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Synthesis, characterization of [{(*N*-methyl-*N*-benzyl)amino}methyl]-ferrocenes and their cyclopalladated complexes: Crystal structure of σ-Pd[(η^5-C_5H_5)Fe(η^5-$C_5H_3CH_2N(CH_3)CH_2C_6H_4NO_2$-4)]Cl($PPh_3$)

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Abstract

Condensation of aminomethylferrocene (**1**) and substituted benzaldehydes resulted in aldimines **2a**–**c** which followed by reduction with sodium borohydride to give **3a**–**c**. *N*-methylation of **3a**–**c** with HCHO/$NaCNBH_3$/HOAc led to **4a**–**c**. Treatment of **4a**–**c** with sodium palladium tetrachloride in the presence of sodium acetate afforded cleanly cyclopalladated **5a**–**c** in which configurations consisted of the R_NR_C, S_NS_C. The preferable activation of $C_{Ferrocenyl}$–H bond over C_{Phenyl}–H bond was also observed. All compounds **2**–**5** were characterized by elemental analysis, IR and ^{1}H NMR. In addition, the molecular structure of **5c** was confirmed by single crystal X-ray diffraction. The possible mechanism for the formation of **5** was also discussed.

Keywords: Ferrocenylamines; *N*-methylation; Cyclopalladation; Stereoselectivity; Crystal

1. Introduction

Transition metals mediated activation of C(sp^2)–H bonds in the aromatic compounds especially those containing nitrogen-chelating atom has attracted much attention [1] in the past decades due to their wide applications in organic synthesis such as Heck reaction [2], Suzuki coupling reaction [3], *etc*. The first example of cyclopalladation of ferrocenylamines, *i.e*., *N*,*N*-dimethylaminomethylferrocene (FcN) was reported by Sokolov et al. [4]. Later, Lopez and co-workers [5] found that treatment of ferrocenylimines [(η^5-C_5H_5)Fe(η^5-$C_5H_4CH_2$—N=CHC_6H_4R)] (R = H, 2-Cl) with sodium palladium tetrachloride in the presence of sodium acetate resulted in two kinds of cyclopalladated complexes either with a σ-Pd–$C_{sp^2,\,Ferrocenyl}$ bond or with a σ-Pd–$C_{sp^2,\,phenyl}$ bond due to the presence of the *endo* effect. In addition, the preferred activations of $C_{Ferrocenyl}$–H bond over C_{Phenyl}–H bond were documented very well in the literatures [6]. Although a large number of cyclopalladated compounds have been described [6], reports on cyclopalladated ferrocenylamines are still rare [5,7] mostly because the lack of suitable substrates. In the recent papers, we described the synthesis and characterization of [{(*N*-methyl-*N*-phenyl)amino}methyl]ferrocenes (PFcN) and their cyclopalladated complexes in which configurations consisted of R_NR_C, S_NS_C [8]. In addition, such stereoselectivity was also observed in cycloplatinated [{(*N*-methyl-*N*-benzyl)amino}methyl]ferrocenes [9]. In order to extend our researches of stereoselective cyclometallation on ferrocenylamines, in this paper, we wish to report the cyclopalladation of [(*N*-methyl-*N*-benzyl)-amino]methylferrocenes (Schemes 1 and 2) starting from aminomethylferrocene and *para*-benzaldehydes, particularly the relationship between the N–Pd coordination modes and the selectivities.

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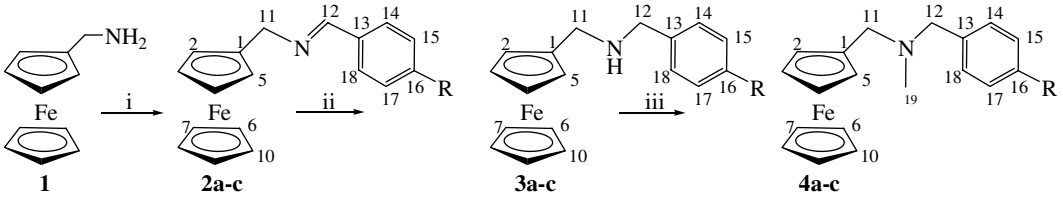
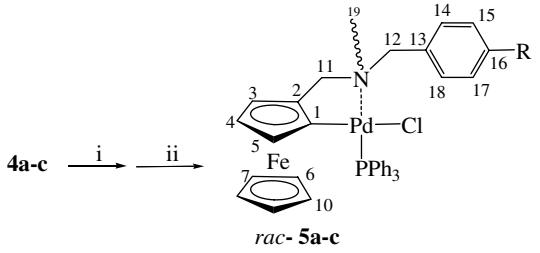


Scheme 1. (i) 4-RC_6H_4CHO(R = MeO (a), H (b), NO_2 (c)), MeOH, reflux 2 h; (ii) $NaBH_4$, methanol/water; (iii) $NaCNBH_3$, HCHO (37%), CH_3CO_2H.



