180 *Organometallics* **1999,** *18,* 180−186

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Synthesis of Fulvalene-Bridged Bimetallic Compounds Containing a Substituted Cyclopentadienyl Group Based on Pauson−Khand Chemistry

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From the Pauson−Khand products 2-ferrocenylcyclopentenone (**2**) and 2-ferrocenyl-3-methylcyclopentenone (**10**) as starting materials, substituted ferrocene complexes (C_5H_5-η^5-C_5H_4)Fe(C_5H_5) (**4**), ($CH_3C_5H_4$-η^5-C_5H_4)Fe(C_5H_5) (**12**), and ($Me_2C_5H_3$-η^5-C_5H_4)Fe(C_5H_5) (**16**) were prepared. Metalation of **4**, **12**, and **16** with Mn(CO)$_5$Br, Cr(CO)$_3$(CH_3CN)$_3$, FeCl$_2$(THF)$_n$, and the deprotonated form of [CpFe(fluorene)]$^+$ resulted in good yields of fulvalenyl-bridged heterobi- and polymetallic compounds. The molecular structures of [1-{(C_5H_4)Fe(C_5H_5)}-2-$CH_3C_5H_4$]Mn(CO)$_3$ (**13**), [2-{(C_5H_4)Fe(C_5H_5)}-1,3-$Me_2C_5H_2$] Mn(CO)$_3$ (**17**), [2-{(C_5H_4)Fe(C_5H_5)}-1,3-$Me_2C_5H_2$]Fe(C_5H_5) (**18**), and [1-{(C_5H_4)Fe(C_5H_5)}-2,3,4,5-Me_4C_5]Fe(C_5H_5) (**23**) are reported.

Introduction

Recently, bimetallic complexes linked by pairs of cyclopentadienyl moieties, as in fulvalene,[1] fluorene,[2] indenyl,[3] pentalene, and indacene,[4] have been reported. Ligands of this type have the ability to hold several metals in close proximity, thereby allowing for the possibility of cooperative effects which can enhance or modify chemical reactivity. Potential uses include new multimetal catalysts,[5] organometallic polymers,[6] heteropolymetallics,[7] redox active compounds,[8] and energy storage devices.[9]

Many examples of fulvalene ligand (Fv)-bridged heterobimetallics are metallocene-based with the formulas [(C_5H_5)Fe(μ-η^5:η^5-Fv)M($C_5R'_5$)][10] and [(C_5H_5)Fe(μ-η^5:η^5-Fv)ML$_x$][11] where ML$_x$ is not a metallocene. There are also many examples of fulvalene-bridged heterobimetallics [M′L′$_y$M(μ-η^5:η^5-Fv)M′L$_x$][12] which are not based on metallocenes. Fulvalene ligands bound to a CpFe moiety have been synthesized by the use of ferrocenyl-substituted alkali-metal cyclopentadienides, with subsequent conversion to fulvalene-bridged heterobimetallics.[11] This methodology is limited by the difficulty of generating ferrocenyl-substituted alkali-metal cyclopentadienides. Herein we report the facile synthesis of ferrocenylcyclopentadiene systems, which provide a general route to multinuclear fulvalene complexes.

One of the strategies used to synthesize cyclopentadienylmetal compounds involves the use of cyclopentenone as a starting material.[13] An effective method for the preparation of cyclopentenones is based on the Pauson−Khand reaction.[14] Recently, we reported the preparation and utilization of substituted cyclopenta-

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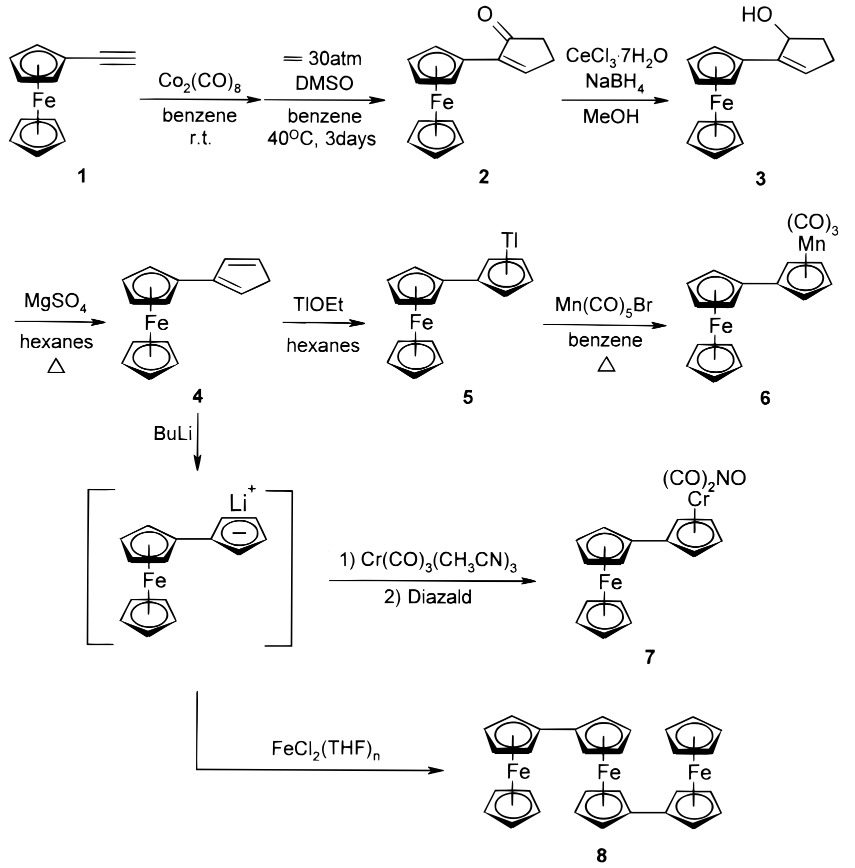
Scheme 1



dienyl ligands obtained from products of Pauson–Khand reactions.[15] Herein we describe the intermolecular Pauson–Khand reaction between ethynylferrocene or ferrocenylpropyne as the alkyne substrate and ethylene or propylene as the alkene substrate, and the use of the products to synthesize some fulvalene-bridged heterobi- and polymetallic compounds containing ferrocenyl groups. To our knowledge, there have been no reports of the use of ethynylferrocene and ferrocenylpropyne as an alkyne substrate in the Pauson–Khand reaction.

