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Stereoselective cyclopalladation of [{(*N*-methyl-*N*-aryl)amino}methyl]ferrocenes: Crystal structure of σ-Pd[ClPPh$_3$(η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_3$CH$_2$N(CH$_3$)C$_6$H$_4$OCH$_3$-4)] · H$_2$O

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Abstract

Stereoselective cyclopalladation of [(*N*-methyl-*N*-aryl)amino]methylferrocenes **1a–f** (aryl = 4-CH$_3$OC$_6$H$_4$(a), 4-CH$_3$C$_6$H$_4$(b), C$_6$H$_5$(c), 4-ClC$_6$H$_4$(d), 3-ClC$_6$H$_4$(e), 3-O$_2$NC$_6$H$_4$(f)) with sodium palladium tetrachloride and followed by treatment with triphenylphosphine resulted in the cyclopalladated complexes **3a–f** (aryl = same as before) in the form of raceme. The structure of **3a** was determined by X-ray single crystal diffraction. Complex **3a** crystallizes in triclinic, space group P-1 with $a = 10.6685(14)$, $b = 10.7412(14)$, $c = 16.795(2)$ Å, $\alpha = 71.879(2)$, $\beta = 85.798(2)$, $\gamma = 64.523(2)°$. The possible mechanism for the formation of **3** was discussed.

Keywords: Ferrocenylamines; Cyclopalladation; Stereoselectivity; Crystal

Cyclopalladation reaction [1] represents one of most powerful methods for the activation of C$_{sp2}$–H bonds and ortho-functionalization in aromatic compounds. The application of cyclopalladated compounds especially those bearing nitrogen-chelating atom have been widely used in organic synthesis such as Heck reaction [2], Suzuki coupling reaction [3], etc. As far as we know, although a lot of cyclopalladated ferrocenylimines have been described [1,4], the cyclopalladations of tertiary ferrocenylamines are still rare mostly because of the lack of suitable substrates. Recently, we reported the synthesis of [{(*N*-methyl-*N*-aryl (or benzyl))amino}methyl]ferrocenes by (i) methylation of imines with methyl iodide to form iminum salts and followed by reduction of latter with sodium borohydride [5a] or (ii) direct reductive methylation of ferrocenylaldimines (or secondary ferrocenylamines) [5b], [c] in one step with sodium cyanoborohydride, aqueous formaldehyde in the presence of glacial acid. And we observed that cycloplatination of aliphatic amines, i.e. [{(*N*-methyl-*N*-benzyl)amino}methyl]ferrocenes resulted in predominately cycloplatinated compounds [6]. These cycloplatinated complexes mainly consist of raceme (R_NR_P and S_NS_P). In order to confirm further this stereoselectivity, in this communication, we wish to report here the first example of cyclopalladation of tertiary aromatic ferrocenylamines, i.e. [{(*N*-methyl-*N*-aryl)amino}methyl]ferrocenes **1a–f** (Scheme 1) and elucidate the relationship between structures of substrates and their selectivities.

The reactions of **1a–f** and sodium palladium tetrachloride were carried out in methanol at room temperature in the presence of sodium acetate (Scheme 1). After the reactions completed, triphenylphosphine was added to split di-μ-chloro adducts. Complexes **3a–f** were obtained after

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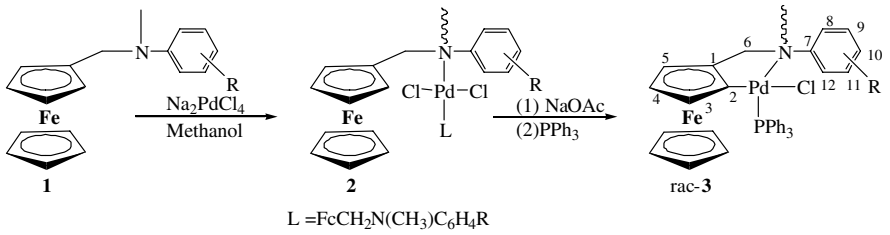


Scheme 1. R = 4-MeO(a), 4-Me(b), H(c), 4-Cl(d), 3-Cl(e), 3-NO_2(f).

