Structural Characterization and Electrochemical Study of Novel Ferrocene Derivatives Prepared from [(β-Ferrocenylvinyl)imino]phosphorane by Aza Wittig Reactions

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A rapid and efficient synthetic procedure has been developed to prepare new ferrocene derivatives such as β-ferrocenylvinyl heterocumulenes and ferrocene-containing imidazole ring bearing one, two, or three ferrocene subunits. The method is based on the aza Wittig reaction of [(β-ferrocenylvinyl)imino]phosphorane **3**, readily available from ferrocenecarboxaldehyde by sequential treatment with ethyl azidoacetate and triphenylphosphine, with isocyanates and further treatment with the appropriate primary amine. The crystal structures of compounds **6c** (monoferrocene derivative), **11c**, and **12b** (biferrocene derivatives) have been determined by single-crystal X-ray methods. The electrochemical properties of these new compounds are also reported.

Considerable attention has been paid in the last few years to supramolecular systems containing a ferrocene unit and a fragment able to act as ligand, with a well-defined geometry because of its fixed intramolecular spacing, toward transition-metal ions; these systems can behave either as chemical sensors[1] or as redox-active and photoactive molecular devices.[2] In addition, supramolecular systems containing more than one metallocene unit have attracted a great deal of attention.[3] In particular, bridging two or three ferrocene subunits generates redox systems which have been the subject of recent studies due to their great potential as partially oxidized species exhibiting mixed-valence behavior or electronic delocalization[4] and as models for poly(ferrocenyl)silane materials.[5] On the other hand, the ferrocene subunit has been incorporated into more complex structures, which then displayed a high degree of nonlinear optical (NLO) behavior, liquid crystalline, ferromagnetic, or catalytic properties.[6]

The present work was undertaken to synthesize and characterize a range of ferrocene-containing species with P- or sp/sp^2/sp^3/N-donor groups which may be able to act as ligand toward transition-metal ions. To our knowledge, no ferrocenylimidazole derivatives have been described, in spite of the fact that ferrocenyl-substituted pyrazoles[7] and many ferrocenyl-substituted pyridines[8] have been studied, especially in the context of the design of redox spectators.

Results and Discussion

We chose to use the [(β-ferrocenylvinyl)imino]phosphorane **3** as a building block for the synthesis of the new ferrocene derivatives. Ferrocenecarboxaldehyde (**1**) underwent Knoevenagel condensation with ethyl azidoacetate in the presence of NaEtO at −15 °C to give the β-ferrocenylvinyl azide **2** in 82% yield. Staudinger reaction of azide **2** with triphenylphosphine in dry dichloromethane at room temperature provided the key intermediate, iminophosphorane **3**, in 93% yield. The ^{1}H NMR spectrum of **3** is characteristic: the ferrocenyl substituent gives rise to a five-proton singlet at 4.04 ppm for the unsubstituted cyclopentadienyl ring and two apparent triplets at 4.17 and 4.87 ppm, respectively, corresponding to the AA′MM′ pattern for the monosub-

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[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1997.

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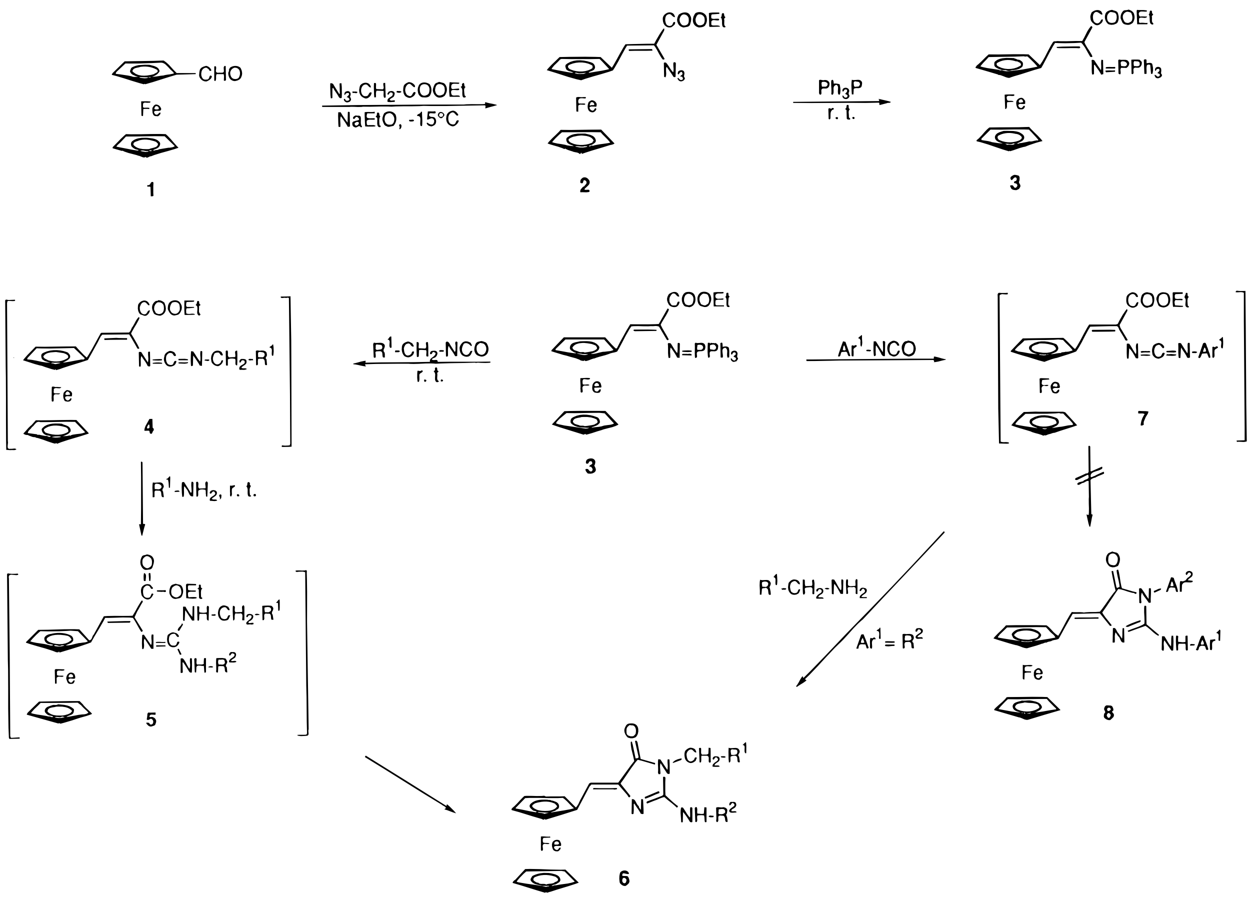
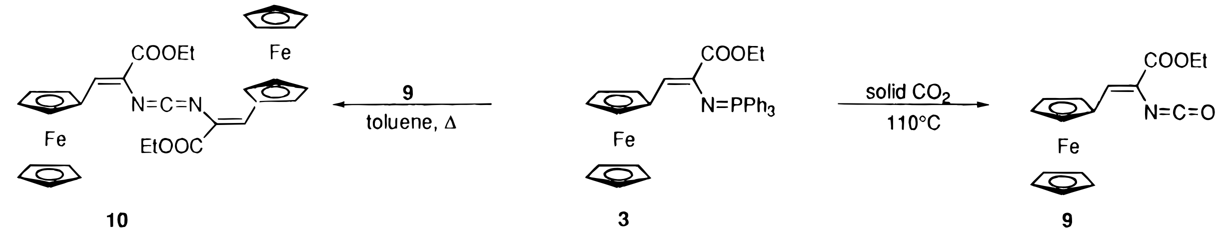
S0276-7333(97)00616-X CCC: $14.00

Scheme 1



Scheme 2



stituted ring. Similar behavior was observed in the ^{13}C NMR spectrum.