Scheme 2. (i) Na_2PdCl_4, NaOAc, MeOH; (ii) PPh_3, MeOH.

2. Results and discussion

2.1. Synthesis of ferrocenylamines 4 and their cyclopalladated compounds 6

Condensation of **1** and *para*-substituted benzaldehydes produced ferrocenylimines **2a**–**c** (Scheme 1) which were followed by reduction with sodium borohydride to give quantitatively *secondary* **3a**–**c**. *N*-methylation [10] of **3a**–**c** with aqueous formaldehyde, sodium cyanoborohydride and acetic acid finally led to **4a**–**c** in the moderate yields.

Treatment of **4a**–**c** with stoichiometric sodium palladium tetrachloride in the presence of sodium acetate in methanol resulted in cleanly cyclopalladated ferrocenylamines **6a**–**c** (Scheme 2). Compounds **6a**–**c** were isolated as red-brown solids in good yields after column chromatography (see Section 3). They are very stable in air and soluble in dichloromethane, chloroform, ethyl acetate, acetone and benzene, but poorly soluble in methanol, particularly insoluble in petroleum ether.

Unlike PFcN which are easily oxidated by sodium palladium tetrachloride [8], **4a**–**c** show a strong anti-oxidation ability toward palladium (II). It is believed that a stronger coordination between **4a**–**c** and Pd than the former and hence reducing the oxidation potential of palladium (II) accounts for such significant different behavior.

2.2. Spectra characterizations of 2–5

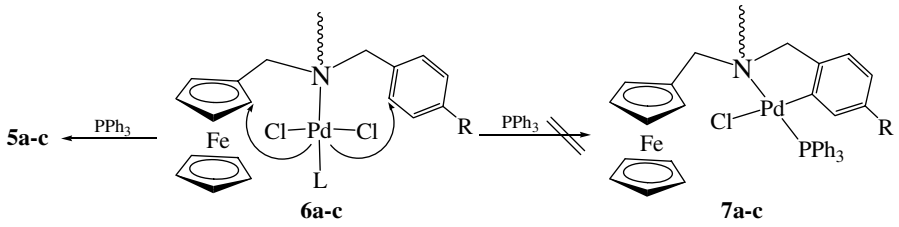
Compounds **2**–**5** were characterized by elemental analysis, IR and ^{1}H NMR. Elemental analyses are in good agreement with the proposed formula. In the IR spectra of **2a**–**c**, a strong absorption band appeared ν 1640 cm^{-1} indicates that the C=N bond exists in these molecules. And these data are in sharp contrast to those of the C=N bond for the other ferrocenylimines [(η^5-C_5H_5)Fe(η^5-$C_5H_4CH{=}N{-}CH_2C_6H_4R$)] ($\sim\nu$ 1620 cm^{-1}) [9] due to their different systems of electron delocalization. In the ^{1}H NMR spectra of **2a**–**c**, a singlet appeared at δ 8.20 ppm corresponds to H12. For **3a**–**c**, the presence of a weak absorption 3300 cm^{-1} in IR and a broad peak δ 2.19 ppm (when D_2O is added this peak disappeared) in ^{1}H NMR both confirm the presence of a N–H group. In **4a**–**c**, a singlet around δ 2.14 ppm is assigned to H19 and this value is very close to those (δ 2.12 ppm) of the other ferrocenylamines [(η^5-C_5H_5)Fe(η^5-$C_5H_4CH_2N(CH_3)CH_2$-C_6H_4R-4)](R=CH_3, Cl) [9].

