Reductive Coupling Reaction of Aryliminomethylferrocenes with Triethyl Orthoformate Induced by Low-valent Titanium

GONG, Jun-Fang[a](龚军芳) WU, Yang-Jie*,[a](吴养洁) CUI, Xiu-Ling[a](崔秀灵)
DU, Chen-Xia[b](杜晨霞) ZHU, Yu[b](朱玉)
[a] *Department of Chemistry, Zhengzhou University, Zhengzhou, Henan 450052, China*
[b] *Henan Provincial Key Laboratory of Applied Chemistry, Zhengzhou University, Zhengzhou, Henan 450052, China*

Reductive coupling reaction of aryliminomethylferrocenes FcCH=NAr [(1, Ar = C_6H_5 (a), *p*-ClC_6H_4 (b), *p*-BrC_6H_4 (c), *p*-$CH_3C_6H_4$ (d), *m*-ClC_6H_4 (e)] with triethyl orthoformate (2) in Zn-$TiCl_4$ system gave three kinds of products: 1,3-diaryl-4,5-diferrocenyl imidazolidines (3), *N*,*N*-disubstituted formamides (4), and 1,2-diferrocenyl ethylene (5). ^1H NMR spectra proved that all the compounds 3 obtained were *dl*-isomers. All the new compounds 3 and 4 were characterized by elemental analysis, ^1H NMR, ^{13}C NMR (for 3) and IR spectra. The molecular structure of 3c was determined by X-ray diffraction.

Keywords Low-valent titanium, reductive coupling reaction, ferrocenyl-substituted compounds, single-crystal structure

Introduction

Low-valent titanium reagents have been widely used in synthetic organic chemistry as reagents for inter- and intra-molecular coupling, reductive elimination and alkylidenation,[1-2] in which coupling reaction plays important roles in many kinds of synthetic methods, such as coupling of aldehydes and ketones to olefins (McMurry reaction),[2] α, β-unsaturated ketones to cyclopentanols,[3] imines to diamines and pyrroles.[4-5] Various reducing agents for the reduction of $TiCl_3$ or $TiCl_4$ have been used to generate low-valent titanium species such as Zn,[3,6] Et_3N,[4-5] $LiAlH_4$,[7] Mg powder,[8] $Mg/HgCl_2$,[9] Sm,[10] *etc*, but these low-valent titanium systems are rarely employed in organometallic compounds. Some examples in this field were the coupling of organometallic carbonyl compounds.[11-14] Recently, Li, *et al*. described an easy and new one-pot synthesis of aryl-substituted imidazolidine derivatives induced by low-valent titanium.[15] Imidazolidines are of great biological interest since they may act as carriers of either pharmacologically active ethylenediamines[16-17] or carbonyl compounds.[18] Owing to their biological activities and in connection with our interest in the study of ferrocenyl-substituted compounds, in this paper we report the synthesis, structure and properties of novel ferrocenyl-substituted compounds obtained from reductive coupling reaction of aryliminomethylferrocenes with triethyl orthoformate induced by low-valent titanium.

Results and discussion

Coupling reaction

Aryliminomethylferrocenes (**1**), treated with Zn-$TiCl_4$ in THF, react with triethyl orthoformate (**2**) for about 50 h to give the corresponding 1,3-diaryl-4,5-diferrocenyl imidazolidines (**3**), *N*,*N*-disubstituted formamides (**4**), and 1,2-diferrocenyl ethylene (**5**) (Scheme 1). All the new compounds **3** and **4** were characterized by elemental analysis, IR and ^1H NMR spectra, additionally, ^{13}C NMR for **3**. The distributions of the products are listed in Table 1. The total yields of **3**, **4**, **5** were moderate (40%—48%). Unfortunately, it was found that the yields of the imidazolidines **3** were rather low and the main products were formamides **4**.

* E-mail: wyj@mail.zzu.edu.cn; Tel: 0371-7763207; Fax: 0371-7979408
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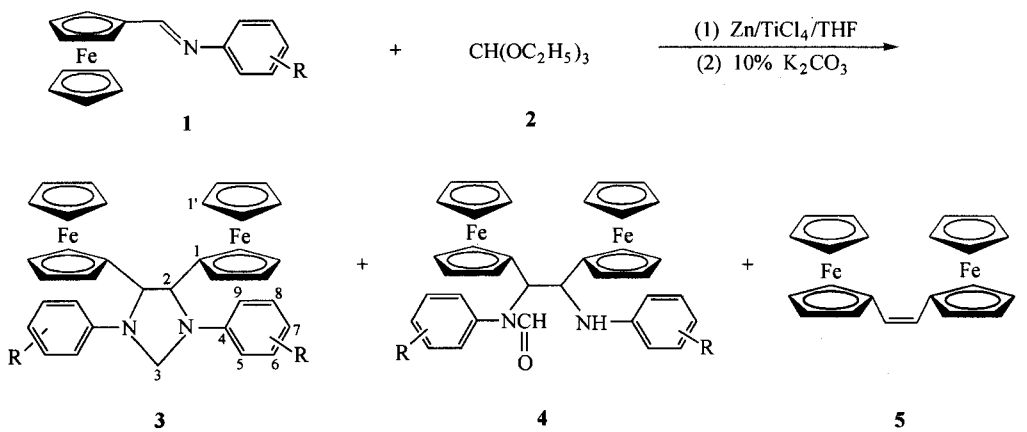
Further study showed that there was no significant change of the distributions of the products by prolonging the reaction time from 50 h to 72 h (for **3a**). This was different from the reaction of benzylideneanilines with triethyl orthoformate reported by Li, *et al*.,[15] where the formamides as reaction intermediates could be converted into imidazolidines by prolonging the reaction time. A possible mechanism was proposed by drawing analogy from the reductive coupling of imines induced by low-valent titanium (Scheme 2).[4,8,9]

