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Journal of Organometallic Chemistry 691 (2006) 987–993
Journal of Organometallic Chemistry
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Ferrocenylamines 2. Reductive methylation of secondary ferrocenylamines and ferrocenylaldimines: Synthesis, characterization of [(*N*-methyl-*N*-aryl)amino]methylferrocenes, 1-[(*N*-methyl-*N*-phenyl)amino]ethylferrocene and crystal structures of $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH_2NHC_6H_4\text{-}Cl\text{-}4)]$ and $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH_2N(CH_3)\text{-}C_6H_4\text{-}OCH_3\text{-}4)]$

Hong-Xing Wang [a,b,*], Ying-Jie Li [a], Rong Jin [c], Ji-Ru Niu [a], Hong-Fei Wu [a], Hui-Chao Zhou [a], Jian Xu [a], Ren-Qing Gao [a], Feng-Ying Geng [a]

[a] *Department of Chemistry, College of Sciences, Tianjin University, Tianjin 300072, People's Republic of China*
[b] *State Key Laboratory of Elemento-organic Chemistry, Nankai University, Tianjin 300071, People's Republic of China*
[c] *Department of Ultrasound, The First Central Hospital of Tianjin, Tianjin 300192, People's Republic of China*

Received 9 July 2005; received in revised form 4 October 2005; accepted 13 October 2005
Available online 15 December 2005

Abstract

The reactions of ferrocenylaldimines (**II**) $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH{=}NC_6H_4\text{-}R)]$ (R = 4-CH_3O (**a**), 4-CH_3 (**b**), H (**c**), 4-Cl (**d**), 3-Cl (**e**), 4-NO_2 (**f**), 3-NO_2 (**g**)) and ferrocenylketimine (**I**) $[(\eta^5\text{-}C_5H_5)Fe\ (\eta^5\text{-}C_5H_4CH_3C{=}NC_6H_5)]$ with sodium borohydride in ethanol or lithium aluminum hydride in THF resulted in secondary ferrocenylamines **3**, **4**. Reductive methylation of **3** (or **II**) and **4** with aqueous formaldehyde and sodium cyanoborohydride all gave out corresponding *N*-methylated tertiary ferrocenylamines **5** $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH_2N(CH_3)C_6H_{\ 4}\text{-}R)]$ (R = same as above mentioned) and **2**, respectively, in good yields. All these tertiary ferrocenylamines **3**–**5** were characterized structurally. The crystal structures of **3d** and **5a** were also determined. Compound **3d** is monoclinic, space group $P2(1)/n$, with $a = 9.7585(14)$ Å, $b = 11.5267(17)$ Å, $c = 13.0830(19)$ Å and $\beta = 97.969(2)°$. Compound **5a** is orthorhombic, space group $Pccn$, with $a = 13.752(2)$ Å, $b = 22.095(3)$ Å, $c = 10.6421(16)$ Å.

Keywords: Ferrocenylimines; Ferrocenylamines; Reductive methylation; Crystal

1. Introduction

Tertiary amines as one kind of important nitrogen-containing ligands are widely used in organic synthesis [1]. Ferrocene since its discovery has attracted much attention in asymmetric catalysis and drug designing owing to its unique structure and low toxicity [1,2], thus, the incorporation of ferrocenyl moiety into amine molecules render ferrocenylamines, the [C,N] bidentate ligands, possess potential planar chirality [1]. Researches of the planar chirality for ferrocene complexes, e.g., Ugi amines [3] on asymmetric synthesis have already established an active field in organometallic chemistry. The planar chirality can be obtained normally by reactions of tertiary ferrocenylamines either with transition metals to form coordinated complexes and then directed the metal to activate *ortho* C–H bonds of the substrates to give out cyclometallated compounds which are potential catalysts in Suzuki

* Corresponding author.
E-mail address: hongxing_wang@hotmail.com (H.-X. Wang).

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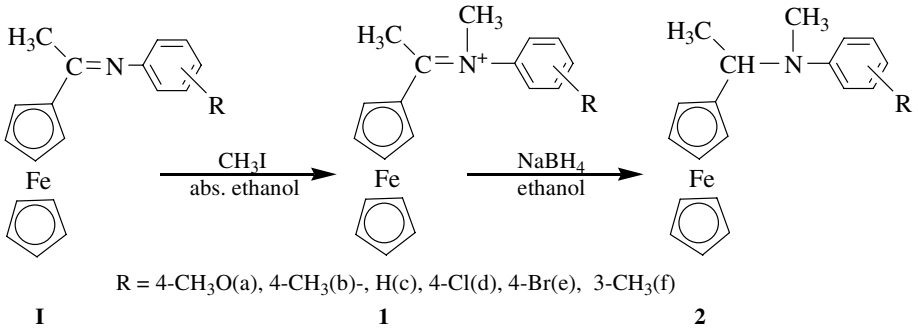
doi:10.1016/j.jorganchem.2005.10.056