For **5a**–**c**, their IR spectra all display two medium absorption bands around ν 1100 and 1000 cm^{-1}, implying that an unsubstituted cyclopentadienyl ring (Cp) is present [11]. In ^{1}H NMR spectra, the δ values of protons in N–CH_3 shifts from upfield $\delta \sim 2.14$ ppm in **4** to downfield $\delta \sim 2.8$ ppm in **5**, suggesting that a N–Pd coordination exists in **5**. Also in ^{1}H NMR spectra of **5**, a broad doublet and a multiplet around $\delta \sim 3.70$, 3.80 ppm are assigned to H5 and H4, respectively, a doublet $\delta \sim 3.90$ ppm is attributed to H3. The protons on substituted phenyl rings all give their corresponding splitting patterns.

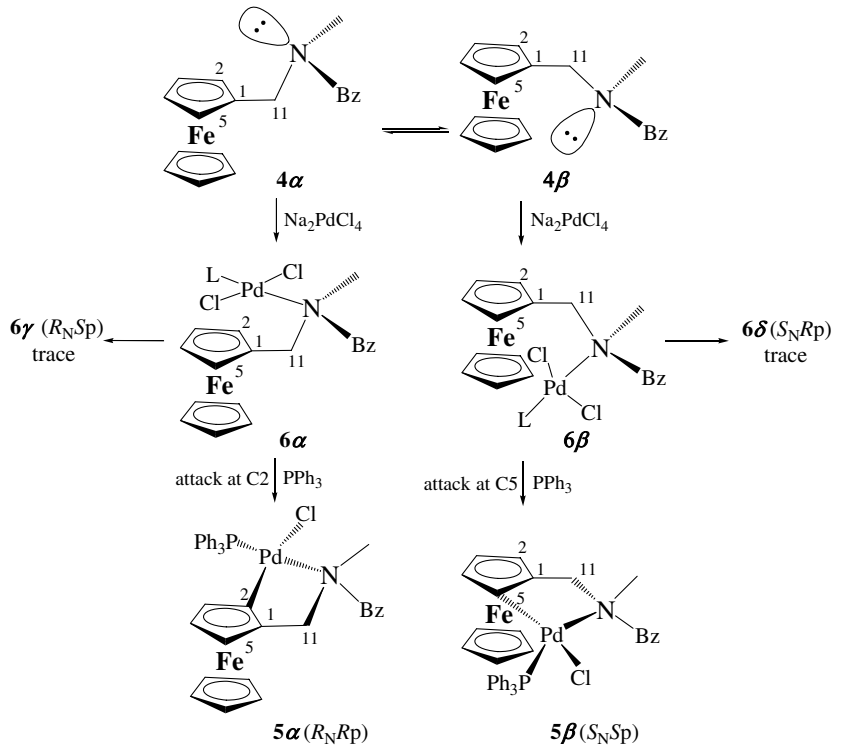
2.3. Chemoselectivity and stereoselectivity

It was observed that cyclopalladations of **4a**–**c** exhibited a preferable activation of $C_{Ferrocenyl}$–H bond over the C_{Phenyl}–H bond. Since **4a**–**c** have two different chemoselective metallation sites (Scheme 3), metallation of these two sites by the coordinated N–Pd complexes **6** can provide stable five membered rings **5** and **7**, respectively. In fact, only **5a**–**c** were isolated in our experiment. The preferable activation of $C_{Ferrocenyl}$–H bond in **4a**–**c** is in good agreement with our early observations [9], *i.e.*, electrophilic substitution of palladium on the ring with higher electron density (Cp ring) is facile than that with lower electron density (phenyl ring).

However, the 0 optical rotations of **5** measured at given conditions (λ = 5893 Å, CH_2Cl_2, 293 K) implies that they probably consist of racemers and this hypothesis is outlined in Scheme 4. Theoretically, two isomers **4α**,**β** are in equilibrium and they will possess the similar conformation to [(*N*-methyl-*N*-4-methylbenzyl)amino]methylferrocene [13]. It can be imaged that after coordination the intermediates **6α**(**β**) (Scheme 4) will keep the stable conformation similar to that of coordinated Pt–FcN complex [12]. The



Scheme 3. The preferred activation of C–H bond on Cp ring over that on phenyl ring. L = $FcCH_2N(CH_3)CH_2C_6H_4$-R.



Scheme 4. The possible mechanism for the formation of **5**. L = $FcCH_2N(Me)CH_2Ar$.

palladium in **6α(β)** either activate C2(5)–H bonds to give a pair of enantiomers **5α(β)** or rotate around C1–C11 bond and then activate C5(2)–H bonds to produce another pair of enantiomers **5γ(δ)**. Since the orientations of palladium in **6α(β)** approach C2–H, C5–H bonds, respectively [12], thus activation of these bonds to yield **5α(β)** will be favored. And in turn, the formation of **5γ(δ)** will not be disfavored due to the steric hindrance between benzyl and H atom in Cp ring when N–Pt moiety rotates around the axis of C1–C11 bond [9].