Scheme 1



Scheme 2

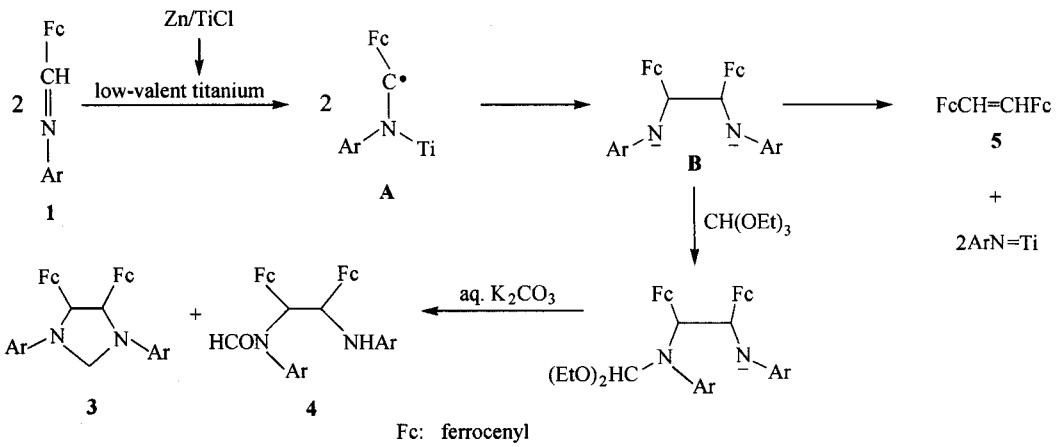


Table 1 Distributions of the products **3**, **4** and **5**

	R	**3**(*dl*, %)	**4** (%)	**5** (%)
a	H	6.0	34.7	7.2
b	*p*-Cl	8.5[a]	28.2	7.5
c	*p*-Br	7.2[b]	26.1	7.6
d	*p*-CH_3	6.4	25.4	8.4
e	*m*-Cl	6.1[a]	32.0	8.1

[a] Contained 0.5 CH_2Cl_2 per molecule;

[b] Contained one CH_2Cl_2 per molecule.

$TiCl_4$ is reduced by Zn dust to give low-valent titanium species. In the initial step, an electron is transferred from low-valent titanium to ferrocenylaldimines (**1**) to give a radical anion **A**, the radical anion dimerizes to form the carbon-carbon bond and generates intermediate **B**. The latter would be transformed to **3** and **4** by reacting with triethyl orthoformate and subsequent base hydrolysis or to **5** by removing two molecules of corresponding titanium complex. The low yields of **3** and **4** may be due to the severe steric crowding of the two vicinal ferrocenyl groups (especially for **3**), which was further confirmed by the single-crystal structure of **3c** as described below.

Spectral properties of the new compounds **3** and **4**

The IR spectra of **3** and **4** were consistent with a monosubstituted ferrocene structure, showing absorptions at ca. 1000 cm^{-1} and 1100 cm^{-1} which were indicative of an unsubstituted Cp ring.[19-20] For **4**, the strong absorptions at 1663—1672 cm^{-1} as well as the middle absorptions at 3333—3400 cm^{-1} belonged to carbonyl stretching vibration of tertiary amide and N—H stretching vibration of secondary amine, respectively. These IR features are in good agreement with the proposed structures for the compounds **3** and **4**.

The ^1H NMR spectra of the compounds **3** were quite simple because of the existence of C_2-symmetric axis and completely consistent with the proposed structure. For example, the ^1H NMR spectrum of **3d** exhibited a singlet at δ 4.22 integrating for the ten protons on the two unsubstituted Cp rings, and four singlets at δ 4.02, 4.06, 4.10 and 4.32, respectively, for the eight protons on the two substituted Cp rings, each singlet integrated for two protons. The two doublets at δ 6.64 and δ 7.09 were for the eight protons on the two 1,4-disubstituted phenyl rings and a singlet at δ 2.27 for the protons of methyl group. The other signals include two singlets at δ 4.66 and δ 5.29 which were assigned to the **CHCH** and CH_2 protons on the imidazolidine ring, respectively. Here ^1H NMR spectroscopy was also used to distinguish the *dl*- and *meso*- isomers of imidazolidines **3**. In *meso*-isomers, the two protons of CH_2 group had different chemical shifts, each signal would be a doublet. While in *dl*-isomers, the two protons were identical with each other and a singlet would appear. It was observed that the ^1H NMR spectra of **3** showed two singlets in the range of δ 4.64—5.36, one belonged to **CHCH** protons and the other to CH_2 protons. So it was believed that all the compounds **3** obtained were *dl*-isomers.

