Reactions of $Fe_2(CO)_9$ with Azine Derivatives: Discovery of New Coordination Modes and Reactivity of New Bimetallic Compounds

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Reaction of N,N′-bis-(3-phenyl-allylidene)-hydrazine (**1**) with $Fe_2(CO)_9$ was studied. When the reaction was carried out in refluxing THF, the three mononuclear compounds $Fe(CO)_3$-[PhCH=CHCH=NN=CHR-*trans*] (**3**), $Fe(CO)_3$[PhCH=CHCH=NN=CHR-*cis*] (**4**), and $Fe(CO)_3$[PhCH=CHCH=N=CHR] (**5**; R = −CH=CHPh) were obtained. In refluxing toluene, the novel dinuclear compound $Fe(CO)_3$[PhCH=CHCH=NN=CHCH=CHPh]$Fe(CO)_3$ (**2**) was obtained. Further treatment of **3**−**5** with $Fe_2(CO)_9$ in refluxing toluene eventually led to **2**. A detailed study of the reaction of **3**−**5** with/without $Fe_2(CO)_9$ allowed us to establish an overall reaction sequence from **1** to **2**. Reaction of the alkyl analogue MeCH=CHCH=NN=CHCH=CHMe (**10**) with $Fe_2(CO)_9$ yielded the two dinuclear compounds $Fe(CO)_3$[MeCH=CHCH=NN=CHCH=CHMe$Fe(CO)_3$ (**11** and **11′)** or the two mononuclear compounds $Fe(CO)_3$[MeCH=CHCH=NN=CHR′-*trans*] (**12**) and $Fe(CO)_3$[MeCH=CHCH=NN=CHR′] (**13**; R′ = −CH=CHMe) and the dinuclear compound *anti*-$Fe(CO)_3$[MeCH=CHCH=N-N=CHCH=CHMe]$Fe(CO)_3$ (**14**), respectively, depending upon the reaction conditions. Treatment of **2** with MeLi yielded the dimeric compound [PhCH=CHCH=NN=CHCH=CHPh]$_2$$Fe_4(CO)_{12}$ (**16**), containing four iron atoms, and treatment with MeLi followed by MeI afforded the dimethyl adduct $Fe(CO)_3$[PhCH=CHCHMeN=NCHMeCH=CHPh]$Fe(CO)_3$ (**17**). The molecular structures of **3**−**5**, **8**, **11**, **11′**, **14**, and **16** were confirmed by X-ray diffraction studies.

Introduction

Azines are 2,3-diazabutadiene derivatives that can be viewed as N−N-linked diimines. They can undergo a wide variety of chemical processes and have interesting chemical properties. Azines have been receiving increased attention due to their potential utility in bond formation reactions,[1] their biological properties,[2] their use in the design of liquid crystals,[3] and other material applications such as polymers[4] and nonlinear optical materials.[5] Recently, azines and pyridyl-substituted azines have been used extensively as ligands for the design and synthesis of novel organometallic compounds[6]

In the reaction of iron carbonyls with azines, the N−N single bond is cleaved in most cases;[7] however, if it is retained, usually only one nitrogen atom is involved in the coordination of the metal. When benzaldazines (R(H)C=NN=C(H)R; R = Ph, *p*-R′-C_6H_4) were used, no

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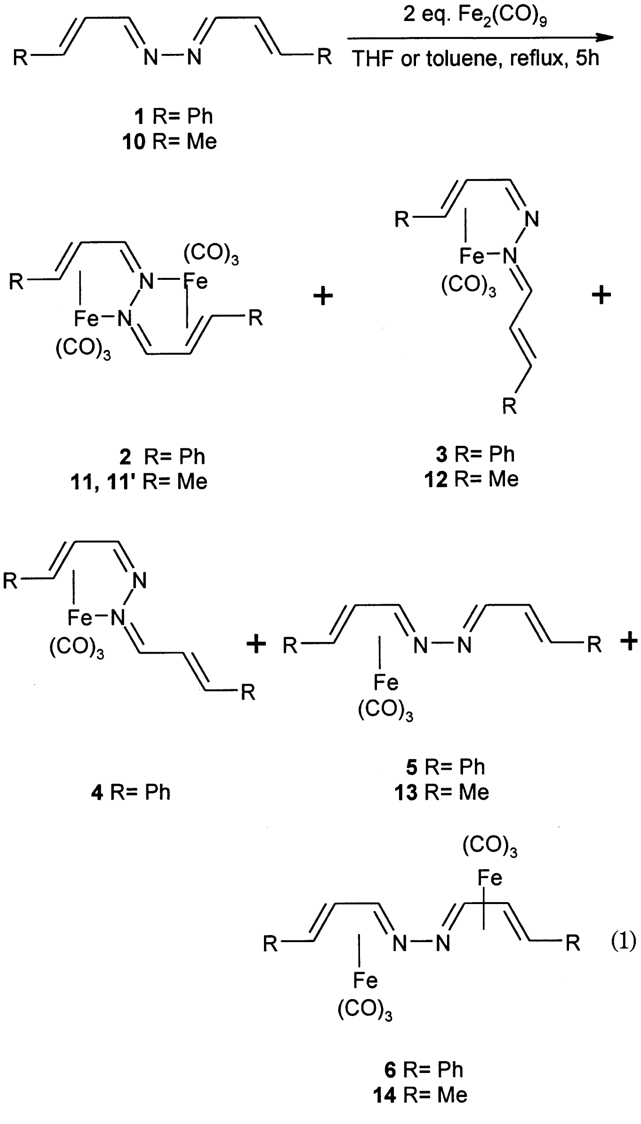
cleavage of the molecule was observed, and the reaction proceeds with ortho proton rearrangement to the azomethine carbon and the metalation of the phenyl ring.[8]