Results and Discussion

Syntheses. To synthesize the required ferrocenyl-substituted cyclopentadienyl ligands, we utilized the high-yield synthesis of cyclopentenones via the intermolecular Pauson–Khand reaction between ethynylferrocene, **1**,[16] and ethylene in the presence of DMSO as a promoter[15b] (Scheme 1). After workup, 1-ferrocenylcyclopentenone, **2**,[17] was obtained as an orange solid in 93% yield. Subsequent reduction with $NaBH_4$ in the presence of cerium chloride afforded the corresponding alcohol, **3**, as an orange solid in quantitative yield. Refluxing a hexane solution of the known[17] **3** with $MgSO_4$ gave the cyclopentadiene **4**[18] in quantitative yield. We found that treatment of a hexane solution of **4** with thallous ethoxide gave its corresponding thallium salt, **5**, as an orange solid in 68% yield. Using **5** as a precursor, cymantrenylferrocene, **6**,[19] was prepared in 52% yield.

Treatment of **4** with BuLi followed by reaction with $Cr(CO)_3(CH_3CN)_3$ afforded **7** as a yellow-orange solid

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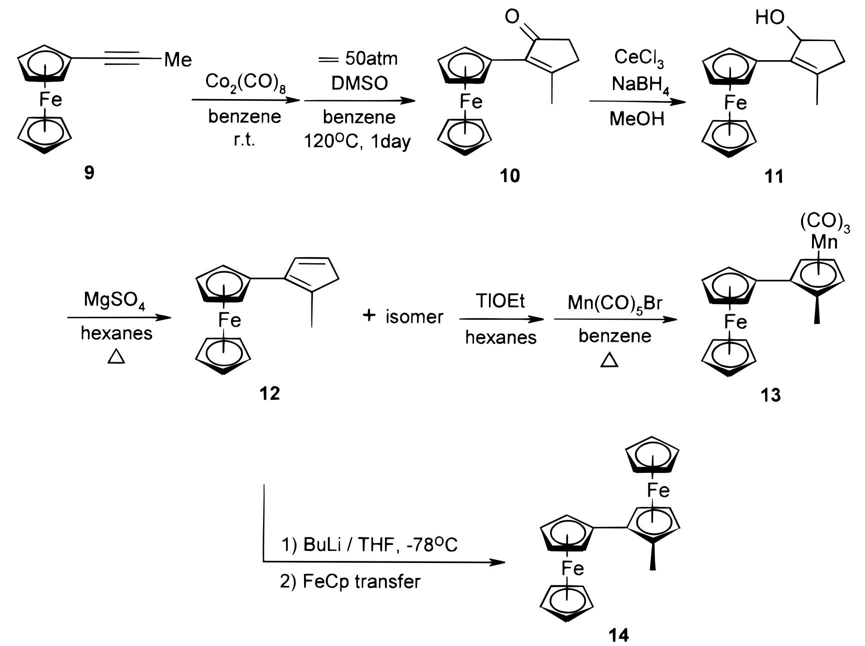
Scheme 2



in 68% yield. When **4** was treated with BuLi and subsequently with $FeCl_2(THF)_n$, terferrocene **8** was obtained in 37% yield. The preparation and oxidation state properties of terferrocene have been reported by several groups.[10d,17c,19] Schottenberger et al.[18] reported the formation and some physical properties of heterotermetallocenes.

To demonstrate the versatility of our methodology, a substituted fulvalene ring system was prepared from ferrocenylpropyne, **9**,[16b] as an alkyne substrate in the intermolecular Pauson−Khand reaction. The reaction between **9** and ethylene in the presence of DMSO gave **10** in 59% yield (Scheme 2). Reduction of **10** was accomplished by addition of $NaBH_4$ in ethanol. Refluxing **11** with $MgSO_4$ in hexane afforded **12** in 62% yield. Treatment of the thallium salt of **12** with $Mn(CO)_5Br$ gave **13** in 40% yield. The structure of **13** was verified by an X-ray study (Figure 1). To make a biferrocene derivative from **12**, a CpFe transfer reaction[20] was utilized. Treatment of **12** with BuLi followed by the addition of the deprotonated form of [(fluorene)FeCp)]PF_6 (generated in situ by the reaction of [(fluorene)FeCp)]PF_6 with K*t*OBu) gave **14** in 78% yield. To introduce another methyl group on the cyclopentadienyl ring, **10** was treated with MeLi (Scheme 3). After reaction, **15** was obtained in 75% yield. In the same way, **16** and **17** were obtained in 33 and 37% yields, respectively, from **15**. The molecular structure of **17** (Figure 2) was verified by an X-ray diffraction study. A biferrocene derivative **18** was obtained in 66.6% yield from **16** by the same procedure used to synthesize **14**.

To synthesize a biferrocene containing three methyl groups on a cyclopentadienyl ring, the intermolecular Pauson−Khand reaction between **9** and propylene was carried out at 160 °C (Scheme 4). After reaction, the Pauson−Khand product **19** was obtained in 40% yield and converted to **20** and **21** in 71 and 53% yields, respectively.