The **CHCH** protons and CH_2 protons could be easily identified by DEPT (135℃) and C,H-COSY spectra since the CH_2 carbon atom (C(3)) would give a reversal peak in the DEPT spectra. The ^{13}C NMR and DEPT spectra of **3c** are shown in Fig. 1 and the C,H-COSY

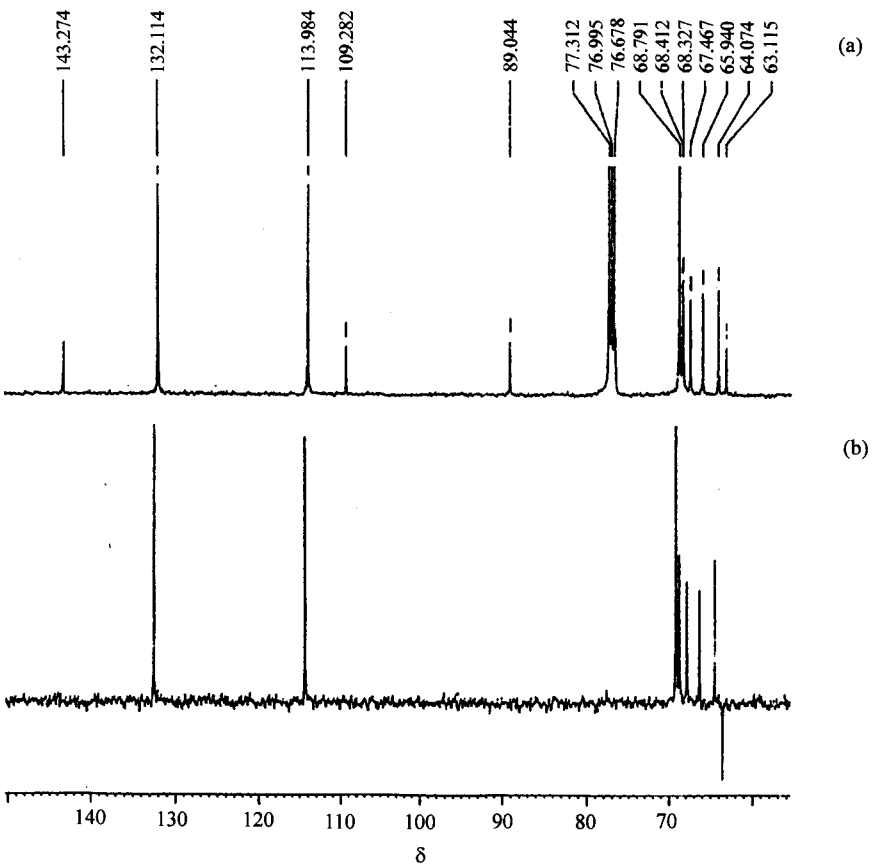


Fig. 1 ^{13}C NMR (a) and DEPT (135℃) (b) spectra of **3c**.

spectrum in Fig. 2. The signal at δ 63.1 was assigned to C(3) since it was reversal. From the C, H-COSY spectrum, it was found that the signal at δ 4.64 was correlated with δ 63.1 and the signal at δ 5.28 correlated with δ 64.1. Therefore it could be concluded that the signal at δ 4.64 belonged to CH_2 protons and the signal at δ 5.28 was for **CHCH** protons. Furthermore, the signal at δ 64.1 was assigned to **CHCH** carbon atoms (C(2)). The quaternary carbon atoms were identified by their relatively low intensity in the ^{13}C NMR spectra and their disappearance in the DEPT spectra. Other carbon atoms in the *N*-phenyl ring were identified by empirical formula. The ^{1}H NMR and ^{13}C NMR spectra of the other compounds **3** were assigned based on the above results.

X-ray single crystal structure of **3c**

The molecular structure of **3c** has been determined by X-ray diffraction method as shown with the atom numbering scheme in Fig. 3. Atomic positional parameters and isotropic temperature factors are given in Table 2. Selected bond distances and angles are presented in Table 3 and 4, respectively.

