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Journal of Organometallic Chemistry 679 (2003) 130–134

Journal of Organometallic Chemistry

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Synthesis, characterization and the crystal structure of 1-[(*N*-methyl-*N*-aryl)amino]ethylferrocenes

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Received 22 January 2003; received in revised form 24 April 2003; accepted 30 April 2003

Abstract

The reactions of ferrocenylketimines [(η^5-$C_5H_4CCH_3$=NAr)Fe(η^5-C_5H_5)] (Ar = a variety of substituted phenyls) with methyl-iodide in refluxed dichloromethane followed by reduction with sodium borohydride in absolute ethanol led to [(η^5-$C_5H_4CH(CH_3)N(CH_3)Ar$)Fe(η^5-C_5H_5)]. Compound [(η^5-$C_5H_4CH(CH_3)N(CH_3)$–C_6H_4–Cl-p)Fe(η^5-C_5H_5)] (**3d**) has been characterized structurally. Compound **3d** is monoclinic, space group $P2_1/n$, with $a = 8.908(2)$ Å, $b = 13.63(1)$ Å, $c = 14.510(3)$ Å and $\beta = 107.03°$.

Keywords: Ferrocenylketimines; Methylation; Reduction; Ferrocenylamines; Crystal structures

1. Introduction

N-Alkyl(or aryl)aminoferrocenes as a kind of important organometallic compounds have attracted a great deal of attention in the past two decades due to their wide application in organic synthesis [1]. For an example, 1-[(*N*,*N*-dimethyl)amino]ethylferrocene not only served as a ligand to transition metals, which was involved in cyclometallation, nucleophilic substitution, and oxidation, etc., but also participated in asymmetric organic synthesis for some optical materials because of its chirality of α carbon atom [1]. To our best knowledge, some of *N*-alkylaminoethylferrocenes have been reported in the literatures [2]; in contrast, the synthesis of *N*-arylaminoethylferrocenes and their properties are still unknown. In the course of our investigation of cyclometallation on ferrocenylketimines [3], we found that these ferrocenylketimines could react with methyl-iodide to form stable imine salts, which were further reduced by sodium borohydride to yield the corresponding *N*-arylaminoethylferrocenes. Ferrocenylketimines could be cyclometallated by palladium, platinum, tin, mercury reagents, etc. [1b,4]. These cyclometallated ferrocenylketimines were found to be used in resolution of racemic α-amino acids [5], Heck reaction [6], as well as insertion of small molecules such as alkynes, alkenes, CO, etc. [7]. In this paper, we will present the details of our study on the synthesis, identification of 1-[(*N*-methyl-*N*-aryl)amino]ethylferrocenes as well as the crystal structure of 1-[(*N*-methyl-*N*-4-chlorophenyl)amino]ethylferrocene.

2. Synthesis and characterization of 1-[(*N*-methyl-*N*-aryl)amino]ethylferrocenes

2.1. *Synthesis of 1-[(N-methyl-N-aryl)amino]ethylferrocenes* ***3a–3f***

The reactions of ferrocenylketimines **1a–1f** with excess methyl-iodide were carried out in dichloromethane (Scheme 1) and the reactions were monitored by TLC. After the reactions completed, the mixtures were cooled down to room temperature and excess sodium borohydride was added. When the reactions finished, water was added to decompose unreacted sodium borohydride. Then the water phases were extracted with dichloromethane and the solvent was

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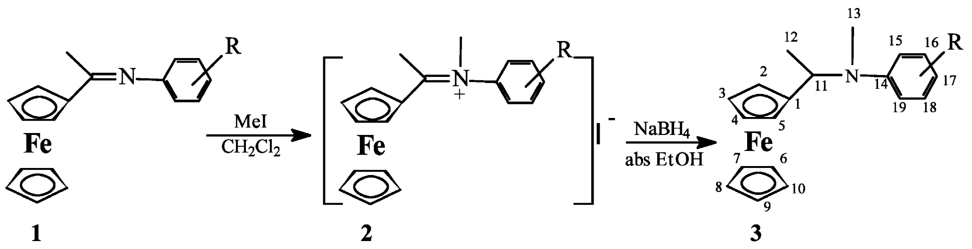
doi:10.1016/S0022-328X(03)00552-7