reaction [4], Heck reaction [5] as well as the other usages [6] or by initial *ortho*-lithiation and followed by substitution to yield [N,P] bidentate ligands. Now, researches on the nitrogen-containing ligands in asymmetric catalysis mainly focus on oxazolinyl type [7–10] or imino form [11], in the contrast, reports on amines in asymmetric catalysis except Hayashi type [1,12] are still rare mostly because of the lack of suitable tertiary ferrocenylamines and their synthetic methods [13], though many of other aromatic tertiary amines have been prepared [14,15]. Therefore, to assess chemical properties of planar chirality of tertiary ferrocenylamines, the synthesis of suitable tertiary ferrocenylamines is necessary. Our previous work [16] demonstrated that tertiary ferrocenylamines could be synthesized by methylation of ferrocenylketimines **I** [17] with methyl iodide and followed by reduction of the corresponding iminium salts **1** to give out tertiary ferrocenylamines **2** (Scheme 1). However, this method has some practical limitations to the tertiary ferrocenylamines which bear electron-withdrawing groups on their phenyl rings. For example, for the ferrocenylketimines bearing electron-donating groups such as methoxy and methyl group, their yields of corresponding ferrocenylamines are only moderate, when the substituent is chlorine, the yield of corresponding **2d** is only 30%. However, replacement of chlorine with nitro group, no corresponding product is obtained. In order to find out a general method to prepare tertiary ferrocenylamines and explore the scope and its limitation, we wish to report here an alternative route in detail to synthesize ferrocenylamines **5**, **2** by reductive methylation [18] of secondary ferrocenylamines **3** (or ferrocenylaldimines **II**), **4**, respectively, with the system composed by aqueous formaldehyde, sodium cyanoborohydride as well as acetic acid (Scheme 2). Experiments show that this method is applicable to prepare tertiary ferrocenylamines no matter what kind of substituents on the phenyl rings. In addition, the reaction condition is mild, and easy to handle.

2. Synthesis and characterization of [(*N*-methyl-*N*-aryl)amino]methylferrocenes

*2.1. Synthesis of [(N-aryl)amino]methylferrocenes **3a–3g** and their N-methylated compounds **5a–5g***

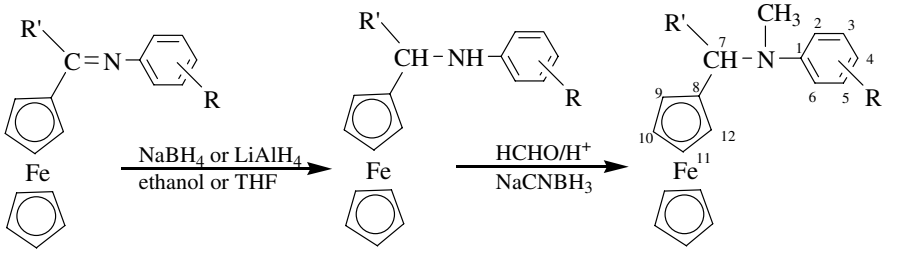
Initially, encouraged by the experiment results as shown in Scheme 1, we tried to obtain tertiary ferrocenylamines **5** with the same procedure as shown in Scheme 1,



R = 4-CH_3O(a), 4-CH_3(b)-, H(c), 4-Cl(d), 4-Br(e), 3-CH_3(f)

I **1** **2**

Scheme 1.



II R' = H, R = 4-MeO(a), 4-Me(b), H(c), 4-Cl(d), 3-Cl(e), 4-NO_2(f), 3-NO_2(g)

I R' = CH_3, R = H

3 R' = H, R = 4-MeO(a), 4-Me(b), H(c), 4-Cl(d), 3-Cl(e), 4-NO_2(f), 3-NO_2(g)

4 R' = CH_3, R = H

5 R' = H, R = 4-MeO(a), 4-Me(b), H(c), 4-Cl(d), 3-Cl(e), 4-NO_2(f), 3-NO_2(g)

2 R' = CH_3, R = H

Scheme 2.

unfortunately, our effort was unsuccessful. An attempt to isolate **5**, **2** by the nucleophilic substitution of secondary ferrocenylamines **3**, **4** (Scheme 2) with methyl iodide, ethyl bromide or benzyl chloride also failed. It is probably that for the former reaction, replacement of methyl group with a hydrogen atom in **I** could not sufficiently stabilize iminium moiety (Scheme 1), hence, only a small amount of products **5** were obtained. The explanation for the latter unsuccessful substitution might be attributed to the weaker nucleophicility of secondary ferrocenylamines **3**, **4**. Finally, we had to turn our attention to search the other method, i.e., reductive methylation [18] starting from secondary amines **3**, **4** with sodium cyanoborohydride, aqueous formaldehyde reagents as shown in Scheme 2.

Reductions of ferrocenylketimines **II**, **I** with sodium borohydride in ethanol or lithium aluminum hydride [19] in THF at room temperature proceeded smoothly. After the reactions completed, in case, when lithium aluminum hydride was used, degassed water was added to decompose the excess reductive reagent. The mixture was extracted with dichloromethane. The organic layer was dried over anhydrous sodium sulfate and removed to give out **3**, **4**.