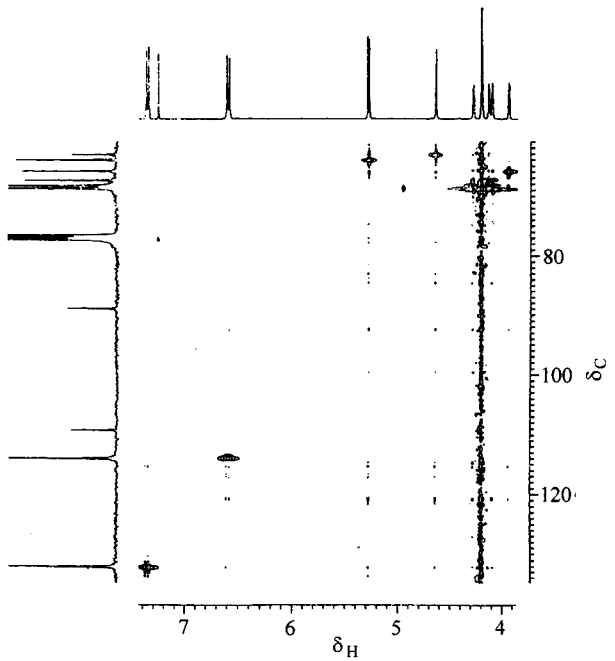


Fig. 2 C, H-COSY spectrum of **3c**.

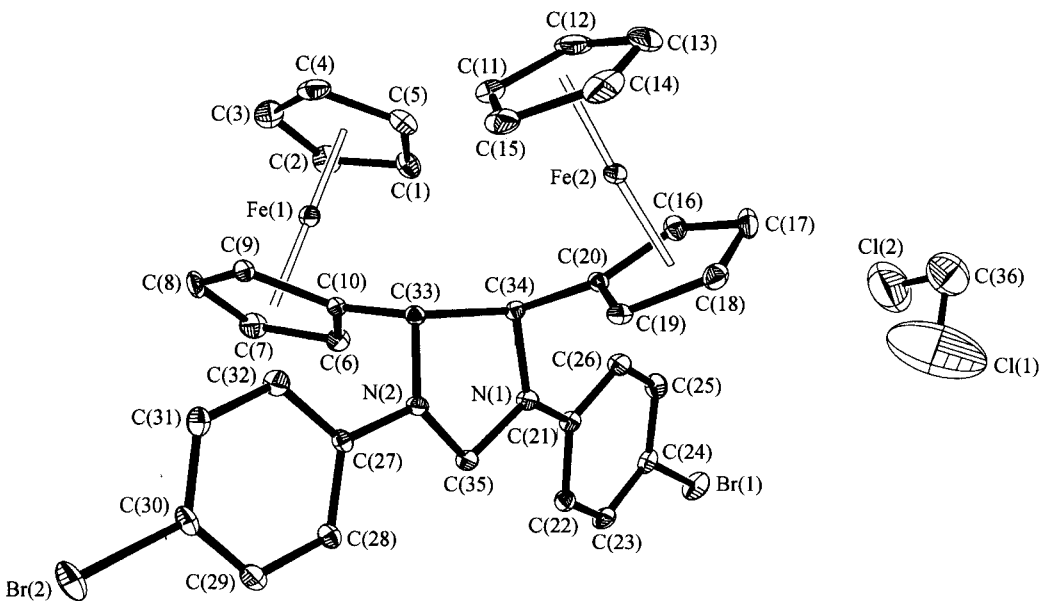


Fig. 3 Molecular structure of **3c**.

The structure determined is completely consistent with that proposed for the compounds **3**, which has been supported by the spectral data. The Cp rings in two ferrocenyl groups are nearly parallel to each other, with the dihedral angles 2.8° and 4.0° respectively. The average Fe—C distances are 0.2029 nm and 0.2036 nm for unsubstituted and substituted Cp rings, respectively, and the average C—C distances in the ferrocenyl moiety are 0.1398 and 0.1416 nm for unsubstituted and substituted Cp rings, respectively. The five-membered imidazolidine ring adopts an envelope-like conformation because of the severe steric crowding of the two vicinal ferrocenyl

Table 2 Atomic coordinates ($nm \times 10^3$) and equivalent isotropic displacement parameters ($nm^2 \times 10$) for **3c**