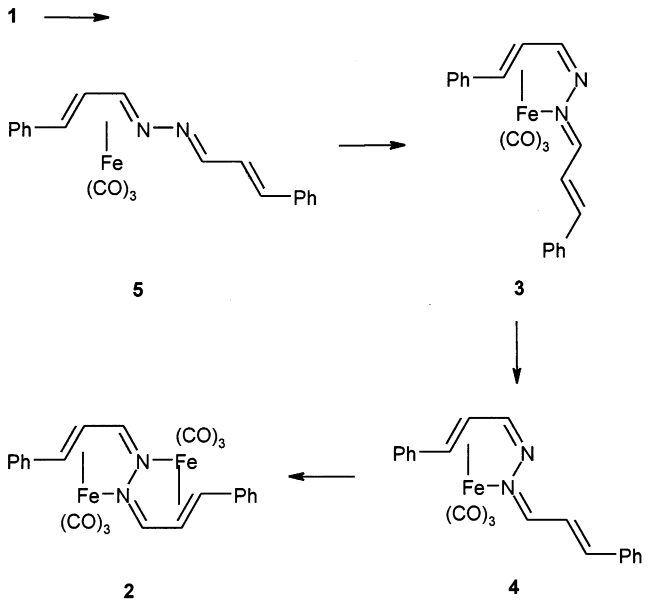
Aza-dienes have been attracted recent attention due to their use as ligands in iron carbonyl complexes[9] and their $Ru_3(CO)_{12}$-catalyzed carbocyclization with ethylene and carbon monoxide to yield lactams and spiropyrrolidin-2-ones.[10] Very recently, we discovered that (η^4-azadiene)$Fe(CO)_3$ acted like cyclopentadiene in the reaction.[11] As an extension of our previous research, we studied the reaction of iron carbonyls $Fe_2(CO)_9$ with *N*,*N*′-bis(3-phenylallylidene)hydrazine (**1**). We aimed to discover whether **1** reacted as an azine and/or azabutadiene derivative in the complex formation. We herein report new reactions of **1** with $Fe_2(CO)_9$.

Results and Discussion

Treatment of **1** with $Fe_2(CO)_9$ in refluxing toluene for 5 h gave the unexpected compound **2** in 45% yield (eq 1). The formation of **2** was confirmed by an X-ray diffraction study. Due to its poor crystallinity, we failed to obtain good X-ray diffraction data suitable for publication; however, we could confirm the molecular structure shown in Scheme 1. The imine carbon is not coordinated to the iron atom. Thus, we could see a characteristic absorption at 1581 cm^{-1}, indicative of a ν(C=N) stretch in the infrared spectrum of **2**. The bonding mode discovered in **2** is not a new one, but it is rare.[12] The same bonding mode was found in the reactions of $FeCl_2(PMe_2Ph)_2$ and *cis*-$Pt(C_6F_5)_2(OC_4H_8)_2$ with diphenyldiazomethane, respectively. The formation of **2** instead of **6** means that the coordination of an iron tricarbonyl to the carbon−carbon double bond and to the farther nitrogen atom is more favorable than the well-known η^4 coordination of an iron tricarbonyl. To obtain some insight into the formation of **2**, we tried to trap intermediates in the reaction by controlling the reaction time and changing the reaction medium (Table 1). Refluxing **1** with $Fe_2(CO)_9$ in toluene for 2 h gave a mixture of **2**−**5** in 10%, 68%, 2%, and 10% yields, respectively (eq 1).



Scheme 1



Treatment of **1** with $Fe_2(CO)_9$ in refluxing THF for 1 h yielded **3** as the sole product in 41% yield. However, when the same reaction was carried out in refluxing THF for 18 h, compounds **3**−**5** were obtained in 60%, 5%, and 7% yields, respectively. Thus, compounds **3**−**5**

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Table 1. Product Distribution

entry	reactant: reactant	reactant: amt of $Fe_2(CO)_9$ (equiv)	solvent	temp (°C)	time (h)	yield (%)[a]: 2	3	4	5
1	**1**	2.0	toluene	110	5	45			
2	**1**	2.0	toluene	110	2	10	68	2	10
3	**1**	2.0	THF	60	1		41		
4	**1**	2.0	THF	60	18		60	5	7
5	**3**	none	toluene	110	8	n.r.[b]			
6	**3**	1.5	toluene	110	7	50		20	
7	**4**	none	toluene	110	2		79		
8	**4**	1.5	toluene	110	7	72			
9	**5**	none	toluene	110	2		68		
10	**5**	1.5	toluene	110	4	55	22	8	

[a] Isolated yield. [b] n.r. = no reaction.

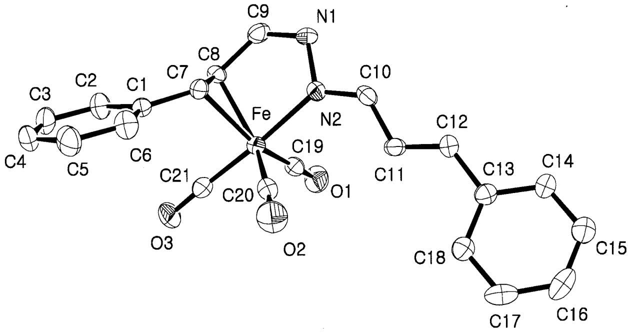


Figure 1. ORTEP view of complex **3**.

seemed to be intermediates on the way to **2**. Interestingly, the expected formation of **6** was not observed. These observations suggest that the bonding mode in **2**−**4** is thermodynamically more favorable than that in **5**. To confirm this speculation, we heated **3**−**5** and observed their transformation.

When **4** and **5** were further heated, they were converted to **3**. However, a thermal transformation of **3** to **4** or **5** was not observed. These observations confirmed that the coordination mode in **2**−**4** is thermodynamically more favorable than that in **5** and that the trans isomer **3** is thermally more stable than the cis isomer **4**. We can temporarily conclude that **2** is synthesized by the following sequences (Scheme 1). The first step is the usual coordination of $Fe(CO)_3$ to azabutadiene to form **5**. The second step is a change of bonding mode from η^4 to π and σ mode via the use of a distant nitrogen atom instead of a nearby nitrogen atom. This change may be responsible for the energy difference between **3** and **5**. Then, **3** isomerized to **4**. The final step is another coordination of $Fe(CO)_3$ to a free C═C bond and a nitrogen atom to form **2**.