Reductive methylation of **3**, **4** with the system composed by sodium cyanoborohydride, aqueous formaldehyde were carried out in acetonitrile solution, acetic acid was then added to maintain the neutral pH value of the mixtures, the reaction progresses were monitored by TLC. After the reactions completed, solvent was removed under reduced pressure. Purification of the crude products by chromatography and further by recrystallization gave out **5**, **2** as very good crystals.

It should be noted that reductive methylation of **II** with the system as mentioned above also afforded tertiary amines **5** (Scheme 3). On the contrary, the conversion from **I** to **2** with reductive methylation method was unsatisfied, because the reaction mixture was much complicated. Obviously, the conversion of **II** into **5** might proceed via secondary ferrocenylamines **3**. In addition, when **3** and **II** were used as starting material, experiments results showed that the yields of **5** were nearly same.

2.2. Spectral characterization of [(N-aryl) amino]methylferrocenes *3a–3g* and their N-methylated compounds *5a–5g*

Elemental analysis of compounds **5** are in consistence with the proposed formulae (see Section 4). The IR spectral features of **3–5** were similar to those as described in our previous paper [17]. Two absorption bands appeared around at ν 1100 and 1000 cm^{-1} corresponded to the structures of mono-substituted ferrocene derivatives [20]. A sharp absorption band displayed around at 3400 cm^{-1} for **3**, **4** indicated that each molecule contained one N–H bond which was indirectly supported by the fact that the absence of N–H absorption band in **5**, **2** are observed, and this fact in turn indicated the conversion of **3**, **4** into **5**, **2** took place actually.

In their NMR spectra, ferrocenylamines **5** all displayed a singlet appeared around at δ2.87 ppm and this corresponded to the methyl group attached directly to nitrogen atom, on the contrary, the NMR of **3d** gave a single peak around δ3.92 ppm which was indicative of a N–H group. Two singlet appeared at δ 4.08 and δ 4.12 ppm, respectively, in ferrocenylamines **3**, **5** were assigned to the four hydrogen atoms of the substituted cyclopentadienyl (Cp) ring, a singlet displayed around at δ4.15 ppm which represented five hydrogen atoms corresponded to the unsubstituted Cp ring. In addition, the hydrogen atoms in a variety of substituted phenyl rings all displayed their corresponding splitting patterns. All of these confirmed that **5**, **2** were mono-substituted tertiary ferrocenylamines.

2.3. The crystal structures of *3d* and *5a*

The crystal structures and crystal packing diagrams of **3d** and **5a** were presented in Figs. 1–4, respectively. Crystallographic data for **3d** and **5a** were given in Table 1, and selected bond lengths and angles were listed in Tables 2 and 3, respectively.

Crystal structures of **3d**, **5a** showed that the bond length between C(10) and C(11) were nearly equal (1.499(3) Å for **3d** and 1.502(4) Å for **5a**) and all of these data were in normal range. However, the bond length between N(1) and C(11) in **3d** (1.450(3) Å) was shorter than that in **5a** (1.466(3) Å), and all of these N(1)–C(11) bond lengths were shorter than that in **2d** (1.473(3) Å) [16]. In addition, the bond length between N(1)–C(12) in **3d** (1.382(3) Å) is shorter than the bond length between N(1)–C(13) in **5a** (1.399(3) Å).

The dihedral angle of C(11)–N(1)–C(12)–C(17) in **3d** was −3.6(4)°, this indicated that the plane consisted of C(12), N(1), C(11) fell in plane of the phenyl ring. In addition, the dihedral angle constructed by C(9)–C(10)–C(11)–

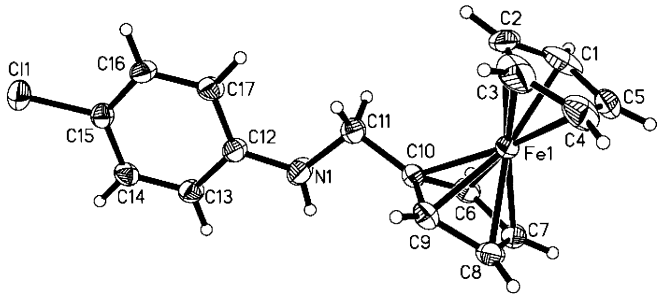
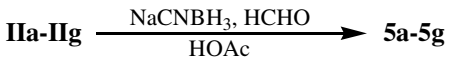


Fig. 1. Molecular structure of **3d** with numbering scheme (torsion angles: C(9)–C(10)–C(11)–N(1): −86.6(3)°, C(11)–N(1)–C(12)–C(17): −3.6(4)°, C(12)–N(1)–C(11)–C(10): 163.1(2)°).



R = 4-MeO(a), 4-Me(b)-, H(c), 4-Cl(d), 3-Cl(e), 4-NO_2(f), 3-NO_2(g)

Scheme 3.