Atom	x	y	z	U(eq)
Fe(1)	-3240(1)	1734(1)	11654(1)	45(1)
Fe(2)	629(1)	1696(1)	7925(1)	43(1)
Br(1)	-4523(1)	-593(1)	8887(1)	76(1)
Br(2)	5337(1)	1663(1)	16463(1)	80(1)
N(1)	-573(3)	766(1)	10514(3)	41(1)
N(2)	942(3)	1160(1)	11851(3)	38(1)
C(2)	-5340(5)	1753(2)	10958(6)	78(2)
C(3)	-4848(6)	2122(2)	11320(6)	86(2)
C(1)	-4624(5)	1618(2)	9976(5)	65(2)
C(5)	-3665(6)	1907(2)	9736(5)	65(2)
C(4)	-3792(6)	2219(2)	10569(6)	80(2)
C(6)	-2333(5)	1219(1)	12325(4)	51(1)
C(7)	-3033(5)	1389(1)	13277(5)	67(2)
C(8)	-2436(5)	1753(2)	13593(4)	62(2)
C(9)	-1358(5)	1819(1)	12852(4)	49(1)
C(10)	-1294(4)	1483(1)	12049(4)	37(1)
C(11)	-60(6)	2190(1)	8702(5)	64(2)
C(12)	-589(7)	2166(2)	7394(6)	90(2)
C(13)	511(8)	2157(2)	6696(6)	106(3)
C(14)	1768(6)	2172(1)	7609(7)	96(2)
C(15)	1399(6)	2187(1)	8886(6)	70(2)
C(16)	-586(5)	1214(1)	7483(4)	51(1)
C(17)	529(6)	1224(1)	6744(5)	65(2)
C(18)	1817(5)	1226(1)	7623(5)	60(2)
C(19)	1512(4)	1216(1)	8920(4)	43(1)
C(20)	27(4)	1210(1)	8825(4)	37(1)
C(21)	-1460(4)	458(1)	10142(4)	41(1)
C(22)	-1354(5)	111(1)	10848(4)	49(1)
C(23)	-2259(5)	-197(1)	10480(5)	54(1)
C(24)	-3291(5)	-168(1)	9396(5)	51(1)
C(25)	-3419(5)	168(1)	8657(5)	58(2)
C(26)	-2510(5)	476(1)	9019(4)	51(1)
C(27)	1884(4)	1278(1)	12932(4)	39(1)
C(28)	2637(5)	1005(1)	13766(4)	49(1)
C(29)	3653(5)	1121(1)	14815(5)	54(1)
C(30)	3939(4)	1508(1)	15036(4)	48(1)
C(31)	3195(5)	1784(1)	14239(4)	51(1)
C(32)	2179(4)	1675(1)	13194(4)	48(1)
C(33)	-206(4)	1408(1)	11185(4)	36(1)
C(34)	-763(4)	1161(1)	9967(4)	34(1)
C(35)	453(4)	760(1)	11708(4)	41(1)
C(36)	-2413(12)	249(3)	4119(11)	297(7)
Cl(1)	-2327(12)	466(2)	5425(8)	380(8)
Cl(2)	-2464(11)	-215(2)	3988(7)	298(5)

Table 3 Selected bond lengths (10^{-1} nm) for **3c**

Fe(1)—C(1)	2.038(5)	Fe(1)—C(2)	2.028(5)
Fe(1)—C(3)	2.027(5)	Fe(1)—C(4)	2.026(5)
Fe(1)—C(5)	2.046(5)	Fe(1)—C(6)	2.040(4)
Fe(1)—C(7)	2.039(5)	Fe(1)—C(8)	2.025(4)
Fe(1)—C(9)	2.033(4)	Fe(1)—C(10)	2.041(4)
N(1)—C(21)	1.371(5)	N(1)—C(35)	1.444(5)
N(1)—C(34)	1.468(5)	N(2)—C(27)	1.374(5)
N(2)—C(35)	1.448(5)	N(2)—C(33)	1.469(5)
C(2)—C(3)	1.381(8)	C(2)—C(1)	1.405(7)
C(3)—C(4)	1.425(8)	C(1)—C(5)	1.407(7)
C(5)—C(4)	1.396(7)	C(6)—C(7)	1.415(7)
C(6)—C(10)	1.417(6)	C(7)—C(8)	1.391(7)
C(8)—C(9)	1.415(7)	C(9)—C(10)	1.430(6)
C(10)—C(33)	1.516(6)	C(20)—C(34)	1.526(6)
C(33)—C(34)	1.538(5)		

groups. C(34), N(1), C(35), N(2) are essentially coplanar with average deviation of 0.0015 nm, and the distance between C(33) and the plane is 0.0589 nm.

The lattice structure of compound **3c** is found to be built around π-π interactions of Br(1)-substituted phenyl rings as well as the weak hydrogen bonds linking H(5) and Br(2) as shown in Fig. 4. The distance of the π-π interactions is 0.342 nm. The length of the hydrogen bonds and the angle of Br(2)-H(5)-C(5) are 0.3015 nm and 109.2°, respectively.

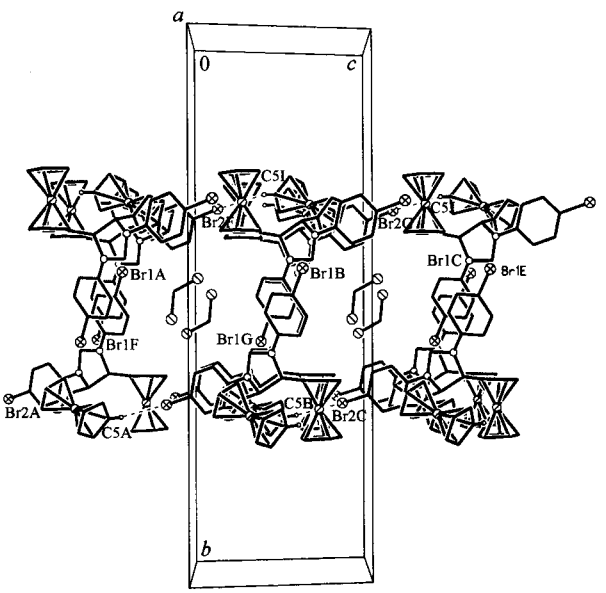


Fig. 4 Lattice structure of compound **3c** viewed along *a* (Hydrogen bonds are shown as dotted lines).

