °C for 4 h and 0 °C for 3 h gave the more polar dienol complexes 2b–e as the major products generally in good yields

Scheme 1

series	2 : 3	Yield
a : R = CH₃ᵃ	22 : 78	30%
b : R = (CH₂)₂CN	73 : 27	90%
c : R = (CH₂)₃CN	92 : 8	93%
d : R = (CH₂)₄CN	95 : 5	74%
e : R = (CH₂)₃CO₂Et	90 : 10	76%

ᵃ The nucleophile of the reaction is (CH₃)₂CuLi and the reaction is performed without boron trifluoride etherate.

(74–93%) and with good diastereomeric excesses (46–90%) as shown in Scheme 1. The relative stereochemistry of 2a has been previously established for its camphanoate ester.[2c] We have unambiguously assigned the relative configuration of 3b by X-ray diffraction analysis (Figure 1). The reason for the inversed stereoselection for the cuprate and the functionalized zinc–copper reagents is not clear. It has been suggested that the reaction of cuprates with 1 could occur "endo" through addition to the iron center or a carbonyl group.[2a] Therefore, it is reasonable to assume that attack of the functionalized zinc–copper species occurred from the opposite face of the Fe(CO)₃ moiety of the *s-cis* conformer (as shown in 1, Scheme 1) would give 2 as the major product.

Intramolecular Nucleophilic Additions. Our cyclization study began with complex 2b. Treatment of 2b with 2.0 molar equiv of LDA at −78 °C under nitrogen for 3 h in tetrahydrofuran (THF) and hexamethylphosphoramide (HMPA, THF–HMPA, 3:1) followed by addition of an excess of trifluoroacetic acid (10 molar equiv) gave two major products in 38% yield (Scheme 2), identified as (σ,η³-allyl)tricarbonyliron complexes 4a (28%) and 4b (10%). None of the desired internal addition product, for example 5, was isolated under an atmosphere of N₂ or CO. Complexes of the (σ,η³-allyl)tricarbonyliron type were previously made by

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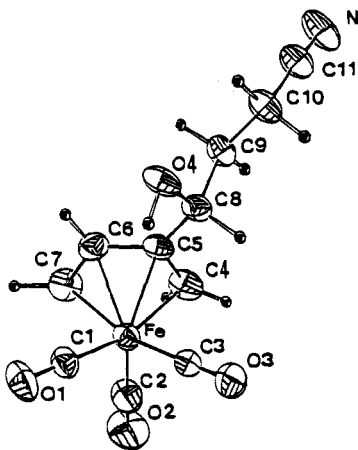
Figure 1. ORTEP drawing of **3b**.

reaction of iron pentacarbonyl with vinylcyclopropane[4] or addition of lithium reagents to (η^5-pentadienyl)Fe-(CO)$_3$ cation salt.[5] NMR studies provided the initial evidence for support of the structural assignments. The ^{1}H NMR spectrum of complex **4a** exhibited the following: a quartet, centered at δ 5.00, assigned to the vinyl proton at C-5; a multiplet, centered at δ 4.62, assigned to the proton at C-3; a doublet, centered at δ 3.70, assigned to the syn proton at C-7; a doublet, centered at δ 2.85, assigned to the anti proton at C-7; a doublet of doublets of doublets, centered at δ 2.17, assigned to one of the two diastereotopic methylene protons at C-2; a doublet of doublets of doublets, centered at δ 2.10, assigned to the other diastereotopic methylene protons at C-2; a broad singlet centered at δ 1.93, assigned to the proton of the hydroxy group; a doublet of doublets, centered at 1.70, assigned to the proton at C-1; a doublet centered at δ 1.40, assigned to the methyl group at C-6. The ^{13}C NMR spectrum of complex **4a** exhibited the following: three signals at δ 210.6 (s), 209.3 (s), 204.1 (s) assigned to C-8 (carbonyl of the tricarbonyliron moiety); a signal at δ 128.4 (s) assigned to C-4; a signal at δ 128.0 (s) assigned to C-9 (carbon of the cyano functionality); a signal at δ 71.3 (d) assigned to C-5; a signal at δ 69.2 (d) assigned to C-3; a signal at δ 49.7 (t) assigned to C-7; a signal at δ 44.8 (t) assigned to C-2; a signal at δ 21.1 (q) assigned to C-6; a signal at δ 3.2 (d) assigned to C-1.

The formation of complex **4** did not follow the mechanism proposed for the intermolecular addition of nucleophiles to (η^4-cyclohexa-1,3-diene)Fe(CO)$_3$ complex.[6] ^{a,b} Unlike most stabilized carbanions added at the unsubstituted internal position of the diene ligand

under kinetically controlled reaction conditions at -78 °C,[1,6] the cyano-stabilized dianion **6** formed by treatment of **2b** with 2.0 molar equiv of LDA attacked at the carbonyl ligand of the Fe(CO)$_3$ moiety to give acyliron dianion intermediate **7** (Scheme 3). Rearrangement of **7** might produce (σ,η^2-alkene)Fe(CO)$_3$ dianion complex **8**, which reacted with CF$_3$COOH to provide the iron hydride species **9**. Hydride addition to the alkene ligand would produce **10**. Complexation of the pendant double bond with the Fe(CO)$_3$ moiety would give (σ,η^3-allyl)-tricarbonyliron complex **4**. The relative stereochemistry of complex **4a** (Figure 2) was confirmed by X-ray diffraction analysis and was consistent with the reaction pathway proposed above. Further manipulation of complex **4a** was demonstrated as follows (Scheme 2). Oxidation cleavage of **4a** with an excess of ceric ammonium nitrate (CAN) provided cyclopentanecarbonitrile derivative **11** (32%, from C-alkylation at C-7) and oxetane derivative **12** (5%, from O-alkylation at C-5 followed by hydrolysis of the cyano group to the carboxylic acid functionality).[7] Under the same reaction conditions, cyclization of the starting complex **3b** also produced a mixture of diastereomeric (σ,η^3-allyl)tricarbonyliron complexes **13a** and **13b** in a 3:2 ratio in 23% total yield, and this result was consistent with the intramolecular cyclization of **2b**.
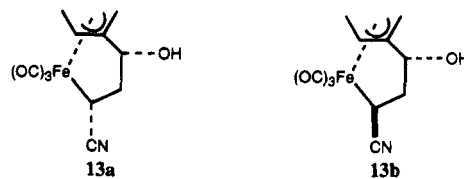
Interestingly, increasing the tether length by one with complex **2c** led to a 9% yield of fused tetracarbonylbicyclo[4.3.0]ferranonanone **14a** and a trace of the epimer **14b**. None of complexes of the (σ,η^3-allyl)-tricarbonyliron type nor fused bicyclo[4.3.0]nonanone **15** was isolated with or without an atmosphere of CO (Scheme 4).[8] As can be seen from Scheme 5, addition of the cyano-stabilized dianion **16** at the internal position of the diene ligand under kinetically controlled reaction conditions (-78 °C) generated homoallyl dianion intermediate **17**. Trapping **17** with trifluoroacetic acid would give iron hydride species **18**, followed by intramolecular alkene insertion (to give **19**). The postulated initial bicyclic intermediate **19** could undergo carbonyl insertion and attach an additional CO at the iron center to form the 18-electron species **14**. Thus, the addition was performed under 1 atm of CO (14 psi) after acid quenching, which increased the yield of bicycloadduct **14a** to 24% after purification by flash column chromatography and recrystallization in hexane (Scheme 4). The low yield of the reaction may be due to the slow decomposition of complex **14**. However, we were able to obtain a single crystal for X-ray diffraction analysis of complex **14a** (Figure 3). ^{13}C NMR study provided the initial evidence for the structural assign-