It is important to note that the iminophosphorane moiety possesses a high complex-forming capacity with a wide variety of metal compounds[9] and metal carbonyls,[10] so **3** could be of valuable interest for the preparation of redox-functionalized metal complexes.

(Vinylimino)phosphorane **3** was converted in a one-flask reaction into the corresponding highly functionalized ferrocenylimidazole **6** in yields higher than 70%. This conversion involves aza Wittig reaction with benzyl or alkyl isocyanates at room temperature and further treatment of the resulting carbodiimide **4** with aliphatic or aromatic primary amines to give ferrocenylguanidines **5** as intermediates, which undergo cyclization at room temperature to give **6**. Compound **3** also reacted with aromatic isocyanates to give the expected carbodiimide **7**, which by reaction with aliphatic amines provided **6** but did not react with aromatic amines at room temperature. At higher temperatures, complex mixtures were obtained, from which the corresponding imidazoles **8** could not be detected (Table 1, Scheme 1). The ^{1}H and ^{13}C NMR spectra of compounds **6** showed the same type of signals for the ferrocene unit as observed in the (vinylimino)phosphorane **3**. An X-ray structure determination confirmed unambiguously the structure **6c** (Figure 1, Table 2).

Table 1. Ferrocenylimidazole Derivatives 6, 11, and 12

compd	R^1	R^2	R^3	yield (%)
6a	CH_3	C_2H_5		86
6b	C_2H_5	C_3H_7		98
6c	C_6H_5	C_6H_5-CH_2		72
6d	C_6H_5	4-H_3C-C_6H_5		65
11a	CH_3	H	H	94
11b	C_2H_5	H	H	86
11c	C_6H_5	H	H	83
11d	CH_3	CH_3	H	62
12a	CH_3	CH_3	H	26
12b	CH_3	CH_3	CH_3	40

(Vinylimino)phosphorane **3** also reacted with solid carbon dioxide at 110 °C in a sealed tube to afford the β-ferrocenylvinyl isocyanate **9** as crystalline solid in 86% yield; however, when the reaction was carried out at

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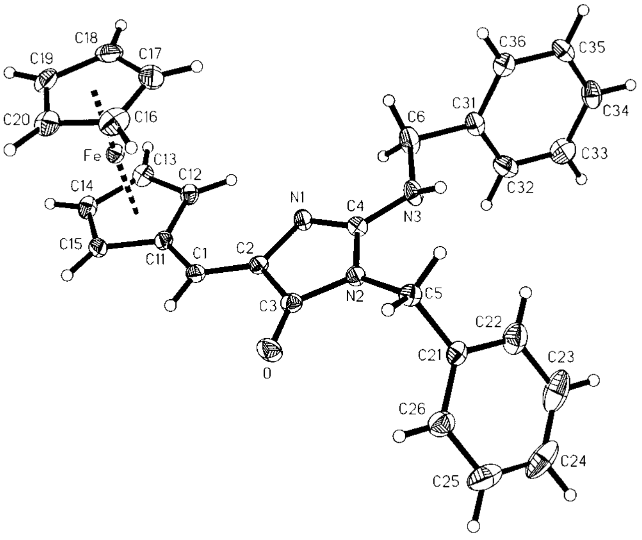

Figure 1. ORTEP plot of **6c** with 50% probability ellipsoids.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 6c

	Lengths (Å)		
O−C(3)	1.231(2)	N(1)−C(4)	1.303(2)
N(1)−C(2)	1.402(2)	N(2)−C(3)	1.372(2)
N(2)−C(4)	1.403(2)	N(2)−C(5)	1.467(2)
N(3)−C(4)	1.346(2)	N(3)−C(6)	1.462(2)
C(1)−C(2)	1.349(2)	C(1)−C(11)	1.447(2)
C(2)−C(3)	1.482(2)		
	Angles (deg)		
C(4)−N(1)−C(2)	105.24(13)	C(3)−N(2)−C(4)	107.04(13)
C(3)−N(2)−C(5)	123.91(13)	C(4)−N(2)−C(5)	128.80(12)
C(4)−N(3)−C(6)	118.31(14)	C(2)−C(1)−C(11)	127.1(2)
C(1)−C(2)−N(1)	127.8(2)	C(1)−C(2)−C(3)	123.17(14)
N(1)−C(2)−C(3)	108.99(13)	O−C(3)−N(2)	124.8(2)
O−C(3)−C(2)	130.9(2)	N(2)−C(3)−C(2)	104.26(13)
N(1)−C(4)−N(3)	125.36(14)	N(1)−C(4)−N(2)	114.46(13)
N(3)−C(4)−N(2)	120.16(14)		

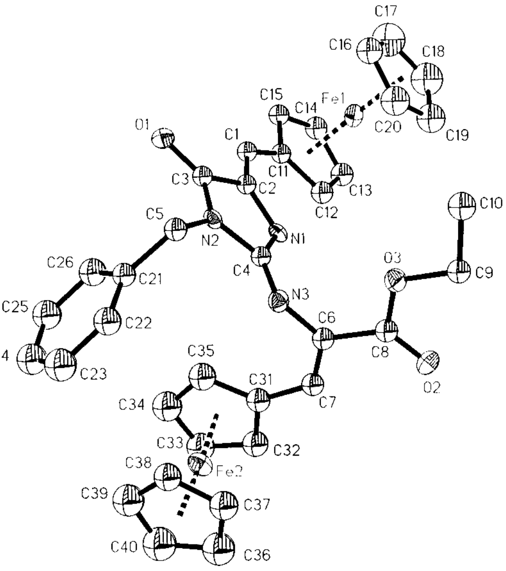

Figure 2. ORTEP plot of **11c** with 50% probability ellipsoids.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 11c