Table 4 Selected bond angles (°) for **3c**

C(21)-N(1)-C(35)	122.1(3)	C(21)-N(1)-C(34)	125.0(3)
C(35)-N(1)-C(34)	111.3(3)	C(27)-N(2)-C(35)	121.3(3)
C(27)-N(2)-C(33)	123.2(3)	C(35)-N(2)-C(33)	107.2(3)
N(1)-C(21)-C(22)	121.8(4)	N(1)-C(21)-C(26)	121.5(4)
N(2)-C(27)-C(32)	121.7(4)	N(2)-C(33)-C(10)	111.3(3)
N(2)-C(27)-C(28)	120.5(4)	N(1)-C(34)-C(20)	110.8(3)
N(1)-C(34)-C(33)	101.0(3)	C(20)-C(34)-C(33)	115.3(3)
N(1)-C(35)-N(2)	103.7(3)	N(2)-C(33)-C(34)	101.1(3)
C(10)-C(33)-C(34)	113.6(3)	C(3)-C(2)-C(1)	108.1(5)
C(2)-C(3)-C(4)	108.0(5)	C(2)-C(1)-C(5)	108.5(5)
C(4)-C(5)-C(1)	107.4(5)	C(5)-C(4)-C(3)	107.9(5)
C(7)-C(6)-C(10)	108.6(4)	C(8)-C(7)-C(6)	107.8(4)
C(7)-C(8)-C(9)	109.2(4)	C(8)-C(9)-C(10)	107.3(4)
C(6)-C(10)-C(9)	107.1(4)	C(6)-C(10)-C(33)	126.8(4)
C(9)-C(10)-C(33)	125.8(4)	C(16)-C(20)-C(34)	125.9(4)
C(19)-C(20)-C(34)	125.6(4)		

Experimental

General

Melting points were measured on a WC-1 apparatus and uncorrected. Elemental analyses were determined with a Carlo Erba 1160 elemental analyzer. IR spectra were recorded on a Perkin-Elmer FTIR 1750 spectrophotometer. ^{1}H NMR, ^{13}C NMR, DEPT and C, H-COSY spectra were recorded on a Bruker DPX 400 spectrometer using $CDCl_3$ as solvent and TMS as an internal standard. All reactions were performed under an argon atmosphere using standard Schlenk techniques. THF was freshly distilled from sodium-benzophenone under argon. Zinc dust was activated by being soaked in 5% HCl, then washed with water, acetone, ether successively and dried *in vacuo*. $TiCl_4$ and triethyl orthoformate were distilled before use. Aryliminomethylferrocenes were prepared according to the published literature.[21] Other chemicals were used as purchased.

Preparation of novel ferrocenyl-substituted compounds: general procedure

A mixture of zinc dust (0.52 g, 8 mmol) and $TiCl_4$ (0.44 mL, 4 mmol) in dry THF (10 mL) was refluxed for 3 h. After cooling to room temperature, a mixed solution of aryliminomethylferrocene (**1**, 2 mmol) and triethyl orthoformate (**2**, 0.66 mL, 4 mmol) was added dropwise. The reaction mixture was refluxed for 50 h, then quenched with 10% K_2CO_3 (60 mL) and extracted with dichloromethane. The organic layer was washed with water and dried over Na_2SO_4. The resulting solution was evaporated *in vacuo* to a minimum amount and subjected to a dry column of silica gel under reduced pressure, then eluted with dichloromethane. The first band afforded mixture of **3** and **5**, the second yellow band gave compounds **4**. Compounds **3** were separated from **5** by preparative TLC developed with petroleum ether (60—90℃)/dichloromethane (3/1). The first yellow band afforded compound **5**, and the second band gave orange-red crystals **3** after the evaporation of the solvent and recrystallization from petroleum ether-dichloromethane.

1,3-*Diphenyl*-4,5-*diferrocenyl imidazolidine* (**3a** (*dl*))

Orange crystals, m.p. 240℃ (dec.); ^{1}H NMR ($CDCl_3$) δ: 4.02 (s, 2H), 4.07 (s, 2H), 4.10 (s, 2H), 4.21 (s, 10H), 4.32 (s, 2H), 4.73 (s, 2H), 5.36 (s, 2H), 6.73—6.78 (m, 6H), 7.26—7.30 (m, 4H); ^{13}C NMR ($CDCl_3$) δ: 63.0 (C(3)), 63.8 (C(2)), 66.2, 67.2, 68.1, 68.6, 68.7 (C(1')), 89.7 (C(1)), 112.4 (C(5), C(9)), 117.1 (C(7)), 129.4 (C(6), C(8)), 144.4 (C(4)); IR (KBr) ν: 1596, 1502, 1386, 1354, 1300, 1105, 994, 743 cm^{-1}; Anal. calcd for $C_{35}H_{32}Fe_2N_2$: C 70.97, H 5.44, N 4.73; found C 71.42, H 5.51, N 4.92.

