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Synthesis, characterization and crystal structures of a novel 1,1′-bisferrocenylimine and its monocyclopalladated derivative

Chen Xu, Jun-Fang Gong, Yan-Hui Zhang, Yu Zhu, Chen-Xia Du, Yang-Jie Wu *

Department of Chemistry, Henan Key Laboratory of Chemical Biology and Organic Chemistry, Key Laboratory of Applied Chemistry of Henan Universities, Zhengzhou University, Daxue Road 75, Zhengzhou, Henan Province 450052, PR China

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Abstract

The synthesis and characterization of a new 1,1′-bisferrocenylimine [{(η^5-C_5H_4)-CH=NCy}$_2$Fe] **4** and its monocyclopalladated derivative **6** are reported. The compound **6** was found to be [PdCl{[(η^5-C_5H_4)-CHO]Fe[(η^5-C_5H_3)-CH=NCy]}(PCy_3)], which was obtained from the reaction of **4** with two mole equivalents of Li_2PdCl_4/NaOAc in methanol at room temperature and subsequent treatment of the resulting product with tricyclohexylphosphine (PCy_3). The X-ray single-crystal structures of the two new compounds are also described.
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Keywords: 1,1′-Bisferrocenylimine; Cyclopalladation; Tricyclohexylphosphine; Crystal structures; Hydrogen bonds

Cyclopalladated compounds containing a Pd—C bond intramolecularly stabilized by one donor atom were first reported in the middle 1960s [1]. Forty years later, the chemistry of these compounds has developed into one of the most fruitful fields in organometallic chemistry [2], and still attracts a great deal of chemical interest. In the palladium-catalyzed carbon–carbon bond and carbon–heteroatom bond forming reactions, palladacycles have shown enormous superiority in many respects due to their ready preparation, facile modification, high activity and comparative stability [3]. For instance Bedford et al. recently demonstrated that isolated or in situ formed trialkylphosphine adducts of dimeric nitrogen-containing palladacycles **1** (Fig. 1, L=PCy_3, P^tBu_3, e.g.) efficiently promoted the Suzuki coupling of both activated and deactivated aryl chlorides [4]. We have also found that tricyclohexylphosphine (PCy_3) adducts of dimeric cyclopalladated ferrocenylimines **2**–**3** are very effective for Suzuki coupling of aryl chlorides with phenylboronic acid [5]. These results are particularly interesting since aryl chlorides are cheaper and more readily available than the corresponding bromides and iodides. On the basis of these findings, we synthesized a novel 1,1′-bisferrocenylimine [{(η^5-C_5H_4)-CH=NCy}$_2$Fe] **4** and studied its cyclopalladation with the aim of getting the corresponding biscyclopalladated tricyclohexylphosphine adducts. However, the double cyclopalladation of **4** with two mole equivalents of Li_2PdCl_4/NaOAc followed by treatment with tricyclohexylphosphine afforded [PdCl{[(η^5-C_5H_4)-CHO]Fe[(η^5-C_5H_3)-CH=NCy]}(PCy_3)] **6**, which arised from the monocyclopalladation of **4** and the hydrolysis of one imino group. Herein we report the synthesis, characterization and crystal structures of **4** and **6** (Scheme 1).

The preparation of **4**, **5** and **6** are as follows: To a solution of 1,1′-diformylferrocene [6] in dry toluene was added cyclohexylamine under nitrogen. Then the mixture was refluxed with stirring in the presence of freshly activated neutral Al_2O_3 for about 3 h until the carbonyl absorption of 1,1′-diformylferrocene disappeared according to IR spectrum. After filtration and evaporation of the solvents, the crude product was recrystallized from dichloromethane–petroleum ether giving brown-red crystals of 1,1′-bisferrocenylimine **4** (yield: 93%) [7]. The following double cyclopalladation reaction was carried out with **4** and two mole equivalents of Li_2PdCl_4 and NaOAc in methanol at

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* Corresponding author. Tel./fax: +86 371 67766667.
E-mail address: wyj@zzu.edu.cn (Y.-J. Wu).