R = *p*-MeO(a), *p*-Me(b), H(c), *p*-Cl(d), *p*-Br(e), *m*-Me(f)

Scheme 1.

removed to yield residue. Recrystallization of the crude products afforded yellowish needles **3a**–**3f**. The structures of **3a**–**3f** were identified by elemental analysis, NMR, IR (see Section 3). In addition, the crystal structure of **3d** was also determined.

2.2. Spectral characterizations of arylaminoethylferrocenes *3a–3f*

All the compounds of **3a**–**3f** displayed two absorption bands around at v 1100 and 1000 cm^{-1} and this feature is in accordance with the structures of mono-substituted ferrocene derivatives [8]. The fact that the absorption band at the region of 3600–3200 cm^{-1} was not observed indicated that no N–H group existed in these molecules. The absence of C=N absorption band (at 1620 cm^{-1}) together with the presence of absorption band at 1300 cm^{-1} confirmed that the reduction of C=N double bond by sodium borohydride was achieved.

In their NMR spectra, a singlet appeared at δ 2.45 ppm corresponded to the CH_3 group which attached directly to nitrogen atom; similarly, a doublet appeared at δ 1.46 ppm was assigned to the methyl group which attached directly to tertiary carbon. These hydrogen nuclei in methyl group split the tertiary hydrogen nuclei (appeared at 5.00 ppm) into quartet, and the coupling constants all were 6.8 Hz, which further confirmed that they were ^3J coupling pattern.

2.3. The crystal structure of *3d*

The crystal structure of **3d** was presented in Fig. 1. The related atomic coordinates, selected bond lengths and angles were listed in Tables 1 and 2, respectively.

From the structure of **3d**, it was found that *N*-phenyl ring was not coplanar with substituted Cp ring, the sp^3-hybridized C(11) caused N atom and substituted Cp ring were not in the same plane. The $\angle$C(1)–C(11)–N(1) (110.4°) was smaller than $\angle$C(1)–C(11)–C(12) (113.3°) and $\angle$N(1)–C(11)–C(12) (112°). The bond lengths of C(11)–N(1) and C(13)–N(1) were 1.473 and 1.465 Å, respectively. However, the bond length of N(1)–C(14) (1.385 Å) was shorter. The plausible explanation comes from the conjugation of π bond and p electrons at N atom. In addition, the average Fe–C bond length in **3d** was 2.039 Å (for substituted Cp ring) and 2.043 Å (for unsubstituted Cp ring), respectively, which were shorter than those (2.041 Å for substituted Cp ring and 2.044 Å for unsubstituted Cp ring) in **1c** [3a]. All these indicated that the structure of **3d** was tightly packed than that of **1c**.

3. Experimental

3.1. Materials and instruments

Melting points were obtained on a WC-1 microscopic apparatus and were uncorrected. Elemental analyses were performed with Carlo Erba 1106 Elemental Analyzer. IR spectra were recorded on a Perkin–Elmer FT-IR 1730 spectrophotometer. ^{1}H-NMR spectra were measured with DPX 400 spectrometer using $CDCl_3$ as a solvent and TMS as an internal standard. All solvents were treated according to the standard methods. Ferrocenylketimines **1a**–**1f** were prepared according to the literature procedures [9].