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Scheme 2
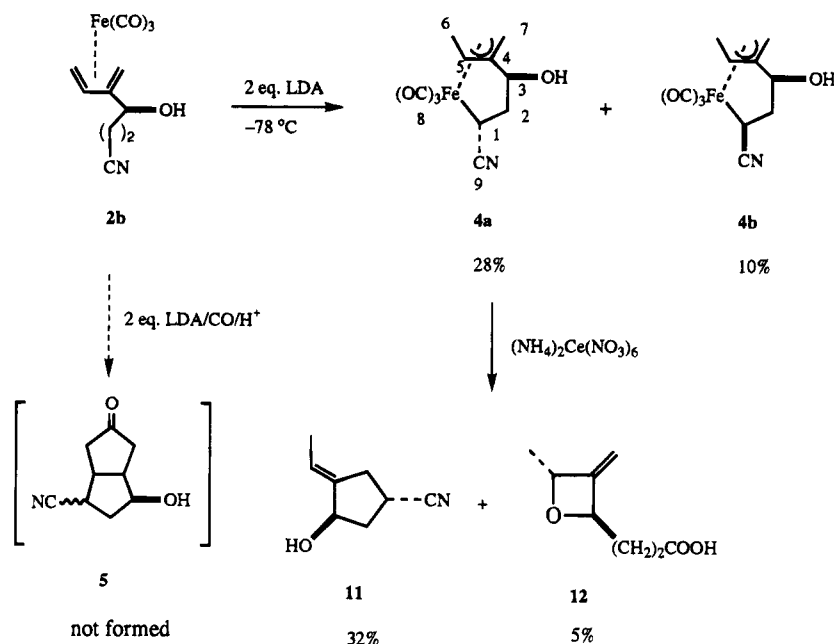
Scheme 3
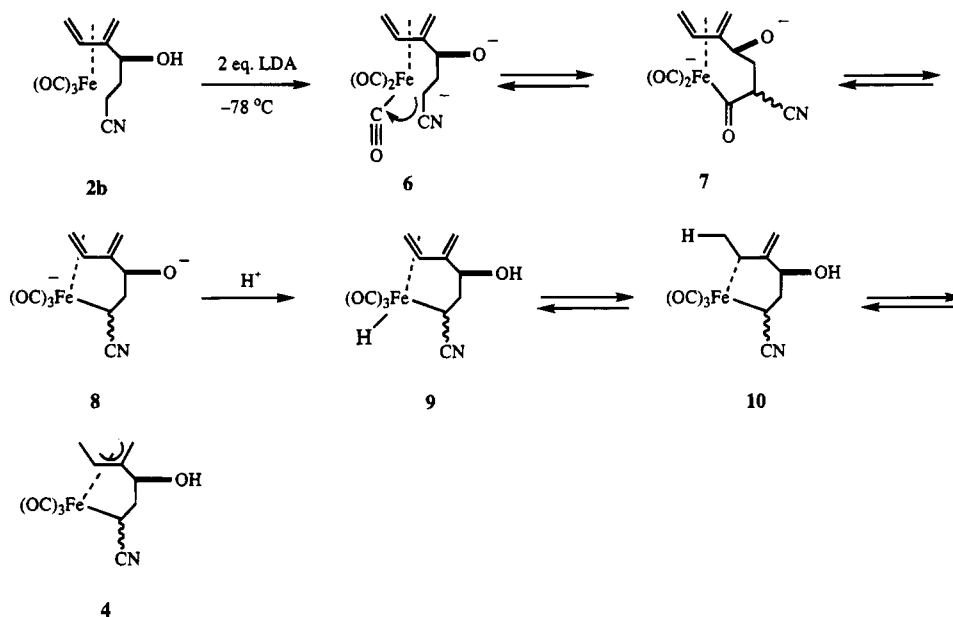
ments. The ^{13}C NMR spectrum of complex **14a** exhibited the following: a signal at δ 263.5 assigned to C-8 (carbonyl of iron acyl functionality); four signals at δ 205.3, 204.9, 202.0, and 199.1 assigned to C-9 (carbonyl of the tetracarbonyliron moiety); a signal at δ 121.1 assigned to C-10 (carbon of the cyano functionality); a signal at δ 73.4 assigned to C-6; a signal at δ 68.4 assigned to C-7; a signal at δ 50.5 assigned to C-2; a signal at δ 32.3 assigned to C-3; two signals at δ 28.1 and 28.2 assigned to C-4, 5; a signal at δ 18.5 assigned to C-1; a signal at δ 8.0 assigned to the methyl carbon at C-11. Nuclear Overhauser enhancement spectroscopy (NOSEY) measurements and X-ray diffraction analysis of complex **14a** confirmed the relative stereochemistry of four stereogenic centers of **14a** and was consistent with the mechanism proposed above. These results from the intramolecular nucleophilic addition are unexpected and unprecedented especially since Semmelhack *et al.* have previously reported on the
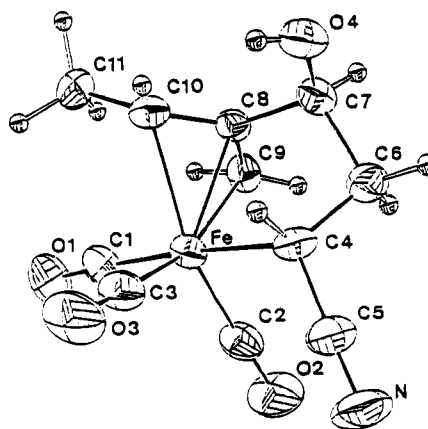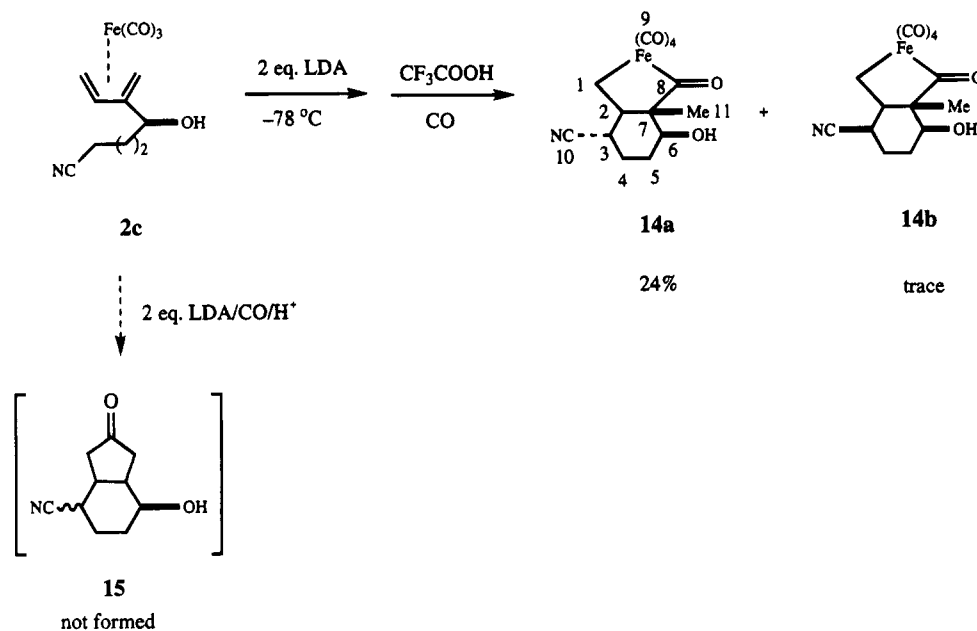

Figure 2. ORTEP drawing of **4a**.

formation of bicyclo[4.3.0]nonanones from a simpler system analogous to **2c**.[8] The reason for the formation
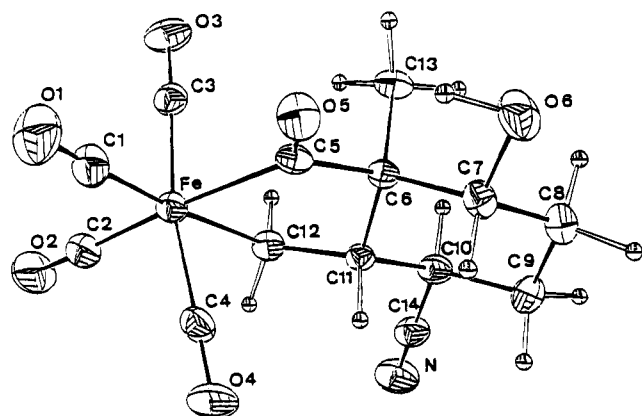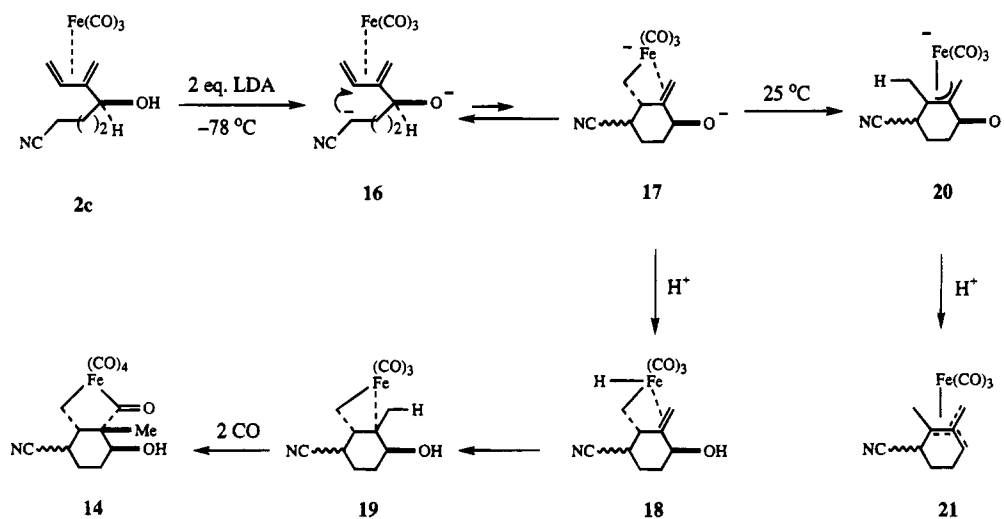
Scheme 4