Compounds **3**− **5** were characterized by X-ray diffraction studies (Figures 1−3). Crystal data and refinement details are given in Table 2, and selected bond distances and angles are given in Table 3. The X-ray crystal structure determinations of **3** and **4** confirm the tetragonal-pyramidal coordination of the iron atom. Two basal positions are occupied by the C═C bond and a nitrogen atom, and the others are occupied by carbonyl ligands. The third carbonyl ligand adopts the apical position of these complexes. Other structural features are similar to those of (η^4-1-azabuta-1,3-diene)$Fe(CO)_3$ derivatives.[9,11] Compounds **3** and **4** are related to each other as cis and trans isomers. The $Fe(CO)_3$ moiety in **3** and **4** coordinates to a C═C bond and one of the nitrogen atoms which is far away from the C═C bond. Thus, the bonding mode found in **2** was confirmed by X-ray diffraction studies of **3** and **4**. The bond distances between Fe and the coordinated nitrogen atoms range from 2.006(5) to 2.068(2) Å, slightly shorter than those of (η^4-1-azabuta-1,3-diene)$Fe(CO)_3$.[13] Compound **5** has the well-known η^4 bonding mode, as found for tricarbonyliron complexes of 1-azabuta-1,3-diene, buta-1,3-diene, and cyclohexa-1,3-dienes.[9c−e,13] The bond lengths found in the tricarbonyliron complexes of **3**−**5**, compared to those of cyclohexa-1,3-dienes and buta-1,3-dienes, correlate very well with the concept of increased back-bonding from the filled iron d orbitals into the π* orbitals of the organic ligand for the heterodiene complexes.

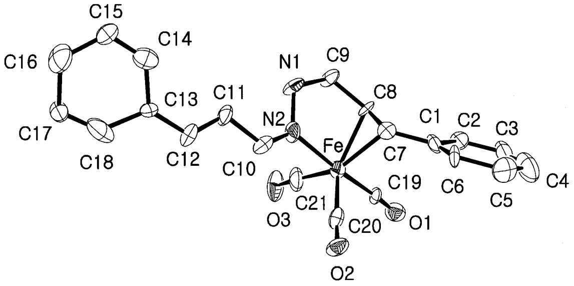


Figure 2. ORTEP view of complex **4**.

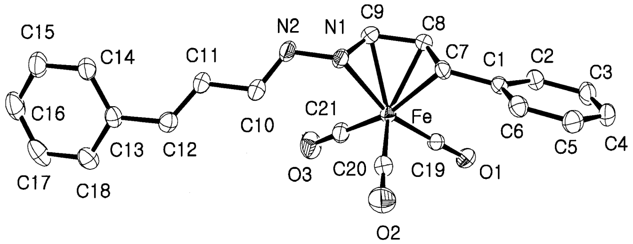
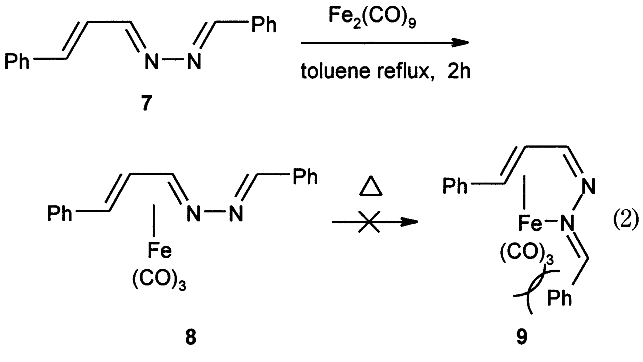


Figure 3. ORTEP view of complex **5**.

Treatment of **7** with $Fe_2CO)_9$ in refluxing toluene for 2 h yielded **8** as the sole product (77%) (eq 2).



Formation of **8** was confirmed by an X-ray diffraction study (Figure 4). The molecular structure of **8** was quite similar to that of the parent complex (η^4-PhCHCHCHN-Ph)$Fe(CO)_3$.[14a,b] As expected, transformation of **8** to **9** was not observed, presumably due to the steric effect. Thus, we expect that the substituent on the free imine

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Table 2. Crystal Data and Structure Refinement Details for 3−5, 8, 11, 11′, 14, and 16

	3	**4**	**5**	**8**	**11**	**11′**	**14**	**16**
formula	$C_{21}H_{16}FeN_2O_3$	$C_{21}H_{16}FeN_2O_3$	$C_{21}H_{16}FeN_2O_3$	$C_{19}H_{14}FeN_2O_3$	$C_{14}H_{12}Fe_2N_2O_3$	$C_{14}H_{12}Fe_2N_2O_3$	$C_{14}H_{12}Fe_2N_2O_3$	$C_{50}H_{38}Fe_4N_4O_{12}$
fw	400.21	400.21	400.21	374.17	415.96	415.96	415.96	1110.24
cryst syst	orthorhombic	triclinic	triclinic	monoclinic	monoclinic	monoclinic	triclinic	orthorhombic
space group	*Pcba*	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/a$	$P2_1/n$	$P\bar{1}$	$P2_12_12_1$
a, Å	6.984(1)	8.067(1)	9.561(1)	13.166(1)	10.821(1)	7.041(1)	7.511(1)	13.273(1)
b, Å	22.873(1)	9.629(1)	9.986(1)	7.444(1)	12.681(1)	13.638(1)	10.217(1)	13.226(1)
c, Å	23.788(1)	12.783(1)	10.494(1)	17.807(1)	12.716(1)	8.952(1)	11.508(1)	28.646(1)
α, deg	90	80.289(2)	85.192(1)	90	90	90	79.250(2)	90
β, deg	90	78.102(2)	72.765(1)	92.573(2)	96.262(1)	96.008(1)	89.994(2)	90
γ, deg	90	83.271(2)	81.1620(1)	90	90	90	89.980(2)	90
V, Å^3	3800.0(6)	954.19(17)	944.80(16)	1743.5(3)	1734.5(3)	854.89(7)	867.62(16)	5028.8(6)
Z	8	2	2	4	4	4	2	4
D(calcd), Mg/m^3	1.399	1.393	1.407	1.426	1.593	1.616	1.592	1.466
θ range, deg	1.71−24.14	1.65−27.58	2.03−27.52	1.14−27.51	1.61−27.49	2.73−27.58	1.80−27.45	3.38−25.26
no. of data collected	16 301	5879	6294	6849	7090	3469	5865	8825
no. of unique data	3011	4309	4321	3989	3979	1953	3933	8835
no. of params refined	244	244	244	226	219	110	219	658
R1($I > \sigma(I)$)	0.0411	0.0514	0.0385	0.0430	0.0452	0.0351	0.0456	0.0443
wR2($I > \sigma(I)$)	0.0966	0.1259	0.1162	0.1021	0.1217	0.0874	0.1052	0.0853
R1(all data)	0.1318	0.1131	0.0529	0.0892	0.0705	0.0644	0.0703	0.1450
wR2(all data)	0.1690	0.1692	0.1336	0.1348	0.1472	0.1128	0.1211	0.0994
GOF	0.944	0.938	1.150	1.031	1.058	1.004	0.950	0.794