As we know, diastereomers can be easily separated by chromatography, fractional crystallization, *etc*. We paid much effort to isolate **5γ(δ)** from **5α(β)** by column chromatography, only a trace product (assumed to be the pair of **5γ(δ)**) was obtained and was not sufficient to identify. Based on the discussion as mentioned above together with the configuration (R_NR_C) of **5c** (Fig. 1), we suggest that **5** consist of a pair **5α(β)**. In addition, the possible coordination of palladium with either isomer **4α** or 4**β** resulting in only a pair of diastereomers **5α,γ** or **5β,δ** is also excluded.

2.4. X-ray single crystal studies of 5c

The molecular structure of **5c** was confirmed by single crystal X-ray diffraction (Fig. 1). Crystallographic data, selected bond lengths and angles are listed in Tables 1 and 2, respectively. X-ray diffraction studies demonstrate that **5c** consists of discrete molecules {$PdCl(PPh_3)[(\eta^5$-$C_5H_5)Fe(\eta^5$-$C_5H_3CH_2N(CH_3)$–$CH_2C_6H_4$–NO_2-4)]} separated by van der Waals contact in which palladium is in a slight distorted square-planar environment, bonded to Cl1, P1, N1 and C29. The deviation of each atom from the mean plane is Pd1, −0.0304; P1, 0.1353; N1, 0.1509; Cl1, −0.1079; C29, −0.1479 Å, respectively. Compound **5c** contains a bicycle, which is formed by the substituted pentagonal ring of the ferrocenyl fragment and a five membered palladacycle with an envelop-like conformation. The bond length N1–Pd1 2.195 Å is slightly longer than that in cyclopalladated FcN (2.170Å) [6h]. In addition, triphenylphosphino moiety adopts a *trans* configuration to N1, with a bond angle N1–Pd1–P1 169.00(9)°. The bond

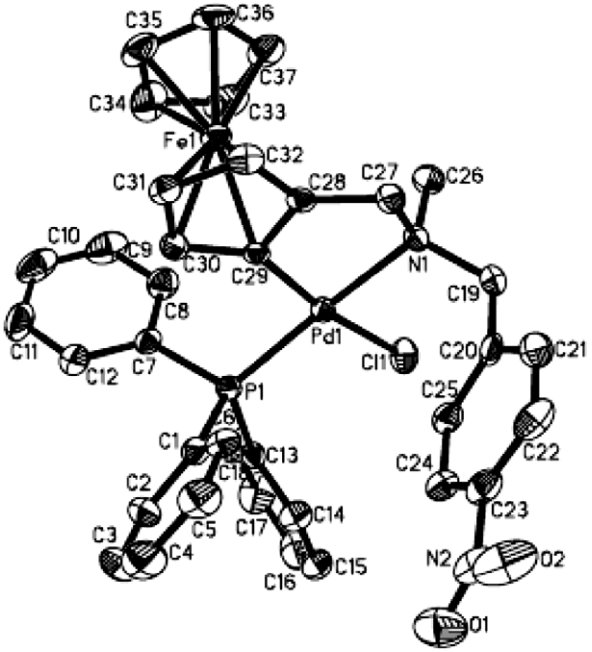


Fig. 1. Crystal structure of **5c** with numbering scheme (H atoms were omitted for clarity).

Table 1
Crystallographic data for **5c**

Compound	**5c**
Empirical formula	$C_{37}H_{34}ClFeN_2O_2PPd$
Formula weight	767.33
Crystal dimensions (mm)	$0.28 \times 0.16 \times 0.10$
Crystal system, space group	monoclinic, $P2(1)/c$
a (Å)	17.451(2)
b (Å)	16.653(3)
c (Å)	11.704(2)
α (°)	90.00
β (°)	105.00(2)
γ (°)	90.00
V (Å^3)	3285.4(8)
Z	4
ρ_{calcd} (g cm^{-3})	1.551
μ (mm^{-1})	1.155
θ Range for data collection (°)	$1.72 \leqslant \theta \leqslant 26.45$
Limiting indices	$-16 \leqslant h \leqslant 21$, $-16 \leqslant k \leqslant 20$, $-14 \leqslant l \leqslant 14$
Reflections collected/unique [$R_{int} = 0.068$]	18330/6731
Reflections [$I > 2\sigma(I)$]	4026
Data/restraints/parameters	6731/0/407
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.042, 0.072
Largest difference in peak and hole (e Å^{-3})	0.513 and −0.538