Scheme 5

Figure 3. ORTEP drawing of **14a**.

of the above unexpected (σ,η^3-allyl)tricarbonyliron complexes and tetracarbonylbicyclo[4.3.0]ferranonanones was not clear. Presumably this might be due to a conformational bias imposed on the functionalized side chain of complexes **2** and **3** due to the chiral alcohol carbon.

Surprisingly, the reaction underwent different pathways at 25 °C (thermally controlled reaction conditions). The putative homoallyl dianion **17** (Scheme 5) could rearranged to the more stable allyl dianion species **20** (presumably via β-hydride elimination—readdition process). Dehydroxylation occurred upon protonation of **20** to lead to complex **21** of the trimethylenemethane type in 49% yield (Scheme 6).[9] A ^{13}C NMR study provided the initial evidence for the structural assignments. The ^{13}C NMR spectrum of complex **21a** exhibited the following: three signals at δ 210.9, 210.7, 210.4 assigned to C-10 (carbonyl of the tricarbonyliron moiety); a signal at δ 120.5 assigned to C-9 (carbon of the cyano functionality); a signal at δ 99.1 assigned to C-2; a signal at δ 84.0 assigned to C-7; a signal at δ 70.8 assigned to C-3; a signal at δ 45.7 assigned to C-1; a signal at δ 33.5 assigned to C-6; two signals at δ 26.5 and 21.5 assigned to C-4, 5; a signal at δ 20.7 assigned to the

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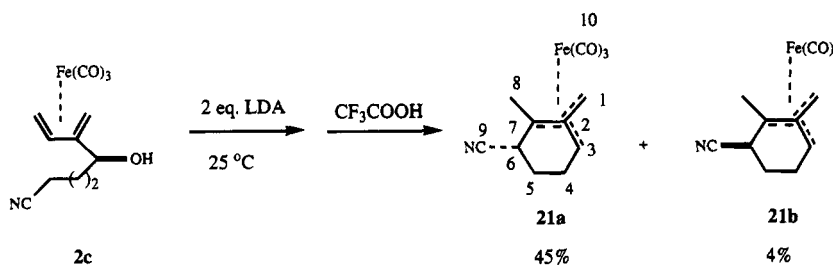
Scheme 6

Table 1. Selected Crystallographic Data for Complexes 3b, 4a, and 14a

	3b	4a	14a
empirical formula	$C_{11}H_{11}NO_4Fe$	$C_{11}H_{11}NO_4Fe$	$C_{14}H_{13}NO_6Fe$
fw	277.06	277.06	347.10
cryst syst	monoclinic	monoclinic	monoclinic
space group	$C2/c$	$P2_1/c$	$P2_1/n$
a, Å	24.535(4)	7.9641(12)	13.425(3)
b, Å	7.660(3)	6.9916(10)	6.287(3)
c, Å	16.1621(12)	22.344(4)	18.346(3)
β, deg	124.426(9)	90.589(14)	106.529(13)
V, Å³	2505.5(10)	1244.1(3)	1484.4(7)
Z	8	4	4
D(calc), mg m⁻³	1.469	1.479	1.553
abs coeff, mm⁻¹	1.20	1.21	3.10
diffractometer	Nonius(CAD-4)	Nonius(CAD-4)	Nonius(CAD-4)
radiation: λ(Mo Kα), Å	0.709 30	0.709 30	0.709 30
temp, °C	25	25	25
T_{min}/T_{max}	0.85/1.00	0.94/1.00	0.96/1.00
residuals: R_F;[a] R_w[a]	0.040; 0.032	0.036; 0.027	0.032; 0.030

[a] The function minimized during the least squares cycles was $R_F = \Sigma(F_o - F_c)/\Sigma F_o$, $R_w = [\Sigma w(F_o - F_c)^2/\Sigma w(F_o)^2]^{1/2}$.

Table 2. Selected Atomic Coordinates and Isotropic Displacement Coefficients for 3b

	x	y	z	B_{iso}, Å²
Fe	0.84766(3)	0.01327(9)	0.20138(5)	4.42(4)
O(1)	0.90065(19)	0.0651(5)	0.0804(3)	7.7(3)
O(2)	0.76987(24)	−0.3035(6)	0.1125(4)	11.2(5)
O(3)	0.74748(19)	0.2820(6)	0.0941(3)	8.0(3)
O(4)	0.92999(17)	0.4152(4)	0.35827(22)	6.02(24)
N	0.9122(3)	0.5231(7)	0.6682(3)	8.4(4)
C(1)	0.88034(23)	0.0449(6)	0.1258(4)	5.2(3)
C(2)	0.8000(3)	−0.1819(8)	0.1456(5)	7.2(5)
C(3)	0.78743(24)	0.1760(7)	0.1356(4)	5.3(3)
C(4)	0.8329(3)	0.0109(7)	0.3165(4)	6.7(4)
C(5)	0.88542(24)	0.1207(6)	0.3399(3)	4.8(3)
C(6)	0.93660(24)	0.0473(7)	0.3362(4)	5.8(3)
C(7)	0.9309(3)	−0.1287(7)	0.3079(4)	7.4(4)
C(8)	0.88415(22)	0.3107(7)	0.3629(3)	4.7(3)
C(9)	0.90344(24)	0.3242(7)	0.4712(3)	5.2(3)
C(10)	0.9021(3)	0.5076(8)	0.5006(3)	6.2(4)
C(11)	0.9090(3)	0.5164(8)	0.5968(4)	6.4(4)

methyl carbon at C-8. The relative stereochemical assignment of **21a** was further confirmed by the X-ray diffraction analysis. Attempted intramolecular cyclization using tethers longer than three methylene groups, for example complex **2d**, gave only the starting complex.

The reactions outlined herein demonstrate that the diastereoselective addition of the highly functionalized zinc—copper reagents RCu(CN)ZnI to (η⁴-2-formylbuta-1,3-diene)tricarbonyliron complex produces dienol complexes with a functionalized side chain at the C-2 position of the diene ligand. The intramolecular iron-mediated cycloaddition is also an unusual method for the formation of (σ,η³-allyl)tricarbonyliron complexes and fused tetracarbonylbicyclo[4.3.0]ferranonanone complexes depending on the length of the side chain.

