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Use of (η^4-1-Azabuta-1,3-diene)tricarbonyliron as a Substitute for Cyclopentadiene in the Synthesis of Sandwich and Half-Sandwich Compounds

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The azadiene-iron complex (η^4-1-azabuta-1,3-diene)tricarbonyliron (**1**) acts as a substitute for cyclopentadiene. New sandwich and half-sandwich compounds **2**−**9** are prepared. Refluxing **1** affords two diasteromeric bis(azaferracyclopentadienyl)iron(II) compounds **2** and **3**. Reaction of **1** with $[CpFe(CO)_2]_2$, $Re(CO)_5BF_4$, and $Mn_2(CO)_{10}$ yields half-sandwich compounds **6**, **7**, and **8**, respectively. Photochemical reaction of **8** with PPh_3 gives a PPh_3-substituted derivative **9**. The molecular structures of **2**, **4**, **5**, **6**, **7**, and **9** have been determined by X-ray diffraction methods.

Introduction

Soon after the discovery of ferrocene in 1951,[1] metal carbonyl complexes containing cyclopentadienyl, benzene, and other carbocyclic ligands began to emerge. The study of these compounds led to important developments in the fields of catalysis, organic synthesis, medicinal chemistry, and materials science.[2]

The isolobal connection allows a joint consideration of inorganic, organic, and organometallic structures.[3] The ferrocene unit is sufficiently stable to tolerate substitution of other elements for carbon in the five-membered ring, and the synthesis of π-complexes containing heterocycles can be analogous to that of corresponding cyclopentadienyl complexes.[4]

Recently, we studied[5] the chemistry of [(1*H*-hydronaphthalene)$Mn(CO)_3$] and attempted to synthesize the iron analogue $[(1H\text{-hydronaphthalene})Fe(CO)_3]^+$ via the reaction of 1,2-dihydronaphthalene with $Fe_2(CO)_9$ followed by a hydride abstraction by trityl cation. However, this procedure was unsuccessful. As described herein, it was found that attempting the same reaction using (η^4-1-azabuta-1,3-diene)tricarbonyliron (**1**) instead of $Fe_2(CO)_9$ as the $Fe(CO)_3$ transfer reagent leads after workup to two unexpected ferrocene-like compounds, $(Cp^{Fe})_2Fe$ ($Cp^{Fe} = \eta^5$-PhCCHCHN(Ph)Fe(CO)$_3$), **2** and **3** (eq 1).

The unexpected formation of **2** and **3** led us to investigate further the chemistry of **1**. Several years ago, in an experiment involving the reaction of $Ru_3(CO)_{12}$ with 3-*N*-diphenylprop-2-enimine, four ruthenium clusters including ruthenium analogues to **2** and **3** were obtained.[6] Azaruthenacyclopentadiene and its relevance to cyclcopentadienyl were recognized and studied in detail by Elsevier's group.[7] The dynamic behavior of $Ru_4(CO)_{10}[R^1C(H){=}C(H)C(H){=}NR^2]$ and its isolobal relationship to $[CpM(CO)_2]_2$ (M = Fe, Ru) had also been studied in detail.[7d] However, no azaferracyclopentadienyl compounds have been reported so far. Herein we report the use of **1** as a substitute for cyclopentadiene in the synthesis of cyclopentadienyl sandwich and half-sandwich compounds. This is a rare example of the use of azaferracyclopentadiene as a cyclopentadienyl ligand

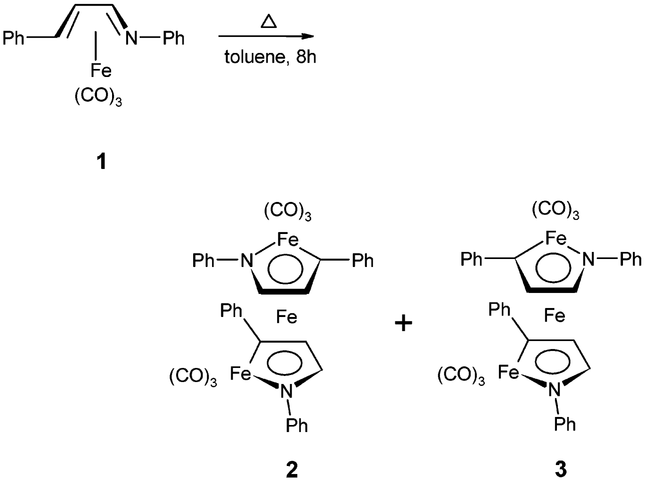

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Table 1. Crystal Data and Structure Refinement for 2, 4, 5, 6, 7, and 9