Table 3. Selected Bond Distances (Å) and Angles (deg) for 3−5, 8, 11, 11′, 14, and 16

Compound **3**							
Fe−C(21)	1.784(8)	Fe−C(7)	2.102(5)	N(1)−N(2)	1.434(6)	Fe−N(2)	2.006(5)
C(21)−Fe−N(2)	172.8(2)	C(20)−Fe−N(2)	88.4(2)	C(19)−Fe−N(2)	95.2(2)	C(8)−Fe−C(7)	40.0(2)
Compound **4**							
Fe−C(19)	1.763(14)	Fe−C(20)	1.84(2)	Fe−C(7)	2.063(12)	N(1)−N(2)	1.375(17)
C(19)−Fe−N(2)	172.8(6)	C(21)−Fe−N(2)	88.5(7)	C(9)−N(1)−N(2)	107.4(11)	C(7)−C(8)−C(9)	118.4(12)
Compound **5**							
Fe−C(19)	1.781(3)	Fe−N(1)	2.0685(19)	Fe−C(8)	2.070(2)	N(1)−N(2)	1.390(3)
C(21)−Fe−C(7)	164.56(10)	C(19)−Fe−N(1)	160.75(10)	C(9)−N(1)−N(2)	112.6(2)	C(7)−C(8)−C(9)	117.5(2)
Compound **8**							
Fe−C(19)	1.796(3)	Fe−N(1)	2.077(3)	Fe−C(8)	2.067(3)	N(1)−N(2)	1.397(3)
C(19)−Fe−C(7)	164.49(12)	C(17)−Fe−C(8)	94.93(14)	C(9)−N(1)−N(2)	113.1(2)	C(7)−C(8)−C(9)	117.8(3)
Compound **11**							
Fe(1)−C(14)	1.769(4)	C(6)−C(7)	1.419(5)	Fe(1)−N(1)	1.999(3)	N(1)−N(2)	1.424(4)
N(2)−C(5)	1.279(4)	C(5)−C(6)	1.457(5)	C(5)−C(6)	1.457(5)	Fe(1)−C(6)	2.050(3)
C(13)−Fe(1)−N(1)	90.51(14)	C(5)−C(6)−C(7)	118.5(3)	C(6)−C(5)−N(2)	123.2(3)	N(1)−N(2)−C(5)	111.1(3)
Compound **11′**							
Fe−C(7)	1.762(4)	C(2)−C(3)	1.434(4)	C(1)−N(1)	1.284(4)	Fe−N(1)#1	2.082(3)
N(1)−N(1)#1	1.435(5)	C(2)−C(1)	1.446(4)	Fe−C(2)	2.055(3)	Fe−C(3)	2.063(3)
C(3)−C(2)−C(1)	117.3(3)	C(7)−Fe−N(1)	175.10(15)	N(1)−Fe−C(3)	85.86(12)	C(2)−Fe−C(3)	40.76(12)
Compound **14**							
Fe−N(1)	2.082(3)	Fe−C(4)	2.054(3)	Fe−C(2)	2.131(3)	N(1)−N(1)#1	1.442(5)
C(2)−C(3)−C(4)	118.3(4)	C(3)−C(4)−N(1)	114.8(4)	C(10)−Fe−C(2)	91.71(16)	Fe−C(10)−O(2)	179.0(4)
Compound **16**							
Fe(1)−C(7)	2.106(6)	C(7)−C(8)	1.399(9)	C(8)−C(9)	1.510(10)	C(9)−N(1)	1.501(7)
N(1)−N(2)	1.280(6)	C(11)−C(30)	1.562(6)	Fe(1)−N(2)	1.984(5)	Fe(2)−N(1)	1.941(5)
C(7)−C(8)−C(9)	119.4(7)	C(8)−C(9)−N(1)	107.1(6)	N(1)−N(2)−C(11)	114.0(5)	C(10)−C(11)−C(12)	114.9(5)

nitrogen may play an important role in the transformation of **5** to **3**.

An alkyl analogue **10** shows a reaction pattern similar to that of **1** (eq 3). However, when **10** was reacted with $Fe_2(CO)_9$ in refluxing toluene for 7 h, two compounds having quite similar ^1H NMR patterns in the ratio of 3:1 were observed in the ^1H NMR spectrum. This means that there may be two structural isomers in the solution. Fortunately, two compounds, **11** and **11′**, were separated by recrystallization. Both compounds were characterized

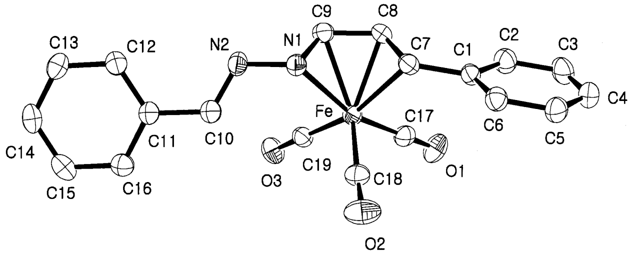


Figure 4. ORTEP view of complex **8**.

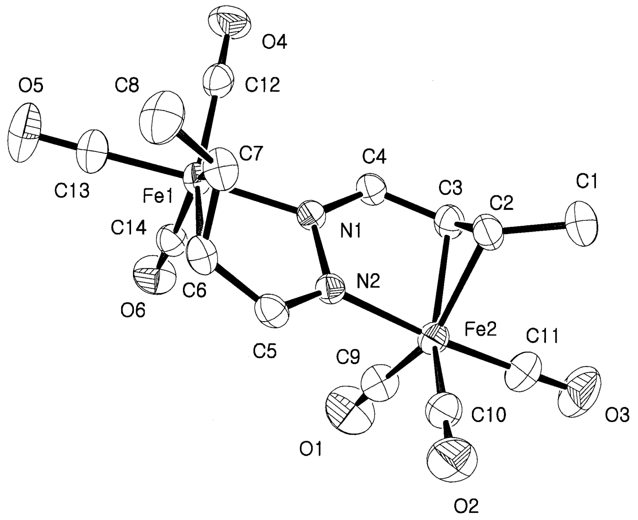


Figure 5. ORTEP view of complex **11**.