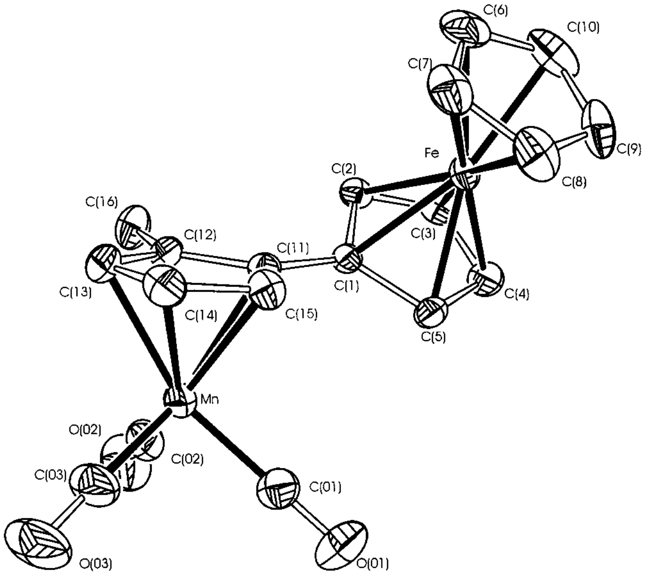


Figure 1. ORTEP drawing and labeling scheme of **13**. Ellipsoids are drawn at 40% probability.

To generate biferrocene derivatives with a systematic variation of methyl substituents, complex **23**, having four methyl groups on a cyclopentadienyl ring, was synthesized from the known compound **22**[21] in 65% yield (Scheme 5).

X-ray Structures of 13, 17, 18, and 23. The molecular structures of **13**, **17**, **18**, and **23** were determined by X-ray diffraction. X-ray crystal structures of **13** and **17** are quite similar to each other. Thus, the X-ray crystal structure of **13** is presented in Figure 1. In the same way, the X-ray crystal structure of **23** is presented in Figure 2. ORTEP drawings of **17** and **18** are available from the Supporting Information. Crystal data and refinement are given in Table 1, and selected bond distances and angles are in Table 2.

The two metal centers in **13** and **17** are coordinated to the fulvalenide ligand in a trans manner. In **13**, the fulvalenide ligand is twisted with the dihedral angle

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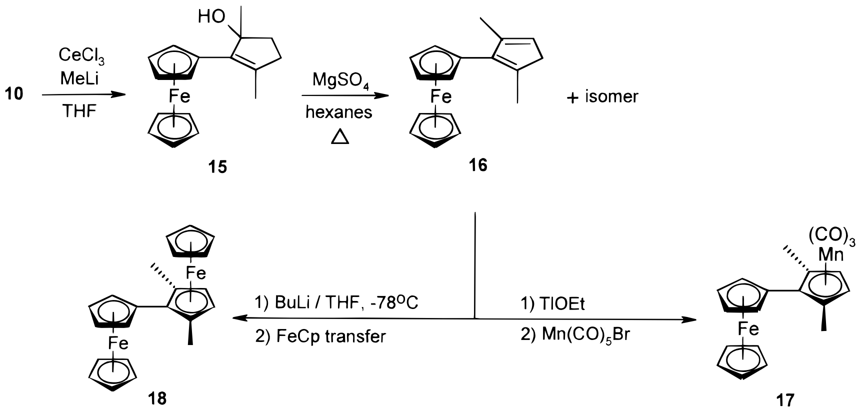
Scheme 3



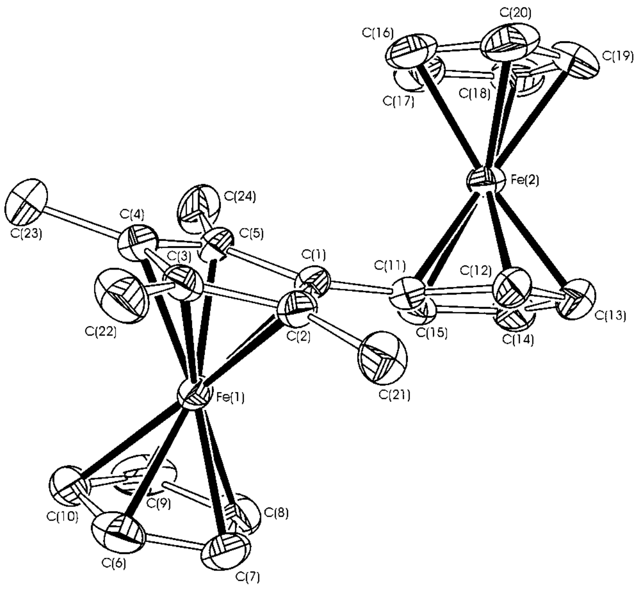


Figure 2. ORTEP drawing and labeling scheme of **23**. Ellipsoids are drawn at 40% probability.

between two Cp rings being 36.9(2)°. For **17**, there are two molecules in the asymmetric unit, with the dihedral angles between the two Cp rings being 28.1(1)° and 31.4(2)°. The Mn atom in **13** and **17** has the usual piano-stool coordination characteristic of the cyclopentadienyl complexes.[22] The Mn atom in **13** is located 1.776(2) Å below the plane of the cyclopentadienyl ring; in **17** the distances are 1.777(1) and 1.772(1) Å.

Compounds **18** and **23** exist in a trans conformation, with the two ions on opposite sides of the fulvalenide moiety, as observed for most biferrocenes. In each ferrocenyl fragment, the cyclopentadienyl rings are eclipsed and nearly parallel (tilt angle: 0.7(2)−3.4(2)°). The dihedral angles between the two Cp rings in the fulvalenide moiety for **18** and **23** are 35.8(1)° and 27.9(2)°, respectively. The importance of the dihedral angle in the rate of electron transfer in biferrocenium salts was pointed out by Dong et al.[23] We are currently studying the oxidation of **14**, **18**, **21**, and **23** to the corresponding biferrocenium cations with respect to electronic structure and rate of intramolecular electron transfer in the biferrocenium cations.