	Lengths (Å)		
O(1)−C(3)	1.235(7)	N(1)−C(2)	1.395(10)
N(1)−C(4)	1.402(13)	N(2)−C(3)	1.350(11)
N(2)−C(4)	1.416(7)	N(2)−C(5)	1.458(10)
N(3)−C(4)	1.249(11)	N(3)−C(6)	1.414(7)
C(1)−C(2)	1.325(12)	C(1)−C(11)	1.457(10)
C(2)−C(3)	1.493(9)	C(6)−C(7)	1.346(8)
C(6)−C(8)	1.478(8)		
	Angles (deg)		
C(2)−N(1)−C(4)	112.3(5)	C(3)−N(2)−C(4)	112.4(6)
C(3)−N(2)−C(5)	124.4(5)	C(4)−N(2)−C(5)	123.1(8)
C(4)−N(3)−C(6)	120.1(6)	C(2)−C(1)−C(11)	131.4(6)
C(1)−C(2)−N(1)	133.7(5)	C(1)−C(2)−C(3)	122.0(6)
N(1)−C(2)−C(3)	104.2(7)	O(1)−C(3)−N(2)	126.3(6)
O(1)−C(3)−C(2)	127.0(8)	N(2)−C(3)−C(2)	106.7(5)
N(3)−C(4)−N(1)	133.5(5)	N(3)−C(4)−N(2)	122.2(7)
N(1)−C(4)−N(2)	104.3(8)	C(7)−C(6)−N(3)	124.8(5)
C(7)−C(6)−C(8)	116.2(5)	N(3)−C(6)−C(8)	118.7(4)
C(6)−C(7)−C(31)	128.2(5)		

160 °C, a mixture of isocyanate **9** (70%) and the bis(β-ferrocenylvinyl)carbodiimide **10** (20%) was obtained. The latter compound can be obtained in 95% yield by intermolecular aza Wittig reaction of the (vinylimino)phosphorane **3** and the vinyl isocyanate **9** in toluene at reflux temperature (Scheme 2). The ^{1}H and ^{13}C NMR spectra of **10** revealed that the two ferrocene subunits are equivalent. Compound **10**, whose structure has been determined by X-ray analysis,[11] represents a novel example of biferrocene compounds in which the bridging unit is an unsaturated carbodiimide.

The present approach to ferrocenylimidazoles enables the design of novel complex ferrocene-containing heterocycles bearing two or three ferrocene subunits. Thus, carbodiimide **10** reacted with α-unsubstituted primary amines in dry dichloromethane at room temperature to give bis(ferrocenyl)imidazole derivatives **11** in yields ranging from 83% to 95% (Table 1, Scheme 3). The ^{1}H and ^{13}C NMR spectra of compounds **11** showed two sets of signals for the two ferrocene subunits, indicating that they are nonequivalent. Namely, in the ^{13}C NMR spectra of **11**, only three resonances are observed for each substituted Cp ring (and one resonance for each unsubstituted ring), implying that the Cp rings undergo rapid rotation. The reaction of **10** with isopropylamine under the same conditions afforded two compounds. The major product (62%) was found to be **11d**, whose spectroscopic properties are nearly identical to those of **11a**−**c**. The minor product **12a** (26%) has the same microanalytical data; however, the ^{1}H and ^{13}C NMR spectra showed striking differences with respect to those of **11d**. The ^{13}C NMR spectrum not only showed separate sets of signals for the two ferrocene subunits, as in **11**, but also showed five separate resonances for each substituted Cp ring, thus indicating the lack of any symmetry element relating to them.[12] When **10** was treated with *tert*-butylamine at room temperature, starting material was recovered unaltered; however, when the reaction was carried out at 100 °C, **12b** was isolated as the only reaction product in 40% yield. The spectroscopic properties of **12b** are nearly identical to those of **12a**. The behavior of carbodiimide **10** toward primary amines can be rationalized by initial formation of a guanidine derivative which undergoes cyclization across either the alkylamino group or the (β-ferroce-

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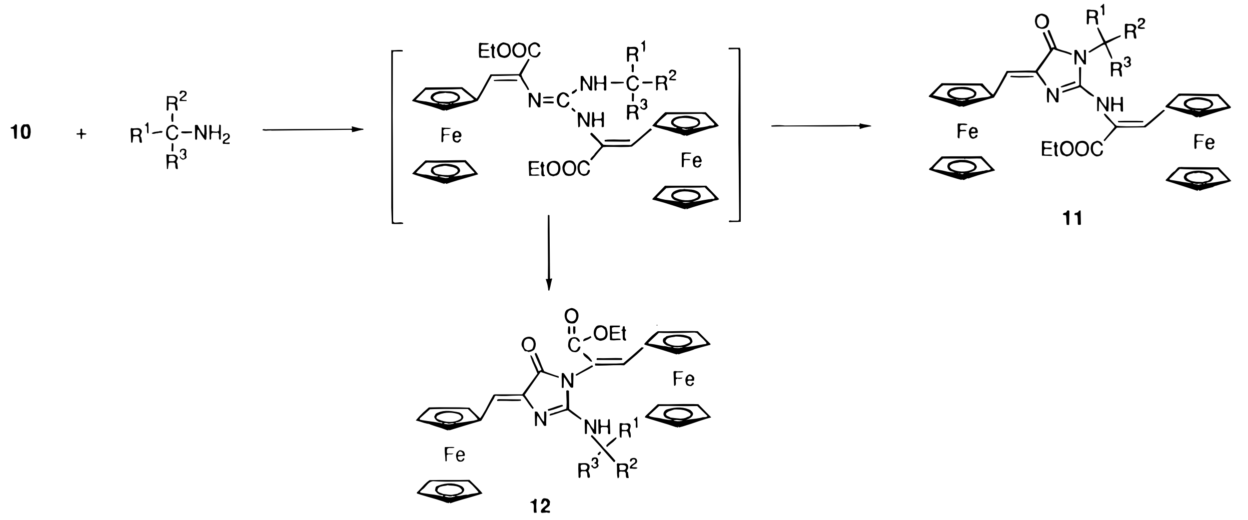
Scheme 3



nylvinyl)amino group, depending on the degree of substitution on the carbon atom adjacent to the amino group.

In order to identify unambiguously the proposed structures, X-ray structure determination of **11** and **12** was performed. The structures **11c** (Figure 2, Table 3) and **12b** (Figure 3, Table 4) reveal that the two ferrocene subunits are orthogonal (Cp11−Cp31 = 86.8° for **11c**, and Cp11−Cp31 = 87.2° for **12b**) with respect to each other, and the intramolecular Fe−Fe separation is almost the same (9.572 Å) for both compounds. A final point is concerned with the conformation of the cyclopentadienyl ring in each subunit. The conformation is, in both subunits, almost eclipsed. It has been pointed out that the energy difference between the two conformers is rather small,[13] and the stability order may be altered through the introduction of substituents on the cyclopentadienyl ring(s).

Carbodiimide **10** also reacted with ferrocenylmethylamine[14] in dichloromethane at room temperature to give the tris(ferrocenyl) compound **13** in 60% yield. The ^{13}C NMR spectrum showed three sets of signals for the three ferrocene subunits (Scheme 4).