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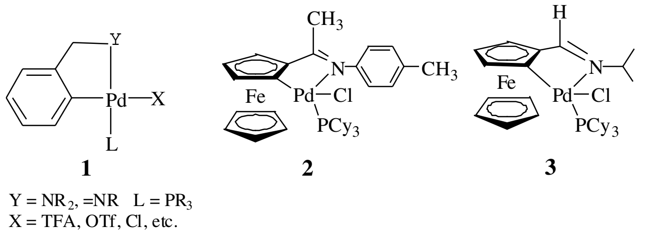
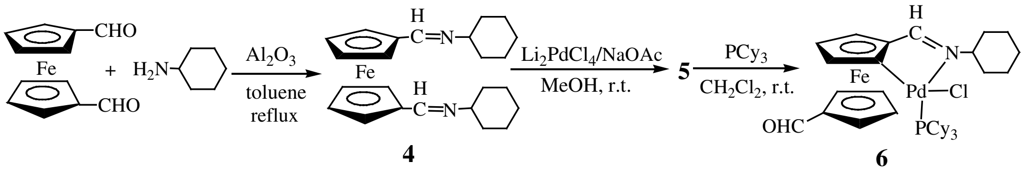


Fig. 1. Examples of adducts resulting from the corresponding dimeric palladacycles with phophines.

room temperature for 24 h. The formed red solids of **5** (yield: 83%) were collected by filtration and washed several times with methanol. Without further purification, complex **5** was treated with two equivalents of PCy_3 in dry CH_2Cl_2 at room temperature for 0.5 h. The product was separated by passing through a short silica gel column with CH_2Cl_2 as eluent, which the first band afforded complex **6** (yield: 42%) [8] after the evaporation of the solvent.

The IR spectrum of 1,1′-diferrocenylimine **4** show $\nu_{C=N}$ at 1639 cm^{-1}, which is similar to that of N-(cyclohexyl)ferrocylideneamine [9], but shifted to higher energy in comparison with those of ferrocenylarylimines [10]. Compared with **4**, the C=N absorption (1622 cm^{-1}) of compound **5** shifts to lower energy, indicating the coordination of nitrogen to palladium. Compound **5** was tentatively assigned to be polymeric or dimeric biscyclopalladated derivatives since no other bands (at about 1639 or 1679 cm^{-1}) were detected in the IR spectrum [11]. For complex **6**, two bands at 1612 and 1679 cm^{-1} are detected in the IR spectrum and these absorptions are ascribed to the stretching of the C=N and C(O)H groups ($\nu_{C(O)H} = 1684$ cm^{-1} for 1,1′-diformylferrocene). The IR spectrum of the reaction mixture of **5** with PCy_3 was also determined and three bands at 1693, 1637 and 1612 cm^{-1} were observed. This suggested that the C(O)H group was formed during the reaction. The ^1H NMR spectrum of **6** also confirms the existence of C(O)H group by the singlet at δ 9.91 ppm. The signals of two Cp rings appear at δ 4.74, 4.61, 4.42 and 4.32 ppm, respectively, which are integrated for seven protons. The above results indicate that **6** is a monocyclopalladated complex. The expected biscyclopalladated tricyclohexylphosphine adducts were not isolated from the reaction of **5** with PCy_3 .

The X-ray crystal structures [12] of compounds **4** and **6** were determined and perspective views of their molecular structures are shown in Figs. 2 and 3, respectively. The two Cp rings in **4** are parallel with a dihedral angle of 0°, and the dihedral angle between two Cp rings in **6** is 3.3°. Owing to the coordination of nitrogen to palladium, the C=N bond distance in **6** (1.275(7) Å) is longer than that in **4** (1.264(3) Å). The angle between the C5—C6 and C5A—C6A is 180° for **4** and the corresponding angle between the C1—C18 and C10—C11 is 75.3° for **6**. Fig. 3 shows clearly that compound **6** is a monocyclopalladated complex. The palladium adopts a distorted square planar configuration defined by the N1, C6, P1, Cl1 atoms and the angels around the Pd1 center are in the range of 81.05–96.52°. The coordinated PCy_3 is *trans* to the imino nitrogen with a P—Pd—N angle of 169.71(12)°. The bicyclic system formed by the palladacycle and the C_5H_3 moiety is approximately coplanar (dihedral angle 7.7°). The Pd1—N1 (2.173(4) Å) and Pd—P (2.2815(13) Å) bond lengths are similar to those of complex **2** (2.170(5) Å and



Scheme 1.