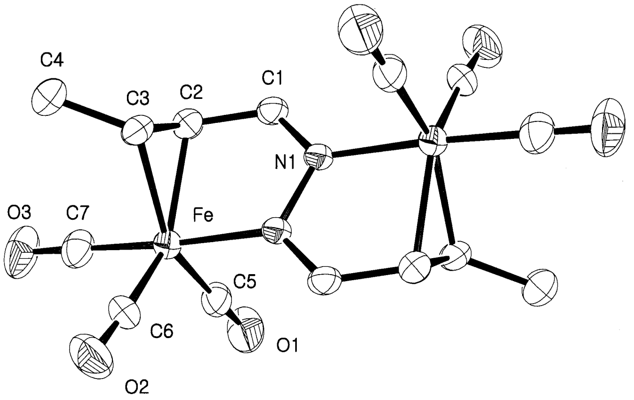
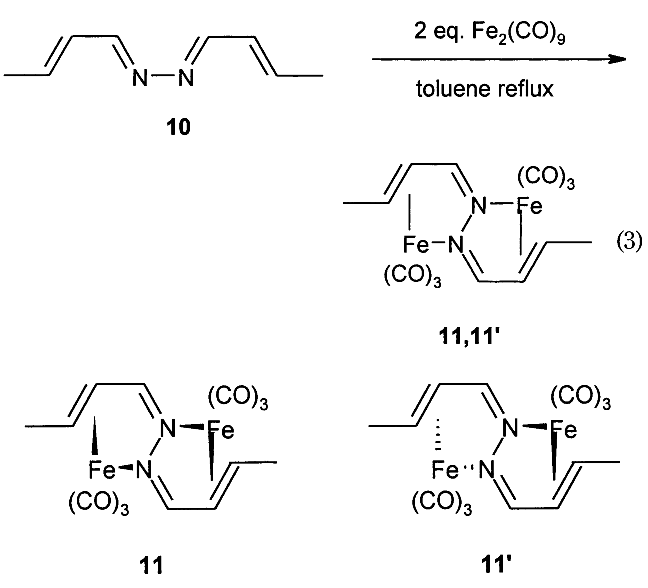


Figure 6. ORTEP view of complex **11′**.

by an X-ray diffraction study (Figures 5 and 6). As expected, both compounds are related to the structural isomers, due to the difference in the bonding modes of the two iron metals. The structure of **11** is almost the same as that of **2**, the two iron metals coordinating to the same face of the azine ligand. In **11′**, each iron metal is coordinated to a different face of the azine ligand. This contrast seems to be due to the steric difference between methyl and phenyl groups.



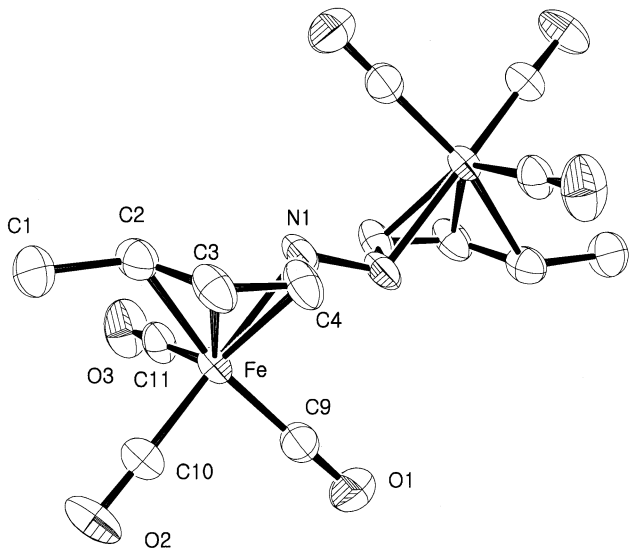
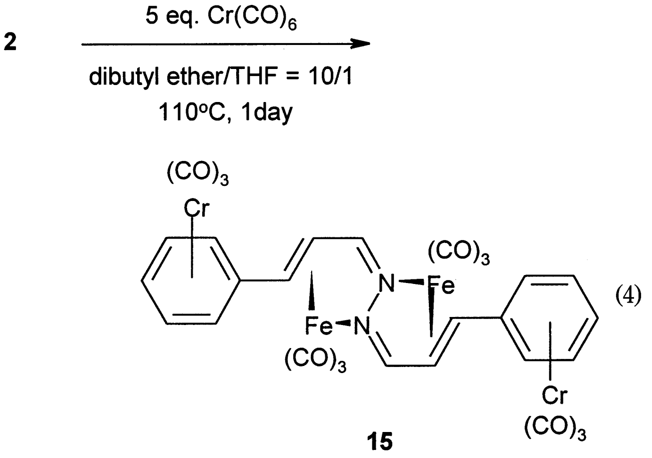


Figure 7. ORTEP view of complex **14**.

Treatment of **10** with Fe$_2$(CO)$_9$ in refluxing THF for 7 h yielded **12**–**14** in 27%, 10%, and 7% yields, respectively (eq 1). Comparison of the ^{1}H NMR spectrum with that of **3** and **5** allowed the assignment of the products to **12** and **13**, and the formation of **14** was verified by an X-ray diffraction study (Figure 7). The two Fe(CO)$_3$ moieties coordinate to the azine ligand in an anti fashion, and the structure of each half of **14** is quite similar to that of the parent complex (η^4-PhCHCHCHN-Ph)Fe(CO)$_3$.[14a,b] When we considered the chemistry of **1**, the formation of **14** was not expected. This seemed to be reflected in its poor yield. When a mixture of **12** and **13** was treated with Fe$_2$(CO)$_9$ in refluxing toluene, a mixture of **11** and **11′** in the ratio 3:1 was obtained in 75% yield. However, refluxing **14** in toluene gave no reaction product.

Next we investigated the reactivity of **2** having a new bonding mode. To determine whether the bimetallic core of **2** may act as a η^6-ligand through C–H activation of the benzyl group, **2** was heated with Cr(CO)$_6$ at 110 °C (eq 4). However, no C–H activation was observed.



Instead, the Cr(CO)$_3$ fragments were coordinated to the free phenyl groups to yield the tetrametallic Cr$_2$Fe$_2$ compound **15**.