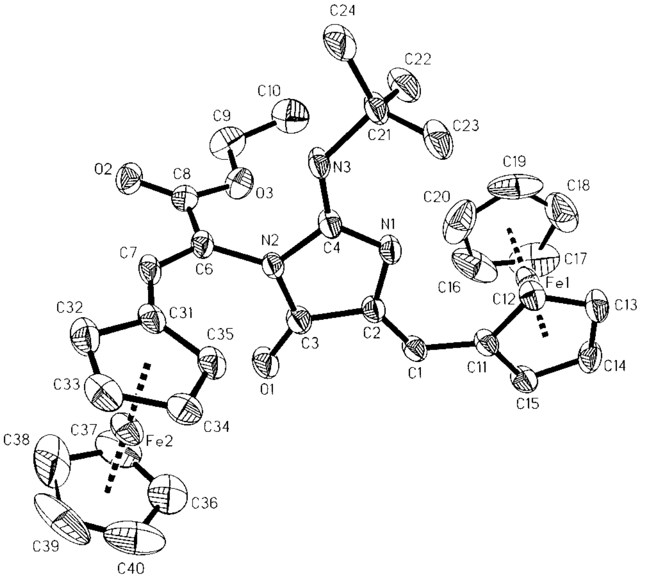
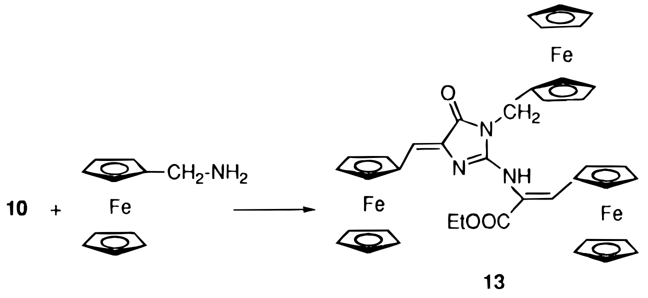


Figure 3. ORTEP plot of **12c** with 50% probability ellipsoids.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 12b·$^1/_2$Et$_2$O

Lengths (Å)			
O(1)−C(3)	1.201(5)	N(1)−C(4)	1.322(5)
N(1)−C(2)	1.401(5)	N(2)−C(4)	1.403(5)
N(2)−C(3)	1.405(5)	N(2)−C(6)	1.424(5)
N(3)−C(4)	1.333(5)	N(3)−C(21)	1.495(5)
C(1)−C(2)	1.327(6)	C(1)−C(11)	1.452(5)
C(2)−C(3)	1.489(5)	C(6)−C(7)	1.351(5)
C(6)−C(8)	1.477(6)	C(7)−C(31)	1.435(6)
Angles (deg)			
C(4)−N(1)−C(2)	105.7(3)	C(4)−N(2)−C(3)	107.6(3)
C(4)−N(2)−C(6)	126.6(3)	C(3)−N(2)−C(6)	122.3(3)
C(4)−N(3)−C(21)	123.9(3)	C(2)−C(1)−C(11)	127.3(4)
C(1)−C(2)−N(1)	127.6(4)	C(1)−C(2)−C(3)	122.5(4)
N(1)−C(2)−C(3)	109.8(3)	O(1)−C(3)−N(2)	125.3(4)
O(1)−C(3)−C(2)	131.6(4)	N(2)−C(3)−C(2)	103.0(3)
N(1)−C(4)−N(3)	126.8(4)	N(1)−C(4)−N(2)	113.7(3)
N(3)−C(4)−N(2)	119.5(3)	C(7)−C(6)−N(2)	123.1(4)
C(7)−C(6)−C(8)	119.3(3)	N(2)−C(6)−C(8)	117.5(3)
C(6)-C(7)-C(31)	130.4(4)		

Scheme 4



The cyclic voltammograms of **6a−c** (Figure 4) show that the ratio of the current intensity of the anodic peak over the intensity of the cathodic peak (i_{pa}/i_{pc}) was approximatly equal to 1 over the potential scan rate range 0.01−0.2 V s^{-1}, and the peak-to-peak separation was 65−67 mV. Under the same experimental conditions, the one-electron oxidation of ferrocene itself displays an E_p of 64 mV, thus indicating that departure from the constant value of 59 mV expected for an

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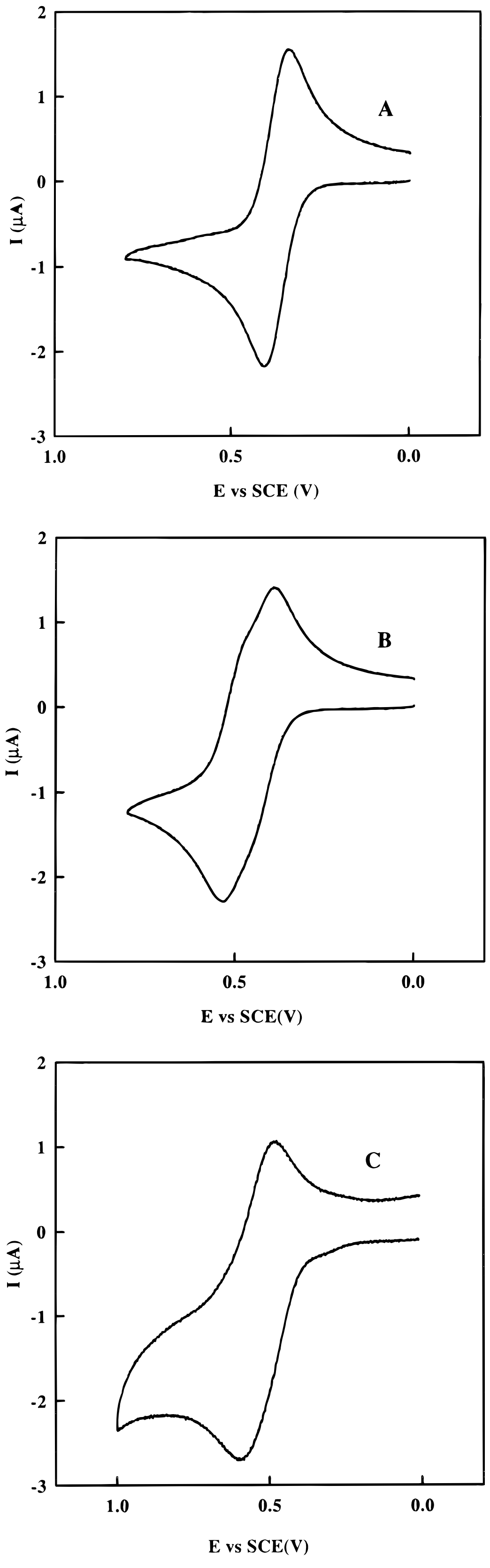

Figure 4. Cyclic voltammograms of (A) **6c** (1 mM) in MeCN/CH_2Cl_2 (1:1) solution containing 0.10 M TBAP, scan rate 0.1 V s^{-1}; (B) **11c** in MeCN/CH_2Cl_2 (1:1) solution containing 0.10 M TBAP, scan rate 0.1 V s^{-1}; (C) **13** (0.25 mM) in DMF solution containing 0.10 M TBAP, scan rate 0.5 V s^{-1}.

electrochemically reversible one-electron trasfer[15] should be due to uncompensated solution resistences. Table 5 shows the half-wave potentials of compounds **6**, and they show the electron-donating abilities of the substituents, which makes the electron removal about 32−53 mV easier when compared with that of ferrocene.