	2	**4**	**5**	**6**	**7**	**9**
formula	$C_{36}H_{24}Fe_3N_2O_6$	$C_{38}H_{28}Fe_3N_2O_8$	$C_{38}H_{28}Fe_3N_2O_8$	$C_{23}H_{17}Fe_2NO_3$	$C_{21}H_{12}FeNO_6Re$	$C_{38}H_{27}FeMnNO_5P$
fw	748.12	808.17	808.17	467.08	616.37	719.37
crystal system	triclinic	triclinic	triclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P1$	$P21/c$	$P21/c$	$P\bar{1}$
a, Å	10.822(1)	10.466(3)	10.791(4)	8.612(3)	11.134(2)	8.542(2)
b, Å	11.601(1)	11.930(4)	11.773(4)	17.627(1)	24.653(5)	10.456(2)
c, Å	13.024(1)	14.661(5)	13.886(7)	26.582(1)	15.114(3)	18.981(4)
α, deg	83.985(2)	77.037(2)	93.645(1)	90	90	81.244(1)
β, deg	82.952(2)	81.664(2)	90.793(1)	94.011(1)	91.460(1)	89.584(1)
γ, deg	79.124(4)	72.343(1)	95.466(2)	90	90	82.354(1)
volume, Å^3	1588.0(2)	1694.03(12)	1752.19(13)	4025.4(3)	4147.79(17)	1660.5(6)
Z	2	2	2	4	4	2
D(calcd), Mg/m^3	1.565	1.584	1.532	0.771	0.987	1.439
no. of reflns collected	10 907	11 510	11 642	14 321	16 604	11 288
no. of unique data	7188	7693	11 642	8801	9414	7580
no. of params refined	424	462	923	523	541	424
R_1 [$I > \sigma(I)$]	0.0797	0.0455	0.0499	0.0445	0.0374	0.0390
wR_2 [$I > \sigma(I)$]	0.2676	0.1075	0.1170	0.1079	0.0939	0.1023
R_1 (all data)	0.1608	0.1267	0.1167	0.1389	0.0866	0.0790
wR_2 (all data)	0.3007	0.1770	0.1702	0.1641	0.1392	0.1444
Gof	1.046	1.006	0.987	0.937	0.971	1.085