length Pd1–$C_{Ferrocenyl}$ 1.988(4) Å is nearly the same as that in cyclopalladated FcN (1.983(1) Å) [6h]. The average C–C bond length in the pentagonal rings 1.415 Å is similar to the values reported for the other ferrocene derivatives [11]. The Fe–C (Cp ring) bond lengths range from 2.024 to 2.097 Å. The two pentagonal rings of the ferrocenyl moiety are planar and nearly parallel (the interplane angle 6.4°). In addition, the Cp rings are also nearly eclipsed.

Table 2
Selected bond lengths (Å) and angles (°) for compound **5c**

Bond lengths (Å)			
Pd1–C29	1.988(4)	N1–C26	1.484(5)
Pd1–N1	2.195(3)	N1–C27	1.500(5)
Pd1–P1	2.224(1)	N1–C19	1.501(5)
Pd1–Cl1	2.395(1)	C27–C28	1.481(5)
Angles (°)			
C29–Pd1–N1	83.05(1)	N1–Pd1–Cl1	91.37(9)
C29–Pd1–P1	91.20(1)	P1–Pd1–Cl1	95.22(4)
N1–Pd1–P1	169.00(9)	C27–N1–Pd1	109.5(2)
C29–Pd1–Cl1	171.99(1)	C28–C29–Pd1	113.0(3)

3. Experimental

3.1. Materials and instruments

Aminomethylferrocene was prepared according to the literature procedure [14], substituted benzaldehydes, lithium aluminum hydride, aqueous formaldehyde, sodium cyanoborohydride, acetic acid, sodium acetate, triphenylphosphine were obtained commercially and used without further purification. Sodium palladium tetrachloride was prepared in our laboratory. All of the solvents were purified with standard methods prior to use. Melting points were obtained from Yanaco micro melting point apparatus and were uncorrected. Elemental analyses were measured from Carlo Erba 1106 Elemental analyzer. ^{1}H NMR spectra were obtained 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.

3.2. Synthesis of ferrocenylaldimines **2**

General procedure: To a stirred solution of aminomethylferrocene (5 mmol) in 20 ml methanol was added dropwise a solution of substituted benzaldehyde (5.5 mmol) in 10 ml ethanol. The mixture was refluxed for 4 h and cooled to room temperature. If no crystal precipitated, the mixture was kept at 5 °C in refrigerator or removed the solvent *in vacuo*. The crude product was recrystallized from ethyl acetate and petroleum ether (60–90 °C) to give out **2a**–**c**.

3.2.1. {(η^5-C_5H_5)Fe(η^5-$C_5H_4CH_2N{=}CHC_6H_4OCH_3$-4)} (**2a**)

Yield: (55%); a red-brown solid; m.p. 67–70 °C. *Anal.* Calc. for $C_{19}H_{19}FeNO$: C, 68.49; H, 5.75; N, 4.20. Found: C, 68.25; H, 5.73; N, 4.19%. FT-IR(KBr): 3092(w), 2935(w), 2888(w), 1641(m), 1604(s), 1512(s), 1315(s), 1258(s), 1167(s), 1104(m), 1028(s), 999(m), 816(s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.85(s, 3H, OCH_3), 4.14(m, 2H, H2, H5), 4.16(s, 5H, η^5-C_5H_5), 4.21(m, 2H, H3, H4), 4.51(s, 2H, H11), 6.93(d, 2H, H15, H17), 7.71(d, 2H, H14, H18), 8.20(s, 1H, H12).

3.2.2. {(η^5-C_5H_5)Fe(η^5-$C_5H_4CH_2N{=}CHC_6H_5$)} (**2b**)

Yield: (65%); a red-brown solid; m.p. 74–76 °C [lit. [6g]: 72–76 °C]. FT-IR(KBr): 3083(w), 2880(w), 1639(s),

1577(m), 1447(m), 1302(s), 1215(m), 1101(s), 1002(s), 809(s), 692(s) cm^{-1}.