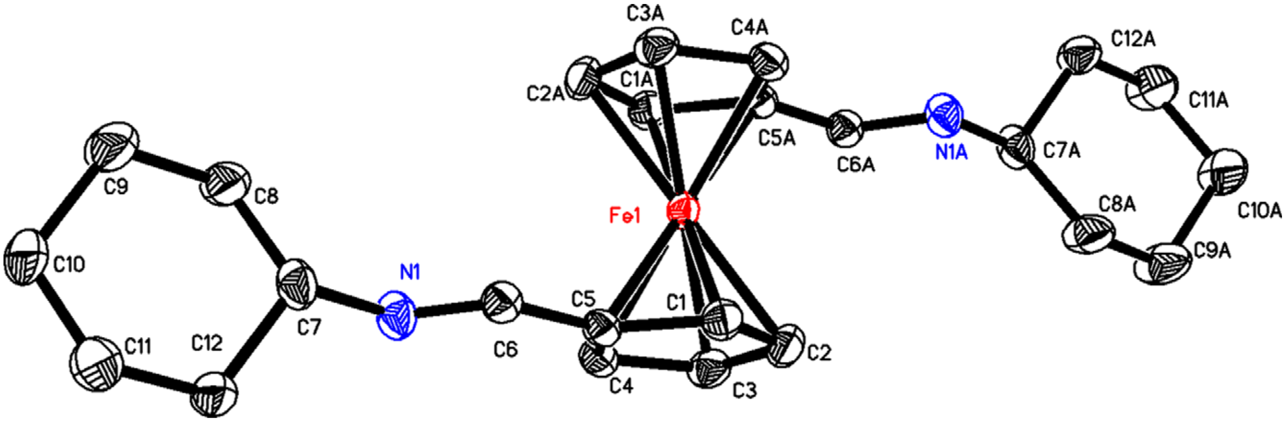


Fig. 2. Molecular structure of complex **4**. Selected bond lengths (Å) and angles (°): N(1)—C(6) 1.264(3), N(1)—C(7) 1.466(2), C(5)—C(6) 1.458(3), C(6)—N(1)—C(7) 117.64(18), N(1)—C(6)—C(5) 123.72(19), C(4)—C(5)—C(6) 127.74(19).