Table 2. Selected Bond Distances (Å) and Angles (deg) for 2, 4, 5, 6, 7, and 9

2							
Fe1−Fe2	2.5210(16)	Fe1−N1	1.957(6)	Fe1−C3	1.966(9)	C2−C3	1.416(11)
C2−C1	1.387(12)	Fe2−N1	2.020(7)	Fe2−C1	2.025(8)	Fe2−C2	2.095(8)
Fe2−C3	2.135(7)	N1−C1	1.403(11)	C3−Fe1−N1	81.2(3)	Fe1−N1−C1	115.8(5)
Fe1−C3−C2	112.8(6)	N1−Fe2−N2	148.7(3)	Fe1−Fe2−Fe3	147.80(7)	C1−Fe2−Fe3	69.7(3)
4							
Fe1−Fe2	2.5314(10)	Fe1−N1	1.973(4)	Fe1−C3	1.985(6)	C2−C3	1.411(7)
C2−C1	1.416(7)	Fe2−N1	2.039(4)	Fe2−C1	2.035(5)	Fe2−C2	2.107(5)
Fe2−C3	2.154(5)	N1−C1	1.393(6)	C3−Fe1−N1	82.5(2)	Fe1−N1−C1	113.9(3)
Fe1−C3−C2	111.7(4)	N1−Fe2−N2	152.12(18)	Fe1−Fe2−Fe3	151.39(4)	C1−Fe2−Fe3	104.34(15)
5							
Fe1−Fe2	2.512(2)	Fe1−N1	1.967(9)	Fe1−C3	1.987(11)	C2−C3	1.431(14)
C2−C1	1.393(15)	Fe2−N1	2.066(9)	Fe2−C1	2.077(11)	Fe2−C2	2.099(10)
Fe2−Fe3	2.113(10)	N1−C1	1.416(14)	C3−Fe1−N1	80.8(4)	Fe1−N1−C1	115.9(7)
Fe1−C3−C2	114.0(8)	N1−Fe2−N2	113.8(3)	Fe1−Fe2−Fe3	151.71(9)	C1−Fe2−Fe3	98.9(3)
6							
Fe1−Fe2	2.4638(11)	Fe1−N1	1.961(4)	Fe1−C9	1.975(5)	C8−C9	1.413(7)
C8−C7	1.422(7)	Fe2−C7	2.006(5)	Fe2−N1	2.011(5)	Fe2−C8	2.060(5)
Fe2−C9	2.071(5)	Fe2−C17	2.044(6)	Fe2−C20	2.098(6)	Fe2−C19	2.080(6)
N1−Fe1−C9	81.1(2)	Fe1−N1−C7	115.4(4)	C7−C8−C9	113.2(5)	Fe1−Fe2−C16	99.68(19)
7							
Fe−Re	2.6834(13)	Fe−N	1.977(7)	Fe−C7	1.954(9)	C7−C8	1.402(12)
N1−C9	1.408(11)	C8−C9	1.412(12)	Re−N	2.232(8)	Re−C7	2.288(9)
Re−C8	2.295(10)	Re−C9	2.266(9)	Fe−C16	1.813(10)	Fe−C17	1.808(3)
N−Fe−C16	93.9(4)	C7−Fe−C18	92.6(4)	C16−Fe−C18	88.9(4)	Fe−Re−C19	84.9(3)
9							
Fe−Mn	2.5634(6)	Fe−N	1.968(3)	Fe−C9	1.971(3)	Fe−P	2.2378(9)
C8−C9	1.403(4)	C7−C8	1.411(5)	N−C7	1.382(4)	Mn−N	2.118(3)
Mn−C7	2.127(3)	Mn−C8	2.155(3)	Mn−C9	2.182(3)	Fe−C34	1.761(3)
P−Fe−Mn	145.97(3)	C9−Fe−N	80.65(11)	Fe−N−C7	116.2(2)	Fe−C9−C8	114.2(2)
P−Fe−C34	94.03(10)	P−Fe−C35	99.17(10)	C34−Fe−C9	95.90(12)	C35−Fe−N	92.86(13)

in the synthesis of ferrocene-type and cymantrene-type compounds.

Results and Discussion

Heating **1** in toluene for 12 h led to the isolation of **2** and **3** in 15% and 18% yields, respectively. The formulation of **2** was confirmed by an X-ray crystal structure determination (see the Supporting Information). Crystal data and refinement are given in Table 1, and selected bond distances and angles are listed in Table 2. Compounds **2** and **3** have identical combustion data and parent ions in mass spectrometry. However, they have quite different ^{1}H NMR spectral data: the azaferracyclic ring protons appeared at δ 6.88 (d, $J = 1.7$ Hz) and 5.89 (d, $J = 1.7$ Hz) ppm for **2** and at δ 8.15 (d, $J = 1.1$ Hz) and 4.71 (d, $J = 1.1$ Hz) for **3**. Many attempts to grow single crystals of **3** suitable for X-ray crystal structure determination were unsuccessful. To obtain some idea about **3**, compounds **4** and **5** were synthesized by refluxing [η^4-(p-$CH_3OC_6H_5$)NCHCHCH(Ph)]Fe(CO)$_3$ and fully characterized by ^{1}H NMR, elemental analysis, and X-ray diffraction (Figures 1 and 2).