Table 5. Cyclic Voltammetry Data of Ferrocenyl Derivatives

compd	$E_{1/2}(1)$, V	$E_{1/2}(2)$, V	$\Delta E_p{}^a$, mV	$\Delta E_{1/2}(1)$, mV	K_c
FcH	0.404		64		
6a	0.355		66		
6b	0.351		67		
6c	0.372		65		
10	0.463	0.539	106	76	19
11c	0.425	0.517	141	92	36

[a] Peak-to-peak separation measured at 100 mV s^{-1}.

Biferrocene derivatives **10** and **11c** exhibit cyclic voltammograms characteristic of superimposed one-electron waves,[16] with a peak-to-peak separation notably higher than the 57 mV expected for a two-electron process involving non-interacting centers.[17] The values of $E_{1/2}(1)$ and $E_{1/2}(2)$ were estimated by using the method outlined by Richarson and Taube.[18] The difference ($E_{1/2}$) between the first and second half-wave potentials gives values of K_c significantly higher than the statitiscal value for **4**, which reveals a small but significant electronic interaction between the two redox centers through the organic chain attached to the ferrocenyl subunits.

The cyclic voltammogram of derivative **13** (Figure 4) shows one oxidation wave at $E_{pa} = 0.603$ V *vs* SCE, which implies that only very weak interactions between the ferrocenyl subunits are presented.

In conclusion, the aza Wittig reaction, which has not been used before in ferrocene chemistry, appears to be a simple but very effective new way to prepare a wide variety of ferrocene derivatives, in which the ferrocene group is conjugated either to a heterocumulene fragment or to a highly functionalized imidazole ring. The method also works for the preparation of bi- and triferrocene derivatives. These relatively complex and unreported structures are prepared under mild reaction conditions, with high yields, and from the readily available starting material [(*β*-ferrocenylvinyl)imino]-phosphorane **3**.

Experimental Section

General Methods. General experimental conditions and spectroscopic instrumentation used have been described.[19]

The cyclic voltammetric measurements were performed with a QUICELTRON potentiostat/galvanostat, controlled by a personal computer and driven by dedicated software. Experiments were carried out in a three-electrode cell. The counter electrode was platinum foil, and the reference was a saturated calomel electrode (SCE). The cyclic voltammetry was performed at a platinum disk working electrode with a variable scan rate.

First, 5 mL of CH_2Cl_2/CH_3CN (1:1) solution containing 0.1 M $[nBu_4N][ClO_4]$ was poured into the cell, followed by 5 mmol of the derivative (10^{-3} M). The same electrodes were used for cyclic voltammetry performed in DMF. Deoxygenation of the

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Table 6. Crystal Data for 6c, 11c, and 12b·$^1/_2$Et$_2$O

	6c	**11c**	**12b·$^1/_2$Et$_2$O**
molecular formula	$C_{28}H_{25}N_3OFe$	$C_{36}H_{33}N_3O_3Fe_2$	$C_{35}H_{40}N_3O_{3.5}Fe_2$
molecular weight	475.36	667.35	670.40
habit	tablet	prism	prism
color	dark red	dark red	dark red
source	liquid diffusion CH_2Cl_2/Et_2O	liquid diffusion $CH_2Cl_2/^iPr_2O$	liquid diffusion CH_3COOEt/*n*-hexane
a, Å	8.007(1)	32.212(3)	11.042(2)
b, Å	23.699(2)	13.216(2)	12.570(2)
c, Å	11.700(1)	21.668(3)	13.440(4)
α, deg			110.18(2)
β, deg	93.88(1)	91.33(1)	92.38(2)
γ, deg			93.43(1)
V, Å^3	2215(1)	6079(1)	1744(1)
Z	4	8	2
λ, Å	0.710 73	0.710 73	0.710 73
temp, K	173(2)	173(2)	173(2)
radiation	Mo Kα	Mo Kα	Mo Kα
monochromator	graphite	graphite	graphite
space group	$P2_1/c$	$C2/c$	$P\bar{1}$
crystal size, mm	0.56 × 0.44 × 0.14	0.32 × 0.30 × 0.28	0.40 × 0.38 × 0.32
absorpt correction	*ψ*-scans	*ψ*-scans	*ψ*-scans
max/min trans, %	0.99/0.74	0.77/0.74	0.95/0.74
diffractometer	Siemens P4	Siemens P4	Siemens P4
scan method	*ω*	*ω*	*ω*
2*θ* range	6.2−50.0	6.2−50.0	6.2−50.2
hkl limits	$\pm h\ -k\ \pm l$	$-h\ +k\ \pm l$	$\pm h\ \pm k\ +l$
reflns measured	8636	5442	5852
independent reflns	3899	2789	5636
R_{int}	0.025	0.036	0.015
$R1^a$	0.0254	0.0516	0.0557
w$R2^b$	0.0668	0.1380	0.2096

[a] $R1 = \sigma||F_o| - |F_c||/\sigma|F_o|$ for reflections with $I > 2\sigma I$. [b] $wR2 = [\sigma[w(F_o^2 - F_c^2)^2]/\sigma[w(F_o^2)^2]]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_o^2)/3$, and *a* and *b* are constants set by the program.

solutions was achieved by bubbling nitrogen for at least 10 min. All of the potential values are referred to SCE.

X-ray Crystallography. Crystals obtained by liquid diffusion from CH_2Cl_2/Et_2O (**6c**), CH_2Cl_2/iPr$_2$O (**11c**), and CH_3COOEt/*n*-hexane (**12b**·$^1/_2$Et$_2$O) were respectively mounted in inert oil on a glass fiber and transferred to the diffractometer (Siemens P4 with LT2 low-temperature attachment), as summarized in Table 6. The data were collected at 173 K using graphite monochromated Mo Kα radiation (0.710 73 Å) according to the *ω*-scans method in the region $6.2 \le 2\theta \le 50.0°$. Unit cell parameters were determined from a least-squares fit of 72 (**6c**), 42 (**11c**), and 74 (**12b**·$^1/_2$Et$_2$O) accurately centered reflections ($9 < 2\theta < 25°$). An absorption correction based on *φ*-scans was applied, with transmision factors 0.74−0.99 (**6c**), 0.74−0.76 (**11c**), and 0.74−0.95 (**12b**·$^1/_2$Et$_2$O). The structures were solved by direct methods and refined on F^2 by means of the full-matrix least-squares method. The N-H hydrogen atom was found in the final Fourier F map and refined as a free variable for all three compounds. Other hydrogen atoms were included using a riding model, except for those of the methyl groups of **6c**, which were refined as rigid. The programs use the neutral atom scattering factors, $\Delta f'$ and $\Delta f''$, and absorption coefficients.[20]