3.2. Preparations of compounds *3a–3f*

General procedure. Ferrocenylketimines **1** (0.3 mmols) were dissolved in 10 ml of dry dichloromethane with the protection of nitrogen gas. Then two equivalents of methyl-iodide was added. The mixtures were refluxed and stirred for 24 h. TLC monitored the reactions until ferrocenylketimines were consumed completely. Later, the mixtures were cooled down to room temperature and petroleum ether (30–60 °C) was added. The corresponding imine salts precipitated and were filtered. The imine salts were dissolved in 20 ml of absolute ethanol and 1.5 equivalents of sodium borohydride was added in portions. The mixtures were stirred vigorously at room temperature until the bubble ceased. The unreacted sodium borohydride was hydrolyzed by water and yellowish solids precipitated and were filtered. If no solids precipitated, the water phase was extracted with chloroform until the color of water phase was near colorless. The organic portions were combined, and the

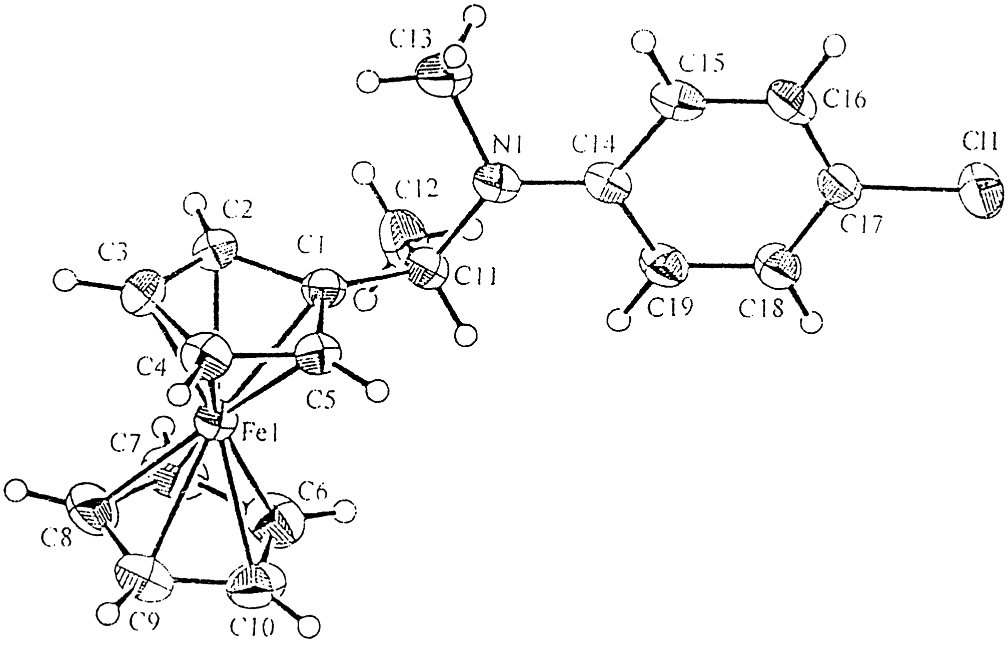


Fig. 1. Molecular structure of **3d**.

Table 1
Atomic coordinates and equivalent isotropic thermal parameters for **3d**

Atom	x	y	z	B_{eq}
Fe	0.01206(4)	0.15932(2)	0.15497(2)	3.526(8)
Cl	−0.2075(1)	−0.53016(6)	0.02498(7)	6.88(2)
N	−0.2729(2)	−0.1100(2)	0.1122(2)	4.63(5)
C(1)	−0.1584(3)	0.0546(2)	0.1300(1)	3.63(4)
C(2)	−0.1987(3)	0.1358(2)	0.1794(2)	4.39(5)
C(3)	−0.2049(3)	0.2212(2)	0.1218(2)	4.91(6)
C(4)	−0.1691(3)	0.1934(2)	0.0365(2)	4.62(5)
C(5)	−0.1415(3)	0.0910(2)	0.0410(1)	3.82(5)
C(6)	0.2250(3)	0.0958(2)	0.2275(2)	6.08(7)
C(7)	0.1771(4)	0.1668(3)	0.2857(2)	6.07(7)
C(8)	0.1677(4)	0.2573(2)	0.2387(2)	5.94(7)
C(9)	0.2037(3)	0.2415(2)	0.1516(2)	5.63(7)
C(10)	0.2364(3)	0.1425(3)	0.1451(2)	5.87(7)
C(11)	−0.1350(3)	−0.0508(2)	0.1626(2)	3.98(5)
C(12)	−0.0925(4)	−0.0626(2)	0.2720(2)	6.15(7)
C(13)	−0.4148(4)	−0.0741(3)	0.1182(3)	7.65(10)
C(14)	−0.2557(2)	−0.2093(2)	0.0975(1)	3.76(5)
C(15)	−0.3872(3)	−0.2663(2)	0.0949(2)	4.51(5)
C(16)	−0.3729(3)	−0.3637(2)	0.0279(2)	4.69(6)
C(17)	−0.2275(3)	−0.4073(2)	0.0544(2)	4.41(5)
C(18)	−0.0966(3)	−0.3549(2)	0.1029(2)	4.48(5)
C(19)	−0.1100(3)	−0.2576(2)	0.1251(2)	4.21(5)