Crystal data and refinement are given in Table 1, and selected bond distances and angles are listed in Table 2. Interestingly, **4** and **5** show the same ^{1}H NMR patterns as those of **2** and **3**, respectively. Thus, the ^{1}H

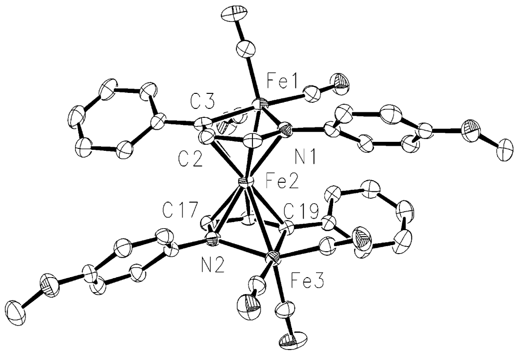


Figure 1. ORTEP drawing of **4**. Thermal ellipsoids are drawn at the 30% probability level.

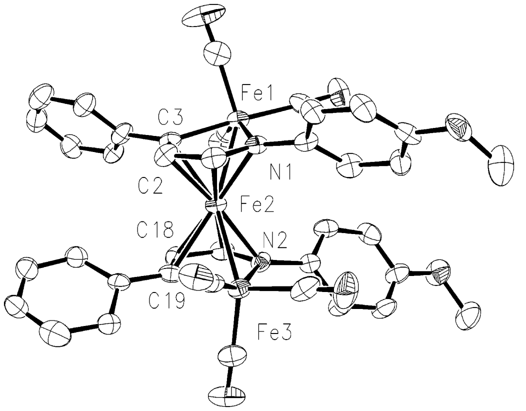
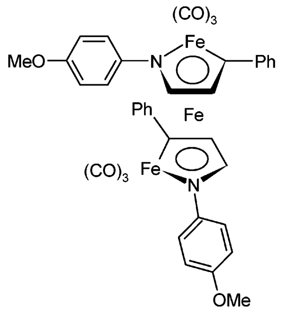


Figure 2. ORTEP drawing of **5**. Thermal ellipsoids are drawn at the 30% probability level.



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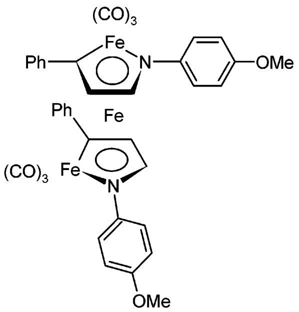

5

NMR and X-ray diffraction study (Figure 2) of **5** allow the assignment of the structure of **3**. According to the X-ray structure determination of **5**, **3** is a diastereomer of **2**. As previously mentioned, the ruthenium analogues to **2** and **3** have been reported.[6a] The two azaruthenacyclopentadienyl rings were in an eclipsed conformation. On the contrary, the azaferracyclopentadienyl rings in **2**, **4**, and **5** are not eclipsed. As in ruthenium analogues, compounds **2**, **3**, **4**, and **5** are isolobally related to ferrocene. They contain two [$Fe(CO)_3(PhCCHCHNPh)$] moieties, both being η^5-coordinated to a central iron atom. They have almost the same crystal structures except for the orientation of the azaferracyclopentadienyl ring. X-ray structure determination of **2** shows that the Fe−Fe bond distances are 2.5210(16) and 2.5182(15) Å, similar to the values found in ferroles,[8] polyiron alkyne,[9] and alkylidyne clusters.[10] Owing to the presence of iron and nitrogen atoms in the ring, the azaferracycloapentadienyl ring is a distorted pentagon and the plane consisting of Fe(1), N(1), C(1), C(2), and C(3) is roughly planar with a maximum deviation of 0.075(4) Å. The Fe(1) atom is displaced outward from the ring plane by 0.061(3) Å, significantly smaller than the displacement (0.188 Å) observed in (η^5-$(OC)_3FeCHCHCHCH$)RhCp.[11] The distances between Fe(2) and carbon atoms on the ring are quite different from each other, ranging from 2.025(8) to 2.135(7) Å, but interestingly the average distance (2.085 Å) between Fe(2) and carbon atoms on the ring is quite close to that (2.080 Å) of ferrocene.[12] The two azaferracyclopentadienyl rings are almost parallel with a dihedral angle of 6.53°. As a result of the steric hindrance between the substituents, the two rings are not eclipsed. A cyclic voltammetric study of **2** shows a reversible couple 166 mV higher than that of ferrocene, presumably due to the presence of an electron-withdrawing group, an iron tricarbonyl moiety. This observation is quite different from that of nickelaferrocene, which forms a ferricinium ion analogue at about the same potential as ferrocene itself.[4d] Attempts to substitute one of the carbonyls on the iron by phosphine under thermal or irradiation conditions were unsuccessful. Thus, it seems that the carbonyls on the iron are quite stable.