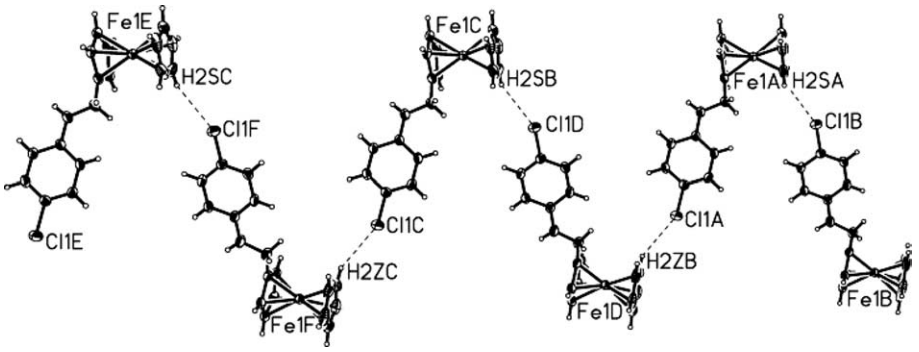


Fig. 2. Crystal packing for compound **3d**.

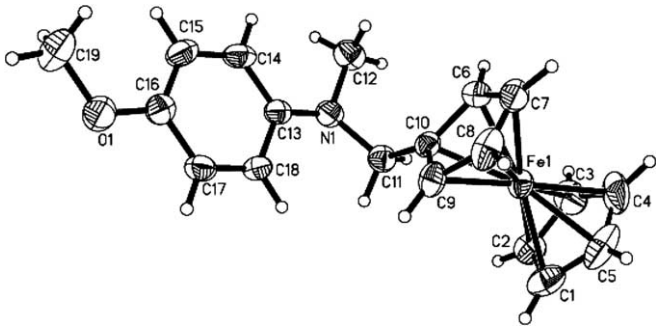


Fig. 3. Molecular structure of **5a** with numbering scheme (torsion angles: C(9)–C(10)–C(11)–N(1): 104.5(3)°, C(12)–N(1)–C(11)–C(10): 75.6(3)°, C(13)–N(1)–C(11)–C(10): −70.0(3)°, C(11)–N(1)–C(13)–C(18): −28.4(4)°, C(12)–N(1)–C(13)–C(18): −172.5(2)°, C(19)–O(1)–C(16)–C(17): 177.5(3)°).

N(1) was −86.6(3)°, which mean that this plane was nearly perpendicular to the substituted Cp ring. A similar conformation in **5a** was also observed. However, the influences of substituents at *para*-position of phenyl rings on the bond lengths of carbon–carbon double bond in phenyl rings were not significant.

The average Fe–C bond lengths in **3d** (2.025 Å for unsubstituted Cp ring, 2.037 Å for substituted Cp ring) and **5a** (2.027 Å for unsubstituted Cp ring, 2.031 Å for substituted Cp ring) were shorter than that in **2d** (2.039 Å for unsubstituted Cp ring, 2.043 Å for substituted Cp ring) [17]. All of these indicated that the structures of **3d**, **5a** were tightly packed than that of **2d**.

For compound **3d**, the molecules are linked with intermolecular Cl···H (Cp ring) interaction to form a helix-like packing (Fig. 2), The distance between adjacent phenyl rings is 5.933 Å, the dihedral angle between adjacent phenyl rings is 27.1°, in addition, the distance between interval phenyl rings is 7.052 Å, and the dihedral angle between interval phenyl rings is 0°. The diameter of the helix is 0.948 Å (The longer side of a right triangle when the distance between Fe1E and Fe1F is defined as the hypotenuse). For compound **5a**, the molecules were linked through weak intermolecular interaction between H7 and O1 (H7–O1, 2.692 Å, C7–H7–O1, 171.2°) to form zig-zag chains (Fig. 4).

Table 1
Crystallographic data for **3d** and **5a**

Compound	**3d**	**5a**
Empirical formula	$C_{17}H_{16}ClFeN$	$C_{19}H_{21}FeNO$
M	325.61	335.22
Crystal dimensions (mm)	$0.48 \times 0.24 \times 0.20$	$0.36 \times 0.24 \times 0.20$
Crystal system, space group	Monoclinic, $P2(1)/n$	Orthorhombic, $Pccn$
a (Å)	9.7585(14)	13.752(2)
b (Å)	11.5267(17)	22.095(3)
c (Å)	13.0830(19)	10.6421(16)
α (°)	90.00	90.00
β (°)	97.969(2)	90.00
γ (°)	90.00	90.00
V (Å^3)	1457.4(4)	3233.7(8)
Z	4	8
ρ_{calcd} (g cm^{-3})	1.484	1.377
μ (mm^{-1})	1.206	0.934
Reflections collected: total/independent/R_{int}	2974/2300/0.0289	2843/2052/0.0330
Data/restraints/parameters	2974/0/181	2843/0/201
Final R_1, wR_2	0.0327, 0.0764	0.0346, 0.0808

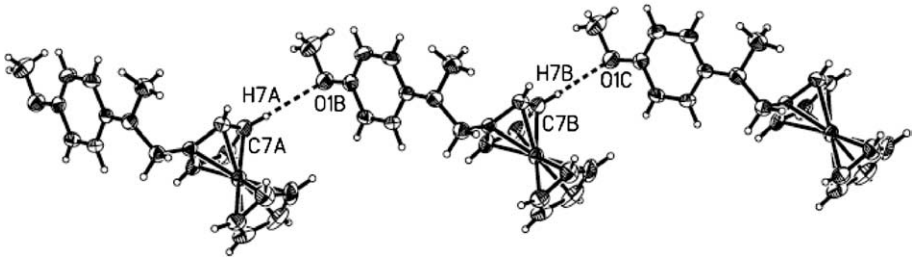


Fig. 4. Crystal packing for compound **5a**.