1,3-Di-(4-chlorophenyl)-4,5-diferrocenyl imidazolidine (**3b** (*dl*))

Red crystals, m.p. 244—246℃; ^{1}H NMR ($CDCl_3$) δ: 3.94 (s, 2H), 4.10 (s, 2H), 4.13 (s, 2H), 4.20 (s, 10H), 4.28 (s, 2H), 4.65 (s, 2H), 5.28 (s, 2H) 5.30 (s, 1H), 6.64 (d, J = 8.8 Hz, 4H), 7.23 (d, J = 8.8 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ: 63.2 (C(3)), 64.1(C(2)), 65.9, 67.4, 68.2, 68.4, 68.7 (C(1')), 89.1 (C(1)), 113.5 (C(5),C(9)), 122.1 (C(7)), 129.2(C(6), C(8)), 142.9 (C(4)); IR (KBr) ν: 1599, 1495, 1386, 1349, 1299, 1105, 1001, 821, 807 cm^{-1}; Anal. calcd for $C_{35}H_{30}Cl_2Fe_2N_2 \cdot 0.5CH_2Cl_2$: C 60.59, H 4.44, N 3.98; found C 60.43, H 4.66, N 3.91.

1,3-Di-(4-bromophenyl)-4,5-diferrocenyl imidazolidine (**3c** (*dl*))

Red crystals, m.p. > 250℃; ^{1}H NMR ($CDCl_3$) δ: 3.94 (s, 2H), 4.10 (s, 2H), 4.13 (s, 2H), 4.20 (s, 10H), 4.28 (s, 2H), 4.64 (s, 2H), 5.28 (s, 2H), 5.30 (s, 2H), 6.59 (d, J = 8.8 Hz, 4H), 7.36 (d, J = 8.8 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ: 63.1 (C(3)), 64.1 (C(2)), 65.9, 67.5, 68.3, 68.4, 68.8 (C(1')), 89.0 (C(1)), 109.3 (C(7)), 114.0 (C(5), C(9)), 132.1 (C(6),C(8)), 143.3 (C(4)); IR (KBr) ν: 1592, 1494, 1386, 1349, 1299, 1105, 1000, 822, 802 cm^{-1}; Anal. calcd for $C_{35}H_{30}Br_2Fe_2N_2 \cdot CH_2Cl_2$: C 51.78, H 3.86, N 3.35; found C 51.84, H 3.79, N 3.44.

1,3-Di-(4-methylphenyl)-4,5-diferrocenyl imidazolidine (**3d** (*dl*))

Orange crystals, m. p. 233—235℃; ^{1}H NMR ($CDCl_3$) δ: 2.27 (s, 6H), 4.02 (s, 2H), 4.06 (s, 2H), 4.10 (s, 2H), 4.22 (s, 10H), 4.32 (s, 2H), 4.66 (s, 2H), 5.29 (s, 2H), 6.64 (d, J = 8.0 Hz, 4H), 7.09 (d, J = 8.0 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ: 20.4 (CH_3), 63.4 (C(3)), 63.9 (C(2)), 66.3, 67.1, 68.0, 68.5, 68.7 (C(1')), 89.9 (C(1)), 112.4 (C(5), C(9)), 126.0 (C(7)), 129.8 (C(6),C(8)), 142.4 (C(4)); IR (KBr) ν: 1619, 1517, 1386, 1344, 1294, 1105, 1000, 820, 803 cm^{-1}; Anal. calcd for $C_{37}H_{36}Fe_2N_2$: C 71.63, H 5.85, N 4.52; found C 71.75, H 6.46, N 4.26.

1,3-Di-(3-chlorophenyl)-4,5-diferrocenyl imidazolidine (**3e** (*dl*))

Red crystals, m.p. 236—238℃; ^{1}H NMR ($CDCl_3$) δ: 3.98 (s, 2H), 4.12 (s, 2H), 4.14 (s, 2H), 4.22 (s, 10H), 4.30 (s, 2H), 4.67 (s, 2H), 5.30 (s, 3H), 6.59—6.61 (m, 2H), 6.70 (s, 2H), 6.74 (d, J = 8.0 Hz, 2H), 7.19 (t, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ: 62.9 (C(3)), 64.0 (C(2)), 65.8, 67.4, 68.3, 68.4, 68.7 (C(1')), 88.8 (C(1)), 110.6 (C(9)), 112.3 (C(5)), 117.2 (C(7)), 130.3 (C(8)), 135.2 (C(6)), 145.3 (C(4)); IR (KBr) ν: 1593, 1563, 1489, 1384, 1353, 1292, 1104, 997, 823, 758, 732 cm^{-1}; Anal. calcd for $C_{35}H_{30}Cl_2Fe_2N_2 \cdot 0.5CH_2Cl_2$: C 60.59, H 4.44, N 3.98; found C 60.09, H 4.54, N 3.86.