Table 3. Selected Atomic Coordinates and Isotropic Displacement Coefficients for 4a

	x	y	z	B_{iso}, Å²
Fe	0.70728(10)	0.92211(11)	0.13908(4)	4.01(4)
O(1)	0.7599(6)	1.2876(7)	0.20077(22)	8.0(3)
O(2)	0.4079(6)	1.0681(7)	0.07785(22)	9.2(3)
O(3)	0.6002(6)	0.7592(8)	0.25241(20)	8.8(3)
O(4)	0.9779(4)	0.5001(6)	0.08800(17)	5.55(21)
N	0.3222(6)	0.5843(9)	0.1032(3)	8.7(4)
C(1)	0.7446(8)	1.1467(9)	0.1752(3)	5.8(4)
C(2)	0.5239(8)	1.0106(9)	0.1029(3)	5.7(3)
C(3)	0.6412(7)	0.8244(8)	0.2079(3)	5.4(3)
C(4)	0.6423(6)	0.6471(7)	0.1063(3)	4.4(3)
C(5)	0.4634(7)	0.6126(9)	0.1048(3)	5.7(4)
C(6)	0.7251(6)	0.6178(8)	0.0464(3)	5.2(3)
C(7)	0.9112(7)	0.6584(8)	0.05787(25)	4.5(3)
C(8)	0.9242(6)	0.8460(8)	0.09262(23)	3.8(3)
C(9)	0.8623(7)	1.0112(8)	0.06533(23)	4.7(3)
C(10)	0.9714(6)	0.8473(8)	0.1532(3)	4.6(3)
C(11)	1.0782(7)	1.0013(10)	0.1821(3)	6.3(3)

Table 4. Selected Atomic Coordinates and Isotropic Displacement Coefficients for Complex 14a

	x	y	z	B_{iso}, Å²
Fe	0.80132(5)	0.64984(11)	0.09690(3)	2.88(3)
O(1)	0.9269(3)	0.3171(6)	0.19491(20)	6.42(22)
O(2)	0.7675(3)	0.9378(7)	0.21612(21)	6.87(24)
O(3)	0.98448(23)	0.8927(6)	0.08860(19)	5.12(19)
O(4)	0.60606(25)	0.4135(6)	0.07808(19)	5.46(20)
O(5)	0.86094(23)	0.3182(5)	0.00888(17)	4.11(17)
O(6)	0.79182(25)	0.2873(5)	−0.14971(17)	4.82(17)
N	0.4751(3)	0.10979(7)	−0.11575(25)	5.51(25)
C(1)	0.8784(4)	0.4474(9)	0.1590(3)	4.2(3)
C(2)	0.7788(3)	0.8257(9)	0.1707(3)	4.2(3)
C(3)	0.9132(3)	0.7986(8)	0.09074(24)	3.32(22)
C(4)	0.6800(3)	0.5045(8)	0.08480(24)	3.43(23)
C(5)	0.8152(3)	0.4844(7)	0.00523(23)	2.70(21)
C(6)	0.7627(3)	0.5890(6)	−0.07220(22)	2.37(18)
C(7)	0.7150(3)	0.4203(7)	−0.13260(23)	3.19(21)
C(8)	0.6529(3)	0.5220(8)	−0.20683(23)	4.0(3)
C(9)	0.5723(3)	0.6788(9)	−0.19664(24)	4.16(24)
C(10)	0.6191(3)	0.8423(8)	−0.13349(23)	3.13(21)
C(11)	0.6732(3)	0.7243(7)	−0.05934(21)	2.40(18)
C(12)	0.7115(3)	0.8567(7)	0.01241(22)	2.90(20)
C(13)	0.8476(3)	0.7191(7)	−0.09327(24)	3.45(23)
C(14)	0.5380(3)	0.9860(8)	−0.1228(3)	3.79(23)

Experimental Section

Table 5. Selected Bond Distances (Å) and Bond Angles (deg) for 3b

(A) Distances			
Fe–C(1)	1.777(5)	Fe–C(7)	2.083(5)
Fe–C(2)	1.795(6)	C(4)–C(5)	1.399(7)
Fe–C(3)	1.758(5)	C(5)–C(6)	1.408(7)
Fe–C(4)	2.086(5)	C(5)–C(8)	1.506(7)
Fe–C(5)	2.050(4)	C(6)–C(7)	1.405(8)
Fe–C(6)	2.050(5)		

(B) Angles			
C(1)–Fe–C(2)	101.0(3)	C(5)–Fe–C(6)	40.16(21)
C(1)–Fe–C(3)	92.41(23)	C(5)–Fe–C(7)	71.36(21)
C(1)–Fe–C(4)	164.37(21)	C(6)–Fe–C(7)	39.73(21)
C(1)–Fe–C(5)	125.07(21)	Fe–C(1)–O(1)	179.1(4)
C(1)–Fe–C(6)	94.54(22)	Fe–C(2)–O(2)	178.2(6)
C(1)–Fe–C(7)	91.17(24)	Fe–C(3)–O(3)	178.3(5)
C(2)–Fe–C(3)	101.6(3)	Fe–C(4)–C(5)	68.8(3)
C(2)–Fe–C(4)	92.8(3)	Fe–C(5)–C(4)	71.6(3)
C(2)–Fe–C(5)	130.30(25)	Fe–C(5)–C(6)	69.9(3)
C(2)–Fe–C(6)	129.7(3)	Fe–C(5)–C(8)	126.7(3)
C(2)–Fe–C(7)	92.1(3)	Fe–C(6)–C(5)	69.9(3)
C(3)–Fe–C(4)	92.03(23)	Fe–C(6)–C(7)	71.4(3)
C(3)–Fe–C(5)	94.72(22)	Fe–C(7)–C(6)	68.8(3)
C(3)–Fe–C(6)	125.33(22)	C(4)–C(5)–C(6)	117.1(5)
C(3)–Fe–C(7)	164.94(23)	C(4)–C(5)–C(8)	120.2(5)
C(4)–Fe–C(5)	39.54(19)	C(6)–C(5)–C(8)	122.7(4)
C(4)–Fe–C(6)	70.75(21)	C(5)–C(6)–C(7)	118.0(5)
C(4)–Fe–C(7)	80.88(23)		

Table 6. Selected Bond Distances (Å) and Bond Angles (deg) for 4a

(A) Distances			
Fe–C(1)	1.789(7)	Fe–C(10)	2.187(5)
Fe–C(2)	1.774(6)	C(7)–C(8)	1.527(8)
Fe–C(3)	1.768(6)	C(8)–C(9)	1.394(8)
Fe–C(4)	2.120(5)	C(8)–C(10)	1.401(8)
Fe–C(8)	2.093(5)	C(10)–C(11)	1.513(8)
Fe–C(9)	2.161(5)		

(B) Angles			
C(1)–Fe–C(2)	91.8(3)	C(9)–Fe–C(10)	67.84(21)
C(1)–Fe–C(3)	89.8(3)	Fe–C(1)–O(1)	175.5(5)
C(1)–Fe–C(4)	172.27(24)	Fe–C(2)–O(2)	177.9(5)
C(1)–Fe–C(8)	108.23(25)	Fe–C(3)–O(3)	179.0(5)
C(1)–Fe–C(9)	89.86(24)	Fe–C(4)–C(5)	113.4(4)
C(1)–Fe–C(10)	89.4(3)	Fe–C(4)–C(6)	108.8(3)
C(2)–Fe–C(3)	106.3(3)	Fe–C(8)–C(7)	114.7(3)
C(2)–Fe–C(4)	87.8(3)	Fe–C(8)–C(9)	73.5(3)
C(2)–Fe–C(8)	122.84(24)	Fe–C(8)–C(10)	74.6(3)
C(2)–Fe–C(9)	91.47(24)	Fe–C(9)–C(8)	68.3(3)
C(2)–Fe–C(10)	159.28(24)	Fe–C(10)–C(8)	67.3(3)
C(3)–Fe–C(4)	82.9(3)	Fe–C(10)–C(11)	115.3(4)
C(3)–Fe–C(8)	126.00(24)	C(5)–C(4)–C(6)	113.3(5)
C(3)–Fe–C(9)	162.22(24)	C(4)–C(6)–C(7)	104.9(4)
C(3)–Fe–C(10)	94.38(24)	C(6)–C(7)–C(8)	107.8(4)
C(4)–Fe–C(8)	78.33(20)	C(7)–C(8)–C(9)	117.9(5)
C(4)–Fe–C(9)	97.86(21)	C(7)–C(8)–C(10)	120.8(5)
C(4)–Fe–C(10)	93.67(20)	C(9)–C(8)–C(10)	120.5(5)
C(8)–Fe–C(9)	38.20(21)	C(8)–C(10)–C(11)	124.2(5)
C(8)–Fe–C(10)	38.14(21)		

Table 7. Selected Bond Distances (Å) and Bond Angles (deg) for 14a

(A) Distances			
Fe–C(1)	1.821(6)	C(6)–C(7)	1.536(6)
Fe–C(2)	1.839(5)	C(6)–C(11)	1.544(5)
Fe–C(3)	1.800(5)	C(7)–C(8)	1.521(6)
Fe–C(4)	1.825(5)	C(8)–C(9)	1.514(7)
Fe–C(5)	2.031(4)	C(9)–C(10)	1.543(7)
Fe–C(12)	2.118(4)	C(10)–C(11)	1.538(6)
C(5)–C(6)	1.542(6)	C(11)–C(12)	1.518(6)