3.2.3. {(η^5-C_5H_5)Fe(η^5-$C_5H_4CH_2N{=}CHC_6H_4NO_2$-4)} (**2c**)

Yield: (80%); a purple solid; m.p. 148–150 °C. *Anal*. Calc. for $C_{18}H_{16}FeN_2O_2$: C, 62.09; H, 4.63; N, 8.05. Found: C, 61.93; H, 4.56; N, 8.01. FT-IR (KBr): 3105(w), 2837(w), 2363(w), 1643(m), 1603(m), 1524(s), 1343(s), 1103(m), 1001(m), 832(m) cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.13(d, 2H, H2, H5), 4.16(s, 5H, η^5-C_5H_5), 4.21(m, 2H, H3, H4), 4.59(2H, s, H11), 7.91(d, 2H, H14, H18), 8.26(d, 2H, H15, H17), 8.33(s, 1H, H12).

3.3. Synthesis of secondary ferrocenylamines **3**

General procedure: To a stirred solution of **2** (3.3 mmol) in 20 ml dry THF was added sodium borohydride (6.6 mmol) under the argon. The mixture was refluxed for 4 h and cooled to room temperature. Solvent was evaporated under reduced pressure. The mixture was extracted with dichloromethane (3×30 ml). The extract was dried over anhydrous sodium sulfate and evaporated *in vacuo*. The residue was recrystallized from ethyl acetate–petroleum ether (60–90 °C) or crystallized from the above mentioned mixture of solvents or purified by column chromatography (silica-gel, ethyl acetate–petroleum ether (60–90 °C) = 1:2, v/v) to give **3a**–**c**.

3.3.1. {(η^5-C_5H_5)Fe(η^5-$C_5H_4CH_2NHCH_2C_6H_4OCH_3$-4)} (**3a**)

Yield: (83%); a yellow liquid. *Anal*. Calc. for $C_{19}H_{21}FeNO$: C, 68.08; H, 6.31; N, 4.18. Found: C, 67.83; H, 6.25; N, 4.12%. FT-IR (KBr): 3298(s), 3093(w), 2934(w), 2835(m), 2363(w), 1611(s), 1512(s), 1456(m), 1355(w), 1247(vs), 1175(s), 1105(m), 1035(s), 999(m), 816(s) cm^{-1}. ^1H NMR($CDCl_3$): δ 1.83(s, 1H, NH), 3.42(s, 3H, OCH_3), 3.49(s, 2H, H11), 3.73(s, 2H, H12), 3.80(d, 2H, H2, H5), 4.09(s, 5H, η^5-C_5H_5), 4.14(t, 2H, H3, H4), 6.86(d, 2H, H15, H17), 7.24(d, 2H, H14, H18).

3.3.2. {(η^5-C_5H_5)Fe(η^5-$C_5H_4CH_2NHCH_2C_6H_5$)} (**3b**)

Yield: (70%); a yellow solid; m.p. 37–39 °C. *Anal*. Calc. for $C_{18}H_{19}FeN$: C, 70.84; H, 6.27; N, 4.59. Found: C, 70.59; H, 6.25; N, 4.55%. FT-IR (KBr): 3319(s), 3084(w), 2934(w), 2858(m), 1494(s), 1451(s), 1330(s), 1103(s), 999(m), 803(s), 729(s), 697(s) cm^{-1}. ^1H NMR($CDCl_3$) δ 1.85(s, 1H, NH), 3.53(s, 2H, H11), 3.82(s, 2H, H12), 4.10(s, 5H, η^5-C_5H_5), 4.11(d, 2H, H2, H5), 4.20(t, 2H, H3, H4), 7.33(m, 5H, H14-H18).

3.3.3. {(η^5-C_5H_5)Fe(η^5-$C_5H_4CH_2NHCH_2C_6H_4NO_2$-4)} (**3c**)

Yield: (90%); a yellow solid; m.p. 97–98 °C. *Anal*. Calc. for $C_{18}H_{18}FeN_2O_2$: C, 61.74; H, 5.18; N, 8.00. Found: C, 61.68; H, 5.15; N, 7.98%. FT-IR (KBr): 3321(s), 3084(w), 2911(w), 1603(w), 1519(s), 1452(w), 1345(s), 1227(w), 1105(m), 1001(w), 859(m), 831(m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.98(s, 1H, NH), 3.64(s, 2H, H11), 3.91(s, 2H, H12), 4.11(s, 5H, η^5-C_5H_5), 4.16(d, 2H, H2, H5), 4.24(m, 2H, H3, H4), 7.61(d, 2H, H14, H18), 8.20(d, 2H, H15, H17).