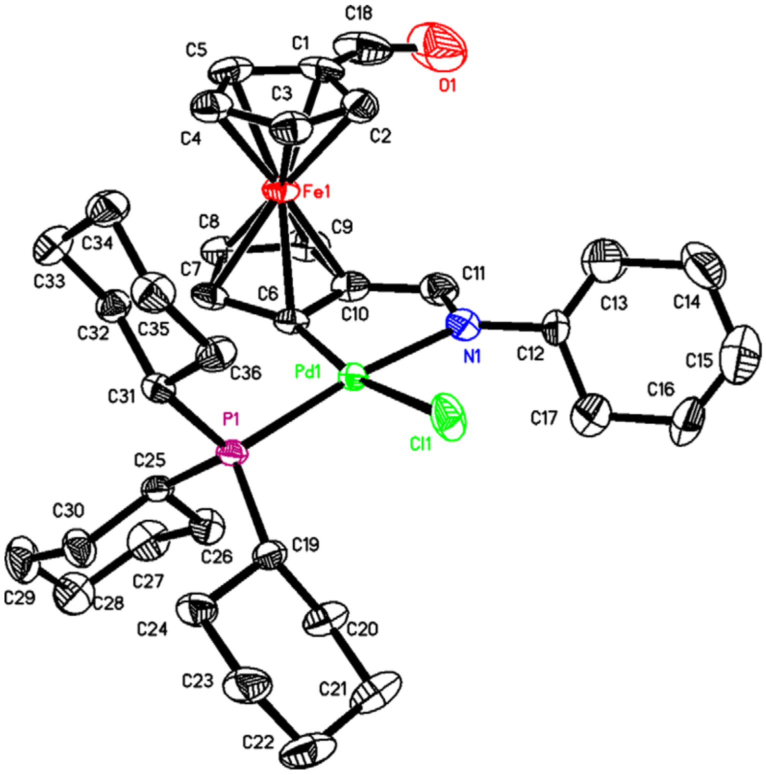


Fig. 3. Molecular structure of complex **6**. Selected bond lengths (Å) and angles (°): Pd(1)—C(6) 2.006(4), Pd(1)—N(1) 2.173(4), Pd(1)—P(1) 2.2815(13), Pd(1)—Cl(1) 2.3814(13), C(11)—N(1) 1.275(7), C(12)—N(1) 1.479(7) and C(6)—Pd(1)—N(1) 81.05(18), C(6)—Pd(1)—P(1) 96.52(14), N(1)—Pd(1)—P(1) 169.71(12), C(6)—Pd(1)—Cl(1) 167.97(13), N(1)—Pd(1)—Cl(1) 91.49(13), P(1)—Pd(1)—Cl(1) 92.44(4), C(11)—N(1)—C(12) 122.3(5).

2.2833(16) Å) [5], while they are longer than those of the related Ph$_3$P adducts [10c,13] [2.135(3), 2.153(6), 2.130(6), 2.114(4) Å and 2.2569(9), 2.236(2), 2.247(2), 2.2356(13) Å] possibly due to the steric bulk of the PCy$_3$ ligand.

In the crystal of **4** there exist intermolecular hydrogen bond between the nitrogen atom of imino group and the adjacent C—H group of Cp ring (N1AJ···H1E = N1F···H1AJ = 2.612 Å,N1AJ ···H1E—C1E = N1F···H1AJ—C1AJ = 154.8°), which are attributed to construct the 2 D layer structure of complex **4**. In complex **6**, chlorine atom not only forms hydrogen bond with the adjacent C—H group of Cp ring, but also forms hydrogen bond with the adjacent C—H group of tricyclohexylphosphine (Cl1C···H5AA = Cl1F···H5AB = 2.774Å,Cl1C···H5AA-

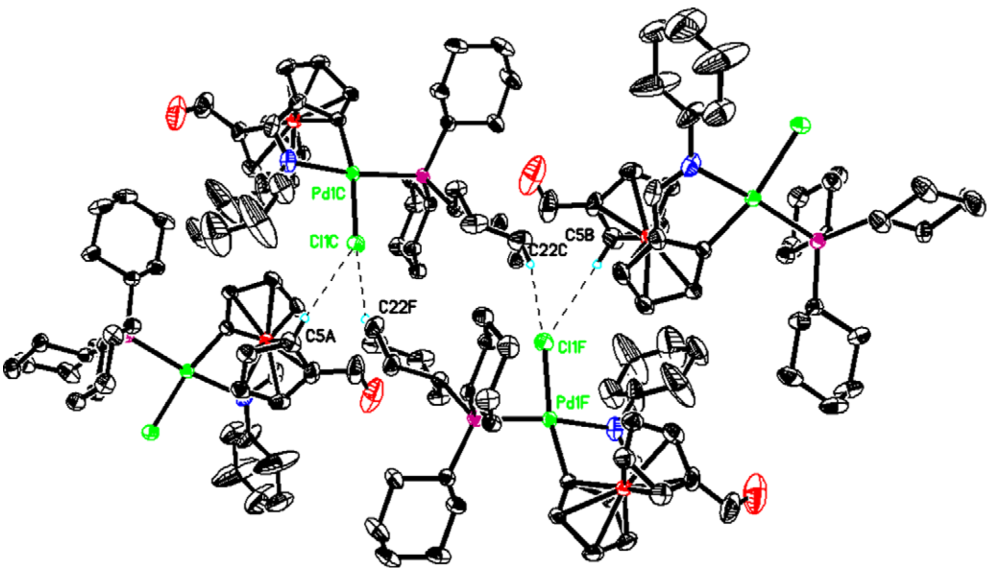


Fig. 4. The hydrogen bonds in complex **6**.

C5A = Cl1F···H5AB—C5B = 148.9° and Cl1C···H22K = Cl1F···H22E = 2.794 Å, Cl1C···H22K—C22F = Cl1F···H22E—C22C = 168.5°) (Fig. 4), which are attributed to construct the 3D network structure of complex **6**.