(B) Angles			
C(1)–Fe–C(2)	98.20(22)	Fe–C(5)–O(5)	124.3(3)
C(1)–Fe–C(3)	93.82(21)	Fe–C(5)–C(6)	114.8(3)
C(1)–Fe–C(4)	93.14(21)	Fe–C(12)–C(11)	106.2(3)
C(1)–Fe–C(5)	89.44(19)	C(5)–C(6)–C(7)	111.0(3)
C(1)–Fe–C(12)	172.21(19)	C(5)–C(6)–C(11)	105.4(3)
C(2)–Fe–C(3)	92.79(20)	C(5)–C(6)–C(13)	106.3(3)
C(2)–Fe–C(4)	93.60(20)	C(7)–C(6)–C(11)	107.9(3)
C(2)–Fe–C(5)	172.36(20)	C(7)–C(6)–C(13)	111.9(3)
C(2)–Fe–C(12)	89.50(19)	C(11)–C(6)–C(13)	114.2(3)
C(3)–Fe–C(4)	169.79(19)	C(6)–C(7)–C(8)	111.5(4)
C(3)–Fe–C(5)	86.51(18)	C(7)–C(8)–C(9)	113.1(3)
C(3)–Fe–C(12)	86.94(17)	C(8)–C(9)–C(10)	111.9(3)
C(4)–Fe–C(5)	86.10(18)	C(9)–C(10)–C(11)	109.4(4)
C(4)–Fe–C(12)	85.17(18)	C(9)–C(10)–C(14)	110.5(3)
C(5)–Fe–C(12)	82.86(17)	C(11)–C(10)–C(14)	111.1(3)
Fe–C(1)–O(1)	177.0(4)	C(6)–C(11)–C(10)	108.8(3)
Fe–C(2)–O(2)	177.9(4)	C(6)–C(11)–C(12)	110.4(3)
Fe–C(3)–O(3)	178.5(4)	C(10)–C(11)–C(12)	117.4(4)
Fe–C(4)–O(4)	179.1(4)		

chlorides with an excess of sodium iodide in refluxing acetone. Diiron nonacarbonyl was obtained by photolysis of iron pentacarbonyl in benzene and acetic acid according to the literature procedure.[10] Functionalized zinc–copper reagents were prepared according to the literature procedures.[11] (η^4-2-Formylbuta-1,3-diene)Fe(CO)$_3$ complex (1) was synthesized according to the known method.[2a] Flash column chromatography, following the method of Still,[12] 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 F$_{254}$ 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 Büchi Rotavapor-R. The term "under nitrogen" implies that the apparatus was evacuated (oil pump) and then filled with nitrogen three times. Melting points were determined in open capillaries with a Thomas-Hoover apparatus and are uncorrected. Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained with a JEOL-EX 400 (400-MHz) spectrometer. Chemical shifts are reported in parts per million with either tetramethylsilane (0.00 ppm) or CHCl$_3$ (7.26 ppm) as internal standard. ^{13}C NMR spectra were recorded with a JEOL-EX 400 (100.4-MHz) spectrometer with CDCl$_3$ (77.0 ppm) as the internal standard. Infrared (IR) spectra were recorded with a JASCO FT/IR-5300 spectrometer. Mass spectra were measured on a JEOL JMS-D 100 spectrometer at an ionization potential of 20 eV and were reported as mass/charge (m/e) with percent relative abundance. High-resolution mass spectra (HRMS) were obtained with an AEI MS-9 double-focusing mass spectrometer and a JEOL JMS SX/SX-102A spectrometer at the Department of Chemistry of National Chung-Hsing University, Central Instrument Center, Taichung, ROC. All X-ray data were collected at 25 °C on an Enraf–Nonius CAD4 diffractometer using Mo Kα radiation (λ = 0.7107 Å) and a graphite monochromator at the Department of Chemistry of National Taiwan Normal University. The crystal structures were solved and refined using the NRCVAX package.[13] The structures were solved by direct methods, the initial model being completed using standard Fourier techniques.

General Procedure for Addition of Functionalized Zinc–Copper Reagents RCu(CN)ZnI to (η^4-2-Formylbuta-1,3-diene)tricarbonyliron Complex (1). A solution of the functionalized zinc–copper reagent (4.0 molar equiv) in THF (5.0 mL) was added to a stirred solution of complex 1 in THF (5.0 mL) at −78 °C under nitrogen followed by addition of boron trifluoride etherate (3.0 molar equiv). The reaction mixture was stirred at −78 °C for 4 h and 0 °C for 3 h. The reaction mixture was then quenched with saturated aqueous

(10) Diiron nonacarbonyl (32 g) was prepared by photolyzing iron pentacarbonyl (66 g) in benzene (150 mL) and acetic acid (42 mL): King, R. B. *Organometallics Synthesis*; Academic Press: New York, 1965; Vol. 1, p 93.

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ammonium chloride solution at 0 °C and was diluted with a mixture of ethyl acetate and hexanes (1/1, 100 mL). 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.

(4S*,5S*,6R*)-(η⁴-4-Hydroxy-5-methylene-6-heptenenitrile)tricarbonyliron Complex (2b). The crude mixture obtained from the addition of the corresponding zinc–copper reagent (22 mmol) to complex 1 (1.2 g, 5.5 mmol) in the presence of BF₃·OEt₂ (2.1 mL, 17 mmol) was purified via flash column chromatography (silica gel, 15% ethyl acetate/85% hexanes) to give complex 2b (1.0 g, 3.7 mmol, 66%) and 3b (0.40 g, 1.3 mmol, 24%), both as yellow oils. 2b: IR (CH₂Cl₂) 3609, 3472, 3054, 2932, 2249, 2052, 1981, 1620, 1443, 1387, 1213, 1186, 1074 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.38 (dd, J = 8.3, 7.8 Hz, 1 H), 4.45 (m, 1 H), 2.64 (t, J = 7.3 Hz, 2 H), 2.55 (br, OH), 2.15 (m, 2 H), 2.07 (d, J = 2.4 Hz, 1 H), 1.78 (dd, J = 7.8, 2.0 Hz, 1 H), 0.18 (dd, J = 8.3, 2.0 Hz, 1 H), 0.14 (d, J = 2.4 Hz, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 210.8, 119.4, 108.6, 83.3, 71.7, 38.6, 37.2, 34.2, 13.9; MS (20 eV) m/e (relative intensity) 277 (M⁺, 1), 249 (4), 221 (49), 193 (100), 175 (13), 153 (7), 113 (58), 83 (7); HRMS (EI) m/e calcd for C₈H₁₁FeNO (M − 3 CO) 193.0190, found 193.0196.

(4R*,5S*,6R*)-(η⁴-4-Hydroxy-5-methylene-6-heptenenitrile)tricarbonyliron complex (3b): mp 55–56 °C; IR (CH₂Cl₂) 3591, 3468, 3071, 3005, 2930, 2857, 2249, 2052, 1983, 1443, 1381, 1209, 1180, 1084 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.61 (dd, J = 8.3, 7.8 Hz, 1 H), 4.12 (m, 1 H), 2.67 (t, J = 7.3 Hz, 2 H), 2.22 (m, 1 H), 2.15 (m, 1 H), 1.80 (dd, J = 7.8, 2.1 Hz, 1 H), 1.79 (d, J = 2.4 Hz, 1 H), 0.27 (d, J = 2.4 Hz, 1 H), 0.23 (dd, J = 8.3, 2.1 Hz, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 210.5, 119.3, 108.5, 80.3, 72.0, 40.1, 38.7, 35.0, 13.8; MS (20 eV) m/e (relative intensity) 277 (M⁺, 1), 249 (14), 221 (67), 193 (100), 175 (19), 149 (14), 113 (19), 97 (17); HRMS (EI) m/e calcd for C₈H₁₁FeNO (M − 3 CO) 193.0190, found 193.0191.