Compound **2** has two free imine carbons. Thus, we expected a nucleophilic addition to the free imine

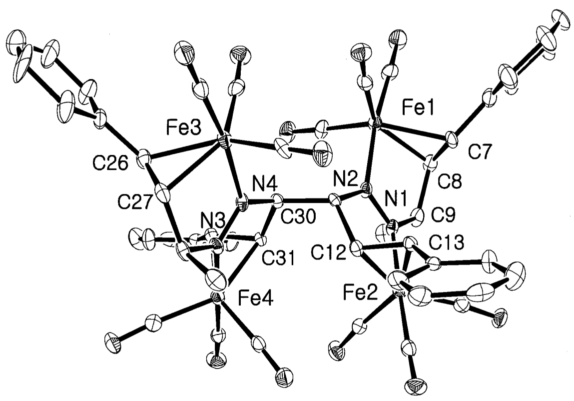
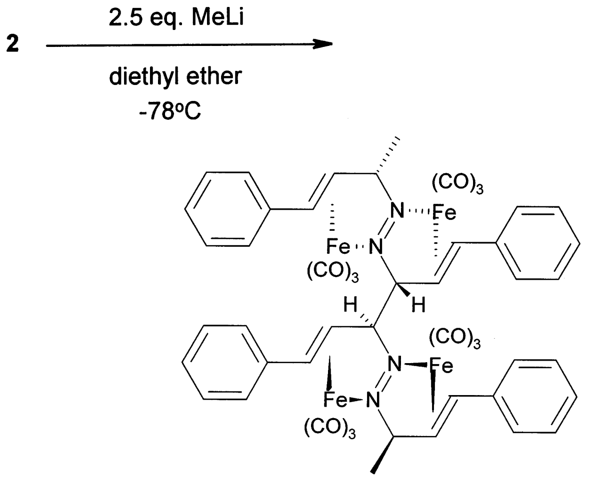


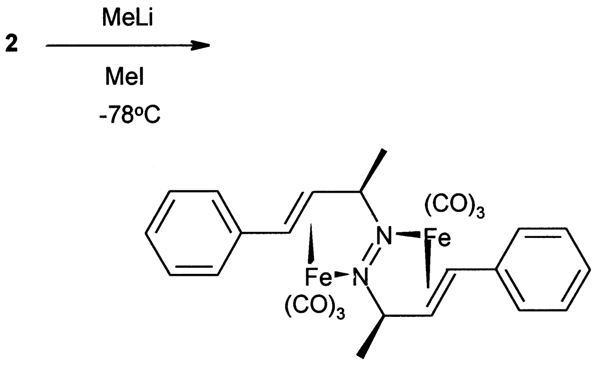
Figure 8. ORTEP view of complex **16**.

carbons. As expected, **2** reacted with a nucleophile. MeLi was added to one of the free imine carbons (eq 5). Surprisingly, the dimeric compound **16**, having four iron tricarbonyl moieties, was obtained as the sole products in 58% yield. This is quite a rare example of a dimerization induced by MeLi. Several years ago, Thomas et al.[15] reported pyrrole formation from the reaction of (1-azabutadiene)tricarbonyliron(0) with methyllithium. Thus, we first expected a pyrrole derivative as a product. The molecular structure of **16** confirmed that the methyl group has been added to the free imine carbon, and the coupling of the resulting diiron species leads to a dimeric structure (Figure 8). The structure of each half of **16** is similar to that of **2**, although the detailed structure of **16** is different from that of **2**.



(5)

Owing to the two free imine carbons of **2**, we expected that there would be a sequential reaction of **2** with a nucleophile and an electrophile. Thus, we investigated the reaction of **2** with MeLi and MeI (eq 6). As expected, the dimethyl adduct **17** was obtained in 91% yield.



17

(6)

Conclusion

We have demonstrated that, using **1** and **10** as ligands, new mono-, bi-, and tetrametallic compounds can be synthesized in good yields. This study discloses new bonding modes in the coordination of **1** and **10** to the iron metal. We expect that these new bonding modes can be expanded to other transition-metal systems.

Experimental Section

General Considerations. 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. ^{1}H 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. High-resolution mass spectra were measured at the Korea Basic Science Institute.

Reaction of 1 with $Fe_2(CO)_9$. Compounds **1**, **7**, and **10** were previously reported.[16] The general procedure for the reaction between **1** and $Fe_2(CO)_9$ in Table 1 is as follows. Compounds **1** (0.30 g, 1.2 mmol) and $Fe_2(CO)_9$ (predetermined amounts in Table 1) were dissolved in 25 mL of THF or toluene. The solution was heated to reflux for the predetermined time. After the solution was cooled to room temperature, the solvent was evaporated by a rotary evaporator. Chromatography of the residue on a silica gel column yielded the compound(s) in Table 1. **2**: ^{1}H NMR ($CDCl_3$) δ 7.97 (d, $J = 3.6$ Hz, 2 H), 7.26–7.06 (m, 1 H), 3.99 (dd, $J = 3.7$, 9.0 Hz, 2 H), 3.62 (d, $J = 9.0$ Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 177.6, 144.3, 128.5, 125.5, 125.1, 63.3, 52.1; IR ν(CO) 2036, 1949 cm^{-1}, ν(CN) 1581 cm^{-1}; HRMS *m/z* calcd 539.9707, obsd 539.9097. Anal. Calcd for $C_{24}H_{16}Fe_2N_2O_6$: C, 53.37; H, 2.99; N, 5.19. Found: C, 53.39; H, 2.98; N, 5.16. **3**: ^{1}H NMR ($CDCl_3$) δ 8.34 (d, $J = 9.8$ Hz, 1 H), 7.94 (br s, 1 H), 7.64–7.21 (m, 11 H), 7.07 (br s, 1 H), 4.58 (d, $J = 6.7$ Hz, 1 H), 3.68 (d, $J = 8.7$ Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 173.1, 169.1, 149.2, 144.6, 134.9, 131.0, 129.2, 128.3, 128.2, 125.2, 124.0, 63.0, 56.3; IR ν(CO) 2029, 1937 cm^{-1}, ν(CN) 1593 cm^{-1}; HRMS *m/z* calcd 400.0510, obsd 400.0515. Anal. Calcd for $C_{21}H_{16}FeN_2O_3$: C, 63.02; H, 4.03; N, 7.00. Found: C, 63.22; H, 4.06; N, 7.08. **4**: ^{1}H NMR ($CDCl_3$) δ 8.00 (br s, 1 H), 7.97 (br s, 1 H), 7.51–7.211 (m, 10 H), 7.03 (br s, 2 H), 4.36 (d, $J = 6.6$ Hz, 1 H), 3.86 (d, $J = 8.4$ Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 174.8, 164.9, 145.5, 144.9, 134.7, 130.7, 129.0, 128.3, 128.2, 125.2, 124.9, 119.8, 63.7, 55.6; IR ν(CO) 2030, 1935 cm^{-1}, ν(CN) 1593 cm^{-1}; HRMS *m/z* calcd 400.0510, obsd 400.0506. Anal. Calcd for $C_{21}H_{16}FeN_2O_3$: C, 63.02; H, 4.03; N, 7.00. Found: C, 63.24; H, 4.04; N, 7.05. **5**: ^{1}H NMR ($CDCl_3$) δ 7.88 (d, $J = 8.1$ Hz, 1 H), 7.45–7.28 (m, 10 H), 6.92 (d, $J = 12.0$ Hz, 2 H), 6.78 (d, $J = 11.0$ Hz, 1 H), 5.57 (d, $J = 7.2$ Hz, 1 H), 3.20 (d, $J = 8.5$ Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 161.1, 140.6, 139.3, 136.5, 129.4, 129.3, 128.9, 127.5, 127.3, 126.9, 125.5, 106.2, 72.2, 60.2; IR ν(CO) 2046, 1972 cm^{-1};