3.4. Synthesis of tertiary ferrocenylamines **4**

General procedure: To a vigorous stirred solution of **3** (2 mmol) and 10 mmol of 37% aqueous formaldehyde in 20 ml of acetonitrile was added 0.20 g (3.2 mmol) of sodium cyanoborohydride. Thirty minutes 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 and 20 ml of 2*N* sodium hydroxide was then added to the residue. The mixture was stirred for 30 min. and extracted with diethyl ether (3×20 ml), and finally separated. The organic layer was dried over anhydrous sodium sulfate and removed to give out crude product which was purified by column chromatography (silica gel, ethyl acetate/petroleum ether (60–90 C°) = 1:5, v/v) to afford **4a**–**c**.

3.4.1. {(η^5-C_5H_5)Fe(η^5-$C_5H_4CH_2N(CH_3)CH_2C_6H_4O$-$CH_3$-4)} (**4a**)

Yield: (80%); a yellow liquid. *Anal*. Calc. for $C_{20}H_{23}FeNO$: C, 68.78; H, 6.64; N, 4.01. Found: C, 68.58; H, 6.60; N, 4.00%. FT-IR (KBr): 3094(w), 2935(w), 2835(m), 1612(s), 1512(s), 1463(m), 1365(w), 1301(m), 1246(s), 1175(s), 1105(s), 1035(s), 1003(s), 815(s) cm^{-1}. ^1H NMR(($CDCl_3$): δ 2.13(s, 3H, H19), 3.46(s, 3H, OCH_3), 3.50(s, 2H, H11), 3.74(s, 2H, H12), 3.82(d, 2H, H2, H5), 4.09(s, 5H, η^5-C_5H_5), 4.15(m, 2H, H3, H4), 6.87(d, 2H, H15, H17)), 7.25(d, 2H, H14, H18).

3.4.2. {(η^5-C_5H_5)Fe(η^5-$C_5H_4CH_2N(CH_3)CH_2C_6H_5$)} (**4b**)

Yield: (75%); a yellow solid; m.p. 39–40 °C. *Anal*. Calc. for $C_{19}H_{21}FeN$: C, 71.49; H, 6.63; N, 4.39. Found: C, 71.21; H, 6.58; N, 4.36%. FT-IR (KBr): 3093(w), 2938(w), 1598(w), 1491(m), 1448(s), 1326(m), 1105(s), 1023(s), 999(m), 810(s), 733(s), 696(m) cm^{-1}. ^1H NMR($CDCl_3$): δ 2.14(s, 3H, H19), 3.46(m, 4H, H11, H12), 4.05(d, 2H, H2, H5), 4.10(s, 5H, η^5-C_5H_5), 4.16(m, 2H, H3, H4), 7.27–7.32(m, 5H, H14-H18).

3.4.3. {(η^5-C_5H_5)Fe(η^5-$C_5H_4CH_2N(CH_3)CH_2C_6H_4NO_2$-4)} (**4c**)

Yield: (85%); a yellow solid; m.p. 66–68 °C. *Anal*. Calc. for $C_{19}H_{20}FeN_2O_2$: C, 62.66; H, 5.53; N, 7.69. Found: C, 62.49; H, 5.48; N, 7.60%. FT-IR (KBr): 3081(w), 2935(w), 2836(w), 1600(w), 1517(s), 1465(w), 1345(s), 1225(w), 1105(m), 1028(m), 1101(w), 857(m), 820(m) cm^{-1}. ^1H NMR($CDCl_3$): δ 2.15(s, 3H, H19), 3.46(s, 2H, H11), 3.51(s, 2H, H12), 4.10(s, 5H, η^5-C_5H_5), 4.14(d, 2H, H2, H5), 4.16(m, 2H, H3, H4), 7.47–8.17(q, 4H, H14, H15, H17, H18).

3.5. Synthesis of cyclopalladated ferrocenylamines 5

General procedure: To a stirred solution of **4** (1 mmol), sodium acetate (82 mg, 1 mmol) in 30 ml methanol was added dropwise a solution of sodium palladium tetrachloride (0.29 g, 1 mmol) in 15 methanol. The mixture was stirred for 4 h at room temperature with protection of argon gas and TLC monitored the reaction progress. Then triphenylphosphine (0.41 g, 1.5 mmol) was added and the mixture was stirred for another 30 min. The solvent was removed *in vacuo*, the residue was purified by column chromatography (silica gel, ethyl acetate/petroleum ether (60–90 C°) = 1:1, v/v) to give **5**.