Table 2
Selected bond lengths (Å) for compounds **3d** and **5a**

3d	(Å)	**5a**	(Å)
Fe(1)–C(1)	2.027(3)	Fe(1)–C(1)	2.036(3)
Fe(1)–C(2)	2.015(3)	Fe(1)–C(2)	2.031(3)
Fe(1)–C(3)	2.015(3)	Fe(1)–C(3)	2.028(3)
Fe(1)–C(6)	2.040(2)	Fe(1)–C(6)	2.028(3)
Fe(1)–C(9)	2.031(2)	Fe(1)–C(9)	2.034(3)
Fe(1)–C(10)	2.030(2)	Fe(1)–C(10)	2.036(2)
C(1)–C(2)	1.428(5)	C(1)–C(2)	1.383(4)
C(2)–C(3)	1.405(6)	C(2)–C(3)	1.394(4)
C(6)–C(10)	1.425(3)	C(6)–C(10)	1.421(4)
C(9)–C(10)	1.419(3)	C(9)–C(10)	1.415(4)
C(10)–C(11)	1.499(3)	C(10)–C(11)	1.502(4)
N(1)–C(11)	1.450(3)	N(1)–C(11)	1.466(3)
N(1)–C(12)	1.382(3)	N(1)–C(12)	1.462(3)
C(12)–C(13)	1.399(3)	N(1)–C(13)	1.399(3)
C(15)–C(16)	1.373(3)	C(13)–C(18)	1.402(4)
C(13)–C(14)	1.380(3)	C(15)–C(16)	1.372(4)
C(14)–C(15)	1.377(3)	C(17)–C(18)	1.369(4)
Cl(1)–C(15)	1.747(2)	C(16)–C(17)	1.387(4)
		O(1)–C(16)	1.378(3)
		O(1)–C(19)	1.420(3)

Table 3
Selected bond angles (°) for compounds **3d** and **5a**

3d	(°)	**5a**	(°)
C(3)–C(2)–C(1)	106.1(3)	C(1)–C(2)–C(3)	109.7(3)
C(9)–C(10)–C(6)	107.0(2)	C(9)–C(10)–C(6)	107.2(3)
C(9)–C(10)–C(11)	125.9(2)	C(9)–C(10)–C(11)	126.9(2)
N(1)–C(11)–C(10)	109.36(19)	N(1)–C(11)–C(10)	114.8(2)
C(12)–N(1)–C(11)	123.7(2)	C(12)–N(1)–C(11)	113.6(2)
C(17)–C(12)–C(13)	118.2(2)	C(13)–N(1)–C(11)	119.1(2)
C(16)–C(15)–C(14)	121.0(2)	C(13)–N(1)–C(12)	117.8(2)
C(16)–C(15)–Cl(1)	119.88(18)	C(14)–C(13)–C(18)	115.6(3)
C(14)–C(15)–Cl(1)	119.13(18)	C(15)–C(16)–C(17)	117.9(3)
		C(15)–C(16)–O(1)	125.5(3)
		O(1)–C(16)–C(17)	116.6(3)
		C(16)–O(1)–C(19)	117.2(2)

3. Conclusion

Reductive methylation of ferrocenylaldimines and their reductive products, i.e., secondary ferrocenylamines with the system composed by sodium cyanoborohydride, aqueous formaldehyde and acetic acid produced *N*-methylated tertiary ferrocenylamines with higher yields. Similarly, reductive methylation of secondary ferrocenylamines derived from ferrocenylketimines with the above system also resulted in the corresponding *N*-methylated products. The synthesis of tertiary ferrocenylamines $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CHRN(CH_3)\text{-}(CH_2)_nC_6H_4\text{-}R')]$ **6**–**10** (**6**, R = Me, $n = 0$; **7**, R = Ph, $n = 0$; **8**, R = H, $n = 1$; **9**, R = Me, $n = 1$; **10**, R = Ph, $n = 1$), the analogues of compounds **5** (and **2**), and their corresponding ferrocenylaminophosphines **11**–**15** as well as the reactions with palladium reagents are now in progress in our laboratory.

4. Experimental

4.1. Materials and instruments

Ferrocenylaldimines and ferrocenylketimine were synthesized according to the literature procedures [18,21], anilines were obtained commercially and used without further purification, sodium borohydride, sodium cyanoborohydride and sodium aluminum hydride were purchased from Aldrich. All of the solvents were purified with standard method prior to use. Melting points were obtained from Yanaco micro melting point apparatus and were uncorrected. Elemental analyses were obtained from Carlo Erba 1106 Elemental analyzer. ^{1}H NMR spectra were measured with Bruker AV-400 spectrometer by using $CDCl_3$ as a solvent and TMS as internal standard. IR spectra were taken on BIO-RAD 3000 spectrophotometer.