solvent was removed to give the crude products. Recrystallization of the crude products from chloroform and ethanol afforded **3**.

3a, yellow rod. Yield 79%. m.p. 83–84 °C. Anal. Found: C, 68.57; H, 6.67; N, 4.22. Calc. for $C_{20}H_{23}FeNO$: C, 68.78; H, 6.64; N, 4.01%. IR (KBr pellet): 1511, 1475, 1462, 1440, 1303, 1247, 1104, 1036, 999, 818, 796, 509 cm^{-1}. ^{1}H-NMR: δ 1.45 (d, 3H, CH_3, $J = 6.8$ Hz), 2.40 (s, 3H, N–CH_3), 3.75 (s, 3H, p-OCH_3), 4.01–4.15 (m, 4H, substituted Cp ring), 4.10 (m, 5H, C_5H_5), 4.83 (q, 1H, C(11)–H, $J = 6.8$ Hz), 6.78 (d, 2H, C(15)–H, C(19)–H, $J = 8.4$ Hz), 6.83 (d, 2H, C(16)–H, C(18)–H, $J = 8.4$ Hz) ppm.

3b, yellow rod. Yield 65%. m.p. 58–59 °C. Anal. Found: C, 71.82; H, 6.95; N, 4.10. Calc. for $C_{20}H_{23}FeN$: C, 72.08; H, 6.96; N, 4.20%. IR (KBr pellet): 1614, 1516, 1469, 1450, 1425, 1297, 1103, 1026, 998, 823, 814, 499 cm^{-1}. ^{1}H-NMR: δ 1.46 (d, 3H, CH_3, $J = 6.8$ Hz), 2.45 (s, 3H, N–CH_3), 2.27 (s, 3H, p-CH_3), 4.08–4.19 (m, 4H, substituted Cp ring), 4.13 (m, 5H, C_5H_5), 4.98 (q, 1H, C(11)–H, $J = 6.8$ Hz), 6.74 (d, 2H, C(15)–H, C(19)–H, $J = 8.0$ Hz), 7.06 (d, 2H, C(16)–H, C(18)–H, $J = 8.0$ Hz) ppm.

3c, yellow rod. Yield 62%. m.p. 76–77 °C. Anal. Found: C, 71.28; H, 6.30; N, 4.35. Calc. for $C_{19}H_{21}FeN$: C, 71.48; H, 6.63; N, 4.39%. IR (KBr pellet): 1594, 1500, 1449, 1310, 1104, 1027, 992, 823, 754, 692, 505 cm^{-1}. ^{1}H-NMR: δ 1.48 (d, 3H, CH_3, $J = 6.8$ Hz), 2.49 (s, 3H, N–CH_3), 4.10–4.21 (m, 4H, substituted Cp ring), 4.14 (m, 5H, C_5H_5), 5.06 (q, 1H, C(11)–H, $J = 6.8$ Hz), 6.72 (t, 2H, C(15)–H, C(19)–H, $J = 7.2$ Hz), 6.82 (d, 2H, C(16)–H, C(18)–H, $J = 8.4$ Hz), 7.25 (m, 1H, C(17)–H) ppm.