Complex **1** has special properties such as fluxionality through the turnstile rotation of the iron tricarbonyl fragment and epimerization via an η^1-imine intermediate.[13] Recently, it has been reported that the H(C3) in **1** is out-of-plane, thus strengthening the Fe−C3 bonding through better π^* back-bonding between the 1-azadiene and $Fe(CO)_3$ molecular fragments.[14] A facile 1,3-hydrogen shift from C3 of the 1-azabuta-1,3-diene to C1 was observed in some related reactions.[15] In expectation of generating a metal hydride, we heated a solution of **1** in xylene-d_{10} at 110 °C for 7−15 h and found a hydride peak at δ −10.0 ppm in an ^1H NMR spectrum even though the amount of the hydride was very small. These observations suggest that compound **1** could be consid-

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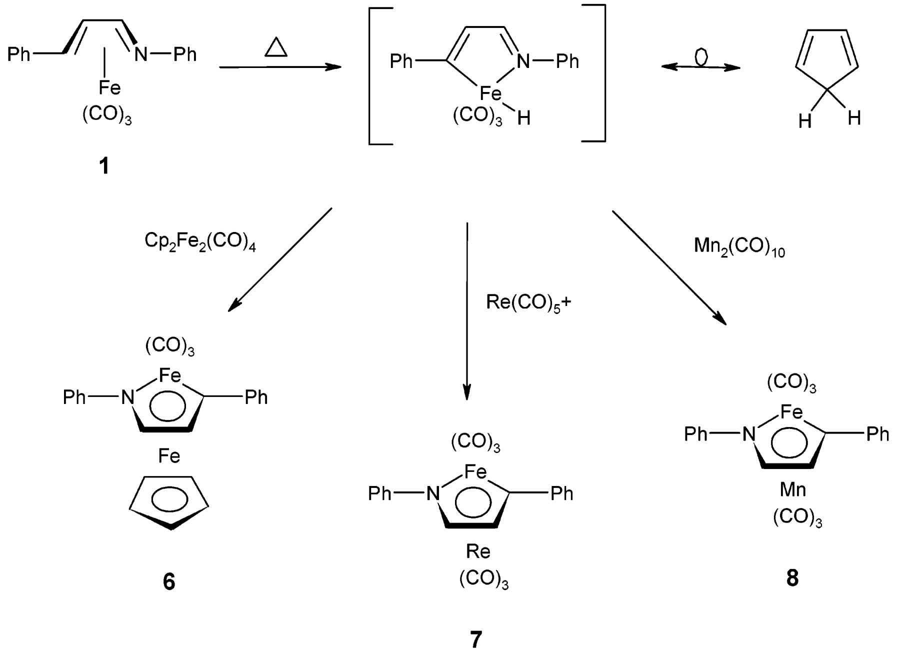
Scheme 1



ered isolobal with cyclopentadiene (C_5H_6) (see the intermediate in Scheme 1) and may allow an understanding of the formation of **2** and **3**.

The use of **1** as a substitute for cyclopentadiene in the synthesis of sandwich and half-sandwich compounds was investigated. Treatment of **1** with $[CpFe(CO)_2]_2$ yielded $Cp^{Fe}FeCp$ (**6**) in 72% yield (Scheme 1).[16]

There is no ruthenium analogue to **6**. The formulation was confirmed by an X-ray crystal structure determination (see the Supporting Information). Crystal data and refinement are given in Table 1, and selected bond distances and angles are listed in Table 2. The overall structure was similar to ferrocene. The iron atom is located 1.614(2) Å below the plane of the azaferracyclopentadienyl ring and 1.687(2) Å above the cyclopentadienyl plane. A cyclic voltammetric study of **6** shows a reversible redox cycle, 124 mV higher than that of ferrocene.