3.5.1. $[PdCl(PPh_3)\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH_2N(CH_3)\text{-}CH_2C_6H_4OCH_3\text{-}4)\}]$ (5a)

Yield: (80%); a red-brown solid; m.p. > 216 °C (dec.). *Anal*. Calc. for $C_{38}H_{37}ClFeNOPPd$: C, 60.66; H, 4.96; N, 1.86. Found: C, 60.38; H, 4.89; N, 1.82%. FT-IR (KBr): 3073(w), 2909(w), 1609(s), 1510(s), 1435(s), 1303(m), 1247(s), 1178(s), 1096(s), 1033(m), 997(m), 806(s), 691(s) cm^{-1}. ^1H NMR($CDCl_3$): δ 2.81(s, 3H, H19), 3.50(m, 2H, H12), 3.65(m, 2H, H11), 3.43(s, 3H, OCH_3), 3.74(s, 5H, η^5-C_5H_5), 3.76(d, 1H, H5), 3.77(m, 1H, H4), 3.84(bs, 1H, H3), 6.80(d, 2H, H15, H17), 6.95(d, 2H, H14, H18), 7.38–7.67(m, 15H, PPh_3).

3.5.2. $[PdCl(PPh_3)\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH_2N(CH_3)\text{-}CH_2C_6H_5)\}]$ (5b)

Yield: (80%); a red-brown solid; m.p. > 221 °C (dec.). *Anal*. Calc. for $C_{37}H_{35}ClFeNPPd$: C, 61.52; H, 4.88; N, 1.94. Found: C, 61.32; H, 4.81; N, 1.96%. FT-IR (KBr): 3090(w), 2932(w), 1595(w), 1490(m), 1450(s), 1103(s), 1021(s), 999(m), 733(s), 696(m) cm^{-1}. ^1H NMR($CDCl_3$): δ 2.80(s, 3H, H19), 3.55(m, 2H, H11), 3.60(m, 2H, H12), 3.70(d, 1H, H5), 3.72(s, 5H, η^5-C_5H_5), 3.78(m, 1H, H4), 3.84(d, 1H, H3), 7.24–7.65(m, 15H, PPh_3), 7.88–8.01(m, 5H, H14, H15, H16, H17, H18).

3.5.3. $[PdCl(PPh_3)\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH_2N(CH_3)\text{-}CH_2C_6H_4NO_2\text{-}4)\}]$ (5c)

Yield: (78%); a red-brown solid; m.p. >228 °C (dec.). *Anal*. Calc. for $C_{37}H_{34}ClFeN_2O_2PPd$: C, 57.91; H, 4.47; N, 3.65. Found: C, 57.82; H, 4.45; N, 3.65%. FT-IR (KBr): 3099(w), 2918(w), 2856(w), 1600(w), 1521(s), 1479(m), 1435(s), 1344(vs), 1096(s), 999(m), 746(s), 692(s) cm^{-1}. ^1H NMR($CDCl_3$): δ 2.84(s, 3H, H19), 3.51(m, 2H, H11), 3.55(m, 2H, H12), 3.71(d, 1H, H5, H4 missing), 3.79(s, 5H, η^5-C_5H_5), 3.91(d, 1H, H3), 7.39–7.65(m, 15H, PPh_3), 8.12(d, 2H, H14, H18), 8.35(d, 2H, H15, H17).

3.6. X-ray determination of 5c

The prismatic single crystal of **5c** suitable for X-ray analysis was obtained by slow evaporation of the mixture of ethyl acetate and petroleum ether (60–90 °C) at room temperature over a period of one week. The single crystal of this complex was mounted on a Bruker SMART CCD diffractometer equipped with a monochromator graphited Mo Kα ($\lambda = 0.71073$ Å) radiation at ambient temperature ($T = 294$ K) using $\omega - 2\theta$ multi-scans technique for data collection. Semi-empirical absorption corrections were applied using SABABS program [15]. The structure was solved by direct methods and refined by full-matrix least-squares procedure on F^2 using the SHELX suite of program [16]. Crystallographic data, selected bond lengths and angles are listed in Tables 1 and 2, respectively.

4. Supplementary materials

Crystallographic data (excluding structure factors) for the structure of **5c** in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-280750. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk.

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