Formamide **4a**

Yellow powder, m.p. 220℃ (dec.); ^{1}H NMR ($CDCl_3$) δ: 3.89—4.80 (m, 20H), 6.59—7.37 (m, 10H), 8.31, 9.96 (2s, 1H); IR (KBr) ν: 3400, 1666, 1601, 1595, 1495, 1269, 1106, 1000, 764 cm^{-1}; Anal. calcd for $C_{35}H_{32}Fe_2N_2O$: C 69.10, H 5.30, N 4.60; found C 69.05, H 5.33, N 4.99.

Formamide **4b**

Yellow powder, m.p. 238℃ (dec.); ^{1}H NMR ($CDCl_3$) δ: 3.87—4.40 (m, 20H), 6.49—7.25 (m, 8H), 8.13, 8.27 (2s, 1H); IR (KBr) ν: 3339, 1672, 1598, 1492, 1267, 1107, 1001, 821 cm^{-1}; Anal. calcd for $C_{35}H_{30}Cl_2Fe_2N_2O$.: C 62.07, H 4.46, N 4.14; found C 61.78, H 4.54, N 4.15.

Formamide **4c**

Yellow powder, m. p. 208—210℃; ^{1}H NMR ($CDCl_3$) δ: 3.88—4.79 (m, 20H), 6.45—7.48 (m, 8H), 8.13, 8.26 (2s, 1H); IR (KBr) ν: 3358, 1671, 1591, 1488, 1264, 1106, 1005, 819 cm^{-1}; Anal. calcd for $C_{35}H_{30}Br_2Fe_2N_2O$: C 54.87, H 3.95, N 3.66; found C 55.31, H 4.05, N 3.93.

Formamide **4d**

Yellow powder, m. p. 204—206℃; ^{1}H NMR

($CDCl_3$) δ: 2.24—2.36 (m, 6H), 3.96—4.79 (m, 20H), 6.48—7.18 (m, 8H), 8.08, 8.33 (2s, 1H); IR (KBr) ν: 3335, 2919, 2850, 1669, 1617, 1511, 1263, 1107, 1002, 805 cm^{-1}; Anal. calcd for $C_{37}H_{36}Fe_2N_2O$: C 69.83, H 5.70, N 4.40; found C 69.62, H 5.34, N 4.62.

Formamide **4e**

Dark red balls, m. p. 184—186℃; ^1H NMR ($CDCl_3$) δ: 3.98—4.39 (m, 20H), 6.46—7.28 (m, 8H), 8.16, 8.31 (2s, 1H); IR (KBr) ν: 3333, 1663, 1598, 1486, 1271, 1108, 1001, 820, 794, 765 cm^{-1}; Anal. calcd for $C_{35}H_{30}Cl_2Fe_2N_2O$: C 62.07, H 4.46, N 4.14; found C 62.52, H 4.49, N 4.17.

1,2-*Diferrocenyl ethylene* **5** [11]

Dark red powder, ^1H NMR ($CDCl_3$) δ: 4.14 (s, 10H), 4.28 (s, 4H), 4.43 (s, 4H), 6.30 (s, 2H).

X-ray single crystal structure determination of **3c**

Crystal data: $C_{35}H_{30}N_2Fe_2Br_2 \cdot CH_2Cl_2$, M_r = 835.06, monoclinic, $P2_1/c$, a = 0.9644(2) nm, b = 3.4302(7) nm, c = 1.0369(2) nm, α = 90.00(0)°, β = 100.08(3)°, γ = 90.00(0)°, V = 3.3772(12) nm^3, Z = 4, D_c = 1.642 g/cm^3, F(000) = 1672, λ = 0.071070 nm, μ(Mo K_α) = 34.12 cm^{-1}.

Data collection: Crystals were grown by slow evaporation of a dichloromethane-petroleum ether solution. A red prismatic crystal of approximate dimensions of 0.30 × 0.30 × 0.20 mm^3 was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS-IV imaging plate area detector with graphite monochromated Mo K_α radiation at 15 ± 1℃. A total of 296.00° oscillation images were collected, each being exposed for 19.0 min. The crystal-to-detector distance was 100.00 mm with the detector at the zero swing position. 6529 unique reflections were measured in the range of $1.19° \leq \theta \leq 27.57°$, 4665 of which had $I > 2\sigma(I)$ and were used in all calculations. Data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied.

Structure solution and refinement: The structure was solved by direct methods[22] and expanded using Fourier techniques and refined by full-matrix least-squares methods. The non-hydrogen atoms were refined isotropically, and the hydrogen atoms were included but not refined. All calculations were performed using the teXsan[23] crystallographic software package of Molecular Structure Corporation. The final residuals R and R_w were 0.080 and 0.108, respectively.

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