When $Re_2(CO)_{10}$ was treated with **1**, no reaction was observed. However, reaction of $Re(CO)_5BF_4$ with **1** gave $Cp^{Fe}Re(CO)_3$ (**7**) in 64% yield (Scheme 1). This is the first example of a metallacyclodienyl rhenium-tricarbonyl complex. The structure of **7** was verified by an X-ray crystal structure determination (Figure 3). Crystal data and refinement are given in Table 1, and selected bond distances and angles are listed in Table 2. The Re atom in **7** has the usual piano-stool coordination characteristic of cyclopentadienyl complexes. The rhenium atom is located 1.908(4) Å below the plane of the azaferracyclopentadienyl ring. The bond distance (2.6834(13) Å) of Re−Fe is much shorter than those found in related iron−rhenium compounds: 2.888(1) Å in nonbridged $CpFe(CO)_2Re(CO)_5$,[17] 2.866(4) Å in double bridged $[(OC)_3Fe(\mu\text{-Br})(\mu\text{-dppm})Re(CO)_3]$,[18] 2.841(1) Å in an acyl-bridged complex $[(OC)_4Fe\{\mu\text{-C(O)Ph}\}Re(CO)_4]$,[19] and 2.7581(1) Å in a μ-alkylidene complex $[(OC)_4Fe(\mu\text{-C(H)Ph)ReCp(CO)_2}]$.[20]

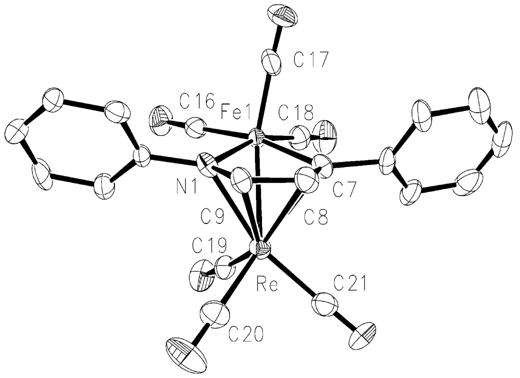
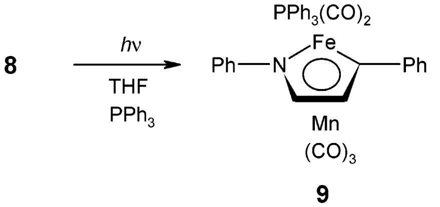


Figure 3. ORTEP drawing of **7**. Thermal ellipsoids are drawn at the 30% probability level.

Reaction of **1** with $Mn_2(CO)_{10}$ led to the isolation of $Cp^{Fe}Mn(CO)_3$ (**8**) in 77% yield (Scheme 1). Compound **8** has a piano-stool structure as in **6**. Surprisingly, treatment of **8** with PPh_3 yielded a PPh_3-substituted derivative (**9**) in 98% yield and a substitution of carbonyl on the iron instead of on the manganese by PPh_3 (eq 2).



9

When we considered the inertness of $CpMn(CO)_3$ toward thermal CO substitution,[21] the formation of **9** could be understood. The structure of **9** was also verified by an

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X-ray crystal structure determination (see the Supporting Information). Crystal data and refinement are given in Table 1, and selected bond distances and angles are listed in Table 2. The crystal structure was quite close to **7** except for the axial phosphine. The manganese atom is located 1.7560(14) Å below the plane of the azaferracyclopentadienyl ring. The bond distance (2.5634(6) Å) of Mn−Fe is close to those found in related iron−manganese compounds: 2.555(2) and 2.567(2) Å in $MnFe_2(\mu\text{-}CO)_2(\mu\text{-}NO)(\mu_3\text{-}NO)Cp_2(\eta\text{-}C_5H_4Me)$[22] and 2.572(1) Å in *trans*-$MnFe[\mu\text{-}C(OEt)](\mu\text{-}CO)(CO)_2Cp(\eta\text{-}C_5H_4\text{-}Me)$.[23] Attempts to synthesize $Cp^{Fe}Cr(CO)_2(NO)$ were not successful.

In conclusion, we have demonstrated that **1** can be considered isolobal with cyclopentadiene (C_5H_6). We expect that the novel chemistry shown by **1** can be extended to other systems, and work in this direction is in progress.