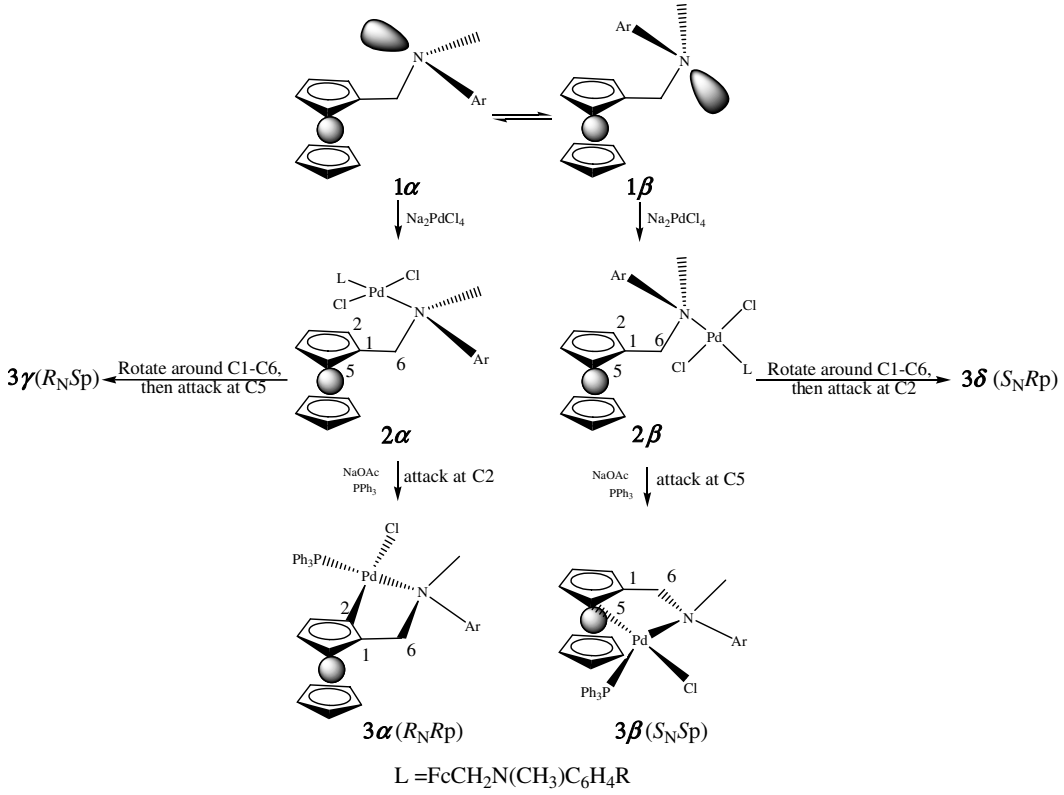
column chromatography (silica gel, ethylacetate/hexane = 1:1, v/v). They are very stable in air, and easily soluble in most organic solvents, but poorly soluble in petroleum ether.

Direct cyclopalladation of **1a–f** with sodium palladium tetrachloride lead to the low yields of **3a–f** ($\leqslant$15%), and this phenomenon is consistence with the literatures reported [4a,7]. An attempt to prepare **3a–f** by transpalladation of their corresponding *ortho*-mercurated **1a–f** gave the similar results. Though the yields of **3a–f** are low, it seems that they are related to the characteristics of substituents in substrates. For example, cyclopalladation of **1a** gives normally **3a** a higher yield (15%). However, the **1d–f** provide comparative lower yields of **3d–f** (<12%).