(5S*,6S*,7R*)-(η⁴-5-Hydroxy-6-methylene-7-octenenitrile)tricarbonyliron Complex (2c). The crude mixture obtained from the addition of the corresponding zinc–copper reagent (27 mmol) to complex 1 (1.5 g, 6.8 mmol) in the presence of BF₃·OEt₂ (2.6 mL, 20 mmol) was purified via flash column chromatography (silica gel, 15% ethyl acetate/85% hexanes) to give complex 2c (1.7 g, 5.8 mmol, 86%) and 3c (0.10 g, 0.50 mmol, 7%), both as yellow oils. 2c: IR (CH₂Cl₂) 3674, 3605, 3063, 2940, 2249, 2049, 1977, 1609, 1458, 1381, 1248, 1184, 1078 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.34 (t, J = 7.8 Hz, 1 H), 4.36 (m, 1 H), 2.47 (t, J = 6.8 Hz, 2 H), 2.08 (d, J = 2.4 Hz, 1 H), 1.97 (m, 4 H), 1.77 (dd, J = 6.8, 2.4 Hz, 1 H), 0.17 (dd, J = 7.8, 2.4 Hz, 1 H), 0.13 (d, J = 2.4 Hz, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 211.0, 119.5, 109.7, 83.0, 72.9, 38.4, 37.7, 37.3, 21.9, 17.0; MS (20 eV) m/e (relative intensity) 263 (M − CO, 2), 235 (79), 207 (100), 189 (86), 154 (24), 127 (74), 113 (14), 83 (8), 49 (7); HRMS (EI) m/e calcd for C₉H₁₃FeNO (M − 3 CO) 207.0347, found 207.0350.

(5R*,6S*,7R*)-(η⁴-5-Hydroxy-6-methylene-7-octenenitrile)tricarbonyliron complex (3c): IR (CH₂Cl₂) 3677, 3590, 3073, 2932, 2249, 2045, 1971, 1609, 1456, 1383, 1217, 1182, 1090 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.60 (t, J = 8.3 Hz, 1 H), 4.02 (m, 1 H), 2.47 (t, J = 6.8 Hz, 2 H), 2.03–1.94 (m, 4 H), 1.79 (dd, J = 7.3, 2.0 Hz, 1 H), 1.76 (d, J = 2.4 Hz, 1 H), 0.27 (d, J = 2.4 Hz, 1 H), 0.22 (dd, J = 8.3, 2.0 Hz, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 210.8, 119.5, 109.6, 80.1, 73.1, 40.2, 38.5, 38.4, 21.8, 17.1; MS (20 eV) m/e (relative intensity) 263 (M − CO, 1), 235 (62), 207 (100), 189 (42), 154 (11), 127 (39), 99 (43), 83 (36), 71 (28), 55 (42); HRMS (EI) m/e calcd for C₉H₁₃FeNO (M − 3 CO) 207.0347, found 207.0352.

(6S*,7S*,8R*)-(η⁴-6-Hydroxy-7-methylene-8-nonenenitrile)tricarbonyliron Complex (2d). The crude mixture obtained from the addition of the corresponding zinc–copper reagent (19 mmol) to complex 1 (1.1 g, 4.9 mmol) in the presence of BF₃·OEt₂ (1.9 mL, 15 mmol) was purified via flash column chromatography (silica gel, 15% ethyl acetate/85% hexanes) to give complex 2d (1.0 g, 3.3 mmol, 70%) and 3d

(0.10 g, 0.20 mmol, 4%), both as yellow oils. 2d: IR (CH₂Cl₂) 3605, 3493, 3056, 2946, 2249, 2045, 1958, 1607, 1462, 1377, 1248, 1155, 1044 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.33 (dd, J = 8.3, 7.8 Hz, 1 H), 4.30 (m, 1 H), 2.40 (t, J = 6.4 Hz, 2 H), 2.07 (d, J = 2.4 Hz, 1 H), 1.94–1.66 (m, 7 H), 0.16 (dd, J = 8.3, 2.0 Hz, 1 H), 0.12 (d, J = 2.4 Hz, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 211.1, 119.6, 110.1, 83.0, 73.3, 38.3, 38.2, 37.4, 25.1, 25.0, 17.1; MS (20 eV) m/e (relative intensity) 249 (M − 2 CO, 60), 221 (100), 203 (82), 148 (6), 113 (17), 83 (5); HRMS (EI) m/e calcd for C₁₀H₁₅FeNO (M − 3 CO) 221.0503, found 221.0501.

(6R*,7S*,8R*)-(η⁴-6-Hydroxy-7-methylene-8-nonenenitrile)tricarbonyliron complex (3d): IR (CH₂Cl₂) 3599, 3488, 3067, 2932, 2249, 2051, 1983, 1609, 1463, 1377, 1283, 1182, 1038 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.59 (dd, J = 8.3, 7.8 Hz, 1 H), 3.99 (t, J = 5.9 Hz, 1 H), 2.40 (t, J = 6.8 Hz, 2 H), 1.89 (m, 2 H), 1.79–1.65 (m, 6 H), 0.25 (d, J = 2.4 Hz, 1 H), 0.22 (dd, J = 8.3, 2.0 Hz, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 210.9, 119.5, 110.0, 80.0, 73.5, 40.4, 38.8, 38.6, 25.3, 24.9, 17.1; MS (20 eV) m/e (relative intensity) 249 (M − 2 CO, 35), 221 (100), 203 (56), 113 (22), 97 (14), 83 (22), 71 (81); HRMS (EI) m/e calcd for C₁₀H₁₅FeNO (M − 3 CO) 221.0503, found 221.0505.

(5S*,6S*,7R*)-(η⁴-Ethyl 5-hydroxy-6-methylene-7-octenoate)tricarbonyliron Complex (2e). The crude mixture obtained from the addition of the corresponding zinc–copper reagent (27 mmol) to complex 1 (1.5 g, 6.8 mmol) in the presence of BF₃·OEt₂ (2.6 mL, 20 mmol) was purified via flash column chromatography (silica gel, 15% ethyl acetate/85% hexanes) to give complex 2e (1.6 g, 4.7 mmol, 69%) and 3e (0.20 g, 0.50 mmol, 7%), both as yellow oils. 2e: IR (CH₂Cl₂) 3605, 3069, 2980, 2050, 1964, 1728, 1449, 1375, 1300, 1188, 1030 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.33 (dd, J = 8.3, 7.3 Hz, 1 H), 4.30 (m, 1 H), 4.16 (q, J = 7.3 Hz, 2 H), 2.41 (t, J = 6.8 Hz, 2 H), 2.30 (br, OH), 2.10 (d, J = 2.4 Hz, 1 H), 1.86 (m, 4 H), 1.72 (dd, J = 7.8, 2.4 Hz, 1 H), 1.27 (t, J = 7.3 Hz, 3 H), 0.13 (dd, J = 8.3, 2.4 Hz, 1 H), 0.11 (d, J = 2.4 Hz, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 211.2, 173.6, 110.2, 82.9, 73.3, 60.4, 38.5, 38.2, 37.5, 33.8, 21.2, 14.1; MS (20 eV) m/e (relative intensity) 282 (M − 2 CO, 25), 254 (100), 236 (35), 208 (60), 174 (18), 162 (12), 148 (13), 135 (26); HRMS (EI) m/e calcd for C₁₁H₁₈FeO₃ (M − 3 CO) 254.0605, found 254.0606.

(5R*,6S*,7R*)-(η⁴-Ethyl 5-hydroxy-6-methylene-7-octenoate)tricarbonyliron complex (3e): IR (CH₂Cl₂) 3596, 3065, 2980, 2051, 1985, 1728, 1460, 1375, 1300, 1271, 1186, 1030 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.59 (dd, J = 8.3, 7.8 Hz, 1 H), 4.15 (q, J = 7.3 Hz, 2 H), 3.99 (m, 1 H), 2.40 (t, J = 6.8 Hz, 2 H), 2.00 (d, J = 2.4 Hz, 1 H), 1.89 (m, 4 H), 1.77 (dd, J = 7.8, 2.4 Hz, 1 H), 1.26 (t, J = 7.3 Hz, 3 H), 0.26 (d, J = 2.4 Hz, 1 H), 0.20 (dd, J = 8.3, 2.4 Hz, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 211.0, 173.5, 110.2, 80.1, 73.5, 60.4, 40.4, 39.2, 38.5, 34.0, 21.1, 14.2; MS (20 eV) m/e (relative intensity) 282 (M − 2 CO, 25), 254 (100), 236 (22), 208 (15), 154 (18), 142 (9), 138 (10), 126 (7); HRMS (EI) m/e calcd for C₁₁H₁₈FeO₃ (M − 3 CO) 254.0605, found 254.0611.