Experimental Section

General Procedures. All reactions were conducted under nitrogen using standard Schlenk-type flasks. Workup procedures were done in air. All solvents were dried and distilled according to standard methods before use. THF was freshly distilled from sodium benzophenone ketyl prior to use. Reagents were purchased from Aldrich Chemical Co. and Strem Chemical Co. and were used as received. IR spectra were obtained in solution or measured as films on NaCl by evaporation of solvent. ^1H NMR spectra were obtained with a Bruker 300 or 500 spectrometer. Elemental analyses were done at the National Center for Inter-University Research Facilities, Seoul National University.

Synthesis of 2 and 3. A solution of **1** (0.30 g, 0.84 mmol) in 15 mL of toluene was heated at reflux for 8 h and then cooled to room temperature. Removal of the solution followed by chromatography on a silica gel column eluting with hexane/diethyl ether (v/v, 20:1) gave **2** and **3** in 0.031 g (15%) and 0.038 g (18%) yields, respectively. **2**: ^1H NMR ($CDCl_3$) δ 7.31−7.06 (m, 20 H), 6.88 (d, 1.7 Hz, 2 H), 5.89 (d, 1.7 Hz, 2 H) ppm; IR νCO 2020, 1948 cm^{-1}; HRMS (M^+) calcd 747.9680, obsd 747.9685. Anal. Calcd for $C_{34}H_{24}Fe_3N_2O_6$: C, 57.80; H, 3.23; N, 3.74. Found: C, 58.00; H, 3.24; N, 3.70. **3**: ^1H NMR ($CDCl_3$) δ 8.15 (d, 1.1 Hz, 2 H), 7.23−7.06 (m, 20 H), 4.71 (d, 1.1 Hz, 2 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.6, 154.4, 149.5, 128.7, 128.6, 127.9, 126.8, 126.6, 125.2, 109.5, 94.6 ppm; IR νCO 2016, 1942 cm^{-1}; HRMS (M^+) calcd 747.9680, obsd 747.9680. Anal. Calcd for $C_{34}H_{24}Fe_3N_2O_6$: C, 57.80; H, 3.23; N, 3.74. Found: C, 57.87; H, 3.26; N, 3.68.

Synthesis of 4 and 5. A solution of $[\eta^4\text{-}(p\text{-}CH_3OC_6H_5)\text{-}NCHCHCH(Ph)]Fe(CO)_3$ (0.30 g, 0.79 mmol) in 15 mL of toluene was heated at reflux for 8 h and then cooled to room temperature. Removal of the solution followed by chromatography on a silica gel column eluting with hexane/diethyl ether (v/v, 20:1) gave **4** in 34 mg (16%) and **5** in 45 mg (21%) yield, respectively. **4**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.32 (m, 4 H), 7.20 (m, 6 H), 6.96 (d, 9.0 Hz, 4 H), 6.87 (d, 1.9 Hz, 2 H), 6.59 (d, 9.0 Hz, 4 H), 5.84 (d, 1.9 Hz, 2 H), 3.77 (s, 6 H) ppm; IR νCO 2016, 1949 cm^{-1}. Anal. Calcd for $C_{38}H_{28}Fe_3N_2O_8$: C, 56.47; H, 3.49; N, 3.47. Found: C, 56.27; H, 3.37; N, 3.53. **5**: Yield 21%; ^1H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, 1.9 Hz, 2 H), 7.17 (m, 10 H), 7.06 (d, 9.0 Hz, 4 H), 6.60 (d, 9.0 Hz, 4 H), 4.71 (d, 1.9 Hz, 2 H), 3.77 (s, 6 H) ppm; IR νCO 2014, 1948 cm^{-1}. Anal. Calcd for $C_{38}H_{28}Fe_3N_2O_8$: C, 56.47; H, 3.49; N, 3.47. Found: C, 56.27; H, 3.48; N, 3.46.

Synthesis of 6. To a solution of **1** (0.20 g, 0.56 mmol) in 15 mL of toluene was added $[CpFe(CO)_2]_2$ (0.20 g, 0.57 mmol). The resulting solution was heated at reflux for 6 h and then cooled to room temperature. Removal of the solution followed by chromatography on a silica gel column eluting with hexane/diethyl ether (v/v, 20:1) gave **6** in 72% yield: ^1H NMR (300 MHz, $CDCl_3$) δ 7.36−7.22 (m, 10 H), 6.56 (d, 1.6 Hz, 2 H), 5.39 (d, 1.6 Hz, 2 H), 4.64 (s, 5 H) ppm; IR νCO 2022,1937 cm^{-1}. Anal. Calcd for $C_{23}H_{17}Fe_2NO_3$: C, 59.14; H, 3.67; N, 3.00. Found: C, 59.12; H, 3.75; N, 3.06.