For **18**, the average distance from the iron atom to the two Cp rings is 1.652(2) Å, and the average distances from two iron atoms to fulvalenide are 1.646(1) and 1.649(1) Å. For **23**, the average distances from the iron atom to the two Cp rings are 1.653(2) and 1.654(2) Å, and those from the iron atom to fulvalenide are 1.643(2) Å (to the plane C1−C5) and 1.648(2) Å (to the plane C11−C15). The average Fe−Cp distances in **18** and **23** are similar to the values found for other biferrocenes.[24]

Electrochemistry for 14, 18, 21, and 23. To evaluate the influence of methyl groups on the oxidation potential of biferrocenes, the electrochemical properties of derivatives **14**, **18**, **21**, and **23** were examined (Table 3). All the complexes show two successive reversible one-electron oxidations. As the number of methyl group increases, the first half-wave potential ($E^1_{1/2}$) shifts negatively while the second half-wave potential ($E^2_{1/2}$) is almost constant, with the separation between $E^1_{1/2}$ and $E^2_{1/2}$ decreasing in the order **23** > **21** > **18** > **14**. This is an anticipated result since methylation results in easier oxidation. This order is entirely predictable since the methylated cyclopentadienyl ring should be the easier to oxidize.

Conclusion

We have demonstrated that by using Pauson−Khand reaction products as starting materials, fulvalenyl bimetallic and trimetallic complexes can be synthesized in good yield. We expect that this methodology can be expanded to include generalized fulvalenyl and cyclopentadienyl ligands.

Experimental Section

General Procedures. All reactions were conducted under nitrogen using standard Schlenk type flasks. Workup procedures were done in air. THF was freshly distilled from sodium

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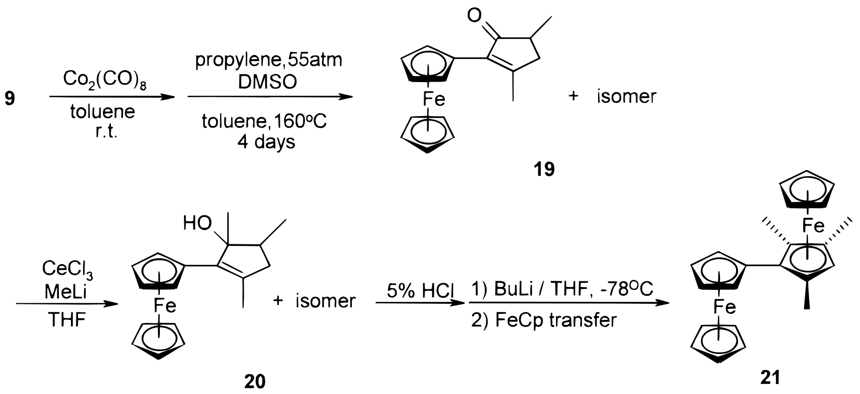
Scheme 4



Scheme 5

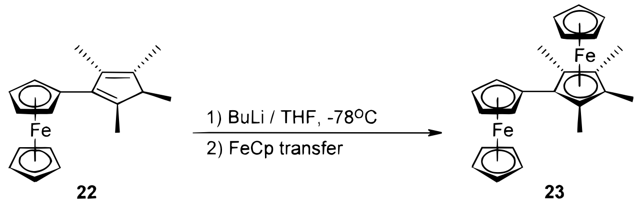


Table 1. Crystal Data and Structure Refinement for 13, 17, 18, and 23

	13	**17**	**18**	**23**
formula	$C_{19}H_{15}FeMnO_3$	$C_{40}H_{34}Fe_2MnO_6$	$C_{22}H_{22}Fe_2$	$C_{24}H_{26}Fe_2$
fw	402.10	832.25	398.10	426.15
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a, Å	10.1192(14)	17.329(2)	8.2325(7)	7.3158(6)
b, Å	10.591(2)	11.447(2)	10.2288(11)	8.0753(7)
c, Å	15.469(2)	18.549(2)	20.603(2)	17.998(2)
α, deg	90	90	90	81.146(8)
β, deg	96.685(11)	109.79(1)	91.387(6)	82.895(8)
γ, deg	90	90	90	65.308(6)
V, Å^3	1646.7(4)	3462.0(7)	1734.4(3)	952.4(2)
Z	4	4	4	2
d(calcd), Mg/m^3	1.622	1.597	1.525	1.486
total no. observns	3065	6312	3279	3639
no. of unique data	2880	6054	3050	3326
2θ range/deg	4.5−50	4.3−50	4−50	4.6−50.4
no. params refined	217	485	305	235
R1	0.0405	0.0308	0.0288	0.0695
wR2	0.1010	0.0689	0.0720	0.1893
GOF on F^2	1.046	1.037	1.092	1.081

benzophenone ketyl prior to use. Most organic compounds were purchased from Aldrich Chemical Co. and were used as received. ^{1}H NMR spectra were obtained with a Bruker-300 or Bruker AMX-500 instrument. IR spectra were recorded on a Shimadzu IR-470 spectrophotometer (spectra measured as films on NaCl by evaporation of the solvent). Elemental analyses were done at the Chemical Analytic Center, College of Engineering, Seoul National University. Mass spectra were recorded on a JEOL JMS AX 505 WA double-focusing mass spectrometer. Melting points were measured on a Thomas-Hoover capillary melting point apparatus and not corrected. Complexes **1**−**6**, **8**−**9**, and **22** have been reported previously.[16−19,21] Formation of known compounds is confirmed by comparing their ^{1}H NMR spectra to the reported values. Compounds **1**, **9**, and **22** were prepared by the known procedures.[16,21]

Synthesis of 2. In a 100 mL steel autoclave were placed ethynyl ferrocene (0.63 g, 3.0 mmol), $Co_2(CO)_8$ (1.0 g, 3.0 mmol), and 30 mL of benzene. After stirring for 1 h at room temperature, TLC indicated the complete consumption of the starting acetylene. DMSO (1 mL, 15 mmol) was added to the steel bomb, and the vessel was closed. After introducing of 30 atm of ethylene, the reaction mixture was stirred at 40 °C for 3 days. After cooling to room temperature and releasing ethylene, the vessel was opened and the solution was filtered on a Celite pad. The filtrate was washed with saturated brine and dried over anhydrous $MgSO_4$. After addition of silica gel (3 g) to the dried solution, the solvent was removed. Flash column chromatography on silica gel eluting with Et_2O and hexane (v/v, 10:1) gave an orange crystalline solid (0.75 g, 93%).^{1}H NMR ($CDCl_3$): δ 7.54 (t, 2.6 Hz, 1 H), 4.76 (t, 1.7 Hz, 2 H), 4.27 (t, 1.7 Hz, 2 H), 4.07 (s, 5 H), 2.59−2.49 (m, 4 H) ppm. Anal. Calcd for $C_{15}H_{14}FeO$: C, 67.70; H, 5.30. Found: C, 67.74; H, 5.26.