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[15] Danks, T. N.; Thomas, S. E. *Tetrahedron Lett.* **1988**, *29*, 1425–1426.

[16] For the synthesis of **1**: Elguero, J.; et al. *Bull. Soc. Chim. Fr.* **1967**, 3005–3019. Mlochowski, J.; Abdel-Latif, F. F.; Kubicz, E.; Said, S. B. *Pol. J. Chem.* **1993**, *67*, 711–722. For the synthesis of **7**: Freche, P.; et al. *Tetrahedron* **1997**, *33*, 2069–2077. For the synthesis of **10**: Brun, P.; et al., *Tetrahedron* **1985**, *41*, 5019–5030.

HRMS *m/z* calcd 400.0510, obsd 400.0510. Anal. Calcd for $C_{21}H_{16}FeN_2O_3$: C, 63.02; H, 4.03; N, 7.00. Found: C, 63.25; H, 4.07; N, 7.00.

Reaction of 7 with $Fe_2(CO)_9$. Compounds **7** (0.20 g, 0.85 mmol) and $Fe_2(CO)_9$ (0.62 g, 1.7 mmol) were dissolved in 20 mL of toluene. The solution was heated to reflux for 2 h. After the solution was cooled to room temperature, the solvent was evaporated to dryness and chromatographed on a silica gel column. Yield: 77%. ^{1}H NMR ($CDCl_3$): δ 8.06 (s, 1 H), 7.62−7.27 (m, 10 H), 5.58 (d, $J = 7.8$ Hz, 1 H), 3.21 (d, $J = 7.8$ Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ 158.7, 138.9, 134.1, 130.2, 128.8, 128.7, 127.3, 126.9, 126.4, 106.2, 71.6, 59.7. IR: ν(CO) 2044, 1975 cm^{-1}, ν(CN) 1597 cm^{-1}. HRMS *m/z* calcd 374.0354, obsd 374.0357. Anal. Calcd for $C_{19}H_{14}FeN_2O_3$: C, 60.99; H, 3.77; N, 7.49. Found: C, 60.99; H, 3.81; N, 7.37.

Reaction of 10 with $Fe_2(CO)_9$. Compounds **10** (0.30 g, 2.2 mmol) and $Fe_2(CO)_9$ (1.60 g, 4.4 mmol) were dissolved in 25 mL of THF or toluene. The solution was refluxed for 7 h. After the solution was cooled to room temperature, the solvent was evaporated to dryness and chromatographed on a silica gel column. When the reaction medium was toluene, a mixture of **11** and **11′** in the ratio of 3:1 was obtained in 58% yield. In THF, **12**−**14** were isolated in 27%, 10% and 7% yield, respectively. IR of a mixture **11** and **11′**: ν(CO) 2025, 1941 cm^{-1}, ν(CN) 1578 cm$^{-1.}$ **11**: ^{1}H NMR ($CDCl_3$) δ 7.65 (d, $J = 3.4$ Hz, 2 H), 3.14 (dd, $J = 3.7$, 8.6 Hz, 2 H), 2.48 (qd, $J = 6.3$, 8.6 Hz, 2 H), 1.62 (d, $J = 6.3$ Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 176.8, 60.3, 59.4, 23.3; HRMS *m/z* calcd 415.9394, obsd 415.9391. Anal. Calcd for $C_{14}H_{12}Fe_2N_2O_6$: C, 40.43; H, 2.91; N, 6.73. Found: C, 40.54; H, 2.91; N, 6.68. **11′**: ^{1}H NMR ($CDCl_3$) δ 7.86 (d, $J = 3.3$ Hz, 2 H), 3.36 (dd, $J = 3.2$, 8.6 Hz, 2 H), 2.59 (qd, $J = 6.3$, 8.6 Hz, 2 H), 1.62 (d, $J = 6.3$ Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 180.2, 61.1, 60.4, 23.6; HRMS *m/z* calcd 415.9394, obsd 415.9391. Anal. Calcd for $C_{14}H_{12}Fe_2N_2O_6$: C, 40.43; H, 2.91; N, 6.73. Found: C, 40.71; H, 2.99; N, 6.64. **12**: ^{1}H NMR ($CDCl_3$) δ 8.03 (d, $J = 10.0$ Hz, 1 H), 7.74 (d, $J = 3.3$ Hz, 1 H), 6.83 (dd, $J = 10.0$, 15.0 Hz, 1 H), 6.52 (dq, $J = 6.9$, 15.0 Hz, 1 H), 3.80 (dd, $J = 3.3$, 9.0 Hz, 1 H), 2.58 (m, 1 H), 2.08 (d, $J = 6.9$ Hz, 3 H), 1.62 (d, $J = 6.3$ Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 214.4, 172.4, 168.7, 149.7, 128.9, 63.5, 59.8, 22.7, 19.7; IR ν(CO) 2021, 1931 cm^{-1}, ν(CN) 1597 cm^{-1}; HRMS *m/z* calcd 276.0197, obsd 276.0201. **13**: ^{1}H NMR ($CDCl_3$) δ 7.56 (d, $J = 9.0$ Hz, 1 H), 6.70 (d, $J = 2.7$ Hz, 1 H), 6.08 (m, 2 H), 4.86 (dd, $J = 2.9$, 8.9 Hz, 1 H), 2.18 (m, 1 H), 1.82 (d, $J = 6.2$ Hz, 3 H), 1.46 (d, $J = 6.4$ Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 214.4, 160.9, 139.6, 129.1, 106.2, 66.3, 56.6, 19.1, 18.8; IR ν(CO) 2048, 1964 cm^{-1}; HRMS *m/z* calcd 276.0197, obsd 276.0194. **14**: ^{1}H NMR ($CDCl_3$) δ 6.61 (d, $J = 3.0$ Hz, 2 H), 4.70 (dd, $J = 2.8$, 9.0 Hz, 2 H), 1.80 (qd, $J = 6.5$, 9.0 Hz, 2 H), 1.33 (d, $J = 6.5$ Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 109.9, 77.1, 55.9, 18.2; IR ν(CO) 2036, 1960 cm^{-1}. Anal. Calcd for $C_{14}H_{12}Fe_2N_2O_6$: C, 40.43; H, 2.91; N, 6.73. Found: C, 40.55; H, 2.87; N, 6.66. HRMS *m/z* calcd 415.9394, obsd 415.9394.