Synthesis of 7. To a solution of **1** (0.20 g, 0.56 mmol) in 15 mL of toluene was added $[Re(CO)_5]BF_4$ (0.35 g, 0.85 mmol). The resulting solution was heated at reflux for 12 h and then cooled to room temperature. Removal of the solution followed by chromatography on a silica gel column eluting with hexane/diethyl ether (v/v, 10:1) gave **7** in 66% yield: ^1H NMR (300 MHz, $CDCl_3$) δ 7.36−7.22 (m, 8 H), 7.15 (d, 2.1 Hz, 1 H), 7.00 (m, 2 H), 5.98 (d, 2.1 Hz, 1 H) ppm; IR νCO 2060, 2008, 1920 cm^{-1}. Anal. Calcd for $C_{21}H_{12}FeNO_6Re$: C, 40.92; H, 1.96; N, 2.27. Found: C, 41.20; H, 1.95; N, 2.23.

Synthesis of 8. To a solution of **1** (0.20 g, 0.56 mmol) in 15 mL of toluene was added $Mn_2(CO)_{10}$ (0.26 g, 0.67 mmol). The resulting solution was heated at reflux for 10 h and then cooled to room temperature. Removal of the solution followed by chromatography on a silica gel column eluting with hexane/diethyl ether (v/v, 20:1) gave **8** in 77% yield: ^1H NMR (300 MHz, $CDCl_3$) δ 7.31−7.25 (m, 8 H), 7.00 (m, 2 H), 6.61 (s, 1 H), 5.64 (s, 1 H) ppm; IR νCO 2058, 1996, 1930 cm^{-1}. Anal. Calcd for $C_{21}H_{12}FeMnNO_6$: C, 51.99; H, 2.49; N, 2.89. Found: C, 52.28; H, 2.43; N, 2.83.

Synthesis of 9. To a solution of **8** (0.10 g, 0.21 mmol) in 15 mL of THF was added PPh_3 (0.066 g, 0.25 mmol). The resulting solution was irradiated with UV light for 2 h. Removal of the solution followed by chromatography on a silica gel column eluting with hexane/diethyl ether (v/v, 10:1) gave **9** in 98% yield: ^1H NMR (300 MHz, $CDCl_3$) δ 7.34−6.91 (m, 23 H), 6.40 (s, 1 H), 6.13 (d, 7.1 Hz, 2 H), 5.61 (s, 1 H) ppm; IR νCO 2008, 1970, 1920, 1905 cm^{-1}. Anal. Calcd for $C_{38}H_{27}FeMnNO_5P$: C, 63.44; H, 3.78; N, 1.95. Found: C, 63.97; H, 3.91; N, 1.82.

Electrochemistry. Cyclic voltammograms were obtained with a BAS CV-50W voltametric analyzer. The working electrode was glassy carbon, with an Ag/AgCl 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.

X-ray Crystal Structural Determinations of 2, 4, 5, 6, 7, and 9. Single crystals of **2**, **4**, **5**, **6**, **7**, and **9** suitable for X-ray diffraction study were grown by slow diffusion of the dichloromethane solution of **2**, **4**, **5**, **6**, **7**, and **9** into hexane in a freezer (at −15 C°). X-ray data for single crystals were collected on an Enraf-Nonius CCD single-crystal X-ray diffractometer at room temperature using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS-97) and refined against all F^2 data (SHELXS-97). All non-hydrogen atoms were refined with anisotropic thermal parameters, and the hydrogen atoms were treated as idealized contributions. Crystal data, details of the data collection, and refinement parameters are listed in Table 1. Selected bond distances and angles are given in Table 2.

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Supporting Information Available: Tables of coordinates, anisotropic displacement parameters, and bond lengths and angles for **2**, **4**, **5**, **6**, **7**, and **9** and ORTEP drawings of **2**, **6**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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