Synthesis of 3. To a solution of **2** (0.80 g, 3.0 mmol) in 25 mL of MeOH was added $CeCl_3 \cdot 7H_2O$ (1.10 g, 3.0 mmol). After stirring for 1 h, $NaBH_4$ (0.22 g, 6.0 mmol) was added slowly to the solution. The reaction mixture was stirred for 20 min until the clear solution turned to a slurry. To quench excess $NaBH_4$ 5 mL of aqueous saturated NH_4Cl solution was poured into the reaction mixture. Excess Et_2O was added to extract a soluble product. The ether extract was dried over $MgSO_4$ and concentrated. An orange solid (0.80 g, 99%) was obtained. ^{1}H NMR ($CDCl_3$): δ 5.91 (s, 1 H), 4.97 (s, 1 H, OH), 4.50 (s, 1 H), 4.43 (s, 1 H), 4.23 (s, 2 H), 4.10 (s, 5 H), 2.56−2.24 (m, 3 H), 1.96−1.83 (m, 2 H) ppm. Anal. Calcd for $C_{15}H_{16}FeO$: C, 67.19; H, 6.01. Found: C, 66.97; H, 5.69.

Synthesis of 4. To a stirred solution of **3** in 200 mL of hexane was added $MgSO_4$ (4 g). The resulting solution was heated at reflux for 5 h. After cooling to room temperature, any solids were filtered off. The filtrate was concentrated to ca. 20 mL and chromatographed on a silica gel column eluting with hexane. An orange solid (0.75 g, 100%) was obtained in quantitative yield. ^{1}H NMR ($CDCl_3$) (major isomer): δ 6.49−6.44 (m, 2 H), 6.33−6.27 (m, 1 H), 4.44 (t, 1.8 Hz, 2 H), 4.23 (t, 1.8 Hz, 2 H), 4.06 (s, 5 H), 3.20 (dd, 1.4, 2.0 Hz, 2 H) ppm; (minor isomer): δ 6.75−6.68 (m, 1 H), 6.46−0.42 (m, 1 H), 6.29−6.26 (m, 1 H), 4.46 (t, 1.7 Hz, 2 H), 4.23 (t, 1.7 Hz, 2 H), 4.08 (s, 5 H), 3.06 (dd, 1.4, 3.1 Hz, 2 H) ppm.

Synthesis of 6. To a stirred solution of **4** (0.55 g, 2.2 mmol) in 30 mL of hexane thallous ethoxide was added dropwise (0.16 mL, 2.2 mmol) under vigorous purging of argon. Orange precipitates formed immediately. After stirring for 20 min, the precipitate **5** was collected and dried (0.70 g, 1.5 mmol, 68%). To a stirred solution of **5** (0.50 g, 1.1 mmol) in 30 mL of benzene was added $Mn(CO)_5Br$ (0.30 g, 1.1 mmol). The solution was heated at reflux for 12 h and cooled to room temperature. Any solids were filtered off, and the filtrate was concentrated to ca. 5 mL and chromatographed on a basic alumina column eluting with hexane and then with Et_2O and hexane (v/v, 1:5). Evaporation of the solvent gave the product **6** in 52% yield.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 13 and 23

			13		
Mn−C(01)	1.786(5)	C(01)−O(01)	1.147(5)	Mn−C(11)	2.171(3)
Mn−C(13)	2.134(4)	C(11)−C(12)	1.416(5)	C(12)−C(16)	1.500(5)
C(1)−C(11)	1.472(5)	Fe−C(1)	2.056(3)	Fe−C(10)	2.043(5)
Mn−C(01)−O(01)	179.2(4)	C(11)−C(12)−C(13)	108.1(3)	C(2)−C(1)−C(11)	126.3(3)
C(2)−C(1)−C(5)	106.8(3)	C(11)−C(12)−C(16)	127.2(4)	C(6)−C(7)−C(8)	107.3(4)
			23		
Fe(1)−C(1)	2.056(4)	Fe(1)−C(3)	2.041(4)	Fe(1)−C(6)	2.044(5)
C(2)−C(21)	1.498(6)	C(1)−C(11)	1.461(6)	Fe(2)−C(11)	2.072(4)
Fe(2)−C(13)	2.033(5)	Fe(2)−C(19)	2.042(5)	C(1)−C(2)	1.433(6)
C(1)−C(2)−C(3)	107.8(4)	C(1)−C(2)−C(21)	127.9(4)	C(2)−C(1)−C(5)	107.5(4)
C(2)−C(1)−C(11)	124.8(4)	C(12)−C(11)−C(15)	105.4(4)	C(6)−C(7)−C(8)	108.5(5)

Table 3. Cyclic Voltammetry Data

compound	$E^1_{1/2}$ (V)[a]	$E^2_{1/2}$ (V)[a]	$\Delta E_{1/2}$(V)[b]
$[Fe(C_5H_4)(C_5H_4)]_2$	−0.12	0.26	0.38
14	−0.13	0.27	0.40
18	−0.16	0.27	0.43
21	−0.19	0.26	0.45
23	−0.26	0.23	0.49

[a] Versus Cp_2Fe/Cp_2Fe^+. [b] Peak separation between waves.

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IR ν(CO): 2012, 1930 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.92 (br s, 2 H), 4.72 (br s, 2 H), 4.38 (br s, 2 H), 4.22 (br s, 2 H), 4.08 (s, 5 H) ppm.