The structures of **3a–f** were identified by elemental analyses, IR and ^{1}H NMR [8]. The IR spectra of **3a–f** display two absorptions around v 1100 and 1000 cm^{-1}, indicating that they all have an unsubstituted cyclopentadienyl ring (Cp) [9]. In ^{1}H NMR spectra of **3a–f**, a singlet around δ 3.83 ppm corresponds to η-C_5H_5, two doublet around δ 3.75 and 4.20 ppm are assigned to C3-H, C5-H, respectively, a triplet around δ 4.12 ppm is attributed to C4-H. In addition, a typical AB coupling system (around δ 3.60 ppm) for C6-H is also observed due to the formation of a five membered palladocycle.

The N atoms in **1a–f** connect three different groups, **1a–f** are undoubtedly chiral amines. However, the determined optical rotations of **3a–f** are 0 under the given conditions (λ = 5893 Å, CH_2Cl_2, 293 K), implying that **3a–f** are probably composed of raceme. The possible mechanism for their formation is illustrated in Scheme 2.

Coordination of palladium with N atoms of two isomers **1**α, β will generate intermediates **2**α, β. Our previous results demonstrated that the orbital occupied by lone-pair electrons in N atom of **1a–f** lies above the substituted Cp ring and points preferably to one of adjacent C–H bonds [10],



Scheme 2. The possible mechanism for the formation of **3**.

one can image that after coordination the palladium in **2**α, β will direct preferably to one of the C–H bonds as mentioned above. And moreover, the N–Pd moiety in **2**α, β could also rotate in principle around the axis of C1–C6 σ bond. Thus, activation of one of its adjacent C–H bonds will produce two racemes **3**α, β and **3**γ, δ. Mostly important, the pair **3**α, β are the diastereomers of another pair **3**γ, δ which can be easily separated by column chromatography. Indeed, we have isolated a trace product which is not sufficient to identify. Based on the optical rotations of **3a**–**f** and in connection with the configuration of **3a** ($R_N R_P$) [11] (Fig. 1), it is believed that **3a**–**f** are composed of the raceme **3**α, β in stead of **3**γ, δ and this result is consistence with our previous observation [6]. The preferable activation of C2-H or C5-H is probably because that the free rotation of N–Pd moiety in **2** α, β around the axis of C1–C6 bond (lead to **3**γ, δ) is retarded due to the steric hindrance between palladium and hydrogen in Cp.

The structure of **3a** was also determined by X-ray single crystal diffraction. Crystallographic studies [12] demonstrates that **3a** consists of discrete molecule σ-Pd[ClPPh$_3$(η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_3$CH$_2$N(CH$_3$)C$_6$H$_4$OCH$_3$-4)] · H$_2$O separated by van der Waals contact in which palladium is in a slight distorted square-planar environment, bonded to N1, Cl1, C10 and P1. The deviations of each atom from the mean plane are Pd1 0.0607, N1-0.1424, Cl1 0.0889, C10 0.1240 and P1 − 0.1313 Å, respectively. Complex **3a** contains two fused five-membered rings, i.e. the substituted pentagonal ring of the ferrocenyl fragment and a five-membered palladocycle with an envelope-like conformation. In addition, P1 adopts a *trans* configuration to N1 with a bond angle N1-Pd1-P1 167.85°. The N–Pd bond length (2.228 Å) is longer than those of cyclopalladated (*N*-methyl-*N*-*tert*-butyl)benzylamine (2.097(3) Å) [13] and *N*,*N*-dimethyl-aminomethylferrocene (2.170(10) Å) [14]. The average C–C bond length of Cp rings (1.419 Å) is similar to the values reported for the other ferrocene derivatives [15]. The Fe-C(ring) bond distances range from 2.024 to 2.080 Å. The two pentagonal rings of the ferrocenyl fragment are planar and nearly parallel (interplanar angle 3.3°).