4.2. Preparation of [(N-methyl-N-aryl)amino]methylferrocenes (**5a**–**5g**) and 1-[(N-methyl-N-phenyl)amino]ethyl-ferrocene (**2**)

4.2.1. Preparation of (N-arylamino)methylferrocenes (**3a**–**3g**) and 1-(N-phenylamino)ehtylferrocene (**4**)

General procedure. To the solutions of ferrocenylaldimines (5 mmol) in ethanol or tetrahydrofuran (20 ml), were added 2.5 equivalents of sodium borohydride or lithium aluminum hydride. When lithium aluminum hydride was used as reductive reagent, 5 ml methanol was added. The mixtures were stirred at room temperature for 12 h and TLC monitored the reactions until they were completed. Forty millilitres of degassed water was then added to decompose the excess reductive reagent. The mixtures were extracted with dichloromethane (3×30 ml), the organic layer was dried with anhydrous sodium sulfate and filtered. Solvent was removed to afford the crude product, and the crude products were recrystallized from dichloromethane–pentane or ethyl acetate–petroleum ether (60–90 °C) and then subjected to chromatography to give out very good crystals.

(N-p-Methoxyphenylamino)methylferrocene (**3a**): yellow solid. Yield 89%. M.p. 50–52 °C. IR (KBr pellet): 3369 (s, N–H), 2992, 1614, 1513, 1460, 1408, 1232, 1180, 1092, 1003, 813 cm^{-1}.

(N-p-Methylphenylamino)methylferrocene (**3b**): yellow solid. Yield 87%. M.p. 62–64 °C. IR (KBr pellet): 3396 (s, N–H), 3099, 2940, 1612, 1517, 1458, 1317, 1249, 1101, 810 cm^{-1}.

(N-Phenylamino)methylferrocene (**3c**): yellow solid. Yield 85%. M.p. 82–84 °C. IR (KBr pellet): 3400 (s, N–H), 3088, 2924, 1602, 1504, 1457, 1427, 1315, 1105, 999, 748 cm^{-1}.

(N-p-Chlorophenylamino)methylferrocene (**3d**): yellow solid. Yield 83%. M.p. 126–128 °C. IR (KBr pellet): 3421 (s, N–H), 3097, 2936, 1595, 1499, 1463, 1400, 1320, 1284, 1102, 998, 818 cm^{-1}. ^{1}H NMR: δ 3.92 (s, 3H, C(9)–H, C(12)–H, NH), 4.18 (s, 2H, C(10)–H, C(11)–H), 4.21 (s,

5H, C_5H_5), 4.27 (s, 2H, C(7)–H), 6.58 (d, 2H, $J = 8.8$ Hz, C(2)–H, C(6)–H), 7.15 (d, 2H, $J = 8.8$ Hz, C(3)–H, C(5)–H) ppm.

*(N-m-Chlorophenylamino)methylferrocene (**3e**)*: yellow solid. Yield 85%. M.p. 78–80 °C. IR (KBr pellet): 3416 (s, N–H), 1597, 1506, 1485, 1321, 1078, 1025, 816, 771 cm^{-1}.

*(N-p-Nitrophenylamino)methylferrocene (**3f**)*: yellow solid. Yield 76%. M.p. 124–126 °C. IR (KBr pellet): 3407 (s, N–H), 3080, 1598, 1499, 1454, 1356, 1296, 1262, 1185, 1112, 1052, 997, 817, 753 cm^{-1}.

*(N-m-Nitrophenylamino)methylferrocene (**3g**)*: yellow solid. Yield 80%. M.p. 86–88 °C. IR (KBr pellet): 3391 (s, N–H), 3092, 1530, 1478, 1350, 1297, 1260, 1100, 994, 811, 734 cm^{-1}.

***1**-(N-phenylamino)ethylferrocene (**4**)*. The starting material was **Ic**, the quantity and procedure were the same as that for preparation of **3a** (82%), yellow solid. M.p. 68–70 °C. ν_{max} (KBr) 3401 (s, N–H), 3089, 2941, 1508, 1498, 1350, 1296, 1260, 1100, 998, 748 cm^{-1}.

4.2.2. Preparation of [(N-methyl-N-aryl) amino]methylferrocenes 5a–5g (2) from secondary amines 3 (4)

General procedure. To a stirred solution of *N*-arylamino methylferrocene (2 mmol) and 10 mmol of 37% aqueous formaldehyde in 18 ml of acetonitrile was added 3.2 mmol of sodium cyanoborohydride, 30 min later, glacial acid was added dropwise until the pH value of the mixture reached neutral. The mixture was stirred at room temperature for 6 h and TLC monitored the reaction until it completed. The solvent was removed under reduced pressure, and 20 ml of 2 N NaOH was then added to the residue. The mixture was extracted with diethyl ether (3×30 ml), and the organic layer was dried over Na_2SO_4 and removed to afford crude product, which was purified by recrystallization and further by chromatography (silica gel, ethyl acetate/hexane) to provide [(*N*-methyl-*N*-aryl)amino]methylferrocenes **5a**–**5g**.