Synthesis of 7. To a stirred solution of **4** (0.33 g, 1.32 mmol) in 30 mL of THF was added *n*-BuLi (1.45 mmol, 0.58 mL of a 2.5 M solution in hexane) at 0 °C. After stirring for 1 h, a THF solution of $Cr(CO)_3(CH_3CN)_3$ (generated in situ by the reaction of $Cr(CO)_6$ (0.58 g, 2.64 mmol) with CH_3CN at reflux overnight) was transferred into the reaction mixture. The resulting solution was heated at reflux for 12 h and then cooled to room temperature. To the solution was added Diazald (0.28 g, 1.3 mmol). The resulting solution was heated at reflux for 2 h, and the solvent was removed. The residue was extracted with diethyl ether (50 mL × 3). To the ether extract was added silica gel (2 g) in 10 mL of hexane. After evaporation of the solvent, chromatography of the crude product on a silica gel column eluting with Et_2O/hexane (v/v, 1:20) gave an orange solid in 68% yield (0.347 g). Mp: 105−106 °C. IR ν(CO): 2008, 1966, 1938, 1879 cm^{-1}; ν(NO) 1678 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.23 (t, 2.3 Hz, 2 H), 5.02 (t, 2.3 Hz, 2 H), 4.36 (t, 1.9 Hz, 2 H), 4.23 (t, 1.9 Hz, 2 H), 4.10 (s, 5 H) ppm. Anal. Calcd for $C_{17}H_{13}CrFeNO_3$: C, 52.74; H, 3.38; N, 3.62. Found: C, 52.59; H, 3.03; N, 3.56.

Synthesis of 8. Compound **4** (0.222 g, 0.888 mmol) was dissolved in 20 mL of THF and cooled to 0 °C. To the solution was added *n*-BuLi (0.4 mL of 2.5 M solution, 1.0 mmol) at 0 °C. The resulting solution was stirred for 1 h and transferred to the THF solution of $FeCl_2(THF)_n$, which was generated by the reaction of $FeCl_2$ (0.05 g, 0.39 mmol) with THF. The reaction mixture was heated at reflux for 12 h. After removal of the solvent, the residue was chromatographed on a silica gel column eluting with hexane. Removal of the solvent gave the product **8** (0.08 g, 37%). ^{1}H NMR ($CDCl_3$): δ 4.17 (t, 1.8 Hz, 4 H), 4.06 (t, 1.8 Hz, 4 H), 4.02 (t, 1.8 Hz, 4 H), 3.95 (t, 1.8 Hz, 4 H), 3.86 (s, 10 H) ppm.

Synthesis of 10. In a 100 mL steel autoclave were placed **9** (1.12 g, 5.0 mmol), $Co_2(CO)_8$ (1.71 g, 5.0 mmol), and 30 mL of benzene. After stirring for 1 h at room temperature, DMSO (1 mL, 15 mmol) was added to the steel bomb and the vessel was closed. After introducing 50 atm of ethylene, the reaction mixture was stirred at 120 °C for 1 day. After cooling to room temperature and releasing ethylene, the vessel was opened and the solution was filtered on a Celite pad. The filtrate was washed with saturated brine and dried. After addition of silica gel (3 g) to the dried solution, the solvent was removed. Flash column chromatography on a silica gel gave an orange crystalline solid (0.83 g, 59%). Mp: 64−65 °C. ^{1}H NMR ($CDCl_3$): δ 4.69 (s, 2 H), 4.28 (s, 2 H), 4.09 (s, 5 H), 2.54−2.46 (m, 4 H), 2.25 (s, 3 H) ppm. Anal. Calcd for $C_{16}H_{16}FeO$: C, 68.60; H, 5.76. Found: C, 68.63; H, 5.43.

Synthesis of 11. To a solution of **10** (0.99 g, 3.5 mmol) in 30 mL of EtOH was added $CeCl_3$ (0.96 g, 3.9 mmol). After stirring for 1 h, $NaBH_4$ (0.27 g, 7.0 mmol) was added slowly to the solution. The reaction mixture was stirred for 30 min until the clear solution turned to a slurry. To quench excess $NaBH_4$, 5 mL of aqueous saturated NH_4Cl solution was poured into the reaction mixture. Excess Et_2O (50 mL × 3)was added to extract a soluble product. The organic layer was washed by water (50 mL × 2). The ether extract was dried over $MgSO_4$ and concentrated. An orange solid (0.92 g, 92%) was obtained. Mp: 73−75 °C. ^{1}H NMR ($CDCl_3$): δ 4.99 (br s, 1 H), 4.51 (d, 1.6 Hz, 1 H), 4.47 (d, 1.6 Hz, 1 H), 4.25 (t, 1.6 Hz, 2 H), 4.12 (s, 5 H), 2.56 (dt, 7.2, 10.3 Hz, 1 H), 2.33−2.19 (m, 2 H), 1.89 (s, 3 H, CH_3), 1.93−1.77 (m, 2 H) ppm. Anal. Calcd for $C_{16}H_{18}FeO$: C, 68.11; H, 6.43. Found: C, 68.29; H, 6.34.

Synthesis of 12. To a stirred solution of **11** (0.83 g, 3.0 mmol) in 200 mL of hexane was added $MgSO_4$ (4 g). The resulting solution was refluxed for 5 h. After filtration of solids, the filtrate was concentrated to ca. 20 mL and chromatographed on a silica gel column eluting with hexane. Removal of the solvent gave the product as an orange solid (0.49 g, 62% yield). According to the ^{1}H NMR spectrum, there were two isomers in the ratio of 9:2. ^{1}H NMR of major isomer ($CDCl_3$): δ 6.64−6.61 (m, 1 H), 6.26−6.23 (m, 1 H), 4.43 (t, 1.9 Hz, 2 H), 4.23 (t, 1.9 Hz, 2 H), 4.11 (s, 5 H), 3.03 (t, 1.4 Hz, 2 H), 2.10 (s, 3 H) ppm. ^{1}H NMR of minor isomer ($CDCl_3$): δ 6.34−6.31 (m, 1 H), 6.28−6.25 (m, 1 H), 4.44 (t, 1.9 Hz, 2 H), 4.22 (t, 1.9 Hz, 2 H), 4.08 (s, 5 H), 3.25−3.23 (m, 2 H), 2.09 (t, 1.7 Hz, 3 H) ppm. Mp: 64−65 °C. Anal. Calcd for $C_{16}H_{16}Fe$: C, 72.75; H, 6.11. Found: C, 72.59; H, 6.34.