Preparation of α-Azido-*β*-ferrocenylpropenoic Acid Ethyl Ester (2). A mixture of ethyl azidoacetate (4.82 g, 37.2 mmol) and ferrocenecarboxaldehyde (**1**, 2.00 g, 9.3 mmol) was added dropwise under nitrogen at −15 °C to a well-stirred solution containing sodium (0.86 g, 37.2 mmol) in 25 mL of anhydrous THF. The reaction mixture was stirred at that temperature for 7 h and then allowed to warm to room temperature. The resultant solution was poured into aqueous 30% ammonium chloride (50 mL) and then extracted with diethyl ether (3 × 50 mL). The combined organic layers were washed with water (3 × 50 mL), dried over anhydrous magnesium sulfate, and filtered. Concentration to dryness yielded a crude material, which was chromatographed on a silica gel column using ethyl acetate/*n*-hexane (1:3) as eluent to give **2** in 82% yield, which was recrystallized form diethyl ether/*n*-hexane (1:1): mp 84−86 °C, red prisms; ^{1}H NMR ($CDCl_3$) *δ* 1.39 (t, 3H, *J* = 7.1 Hz), 4.15 (s, 5H), 4.33 (q, 2H, *J* = 7.2 Hz), 4.40 (t, 2H, *J* = 1.7 Hz), 4.47 (t, 2H, *J* = 1.7 Hz), 6.78 (s, 1H); ^{13}C NMR ($CDCl_3$) *δ* 14.3, 61.9, 69.6, 70.8, 70.7, 122.5, 127.6, 163.5; EI-MS *m/z* (relative intensity) 325 (M$^+$, 8), 224 (100), 121 (54). Anal. Calcd for $C_{15}H_{15}N_3O_2Fe$: C, 55.41; H, 4.65; N, 12.99. Found: C, 55.54; H, 4.76; N, 13.34.

Preparation of *β*-Ferrocenyl-α-[(Triphenylphosphoranylidene)amino]propenoic Acid Ethyl Ester (3). To a solution of **2** (0.25 g, 0.8 mmol) cooled at 0 °C in anhydrous dichloromethane (10 mL) was added a solution of Ph_3P (0.22 g, 0.9 mmol) in the same solvent (5 mL) dropwise under nitrogen. The resultant mixture was then allowed to warm at room temperature and stirred for 24 h. The solvent was removed under reduced pressure, and the crude solid was chromatographed on a silica gel column using ethyl acetate/*n*-hexane (1:3) as eluent to give **3** in 93% yield, which was recrystallized from dichloromethane/diethyl ether/*n*-hexane (1:2:1): mp 142−144 °C, red prisms; ^{1}H NMR ($CDCl_3$) *δ* 0.97 (t, 3H, *J* = 7.1 Hz), 3.82 (q, 2H, *J* = 7.2 Hz), 4.04 (s, 5H), 4.17 (t, 2H, *J* = 1.8 Hz), 4.87 (t, 2H, *J* = 1.7 Hz), 6.52 (d, 1H, $^4J_{PH}$ = 6.3 Hz), 7.39−7.45 (m, 9H) 7.76 (ddd, 6H, $^3J_{PH}$ = 12, ^3J = 7.8, and ^4J = 1.6 Hz); ^{13}C NMR ($CDCl_3$) *δ* 14.1, 60.4, 68.3, 68.9, 69.7, 82.9, 117.0 (d, $^3J_{PC}$ = 20.6 Hz), 128.1 (d, $^3J_{PC}$ = 20.6 Hz), 130.8 (d, $^4J_{PC}$ = 20.6 Hz), 132.4 (d, $^2J_{PC}$ = 9.6 Hz), 133.5 (d, $^1J_{PC}$ = 102.7 Hz), 134.1 (d, $^2J_{PC}$ = 7.1 Hz), 167.7 (d, $^3J_{PC}$ = 20.6 Hz); ^{31}P NMR ($CDCl_3$) *δ* 4.9; EI-MS *m/z* (relative intensity) 559 (M$^+$, 100), 226 (16), 183 (59), 121 (57). Anal. Calcd for $C_{33}H_{30}NO_2PFe$: C, 70.85; H, 5.41; N, 2.51. Found: C, 70.61; H, 5.59; N, 2.29.

General Procedure for the Preparation of Ferrocenylimidazoles 6. To a solution of iminophosphorane **3** (0.25 g, 0.5 mmol) in anhydrous dichloromethane (15 mL) was added the appropriate isocyanate (0.5 mmol) in the same solvent (5 mL). The resultant reaction mixture was stirred at room

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(20) *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, 1992; Vol. C, pp 193−199, 219−222, and 500−502.

temperature for 24 h. The corresponding amine (0.5 mmol) was then added, and the reaction mixture was stirred at that temperature for 24 h. The solution was concentrated to dryness, and the residual material was chromatographed on a silica gel column using ethyl acetate/*n*-hexane (1:3) as eluent to give compounds **6**, which were recrystallized from the appropriate solvent.

6a: yield 86%; mp 197−198 °C; red prisms (dichloromethane/diethyl ether 1:3); IR (Nujol) 3326, 1686, 1652 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.23 (t, 3H, J = 7.2 Hz), 1.35 (t, 3H, J = 7.2 Hz); 3.55−3.67 (m, 4H)), 4.13 (s, 5H), 4.37 (br s, 2H), 4.66 (m, 1H), 4.94 (br s), 6.59 (s, 1H); ^{13}C NMR (CDCl$_3$) δ 14.3, 15.0, 33.8, 36.9, 69.4, 70.2, 70.7, 79.2, 118.8, 137.6, 155.3, 169.2; EI-MS *m/z* (relative intensity) 351 (M$^+$, 100), 286 (74), 121 (60). Anal. Calcd for $C_{18}H_{21}N_3OFe$: C, 61.55; H, 6.03; N, 11.96. Found: C, 61.93; H, 6.21; N, 11.67.

6b: yield 98%; mp 134−135 °C; red prisms (dichloromethane/diethyl ether 1:3); IR (Nujol) 3318, 1686, 1644 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.96 (t, 3H, J = 7.5 Hz), 1.04 (t, 3H, J = 7.5 Hz), 1.63 (qn, 3H, J = 7.4 Hz), 1.76 (qn, 3H, J = 7.3 Hz), 3.47−3.56 (m, 4H), 4.13 (s, 5H), 4.38 (t, 2H, J = 1.8 Hz), 4.49 (m, 1H), 4.93 (br s, 2H), 6.59 (s, 1H); ^{13}C NMR (CDCl$_3$) δ 11.4, 11.5, 22.4, 22.9, 40.7, 43.7, 69.4, 70.2, 70.7, 79.3, 118.8, 137.5, 155.6, 169.4; EI-MS *m/z* (relative intensity) 379 (M$^+$, 100), 314 (26), 121 (51). Anal. Calcd for $C_{20}H_{25}N_3OFe$: C, 63.34; H, 6.64; N, 11.08. Found: C, 63.59; H, 6.22; N, 11.43.