*(N-methyl-N-p-methoxyphenylamino)methylferrocene (**5a**)*: yellow needle crystal. Yield 88%. M.p. 82–84 °C. Anal. Found: C, 67.78; H, 6.55; N, 4.37. Calc. For $C_{19}H_{21}FeNO$: C, 68.08; H, 6.31; N, 4.18%. IR (KBr pellet): 3081, 2934, 1512, 1475, 1243, 1180, 1092, 1028, 818 cm^{-1}. ^1H NMR: δ 2.76 (s, 3H, *N*–CH_3), 3.76 (s, 3H, OCH_3), 4.07 (s, 2H, C(9)–H, C(12)–H), 4.10 (s, 2H, C(10)–H, C(11)–H), 4.13 (s, 5H, C_5H_5), 4.17 (s, 2H, C(7)–H), 6.77 (d, 2H, $J = 9.2$ Hz, C(2)–H, C(6)–H), 6.82 (d, 2H, $J = 9.2$ Hz, C(3)–H, C(5)–H) ppm.

*(N-methyl-N-p-methylphenylamino)methylferrocene (**5b**)*: yellow needle crystal. Yield 85%. M.p. 72–74 °C. Anal. Found: C, 71.39; H, 6.91; N, 4.60. Calc. For $C_{19}H_{21}FeN$: C, 71.49; H, 6.63; N, 4.39%. IR (KBr pellet): 3089, 2939, 1613, 1517, 1188, 1096, 809 cm^{-1}. ^1H NMR: δ 2.25 (s, 3H, Ar–CH_3), 2.81 (s, 3H, *N*–CH_3), 4.07 (s, 2H, C(9)–H, C(12)–H), 4.13 (s, 2H, C(10)–H, C(11)–H), 4.14 (s, 5H, C_5H_5), 4.22 (s, 2H, C(7)–H), 6.71 (d, 2H, $J = 8.4$ Hz, C(2)–H, C(6)–H), 7.03 (d, 2H, $J = 8.4$ Hz, C(3)–H, C(5)–H) ppm.

*(N-methyl-N-phenylamino)methylferrocene (**5c**)*: yellow rod. Yield 87%. M.p. 52–54 °C. Anal. Found: C, 70.73; H, 6.40; N, 4.79. Calc. For $C_{18}H_{19}FeN$: C, 70.84; H, 6.27; N, 4.59%. IR (KBr pellet): 3095, 1594, 1502, 1261, 1190, 1101, 1031, 817, 784 cm^{-1}. ^1H NMR: δ 2.88 (s, 3H, *N*-CH_3), 4.09 (s, 2H, C(9)–H, C(12)–H), 4.15 (s, 2H, C(10)–H, C(11)–H), 4.16 (s, 5H, C_5H_5), 4.28 (s, 2H, C(7)–H), 6.71–7.24 (m, 5H, C(2)–H–(5)–H) ppm.

*(N-methyl-N-p-chlorophenylamino)methylferrocene (**5d**)*: yellow needle crystal. Yield 85%. M.p. 98–100 °C. Anal. Found: C, 63.80; H, 5.63; N, 4.29. Calc. For $C_{19}H_{18}ClFeN$: C, 63.65; H, 5.34; N, 4.12%. IR (KBr pellet): 3095, 2941, 1595, 1502, 1373, 1329, 1253, 1198, 1102, 999, 804 cm^{-1}. ^1H NMR: δ 2.85 (s, 3H, *N*-CH_3), 4.09 (s, 2H, C(9)–H, C(12)–H), 4.13 (s, 2H, C(10)–H, C(11)–H), 4.15 (s, 5H, C_5H_5), 4.24 (s, 2H, C(7)–H), 6.68 (d, 2H, $J = 8.8$ Hz, C(2)–H, C(6)–H), 7.14 (d, 2H, $J = 8.8$ Hz, C(3)–H, C(5)–H) ppm.

*(N-methyl-N-m-chlorophenylamino)methylferrocene (**5e**)*: yellow needle crystal. Yield 87%. M.p. 82–84 °C. Anal. Found: C, 63.39; H, 5.56; N, 4.36. Calc. For $C_{19}H_{18}ClFeN$: C, 63.65; H, 5.34; N, 4.12%. IR (KBr pellet): 3091, 2943, 1592, 1492, 1363, 1257, 1099, 985, 825, 753 cm^{-1}. ^1H NMR: δ 2.87 (s, 3H, *N*–CH_3), 4.09 (s, 2H, C (9)–H, C(12)–H), 4.15 (s, 2H, C(10)–H, C(11)–H), 4.16 (s, 5H, C_5H_5), 4.26 (s, 2H, C(7)–H), 6.65 (t, 2H, $J = 8.0$ Hz, $J = 7.6$ Hz, C(2)–H, C(4)–H), 6.73 (s, 1H, C(6)–H), 7.12 (t, 1H, $J = 8.0$ Hz, $J = 8.4$ Hz, C(5)–H) ppm.