Synthesis of 13. In a 100 mL of Schlenk flask, **12** (0.17 g, 0.65 mmol) and 50 mL of hexane were placed under Ar. Thallous ethoxide (0.05 mL, 0.65 mmol) was added dropwise to the solution under Ar. Orange precipitates formed immediately. After stirring for 20 min, the precipitates (0.17 g, 59%) were collected in a frit and dried in vacuo. To a stirred solution of thallium salt (0.17 g, 0.36 mmol) in 20 mL of benzene was added $Mn(CO)_5Br$ (0.10 g, 0.36 mmol). The solution was heated at reflux for 12 h and cooled to room temperature. Any solids were filtered off, and the filtrate was concentrated to ca. 5 mL and chromatographed on a basic alumina column eluting with hexane and then with Et_2O and hexane (v/v, 1:5). Evaporation of the solvent gave an orange solid **13** in 40% yield (97 mg). Mp: 81−84 °C. IR ν(CO): 2008, 1934 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.91 (dd, 2.1, 2.5 Hz, 1 H), 4.57 (dd, 2.1, 2.5 Hz, 1 H), 4.60 (t, 2.7 Hz, 1 H), 4.44 (d, 1.7 Hz, 1 H), 4.40 (d, 1.7 Hz, 1 H), 4.26 (t, 1.7 Hz, 2 H), 4.13 (s, 5 H), 2.16 (s, 3 H) ppm. Anal. Calcd for $C_{19}H_{15}FeMnO_3$: C, 56.75; H, 3.76. Found: C, 56.88; H, 3.47.

Synthesis of 14. Compound **12** (0.15 g, 0.568 mmol) was dissolved in 10 mL of THF and cooled to −78 °C. *n*-BuLi (0.23 mL, 2.5 M in pentane) was added slowly to the solution and stirred at − 78 °C for 1 h. The deprotonated species of $[(fluorene)FeCp]PF_6$ (generated in situ by the reaction of 0.245 g of $[(fluorene)FeCp]PF_6$ with 0.57 mL of KO*t*-Bu (1.0 M in

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THF) in 10 mL of THF at 0 °C) was added via cannula to the above solution at −78 °C. The resulting solution was stirred, allowed to warm to room temperature over 1 h, and heated at 60 °C for 24 h. After the solution was cooled under N_2, the solution was filtered and the filtrate was evaporated and chromatographed on a flash silica gel column eluting with hexane and diethyl ether (v/v, 20:1). After removal of the solvent, an orange solid was obtained in 78% yield (0.17 g). Mp: 129−130 °C. ^{1}H NMR ($CDCl_3$): δ 4.42 (m, 2 H), 4.31 (m, 1 H), 4.19 (m, 2 H), 4.05 (s, 5 H), 4.03 (m, 1 H), 4.01 (m, 1 H), 3.95 (s, 5 H), 2.16 (s, 3 H) ppm; Anal. Calcd for $C_{21}H_{20}Fe_2$: C, 65.67; H, 5.25. Found: C, 65.76; H, 4.98.

Synthesis of 15. To a solution of **10** (0.62 g, 2.2 mmol) in 30 mL of THF was added $CeCl_3$ (0.60 g, 2.42 mmol). The reaction mixture was heated at reflux for 1 h and cooled to 0 °C. MeLi (1.9 mL of 1.4 M in diethyl ether, 2.66 mmol) was added to the solution at 0 °C. The resulting solution was stirred for at 0 °C for 1 h, allowed to warm to room temperature, quenched by 5 mL of saturated aqueous NH_4Cl, and extracted by addition of excess diethyl ether (50 mL × 3). The separated ether layer was washed by water (50 mL × 2). The ether layer was dried over anhydrous $MgSO_4$ and evaporated. Yield: 0.48 g (75%), orange solid; mp 118−120 °C. ^{1}H NMR ($CDCl_3$): δ 1.55 (s, 3 H), 1.95 (s, 3 H), 1.88−2.08 (m, 2 H), 2.16−2.39 (m, 2 H), 4.12 (s, 5 H), 4.24 (m, 1 H), 4.26 (m, 1 H), 4.48 (t, 1.2 Hz, 1 H), 4.61 (t, 1.2 Hz, 1 H) ppm. Anal. Calcd for $C_{17}H_{20}FeO$: C,68.94; H, 6.81. Found: C, 68.77; H, 6.42.

Synthesis of 16. To a solution of **15** (0.89 g, 3 mmol) in 200 mL of hexane was added $MgSO_4$ (4.0 g). The resulting solution was heated at reflux for 5 h. After filtration of solids, the filtrate was concentrated to ca. 20 mL and chromatographed on a silica gel column eluting with hexane. Removal of the solvent gave the product as an orange solid. Mp: 63 °C (dec). Yield: 0.284 g (33%). ^{1}H NMR ($CDCl_3$): δ 2.16 (s, 3 H), 2.22 (q, 1.1 Hz, 3 H), 2.83 (q, 1.1 Hz, 2 H), 4.12 (s, 5 H), 4.24 (t, 1.1 Hz, 2 H), 4.40 (t, 1.1 Hz, 2 H), 5.89 (q, 1.0 Hz, 1 H) ppm. Anal. Calcd for $C_{17}H_{18}Fe$: C, 73.40; H, 6.52. Found: C, 73.45; H, 6.56.