(σ,η³-Allyl)tricarbonyliron Complex 4a. To a solution of diisopropylamine (0.80 mL, 5.8 mmol) in 3.0 mL of THF under nitrogen at −78 °C was added rapidly (neat, via syringe) a solution of *n*-butyllithium (3.6 mL, 5.8 mmol, 1.6 M) in hexane followed by addition of HMPA (1.0 mL). The reaction mixture was stirred at −78 °C for 20 min. A solution of complex 2b (0.66 g, 2.4 mmol) in THF (3.0 mL) was added dropwise via syringe. The mixture was stirred at −78 °C for 3 h. The reaction mixture was then quenched with trifluoroacetic acid (1.5 mL) via a syringe needle and was stirred at 25 °C for 30 min. After this time, the reaction mixture was diluted with a mixture of ethyl acetate and hexanes (1/1, 100 mL). 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. The crude mixture was purified via flash column chromatography (silica gel, 15% ethyl acetate/85% hexanes) to give complex 4a

(190 mg, 0.67 mmol, 28%) and **4b** (63 mg, 0.23 mmol, 10%), both as yellow oils. **4a**: mp 115 °C dec; IR (CH$_2$Cl$_2$) 3599, 3407, 3056, 2988, 2203, 2068, 2004, 1607, 1441, 1424, 1263, 1103, 1059 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.00 (q, J = 6.8 Hz, 1 H), 4.62 (m, 1 H), 3.70 (d, J = 2.0 Hz, 1 H), 2.85 (d, J = 2.0 Hz, 1 H), 2.17 (ddd, J = 13.7, 4.9, 3.9 Hz, 1 H), 2.10 (ddd, J = 13.7, 9.8, 4.9 Hz, 1 H), 1.93 (br, OH), 1.70 (dd, J = 9.8, 3.9 Hz, 1 H), 1.40 (d, J = 6.8 Hz, 3 H); ^{13}C NMR (100.4 MHz, CDCl$_3$) δ 210.6, 209.3, 204.1, 128.4, 128.0, 71.3, 69.2, 49.7, 44.8, 21.1, 3.2; MS (70 eV) *m/e* (relative intensity) 277 (M$^+$, 1), 249 (21), 221 (16), 193 (31), 191 (33), 175 (100), 148 (45), 140 (18), 79 (23), 56 (30); HRMS (EI) *m/e* calcd for C$_8$H$_{11}$-FeNO (M − 3 CO) 193.0190, found 193.0196.

(σ,η^3-Allyl)tricarbonyliron Complex 4b: mp 131 °C dec; IR (CH$_2$Cl$_2$) 3598, 3434, 3057, 2924, 2205, 2068, 2008, 1609, 1441, 1424, 1246, 1066 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.16 (q, J = 6.8 Hz, 1 H), 4.09 (m, 1 H), 3.66 (d, J = 2.0 Hz, 1 H), 2.93 (d, J = 2.0 Hz, 1 H), 2.34 (ddd, J = 12.7, 4.9, 3.9 Hz, 1 H), 2.20 (br, OH), 2.12 (ddd, J = 12.7, 11.2, 4.9 Hz, 1 H), 1.44 (d, J = 6.8 Hz, 3 H), 1.20 (dd, J = 11.2, 3.9 Hz, 1 H); ^{13}C NMR (100.4 MHz, CDCl$_3$) δ 210.2, 209.4, 204.0, 127.6, 126.4, 75.4, 68.5, 52.4, 43.9, 20.5, −1.05; MS (70 eV) *m/e* (relative intensity) 277 (M$^+$, 5), 249 (34), 221 (33), 193 (57), 191 (43), 175 (100), 148 (51), 140 (57), 110 (9), 85 (26), 59 (14); HRMS (EI) *m/e* calcd for C$_8$H$_{11}$FeNO (M − 3 CO) 193.0190, found 193.0207.

(1S*,3R*)-3-Hydroxy-4-ethylidenecyclopentanecarbonitrile (11). Ceric ammonium nitrate (10 g, 20 mmol), **4a** (0.40 g, 1.4 mmol), and ethanol (50 mL) were stirred together at room temperature under nitrogen for 18 h. The solvent was partially removed under reduced pressure, and the residue was diluted with water (100 mL), extracted with methylene chloride (3 × 50 mL), washed with brine (3 × 50 mL), 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/80% hexanes) to give **11** (63 mg, 0.46 mmol, 32%) and **12** (12 mg, 0.10 mmol, 5%), both as colorless oils. **11**: IR (CH$_2$Cl$_2$) 3599, 3490, 3065, 2924, 2243, 1686, 1634, 1445, 1381, 1289, 1136, 1026 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.73 (q, J = 6.8 Hz, 1 H), 4.53 (d, J = 4.4 Hz, 1 H), 3.19 (dddd, J = 10.7, 9.3, 8.3, 6.4 Hz, 1 H), 2.88 (dd, J = 16.6, 8.3 Hz, 1 H), 2.49 (dd, J = 16.6, 9.3 Hz, 1 H), 2.18 (dd, J = 13.2, 6.4 Hz, 1 H), 1.98 (ddd, J = 13.2, 10.7, 4.4 Hz, 1 H), 1.65 (d, J = 6.8 Hz, 3 H); ^{13}C NMR (100.4 MHz, CDCl$_3$) δ 142.0, 122.4, 74.0, 39.6, 31.8, 25.2, 14.7; MS (20 eV) *m/e* (relative intensity) 137 (M$^+$, 83), 122 (100), 120 (28), 108 (21), 95 (37), 84 (44), 69 (31), 67 (22); HRMS (EI) *m/e* calcd for C$_8$H$_{11}$NO (M$^+$) 137.0841, found 137.0836.

(2R*,4R*)-2-(Carboxyethyl)-3-methylene-4-methyloxetane (12). IR (CH$_2$Cl$_2$) 3399, 3055, 2930, 1782, 1734, 1636, 1458, 1379, 1217, 1180, 1036 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.50 (q, J = 6.8 Hz, 1 H), 5.44 (s, 1 H), 5.40 (s, 1 H), 5.04 (t, J = 7.3 Hz, 1 H), 2.60 (dd, J = 9.8, 7.3 Hz, 2 H), 2.47 (m, 1 H), 2.17 (m, 1 H), 1.53 (d, J = 6.8 Hz, 3 H); ^{13}C NMR (100.4 MHz, CDCl$_3$) δ 176.0, 144.5, 115.2, 79.2, 78.7, 28.6, 28.3, 18.7; MS (20 eV) *m/e* (relative intensity) 156 (M$^+$, 2), 139 (48), 127 (48), 111 (100), 97 (22), 93 (33), 85 (47), 69 (30), 55 (69); HRMS (EI) *m/e* calcd for C$_8$H$_{11}$O$_2$ (M − OH) 139.0759, found 139.0764.

(σ,η^3-Allyl)tricarbonyliron Complex 13a. To a solution of diisopropylamine (0.5 mL, 3.8 mmol) in 3 mL of THF under nitrogen at −78 °C was added rapidly (neat, via syringe) a solution of n-butyllithium (2.4 mL, 3.8 mmol, 1.6 M) in hexane followed by addition of HMPA (1.0 mL). The reaction mixture was stirred at −78 °C for 20 min. A solution of complex **3b** (0.43 g, 1.6 mmol) in THF (3.0 mL) was added dropwise via syringe. The mixture was stirred at −78 °C for 3 h. The reaction mixture was then quenched with trifluoroacetic acid (1.5 mL) via a syringe needle and was stirred at 25 °C for 30 min. After this time, the reaction mixture was diluted with a mixture of ethyl acetate and hexanes (1/1, 100 mL). 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. The crude mixture was purified via flash column chromatography (silica gel, 20% ethyl acetate/80% hexanes) to give complex **13a** (60 mg, 0.22 mmol, 14%) and **13b** (40 mg, 0.14 mmol, 9%), both as yellow oils. **13a**: mp 92 °C dec; IR (CH$_2$Cl$_2$) 3599, 3445, 3052, 2988, 2203, 2064, 2008, 1609, 1445, 1393, 1265, 1113, 1059 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.62 (q, J = 7.0 Hz, 1 H), 4.47 (m, 1 H), 4.23 (d, J = 2.0 Hz, 1 H), 2.82 (d, J = 2.0 Hz, 1 H), 2.19 (ddd, J = 13.6, 4.8, 4.4 Hz, 1 H), 2.07 (ddd, J = 13.6, 8.8, 4.8 Hz, 1 H), 1.66 (br, OH), 1.60 (dd, J = 8.8, 4.4 Hz, 1 H), 1.44 (d, J = 7.0 Hz, 3 H); ^{13}C NMR (100.4 MHz, CDCl$_3$) δ 210.4, 209.6, 204.3, 128.7, 72.0, 69.8, 50.0, 44.1, 20.6, 1.9; MS (20 eV) *m/e* (relative intensity) 277 (M$^+$, 1), 249 (47), 221 (19), 193 (100), 175 (36), 148 (38), 140 (16), 86 (14); HRMS (EI) *m/e* calcd for C$_8$H$_{11}$FeNO (M − 3 CO) 193.0190, found 193.0194.