*(N-methyl-N-p-nitrophenylamino)methylferrocene (**5f**)*: yellow rod. Yield 76%. M.p. 160–162 °C. Anal. Found: C, 61.52; H, 5.31; N, 8.29. Calc. For $C_{18}H_{18}FeN_2O_2$: C, 61.74; H, 5.18; N, 8.00%. IR (KBr pellet): 3101, 2914, 1594, 1476, 1293, 1201, 1107, 997, 826, 752 cm^{-1}. ^1H NMR: δ 3.06 (s, 3H, *N*–CH_3), 4.15 (s, 2H, C(9)–H, C(12)–H), 4.19 (s, 2H, C(10)–H, C(11)–H), 4.21 (s, 5H, C_5H_5), 4.38 (s, 2H, C(7)–H), 6.68 (d, 2H, $J = 9.6$ Hz, C(2)–H, C(6)–H), 8.10 (d, 2H, $J = 9.6$ Hz, C(3)–H, C(5)–H) ppm.

*(N-methyl-N-m-nitrophenylamino)methylferrocene (**5g**)*: yellow rod. Yield 83%. M.p. 94–96 °C. Anal. Found: C, 61.48; H, 5.40; N, 8.10. Calc. For $C_{18}H_{18}FeN_2O_2$: C, 61.74; H, 5.18; N, 8.00%. IR (KBr pellet): 3090, 2943, 1613, 1517, 1344, 1206, 1106, 994, 817, 739, 500 cm^{-1}. ^1H NMR: δ 2.98 (s, 3H, *N*-CH_3), 4.13 (s, 2H, C(9)–H, C(12)–H), 4.17 (s, 2H, C(10)–H, C(11)–H), 4.20 (s, 5H, C_5H_5), 4.33 (s, 2H, C(7)–H), 7.01 (d, 1H, $J = 8.4$ Hz, C(2)–H), 7.31 (t, 1H, $J = 8.4$ Hz, $J = 8.0$ Hz, C(5)–H), 7.50 (d, 1H, $J = 8.0$ Hz, C(4)–H), 7.58 (s, 1H, C(6)–H) ppm.

***1**-[(N-methyl-N-phenyl)amino]ethylferrocene* (**2**). The starting material was **4**, the quantity and procedure were the same as that for preparation of **5a** (87%), yellow needle crystal. M.p 74–76 °C (lit. [16] 75–77 °C). IR and NMR spectra were the same as authentic sample.

4.2.3. Preparation of [(N-methyl-N-aryl)amino] methylferrocenes 5a–5g from ferrocenylaldimines II

To the stirred solution of ferrocenylaldimines **II** (2 mmol) and 38% aqueous formaldehyde in acetonitrile (20 ml), was added three equivalents of sodium cyanoborohydride. One hour later, glacial acid was added dropwise until the pH value of the mixture reached neutral. The mixture was stirred for another 6 h at room temperature and TLC monitored the reaction until it was completed. The following work-up procedure was same as mentioned above to give out corresponding ferrocenylamines **5a**–**5g**.

4.3. Crystal structures determination for 3d, 5a

Crystals of **3d** and **5a** were grown by slow evaporation of the mixture of hexane and ethyl acetate. In each case a suitable crystal was coated with hydrocarbon oil and attached to the tip of a glass fiber, which was then transferred to a Bruker SMART CCD diffractometer equipped with a graphite monochromator graphited Mo Kα ($\lambda = 0.71073$ Å) radiation at ambient temperature ($T = 294$ K) using ω–2θ multi-scans technique with the range of $2.36° \leqslant \theta \leqslant 26.37°$ (for **3d**) and $1.74° \leqslant \theta \leqslant 25.01°$ (for **5a**) for data collection. Semi-empirical absorption corrections were applied using SADABS program [22]. The structure was solved by direct methods and refined by full-matrix least-squares procedure on F^2 using the SHELX suite of program [23]. The value of R_1 was given based on F_o with a typical threshold of $F^2 \geqslant 2\sigma(F^2)$. The weighted R-factor wR was based on F^2 with $w = 1/[\sigma^2(F_o^2) + (0.0423P)^2 + 0.3954P]$, where $P = (F_o^2 + 2F_c^2)/3$ (for **3d**) and $w = 1/[\sigma^2(F_o^2) + (0.0463P)^2 + 1.5780P]$, where $P = (F_o^2 + 2F_c^2)/3$ (for **5a**). Crystallographic data are summarized in Table 1. Selected bond lengths and angles for the two structures are collected in Tables 2 and 3.

5. Supplementary materials

Crystallographic data (excluding structure factors) for the structure of **3d**, **5a** in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC 271789 and 271790. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: 144 0 1223 336033 or deposit@ccdc.cam.ac.uk).

Acknowledgements

We are grateful to the Natural Scientific Foundation of Tianjin City, People's Republic of China, for their generous support for this Research (Grant No. 033609011). Partial support for this Project from Opening Fund of Ministry of Science and Technology, People's Republic of China, is also acknowledged.

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