Synthesis of 17. In a 100 mL Schlenk flask, compound **14** (0.29 g, 1. mmol) and 50 mL of hexane were placed under Ar. Thallous ethoxide (0.08 mL, 1.13 mmol) was added dropwise to the hexane solution of **14** under Ar. Orange precipitates formed immediately. After stirring for 20 min, the precipitates were collected in a frit and dried in a vacuum. To a solution of thallium salt (0.315 g, 0.655 mmol) obtained in the above was added $Mn(CO)_5Br$ (0.18 g, 0.655 mmol). The resulting solution was heated at reflux for 12 h and cooled to room temperature. Any solids were filtered off, and the filtrate was concentrated to ca. 5 mL and chromatographed on basic alumina eluting with hexane and then with diethyl ether and hexane (v/v, 1:5). Evaporation of the solvent gave an orange solid in 37% yield (0.10 g). Mp: 95−96 °C. IR ν(CO): 2004, 1934 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.19 (s, 6 H), 4.19 (s, 5 H), 4.29 (t, 1.7 Hz, 2 H), 4.42 (t, 1.7 Hz, 2 H), 4.46 (s, 2 H) ppm. Anal. Calcd for $C_{20}H_{17}FeMnO_3$: C, 57.73; H, 4.12. Found: C, 57.44; H, 4.11.

Synthesis of 18. The same procedure as the synthesis of **14** was employed except **16** was used instead of **12**. The product was obtained as an orange solid. Yield: 66.6%. Mp: 141−142 °C. ^{1}H NMR ($CDCl_3$): δ 2.20 (s, 6 H), 3.87 (s, 5 H), 4.00 (s, 2 H), 4.09 (s, 5 H), 4.24 (t, 1.7 Hz, 2 H), 4.45 (t, 1.7 Hz, 2 H) ppm. Anal. Calcd for $C_{22}H_{22}Fe_2$: C, 66.37; H, 5.57. Found: C, 66.43; H, 5.27.

Synthesis of 19. The same procedure as the synthesis of **10** was employed except propylene was used instead of ethylene. An orange solid was produced. Mp: 42−43 °C. Yield: 40%. ^{1}H NMR ($CDCl_3$): δ 1.24 (d, 7.53 Hz, 3 H), 2.09 (d, 18.67 Hz, 1 H), 2.79 (dd, 6.9, 18.51 Hz, 1 H), 2.22 (s, 3 H), 2.45 (m, 1 H), 4.08 (s, 5 H), 4.27 (m, 2 H), 4.68 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ 16.78, 18.85, 39.95, 41.38, 68.27, 69.16, 135.18, 166.65, 209.89 ppm. HRMS *m*/*z*: (M^+) calcd 294.0707, obsd 294.0702.

Synthesis of 20. The same procedure as the synthesis of **15** was employed except **19** was used instead of **10**, producing an orange solid. Mp: 118−120 °C. Yield: 71%. ^{1}H NMR ($CDCl_3$): δ 1.04 (d, 6.84 Hz, 3 H), 1.41 (s, 3 H), 1.93 (s, 3 H), 1.92−2.04 (m, 2 H), 2.38 (m, 1 H), 4.13 (s, 5 H), 4.25 (m, 2 H), 4.42 (m, 1 H), 4.57 (m, 1 H) ppm. Anal. Calcd for $C_{22}H_{22}Fe_2$: C, 69.69; H, 7.15. Found: C, 69.77; H, 6.80.

Synthesis of 21. The same procedure as the synthesis of **18** was employed except **20** was used instead of **15**, producing an orange solid. Mp: 88−91 °C. Yield: 53%. ^{1}H NMR ($CDCl_3$): δ 1.91 (s, 3 H), 2.12 (s, 3 H), 2.16 (s, 3 H), 3.79 (s, 5 H), 4.05 (s, 1 H), 4.10 (s, 5 H), 4.22 (m, 2 H), 4.40 (m, 2 H) ppm. Anal. Calcd for $C_{23}H_{24}Fe_2$: C,67.03; H, 5.87. Found: C, 67.15; H, 6.08.

Syntheses of 23. The same procedure as the synthesis of **18** was employed except **22** was used instead of **15** producing an orange solid. Mp: 129−130 °C. Yield: 65.4%. ^{1}H NMR ($CDCl_3$): δ 4.37 (d, 1.6 Hz, 2 H), 4.22 (t, 1.5 Hz, 2 H), 4.11 (s, 5 H), 3.67 (s, 5 H), 2.16 (s, 6 H), 1.95 (s, 6 H) ppm. Anal. Calcd for $C_{24}H_{26}Fe_2$: C, 67.64; H, 6.15. Found: C, 67.46; H, 5.88.

X-ray Crystal Structure Determinations of 13, 17, 18, and 23. Crystals of **13** and **17** were grown by slow evaporation of a pentane solution of **13** and **17**, respectively. Crystals of **18** and **23** were grown by slow evaporation of a diethyl ether and pentane solution of **18** and **23,** respectively. Diffraction was measured by an Enraf-Nonius CAD4 diffractometer with a $\omega-2\theta$ scan method. Unit cells were determined by centering 25 reflections in the approximate 2θ range. Other relevant experimental details are in the Supporting Information. The structure was solved by direct methods using SHELXS-86 and refined by full-matrix least-squares with SHELXL-93. All non-hydrogen atoms were refined with anisotropic temperature factors; hydrogen atoms were refined isotropically using the riding model with 1.2 times the equivalent isotropic temperature factors of the atoms to which they are attached.

Electrochemical Studies. Cyclic voltammograms were obtained with a BAS CV-50W voltametric analyzer. The working electrode was platinum, with a Ag/AgCl reference electrode separated from the test solution by a salt-bridge containing the solvent and supporting electrolyte. The auxiliary electrode was a platinum wire. Solutions studied were 1 mM in solute and 0.1 M in tetrabutylammonium hexafluorophosphate as supporting electrolyte. HPLC grade dichloromethane was used. A dinitrogen atmosphere was maintained over the solution during the experiment. The system was calibrated against ferrocene.

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Supporting Information Available: Tables of atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom positional and displacement parameters for **13**, **17**, **18**, and **23** and ORTEP drawings of **17** and **18** (36 pages). Ordering information is given on any current masthead page.

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