(σ,η^3-Allyl)tricarbonyliron complex 13b: mp 86 °C dec; IR (CH$_2$Cl$_2$) 3597, 3443, 3052, 2988, 2205, 2068, 2006, 1607, 1422, 1395, 1256, 1057, 1026 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.40 (q, J = 6.6 Hz, 1 H), 4.25 (d, J = 2.0 Hz, 1 H), 3.87 (m, 1 H), 2.79 (d, J = 2.0 Hz, 1 H), 2.35 (ddd, J = 12.8, 5.3, 4.0 Hz, 1 H), 1.97 (ddd, J = 12.8, 12.3, 5.3 Hz, 1H), 1.40 (d, J = 6.6 Hz, 3 H), 1.14 (dd, J = 12.3, 4.0 Hz, 1 H); ^{13}C NMR (100.4 MHz, CDCl$_3$) δ 210.4, 209.1, 203.9, 127.7, 126.6, 75.7, 73.3, 49.3, 43.5, 21.2, −2.1; MS (20 eV) *m/e* (relative intensity) 277 (M$^+$, 4), 249 (51), 221 (22), 193 (100), 175 (47), 148 (49), 140 (24), 110 (37), 85 (55); HRMS (EI) *m/e* calcd for C$_8$H$_{11}$FeNO (M − 3 CO) 193.0190, found 193.0193.

Fused Tetracarbonylbicyclo[4.3.0]ferranonanone 14a. To a solution of diisopropylamine (0.40 mL, 2.7 mmol) in 3 mL of THF under nitrogen at −78 °C was added rapidly (neat, via syringe) a solution of n-butyllithium (1.7 mL, 2.7 mmol, 1.6 M) in hexane followed by addition of HMPA (1.0 mL). The reaction mixture was stirred at −78 °C for 20 min. A solution of complex **2c** (0.33 g, 1.1 mmol) in THF (3.0 mL) was added dropwise via syringe. The mixture was stirred at −78 °C for 3 h. The reaction mixture was then quenched with trifluoroacetic acid (1.5 mL) via a syringe needle. Carbon monoxide was introduced to the system via a syringe needle and was pressurized to ca. 2.0 psig (always keeping a positive pressure on the system) as measured by a regulator at the CO cylinder. The CO pressure was then released via an additional needle, and the CO was allowed to flow through the system. The gas exit needle was removed, and the closed system was pressurized to ca. 14 psig with CO. The reaction mixture was stirred at 25 °C under CO for 40 h. After this time, the reaction mixture was diluted with a mixture of ethyl acetate and hexanes (1/1, 100 mL). 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. The crude mixture was purified via flash column chromatography (silica gel, 15% ethyl acetate/85% hexanes) to give complex **14a** (58 mg, 0.17 mmol, 24%) and a trace of **14b** (less than 2%), both as yellow oils. **14a**: mp 145 °C dec; IR (CH$_2$Cl$_2$) 3684, 3536, 3056, 2957, 2255, 2110, 2037, 1983, 1726, 1659, 1464, 1379, 1292, 1138, 1067 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.67 (dd, J = 11.2, 4.9 Hz, 1 H), 3.29 (d, J = 1.5 Hz, OH), 2.46 (dd, J = 13.2, 5.4 Hz, 1 H), 2.43 (dd, J = 12.2, 3.9 Hz, 1 H), 2.13 (dd, J = 13.2, 9.8 Hz, 1 H), 2.12 (m, 1 H), 1.87 (m, 1 H), 1.66 (ddd, J = 12.2, 9.8, 5.4 Hz, 1 H), 1.56 (ddd, J = 12.2, 4.4, 3.9 Hz, 1 H), 1.23 (m, 1 H), 0.89 (s, 3 H); ^{13}C NMR (100.4 MHz, CDCl$_3$) δ 263.5, 205.3, 204.9, 202.0, 199.1, 121.1, 73.4, 68.4, 50.5, 32.3, 28.1, 28.0, 18.5, 8.0; MS (20 eV) *m/e* (relative intensity) 347 (M$^+$, 1), 319 (9), 291 (27), 263 (48), 235 (100), 207 (65), 189 (23), 167 (30), 126 (12), 93 (6); HRMS (EI) *m/e* calcd for C$_{10}$H$_{13}$FeNO$_2$ (M − 3 CO) 235.0296, found 235.0292.

(Trimethylenemethane)tricarbonyliron Complex 21a. To a solution of diisopropylamine (0.35 mL, 2.4 mmol) in 3.0 mL of THF under nitrogen at −78 °C was added rapidly (neat,

via syringe) a solution of *n*-butyllithium (1.5 mL, 2.4 mmol, 1.6 M) in hexane followed by addition of HMPA (1.0 mL). The reaction mixture was stirred at −78 °C for 20 min. A solution of complex **2c** (0.29 g, 1.0 mmol) in THF (3.0 mL) was added dropwise via syringe at −78 °C. The mixture was stirred at 25 °C for 4 h. The reaction mixture was then quenched with trifluoroacetic acid (1.5 mL) via a syringe needle. Carbon monoxide was introduced to the system via a syring needle and was pressurized to ca. 2.0 psig (always keeping a positive pressure on the system) as measured by a regulator at the CO cylinder. The CO pressure was then released via an additional needle, and the CO was allowed to flow through the system. The gas exit needle was removed, and the closed system was pressurized to ca. 14 psig with CO. The reaction mixture was stirred at 25 °C under CO for 36 h. After this time, the reaction mixture was diluted with a mixture of ethyl acetate and hexanes (1/1, 100 mL). 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. The crude mixture was purified via flash column chromatography (silica gel, 5% ethyl acetate/ 95% hexanes) to give complex **21a** (0.12 g, 0.45 mmol, 45%) and **21b** (12 mg, 0.04 mmol, 4%), both as yellow oils. **21a:** mp 82−83 °C; IR (CH₂Cl₂) 3056, 2951, 2240, 2056, 1995, 1460, 1424, 1385, 1281, 1150, 1041 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.12 (dd, *J* = 10.3, 5.9 Hz, 1 H), 3.01 (s, 1 H), 2.23 (s, 1 H), 2.03 (m, 2 H), 1.78 (m, 2 H), 1.63 (s, 1 H), 1.53 (s, 3 H); ¹³C

NMR (100.4 MHz, CDCl₃) δ 210.9, 210.7, 210.4, 120.5, 99.1, 84.0, 70.8, 45.7, 33.5, 26.5, 21.5, 20.7; MS (20 eV) *m/e* (relative intensity) 273 (M⁺, 8), 245 (48), 217 (21), 189 (78), 162 (100), 56 (7); HRMS (EI) *m/e* calcd for C₉H₁₁FeN (M − 3 CO) 189.0241, found 189.0243.

(Trimethylenemethane)tricarbonyliron complex 21b: IR (CH₂Cl₂) 3056, 2951, 2234, 2054, 1991, 1458, 1424, 1385, 1262, 1171, 1051 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.16 (s, 1 H), 3.02 (d, *J* = 6.4 Hz, 1 H), 2.36 (s, 1 H), 2.35 (m, 1 H), 1.98−1.84 (m, 3 H), 1.80 (s, 1 H), 1.59 (s, 3 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 210.9, 210.7, 210.4, 120.7, 100.0, 84.4, 71.4, 46.6, 32.7, 26.5, 21.2, 20.7; MS (20 eV) *m/e* (relative intensity) 273 (M⁺, 34), 245 (9), 217 (43), 189 (100), 162 (19), 56 (8); HRMS (EI) *m/e* calcd for C₉H₁₁FeN (M − 3 CO) 189.0241, found 189.0240.

Supplementary Material Available: Tables of crystallographic data, positional parameters, and bond lengths and angles for **3b**, **4a**, **14a**, and **21a**, and an ORTEP diagram for **21a** (14 pages). Ordering information is given on any current masthead page.

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