Synthesis of 15. Compounds **2** (0.10 g, 0.19 mmol) and $Cr(CO)_6$ (0.21 g, 0.95 mmol) were dissolved in a solvent mixture of dibutyl ether (25 mL) and THF (5 mL). The solution was heated to reflux for 3 days. After the solution was cooled to room temperature, the solvent was evaporated to dryness and chromatographed on a silica gel column. Yield: 93% (0.14 g). **15**: ^{1}H NMR ($CDCl_3$) δ 7.99 (d, 4.1 Hz, 2 H), 5.54 (m, 4 H), 5.41 (t, 6.7 Hz, 2 H), 5.14 (m, 2 H), 4.71 (d, 6.8 Hz, 2 H), 3.62 (dd, 4.7, 8.9 Hz, 2 H), 2.87 (d, 8.9 Hz, 2 H); ^{13}C NMR (CD_2Cl_2) δ 177.3, 116.0, 94.2, 93.1, 91.1, 88.6, 84.4, 58.6, 50.2; IR ν(CO) 2044, 1952, 1872 cm^{-1}, ν(CN) 1574 cm^{-1}. Anal. Calcd for $C_{24}H_{16}Cr_2Fe_2N_2O_{12}$: C, 44.37; H, 1.99; N, 3.45. Found: C, 43.94; H, 2.00; N, 3.20.

Synthesis of 16. Compound **2** (0.10 g, 0.19 mmol) was dissolved in 20 mL of diethyl ether. The solution was cooled to −78 °C. To the cold solution was added MeLi (0.40 mmol). The resulting solution was stirred at −78 °C for 10 h. After the solution was warmed to room temperature, the solution was quenched by addition of 0.2 mL of water. After the solution was dried over anhydrous $MgSO_4$, the solution was filtered, evaporated to dryness, and chromatographed on a silica gel column. Yield: 58% (0.06 g). **16**: ^{1}H NMR ($CDCl_3$) δ 7.31−7.10 (m, 20 H), 6.19 (s, 2 H), 5.79 (d, $J = 6.9$ Hz, 2 H), 4.26 (d, $J = 11.0$ Hz, 2 H), 3.69 (d, $J = 11.0$ Hz, 2 H), 3.07 (d, $J = 10.0$ Hz, 2 H), 2.85 (d, $J = 11.0$ Hz, 2 H), 2.00 (d, $J = 6.6$ Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 142.6, 141.9, 128.6, 128.5, 126.1, 125.9, 93.4, 88.7, 77.9, 61.1, 60.9, 53.2, 47.5, 20.7; IR ν(CO) 2026, 1972, 1944 cm^{-1}; HRMS (M + H) *m/z* calcd 1110.9962, obsd 1110.9972. Anal. Calcd for $C_{50}H_{38}Fe_4N_4O_{12}$: C, 54.09; H, 3.45; N, 5.05. Found: C, 54.07; H, 3.57; N, 5.01.

Synthesis of 17. A solution of **2** (0.10 g, 0.19 mmol) in 10 mL of diethyl ether was cooled to −78 °C. To the cold solution was added MeLi (0.29 mmol). After the solution was stirred at −78 °C for 2 h, an excess of MeI was added. The resulting solution was stirred at −78 °C for 2 h. After the solution was warmed to room temperature, the reaction was quenched by addition of 0.1 mL of water. After the solution was dried over anhydrous $MgSO_4$ (0.5 g), it was filtered and evaporated to dryness. Chromatography of the residue on a silica gel column with *n*-hexane as eluent gave **17** in 91% yield (0.096 g). **17**: ^{1}H NMR ($CDCl_3$) δ 7.26−7.05 (m, 10 H), 5.38 (q, $J = 6.6$ Hz, 2 H), 3.97 (d, $J = 11.0$ Hz, 2 H), 2.89 (d, $J = 11.0$ Hz, 2 H), 1.67 (d, $J = 6.7$ Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 143.6, 128.9, 126.6, 125.9, 86.9, 59.0, 54.4, 19.6; IR ν(CO) 2024, 1968, 1940 cm^{-1}; HRMS *m/z* calcd 570.0177, obsd 570.0175. Anal. Calcd for $C_{26}H_{22}Fe_2N_2O_6$: C, 54.77; H, 3.89; N, 4.91. Found: C, 55.18; H, 4.03; N, 4.87.

X-ray Structure Determinations of 3−5, 8, 11, 11′, 14, and 16. Single crystals of **3**−**5**, **8**, **11**, **11′**, **14**, and **16** suitable for X-ray diffraction study were grown by slow diffusion of the dichloromethane solutions of **3**−**5**, **8**, **11**, **11′**, **14**, and **16** 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 ($\lambda = 0.710\,73$ 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. The crystal structure of **16** was assigned as the noncentric $P2_12_12_1$ space group on the basis of the systematic absences of the reflection data. However, the refinement of the structure with either enantiomeric configuration gave a Flack parameter of around 0.5. The refinement of the structure as a racemic twinned structure gave better agreement. Crystal data, details of the data collection, and refinement parameters are listed in Table 2. Selected bond distances and angles are given in Table 3.

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Supporting Information Available: Tables of atomic positions, anisotropic thermal parameters, bond lengths and angles, and hydrogen coordinates for **3**−**5**, **8**, **11**, **11′**, **14**, and **16** and IR spectra of **2**−**5**, **8**, **11**, **11′**, and **12**−**15**. This material is available free of charge via the Internet at http://pubs.acs.org. Structure factor tables are available from the authors.

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