3d, yellow rod. Yield 30%. m.p. 96–98 °C. Anal. Found: C, 64.39; H, 5.51; N, 3.88. Calc. for $C_{19}H_{20}ClFeN$: C, 64.52; H, 5.70; N, 3.96%. IR (KBr pellet): 1593, 1495, 1470, 1428, 1303, 1105, 1022, 998, 828, 814, 501 cm^{-1}. ^{1}H-NMR: δ 1.47 (d, 3H, CH_3, $J = 6.8$ Hz), 2.46 (s, 3H, N–CH_3), 4.06–4.19 (m, 4H, substituted Cp ring), 4.14 (m, 5H, C_5H_5), 4.97 (q, 1H, C(11)–H, $J = 6.8$ Hz), 6.72 (d, 2H, C(15)–H, C(19)–H,

Table 2
Selected bond lengths (Å) and bond angles (°) for **3d**

Bond lengths			
Fe–C(1)	2.041(2)	Fe–C(2)	2.040(2)
Fe–C(3)	2.037(3)	Fe–C(4)	2.039(2)
Fe–C(5)	2.039(2)	Fe–C(6)	2.036(2)
Fe–C(7)	2.031(3)	Fe–C(8)	2.046(3)
Fe–C(9)	2.050(3)	Fe–C(10)	2.053(3)
Cl(1)–C(17)	1.750(3)	N(1)–C(11)	1.473(3)
N(1)–C(13)	1.465(4)	N(1)–C(14)	1.385(3)
C(1)–C(2)	1.420(3)	C(1)–C(5)	1.434(3)
C(1)–C(11)	1.507(3)	C(2)–C(3)	1.424(4)
C(3)–C(4)	1.418(4)	C(4)–C(5)	1.414(4)
C(6)–C(7)	1.410(5)	C(6)–C(10)	1.367(4)
C(7)–C(8)	1.400(4)	C(8)–C(9)	1.408(4)
C(9)–C(10)	1.390(4)	C(11)–C(12)	1.528(3)
C(14)–C(15)	1.409(3)	C(14)–C(19)	1.405(3)
C(15)–C(16)	1.378(4)	C(16)–C(17)	1.374(4)
C(17–)C(18)	1.372(3)	C(18)–C(19)	1.379(3)
Bond angles			
C(11)–N(1)–C(14)	119.9(2)	C(11)–N(1)–C(13)	120.2(2)
C(2)–C(1)–C(11)	128.1(2)	C(13)–N(1)–C(14)	118.7(2)
C(1)–C(2)–C(3)	108.3(2)	C(2)–C(1)–C(5)	107.1(2)
C(3)–C(4)–C(5)	107.7(2)	C(5)–C(1)–C(11)	124.8(2)
C(7)–C(6)–C(10)	108.3(3)	C(2)–C(3)–C(4)	108.3(2)
C(7)–C(8)–C(9)	107.8(3)	C(1)–C(5)–C(4)	108.6(2)
C(6)–C(10)–C(9)	107.9(3)	C(6)–C(7)–C(8)	107.5(3)
N(1)–C(11)–C(12)	112.0(2)	C(8)–C(9)–C(10)	108.5(3)
N(1)–C(14)–C(15)	120.1(2)	N(1)–C(11)–C(1)	110.4(2)
C(15)–C(14)–C(19)	116.6(2)	C(1)–C(11)–C(12)	113.3(2)
C(15)–C(16)–C(17)	119.7(2)	N(1)–C(14)–C(19)	123.2(2)
Cl(1)–C(17)–C(18)	119.4(2)	C(14)–C(15)–C(16)	121.6(2)
C(17)–C(18)–C(19)	120.2(2)	Cl(1)–C(17)–C(16)	120.0(2)
C(14)–C(19)–C(18)	121.3(2)	C(16)–C(17)–C(18)	120.5(2)

$J = 8.8$ Hz), 7.18 (d, 2H, C(16)–H, C(18)–H, $J = 8.8$ Hz) ppm.