6c: yield 72%; mp 186−188 °C; red prisms (ethyl acetate/*n*-hexane 1:3); IR (Nujol) 3333, 1682, 1647 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.12 (s, 5H), 4.39 (t, 2H, J = 1.8 Hz), 4.59 (s, 3H), 4.76 (s, 2H), 4.95 (br s, 2H), 6.72 (s, 1H), 7.20−7.31 (m, 10H); ^{13}C NMR (CDCl$_3$) δ 42.8, 45.7, 69.5, 70.5, 70.9, 78.9, 120.5, 127.0, 127.5, 127.6, 128.2, 128.7, 129.2, 135.4, 136.9, 138.1, 155.4, 169.2; EI-MS *m/z* (relative intensity) 475 (M$^+$, 29), 91 (100). Anal. Calcd for $C_{28}H_{25}N_3OFe$: C, 70.75; H, 5.30; N, 8.84. Found: C, 70.39; H, 5.47; N, 9.09.

6d: yield 68%; mp 186−188 °C; red prisms (dichloromethane/diethyl ether 1:3); IR (Nujol) 3361, 1705, 1658 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.27 (s, 3H), 4.15 (s, 5H), 4.40 (t, 2H, J = 1.8 Hz), 4.70 (s, 3H), 4.99 (t, 2H, J = 1.8 Hz), 6.73 (s, 1H), 7.39−7.61 (m, 9H); ^{13}C NMR (CDCl$_3$) δ 21.2, 45.8, 69.5, 70.4, 70.8, 79.0, 120.2, 127.2, 127.8, 128.0, 128.8, 129.3, 130.8, 136.8, 138.2, 139.2, 154.6, 168.6; EI-MS *m/z* (relative intensity) 475 (M$^+$, 58), 121 (73), 91 (100). Anal. Calcd for $C_{28}H_{25}N_3OFe$: C, 70.75; H, 5.30; N, 8.84. Found: C, 70.43; H, 5.49; N, 8.67.

α-(Ethoxycarbonyl)-*β*-ferrocenylvinyl Isocyanate (9). A mixture of iminophosphorane **3** (0.25 g, 0.5 mmol), dry toluene (30 mL), and solid CO$_2$ (0.4 g) was heated in a sealed tube at 110 °C for 12 h. After cooling, the solvent was removed under reduced pressure, and the residue was chromatographed on a silica gel column using dichloromethane/*n*-hexane (1:2) as eluent to give **9** in 86% yield, which was recrystallyzed from dichloromethane/diethyl ether/*n*-hexane (1:2:1): mp 104−105 °C; red prisms; IR (Nujol) 2232, 1698, 1637 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.32 (t, 3H, J = 7.1 Hz), 4.09 (s, 5H), 4.27 (q, 2H, J = 7.1 Hz), 4.36 (t, 2H, J = 1.8 Hz), 4.70 (t, 2H, J = 1.8 Hz), 6.73 (s, 1H); ^{13}C NMR (CDCl$_3$) δ 14.3, 62.6, 69.6, 70.6, 71.0, 76.1, 130.1, 131.2, 164.3; EI-MS *m/z* (relative intensity) 525 (M$^+$, 68), 121 (100). Anal. Calcd for $C_{16}H_{15}NO_3Fe$: C, 59.10; H, 4.65; N, 4.31. Found: C, 59.46; H, 4.79; N, 4.16.

Bis[α-(Ethoxycarbonyl)-*β*-ferrocenylvinyl]carbodiimide (10). A mixture of iminophosphorane **3** (0.38 g, 0.7 mmol), isocyanate **9** (0.22 g, 0.7 mmol), and dry toluene (30 mL) was heated at reflux temperature for 2 h. After cooling, the solution was concentrated to dryness, and the residue was chromatographed on a silica gel column using dichloromethane as eluent to give **10** in 99% yield, which was recrystallized from dichloromethane/diethyl ether (1:1): mp 195−197 °C; red prisms; IR (Nujol) 2132, 2069, 1700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.36 (t, 6H, J = 7.1 Hz), 4.20 (s, 10H), 4.29 (q, 4H, J = 7.1 Hz), 4.41 (t, 4H, J = 1.9 Hz), 4.90 (t, 4H, J = 1.8 Hz), 7.01 (s, 2H); ^{13}C NMR (CDCl$_3$) δ 14.3, 61.7, 69.6, 70.6, 70.9, 77.2, 122, 130.0, 133.9, 164.4; EI-MS *m/z* (relative intensity) 606 (M$^+$, 32), 121 (100). Anal. Calcd for $C_{31}H_{30}N_2O_4Fe_2$: C, 61.41; H, 4.99; N, 4.62. Found: C, 61.75; H, 4.82; N, 4.44.

Reaction of Carbodiimide 10 with Primary Amines. General Procedure. To a solution of carbodiimide **10** (0.25 g, 0.41 mmol) in dry dichloromethane (15 mL) was added the corresponding amine (0.41 mmol). The resultant reaction mixture was stirred at room temperature for 24 h. The solution was concentrated to dryness, and the residual material was chromatographed on a silica gel column using diethyl ether/*n*-hexane (1:3) (for **11a** and **11b**) or ethyl acetate/*n*-hexane (1:3) (for **11c**, **11d**, **12a**, **12b**, and **13**) as eluents to give **11** and/or **12**, or **13**, which were recrystallized from the appropriate solvent.

11a: yield 94%; mp 68−70 °C; red prisms (dichloromethane/diethyl ether 1:3); IR (Nujol) 3276, 1681, 1659 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.37 (t, 3H, J = 7.2 Hz), 1.43 (t, 3H, J = 7.2 Hz), 3.93 (q, 2H, J = 6.9 Hz), 4.07 (s, 5H), 4.15 (s, 5H), 4.25 (t, 2H, J = 1.8 Hz), 4.29−4.33 (m, 6H), 4.58 (t, 2H, J = 1.8 Hz), 6.33 (s, 1H), 7.00 (s, 1H), 7.13 (s, 1H); ^{13}C NMR (CDCl$_3$) δ 13.7, 14.4, 34.4, 61.5, 68.7, 69.6, 69.5, 70.2, 70.3, 70.4, 77.3, 78.0, 108.7, 125.9, 127.9, 130.7, 144.6, 163.5, 166.6; EI-MS *m/z* (relative intensity) 605 (M$^+$, 15), 121 (100). Anal. Calcd for $C_{31}H_{31}N_3O_3Fe_2$: C, 61.51; H, 5.16; N, 6.94. Found: C, 61.28; H, 5.40; N, 6.71.