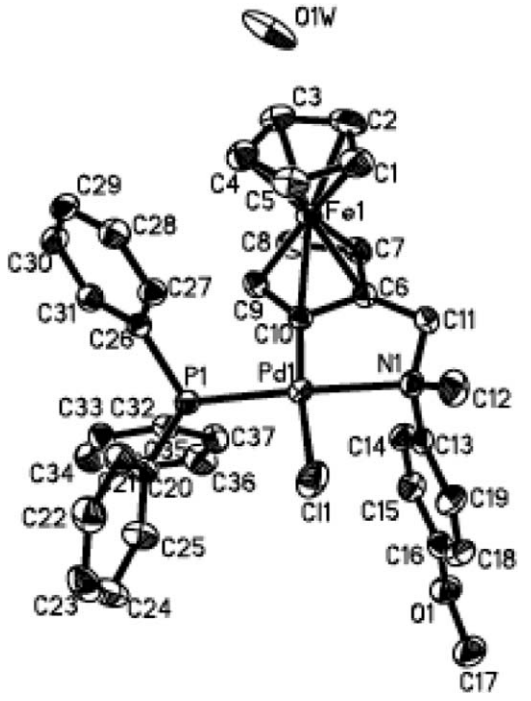


Fig. 1. Molecular structure of **3a** with numbering scheme (H atoms were omitted for clarity. Bond lengths in Å, Pd1-C10 1.996(4), Pd1-N1 2.228(3), Pd1-P1 2.2361(10), Pd1-Cl1 2.3770(12), N1-C13, 1.466(5), O1-C17 1.417(7). Bond angles in °, C10-Pd1-N1 81.70(15), C10-Pd1-P1 92.04(11), N1-Pd1-P1 167.89(9), C10-Pd1-Cl1 174.00(12), C11-N1-Pd1 93.10(10)).

Supplementary data

Crystallographic data (excluding structure factors) for the structure of **3a** in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 284688. 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 e-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements

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[8] Preparation of **3a–f**: To the stirred solution of **1** (2 mmol) [5b] and sodium acetate (2 mmol) in the mixture of methanol (20 ml) and dichloromethane (5 ml), was added dropwise a solution of equivalent sodium palladium tetrachloride in methanol. TLC monitored the reactions until palladium was consumed up. Without isolation, a solution of 1.5 equivalents triphenylphosphine in methanol was added, 1 h later, the mixtures were filtered and the solvent was removed. The residues were purified by column chromatography (silica gel, ethyl acetate/hexane = 1:1, v/v), the second band of eluant was collected, solvent was removed to afford **3** as red-purple powders. **3a**, red solid, yield 15%, melting point 156–158 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.16 (s, 3H, N-CH_3), 2.79 (s, 3H, OCH_3), 3.59 (m, 2 H, C6-H), 3.78 (d, 1H, C3-H), 3.80 (s, 5H, η-C_5H_5), 4.07 (m, 1H, C4-H), 4.15 (d, 1H, C5-H), 6.87–6.90 (q, 4H, C8-H, C9-H, C11-H, C12-H), 7.36–7.77 (m, 15H, PPh_3); IR(KBr) ν: 3055, 2911, 1506, 1435, 1248, 1095, 999, 827, 741, 693 cm^{-1}; Anal. Calcd. for $C_{37}H_{35}ClFeNOPPd$: C 60.19, H 4.78, N 1.90; Found C 59.89, H 4.75, N 1.89. 3b, red solid, yield 14%, melting point 156–158 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.08 (s, 3H, Ar-CH_3), 2.24 (s, 3H, N-CH_3), 3.55 (m, 2H, C6-H), 3.76 (d, 1H, C3-H), 3.81 (s, 5H, η-C_5H_5), 4.10 (m, 1H, C4-H), 4.14 (d, 1H, C5-H), 6.88–6.91 (q, 4H, C8-H, C9-H, C11-H, C12-H), 7.36-7.75 (m, 15H, PPh_3); IR(KBr) ν: 3059, 2927, 1509, 1434, 1099, 998, 819, 691 cm^{-1}; Anal. Calcd. for $C_{37}H_{35}ClFeNPPd$: C 61.52, H 4.88, N 1.94; Found C 61.23, H 4.86, N 1.94. 3c, red solid, yield 14%, melting point 130–132 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.26 (s, 3H, N-CH_3), 3.58 (m, 2H, C6-H), 3.75 (d, 1H, C3-H), 3.83 (s, 5H, η-C_5H_5), 4.12 (m, 1H, C4-H), 4.20 (d, 1H, C5-H), 6.89–7.72 (m, 20H, Ar-H); IR(KBr) ν: 3055, 2924, 1595, 1498, 1436, 1098, 999 cm^{-1}; Anal. Calcd. for $C_{36}H_{33}ClFeNPPd$: C 61.04, H 4.70, N 1.98; Found C 60.79, H 4.66, N 1.97. 3d, red solid, yield 12%, melting point 138–140 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.17 (s, 3H, N-CH_3), 3.62 (m, 2H, C6-H), 3.76 (d, 1H, C3-H), 3.83 (s, 5H, η-C_5H_5), 4.13 (m, 1H, C4-H), 4.22 (d, 1H, C5-H), 6.91–7.07 (q, 4H, C8-H, C9-H, C11-H, C12-H), 7.36-7.69 (m, 15H, PPh_3); IR(KBr) ν: 3055, 2925, 1595, 1499, 1435, 1096, 998, 810, 745, 692 cm^{-1}; Anal. Calcd. for $C_{36}H_{32}Cl_2FeNPPd$: C 58.21, H 4.34, N 1.89; Found C 58.10, H 4.32, N 1.88. 3e, red solid, yield 12%, m.p.134–136 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.16 (s, 3H, N-CH_3), 3.62 (m, 2H, C6–H), 3.75 (d, 1H, C3–H), 3.80 (s, 5H, η-C_5H_5), 4.11 (m, 1H, C4-H), 4.21 (d, 1H, C5-H), 6.59–7.71 (m, 19H, Ar-H); IR(KBr) ν: 3055, 2926, 1597, 1482, 1435, 1097, 999, 745, 692 cm^{-1}; Anal. Calcd. for $C_{36}H_{32}Cl_2FeNPPd$: C 58.21, H 4.34, N 1.89; Found C 57.91, H 4.28, N 1.88. 3f, red solid, yield 7%, m.p. 174–176 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.18 (s, 3H, N-CH_3), 3.64 (m, 2H, C6-H), 3.77 (d, 1H, C3-H), 3.82 (s, 5H, η-C_5H_5), 4.15 (m, 1H, C4-H), 4.27 (d, 1H, C5-H), 6.82–7.89 (m, 19H, Ar-H); IR(KBr) ν: 3054, 295, 1595, 1533, 1498, 1435, 1342 1099, 998, 692 cm^{-1}; Anal. Calcd. for $C_{36}H_{32}ClFeN_2O_2PPd$: C 57.40, H 4.28, N 3.72; Found C 57.12, H 4.25, N 3.70.

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[12] Intensity data for single crystal of complex **3a** were collected on a Bruker SMART CCD diffractometer with graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K. The structure was solved by direct methods and refined by full-matrix least-squares techniques with anisotropic thermal factors for all non-hydrogen atoms. All calculations were performed using the SHELX suite of program [16]. Crystal data: crystal dimensions: $0.32 \times 0.20 \times 0.14$ mm^3, FW = 756.35, triclinic, space group P-1, $a = 10.6685(14)$ Å, $b = 10.7412(14)$ Å, $c = 16.795(2)$ Å, $\alpha = 71.879(2)°$, $\beta = 85.798(2)°$, $\gamma = 64.523(2)°$, $V = 1647.1(4)$ Å^3, $Z = 2$, $D_c = 1.525$ mg/m^3, $F(000) = 772$, $R = 0.0441$.

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