In conclusion, we have synthesized a novel 1,1′-bisferrocenylimine $[\{(\eta^5\text{-}C_5H_4)\text{-}CH{=}NCy\}_2Fe]$ **4** and obtained its monocyclopalladated complex $[PdCl\{[(\eta^5\text{-}C_5H_4)\text{-}CHO]Fe[(\eta^5\text{-}C_5H_3)CH{=}NCy]\}(PCy_3)]$ **6**. Applications involving **6** in palladium-catalyzed reactions are currently under investigation in our laboratory.

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Appendix A. Supplementary data

Crystallographic data for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Center. CCDC No. 284579, **4**; 287209, **6**. Copies of these information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2006.02.008.

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[7] Characterization data for **4**: m.p. = 117–118 °C. Found (calcd.) % for $C_{24}H_{32}FeN_2$: C, 71.34 (71.29); H, 7.94 (7.98); N 6.90 (6.93). IR (KBr, cm^{-1}): 2923s, 2850m, 1639s (C=N), 1446m, 1385m, 1328m, 1245m, 1076m, 1047m, 886w, 824s; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.10 (s, 2H, —CH=N—), 4.61 (s, 4H, C_5H_4), 4.33 (s, 4H, C_5H_4), 3.03 (m, 2H, N—C*H*C_5H_{10}), 1.82 (m, 4H, —C_6H_{11}), 1.70 (m, 6H, —C_6H_{11}), 1.55 (m, 4H, —C_6H_{11}), 1.31 (m, 6H, —C_6H_{11}). ESI-MS $(M+H)^+$ *m/z*: 405.

[8] Characterization data for **6**: m.p. 250 °C. Found (calcd.) % for $C_{36}H_{53}ClFeNOPPd$: C, 58.13 (58.08); H, 7.15 (7.18); N 1.83 (1.88). IR (KBr, cm^{-1}): 2927s, 2851s, 1679m (CHO), 1612m (C=N), 1448m, 1369w, 1243w, 1063w, 822w, 740w. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, ppm): δ 45.25. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 9.91 (s, 1H, —CHO), 8.00 (s, 1H, —CH=N—), 4.74 (s, 1H, C_5H_3), 4.61 (m, 4H, C_5H_4), 4.42 (s, 1H, C_5H_3), 4.32 (m, 2H, C_5H_3+N—C*H*C_5H_{10}), 1.24–2.53 (m, 43H, PCy_3 + —C_6H_{11}). ESI-MS $(M{-}Cl)^+$ *m/z*: 708.

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[12] Crystals of **4** and **6** were obtained by recrystallization from dichloromethane–petroleum ether at r.t.. Crystal data for **4**: $C_{24}H_{32}FeN_2$, $0.20 \times 0.20 \times 0.18$ mm^3, Monoclinic, C2/c, $a = 20.795(4)$ Å, $b = 11.117(2)$ Å, $c = 9.5532(19)$ Å, $\alpha = \gamma = 90°$, $\beta = 99.92(3)°$, $V = 2175.5(8)$ Å^3, $Z = 4$, $D_{\text{Calc}} = 1.235$ Mg/m^3, $\mu = 0.703$ mm^{-1}, $F(000) = 864$. Crystal data for **6**: $C_{36}H_{53}ClFeNOPPd$, $0.20 \times 0.18 \times 0.16$ mm^3, Monoclinic, P2(1)/c, $a = 10.491(2)$ Å, $b = 14.116(3)$ Å, $c = 24.020(5)$ Å, $\alpha = \beta = 90°$, $\gamma = 101.58(3)°$, $V = 3484.6(12)$ Å^3, $Z = 4$, $D_{\text{Calc}} = 1.417$ Mg/m^3, $\mu = 1.083$ mm^{-1}, $F(000) = 1548$. Intensity data of the complexes **4** and **6** were measured on a Rigaku–Raxis-IV X-ray diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 291(2) K. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares using the SHELXTL-97 program package giving a final $R_1 = 0.0311$, w$R_2 = 0.0707$ and 1893 unique reflections with $I > 2\sigma(I)$ for **4** and $R_1 = 0.0514$, w$R_2 = 0.0950$ and 5922 unique reflections with $I > 2\sigma(I)$ for **6**. Non-hydrogen atoms were refined anisotropically, the hydrogen atoms were computed and refined isotropically using a riding model.

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