3e, yellow rod. Yield 30%. m.p. 91–93 °C. Anal. Found: C, 57.32; H, 4.84; N, 3.70. Calc. for $C_{19}H_{20}BrFeN$: C, 57.32; H, 5. 06; N, 3.52%. IR (KBr pellet): 1587, 1494, 1428, 1303, 1104, 1022, 998, 828, 811, 501 cm^{-1}. ^1H-NMR: δ 1.47 (d, 3H, CH_3, $J = 6.8$ Hz), 2.46 (s, 3H, N–CH_3), 4.06–4.19 (m, 4H, substituted Cp ring), 4.14 (m, 5H, C_5H_5), 4.97 (q, 1H, C(11)–H, $J = 6.8$ Hz), 6.67 (d, 2H, C(15)–H, C(19)–H, $J = 8.8$ Hz), 7.30 (d, 2H, C(16)–H, C(18)–H, $J = 9.2$ Hz) ppm.

3f, yellow rod. Yield 57%. m.p. 78–79 °C. Anal. Found: C, 72.26; H, 7.12; N, 4.33. Calc. for $C_{20}H_{23}FeN$: C, 72.08; H, 6.96; N, 4.20%. IR (KBr pellet): 1599, 1586, 1495, 1474, 1459, 1294, 1105, 1023, 996, 830, 813, 501 cm^{-1}. ^1H-NMR: δ 1.46 (d, 3H, CH_3, $J = 6.8$ Hz), 2.33 (s, 3H, m-CH_3), 2.48 (s, 3H, N–CH_3), 4.11–4.20 (m, 4H, substituted Cp ring), 4.14 (m, 5H, C_5H_5), 5.04 (q, 1H, C(11)–H, $J = 6.8$ Hz), 6.55 (d, 2H, C(15)–H, C(19)–H, $J = 6.8$ Hz), 6.63 (m, 1H, C(16)–H), 7.14 (t, 1H, C(17)–H, $J = 8.0$ Hz) ppm.

3.3. Crystal structure determination for **3d**

3.3.1. Crystal data of **3d**

$C_{19}H_{20}ClFeN$, $M_r = 357.67$, monoclinic, $P2_1/n$ (No. 14), $a = 8.908(2)$ Å, $b = 13.63(1)$ Å, $c = 14.510(3)$ Å, $\beta = 107.03(2)°$, $V = 1684.4000$ Å^3, $Z = 4$, $D_c = 1.395$ g cm^{-3}, $F(0\,0\,0) = 736.00$, $\lambda = 0.71070$ Å, μ(Mo–K$_\alpha$) = 10.48 cm^{-1}.

3.3.2. Data collection for **3d**

Yellow prismatic crystal of **3d** with approx. dimension of $0.60 \times 0.50 \times 0.20$ mm^3 was mounted on a Rigaku RAXIS-IV imaging plate area detector. Unit cell parameters were determined with $2\theta \leq 55.1°$ and refined with the least-squares method. 22/5° oscillation frames in the range 1–110° and exposure of 10 min per frame were measured. The distance between the crystal and the board was 105 mm. Intensities were collected with graphite monochromated Mo–K$_\alpha$ radiation by using $\omega - 2\theta$ scan technique. A total of 3386 reflections were measured, 2802 reflections were considered as observed applying the condition $I > 3\sigma(I)$. Data were corrected for Lorentz and polarization effects and also for absorption by an empirical method using the program DIFABS [10].

3.3.3. Structure solution and refinement

The structure was solved by heavy-atom Patterson methods and expanded by using Fourier techniques. All calculations were performed by using the teXsan software package [11]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final R factors were 0.036 ($R_w = 0.051$). The ratio of reflection/parameter was approximately 14. The maximum peak on the final difference Fourier map corresponded to 0.19 e Å^{-3}.

Acknowledgements

We are grateful to the National Natural Science Foundation of China for financial support of this project. The Postdoctoral Fellowship of China (1999) is also acknowledged.

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