11b: yield 86%; mp 79−80 °C; red prisms (dichloromethane/diethyl ether/*n*-hexane 1:1:4); IR (Nujol) 3275, 1684, 1655 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.05 (t, 3H, J = 7.4 Hz), 1.36 (t, 3H, J = 7.2 Hz), 1.89 (sext, 2H, J = 7.5 Hz), 3.82 (m, 2H), 4.07 (s, 5H), 4.14 (s, 5H), 4.20 (t, 2H, J = 1.9 Hz), 4.23−4.34 (m, 6H), 4.57 (t, 2H, J = 1.9 Hz), 6.33 (s, 1H), 7.08 (s, 1H), 7.26 (s, 1H); ^{13}C NMR (CDCl$_3$) δ 11.4, 14.4, 21.6, 61.4, 68.7, 69.5, 69.6, 70.2, 70.3, 70.4, 77.3, 78.0, 108.7, 125.7, 127.0, 130.6, 144.7, 163.8, 165.9; EI-MS *m/z* (relative intensity) 619 (M$^+$, 14), 573 (11), 121 (100). Anal. Calcd for $C_{32}H_{33}N_3O_3Fe_2$: C, 62.06; H, 5.37; N, 6.79. Found: C, 62.29; H, 5.16; N, 6.92.

11c: yield 83%; mp 174−176 °C; red prisms (dichloromethane/diethyl ether 1:3); IR (Nujol) 3309, 1682, 1657 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.36 (t, 3H, J = 7.1 Hz), 4.06 (s, 5H), 4.08 (s, 5H), 4.16 (t, 2H, J = 1.8 Hz), 4.25−4.33 (m, 8H), 5.05 (s, 2H), 6.38 (s, 1H), 7.01 (s, 1H), 7.09 (s, 1H), 7.32−7.41 (m, 3H), 7.53−7.55 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 14.4, 42.7, 61.4, 68.7, 69.4, 69.5, 70.3, 70.4, 70.5, 77.2, 77.8, 109.2, 125.7, 127.2, 127.5, 128.3, 128.6, 130.3, 136.7, 144.5, 163.7, 165.9; EI-MS *m/z* (relative intensity) 667 (M$^+$, 6), 191 (100), 121 (41). Anal. Calcd for $C_{36}H_{33}N_3O_3Fe_2$: C, 64.79; H, 4.98; N, 6.30. Found: C, 64.56; H, 5.13; N, 6.48.

11d (R_f = 0.44): yield 62%; mp 61−63 °C; red prisms; IR (Nujol) 3267, 1659, 1105 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.35 (t, 3H, J = 7.1 Hz), 1.64 (d, 6H, J = 7.0 Hz), 4.05 (s, 5H), 4.14 (s, 5H), 4.21−4.34 (m, 8H), 4.55 (t, 2H, J = 1.8 Hz), 4.78 (sept, 1H, J = 7.0 Hz), 6.26 (s, 1H), 6.82 (br s, 1H), 7.11 (s, 1H); ^{13}C NMR (CDCl$_3$) δ 14.4, 19.8, 44.4, 61.4, 68.6, 69.4, 69.5, 70.1, 70.2, 70.3, 77.5, 78.1, 107.9, 125.8, 126.3, 131.0, 144.7, 163.6, 165.8; EI-MS *m/z* (relative intensity) 619 (M$^+$, 11), 121 (100). Anal. Calcd for $C_{32}H_{33}N_3O_3Fe_2$: C, 62.06; H, 5.37; N, 6.78. Found: C, 62.35; H, 5.19; N, 6.54.

12a (R_f = 0.22): yield 26%; mp 213−214 °C; red prisms; IR (Nujol) 3285, 1704, 1656 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.16 (d, 3H, J = 6.6 Hz), 1.25 (d, 3H, J = 6.6 Hz), 1.30 (t, 3H, J = 6.9 Hz), 4.04 (d, 1H, J = 7.8 Hz), 4.17 (s, 5H), 4.22 (s, 5H), 4.25−4.46 (m, 9H), 4.97 (br s, 1H), 5.09 (br s, 1H), 6.70 (s, 1H), 7.92 (s, 1H); ^{13}C NMR (CDCl$_3$) δ 14.2, 22.7, 22.8, 43.9, 61.6, 68.9, 69.6, 70.2, 70.3, 70.4, 70.7, 71.0, 71.9, 72.7, 72.9, 73.7, 79.2, 115.6, 118.9, 137.2, 145.2, 152.9, 163.9, 168.3; EI-MS *m/z* (relative intensity) 619 (M$^+$, 100), 121 (18). Anal. Calcd for $C_{32}H_{33}N_3O_3Fe_2$: C, 62.06; H, 5.37; N, 6.78. Found: C, 61.69; H, 5.54; N, 7.08.

12b: yield 40%; mp 116−118 °C; red prisms (ethyl acetate/*n*-hexane 1:2); IR (Nujol) 3344, 1710, 1652 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.31 (t, 3H, J = 7.1 Hz), 1.47 (s, 9H), 4.04 (s, 1H), 4.16 (s, 5H), 4.22 (s, 5H), 4.25−4.47 (m, 8H), 4.98 (br s, 1H), 5.09 (br s, 1H), 6.68 (s, 1H), 7.91 (s, 1H); ^{13}C NMR (CDCl$_3$) δ

14.2, 28.9, 52.4, 61.5, 69.0, 69.5, 70.2, 70.3, 70.4, 70.7, 70.9, 71.9, 72.5, 72.8, 73.7, 79.1, 115.7, 118.8, 137.2, 145.2, 151.8, 163.9, 167.7; EI-MS *m*/*z* (relative intensity) 633 (M^+, 100), 121 (77). Anal. Calcd for $C_{33}H_{35}N_3O_3Fe_2$: C, 62.58; H, 5.57; N, 6.64. Found: C, 62.19; H, 5.39; N, 6.82.

13: yield 60%; mp 216−217 °C; orange prisms (dichloromethane/diethyl ether 1:1); IR (Nujol) 3349, 1678, 1659 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.37 (t, 3H, $J = 7.2$ Hz), 4.04 (s, 5H), 4.14 (s, 5H), 4.15 (t, 2H, $J = 1.5$ Hz), 4.21 (t, 2H, $J = 1.8$ Hz), 4.22 (s, 5H), 4.27−4.33 (m, 6H), 4.51 (t, 2H, $J = 1.8$ Hz), 4.56 (t, 2H, $J = 1.8$ Hz), 4.78 (s, 2H), 6.29 (s, 1H), 6.91 (s, 1H), 7.11 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.5, 38.6, 61.5, 68.2, 68.7, 68.8, 69.5, 69.6, 70.1, 70.2, 70.4, 70.6, 77.1, 78.8, 83.5, 108.7, 125.7, 126.8, 130.7, 144.4, 163.3, 166.0; EI-MS *m*/*z* (relative intensity) 776 ($M^+ + 1$, 81). Anal. Calcd for $C_{40}H_{37}N_3O_3Fe_3$: C, 61.97; H, 4.81; N, 5.42. Found: C, 61.80; H, 4.89; N, 5.63.

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Supporting Information Available: A listing of all refined and calculated atomic coordinates, all the anisotropic thermal parameters, and full bond lengths and angles for compounds **6c** and **11c** and **12b**·$^1/_2Et_2O$ (20 pages). See any current masthead page for ordering information and Internet access instructions.

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