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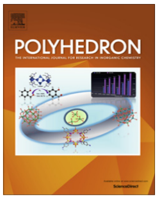

A novel cyclopalladated complex with a diferrocenyl Schiff base ligand: Synthesis, structure, electrochemical and catalytic properties

Li-Min Han, Chun-Long Ke, Dan-Zhao Zhang, Yuan-Yuan Gao, Ning Zhu, Rui-Jun Xie, Ya-Qi Wang, Quan-Ling Suo *

Chemical Engineering College, Inner Mongolia University of Technology, Hohhot 010051, PR China

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ABSTRACT

The N-(diferrocenylmethylene)aniline Schiff base $Fc_2C=NPh$ (**1**) (Fc = ferrocenyl, Ph = phenyl) was synthesized by the reaction of diferrocenyl-methanone with aniline, and its structure was determined for the first time in this paper. The crystal structure of the novel cyclopalladated complex $(Fc_2C=NPh)PdClPPh_3$ (**2**) was analyzed by single crystal X-ray diffraction. The structure of ligand **1** displays an anti-configuration for the ferrocenyl groups bonded to the C atom of the C═N bond lying on the opposite side to the phenyl ring. The structure of complex **2** shows a four-coordinated structural type and the two ferrocenyl moieties bridged through the C atom of the C═N bond remain in the anti-configuration; the structure also contains a bicyclic system of the coordinated Cp ring and a five-membered metallacycle. The electrochemical properties of ligand **1** and complex **2** were studied by cyclic voltammetry, and the results reveal that there is a stronger electronic communication between the two ferrocenyl units in **2**. The results of a catalytic evaluation show that complex **2** is highly active as a catalyst for the Suzuki C—C coupling reaction and the biphenyl product gotten in this reaction can be obtained in 93% yield.

1. Introduction

The chemistry of cyclopalladated compounds has attracted much research interest in past years because of their varied structural features [1–5], as well as for their broad applications in organic synthesis [6], electrochemistry [7], catalysis [8] and liquid crystals [9]. Imine palladacycles, as promising catalysts, have widely been used in Heck, Suzuki, Sonogashira and Buchwald–Hartwig coupling reactions [3,10,11]. Bisferrocenyldiimine compounds, such as $Fc(CH_3)CNCH_2CH_2NC(CH_3)Fc$ (Fc = ferrocenyl), and their complexes, in which two ferrocenyl units are located on two different carbon atoms from two imine groups, have been prepared and their electrochemical properties researched [12,13]. However, investigations on the synthesis, structure and properties of the diferrocenylimine compound Fc_2CNPh (Ph = phenyl) are relatively rare. In 1977, one paper reported the synthesis of a diferrocenylimine [14], but its structure and coordination have not been investigated.

To explore the coordination ability and electrochemical properties of the diferrocenylimine ligand, in which the two bulky ferrocenyl units are bonded to one carbon atom of the imine group, a novel diferrocenylimine cyclopalladated complex $(Fc_2C=NPh)PdClPPh_3$ (**2**) has been synthesized and its crystal structure was studied by single crystal X-ray diffraction in this paper.

The electrochemical investigation on the diferrocenylimine ligand **1** and its complex **2** shows that there is a stronger electronic communication between the two ferrocenyl units in **2**. Complex **2** was used as a catalyst for the Suzuki C—C coupling reaction and was found to be highly active.

2. Experimental

2.1. General procedures

All reactions were carried out under an atmosphere of dry argon using standard Schlenk techniques and monitored with thin-layer chromatography (TLC). Solvents were freshly dried and distilled before use. FcCOFc (Fc = ferrocenyl) and Li_2PdCl_4 were prepared using the methods found in the literature [15,16]. $PhNH_2$, PPh_3 (Ph = phenyl), NaOAc (Ac = CH_3CO), $TiCl_4$, C_6H_5I, $C_6H_5B(OH)_2$ and $K_3PO_4{\cdot}7H_2O$ were purchased from Alfa-Aesar and used as received. Column chromatographic separations and purifications were performed on 200–300 mesh silica gel.

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* Corresponding author. Tel./fax: +86 471 6575675.
E-mail address: szj010062@163.com (Q.-L. Suo).

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^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-500 MHz spectrometer. FT-IR spectra were measured on a Nicolet FT-IR spectrometer using KBr discs. Elemental analyses were carried out on an Elementar var III-type analyzer. Mass spectra were determined using a Shimadzu LCMS-2020 instrument.

Cyclic voltammetry was performed on a CHI-760C electrochemical analyzer using a platinum disk working electrode, an Ag|AgCl reference electrode and a platinum wire auxiliary electrode. The working electrode surface was polished with 0.05 μm alumina before each run. The samples were dissolved in a mixture of CH_3CN and CH_2Cl_2 with a concentration of 3.0×10^{-4} M. The supporting electrolyte was tetra-*n*-butylammonium hexafluorophosphate (TBAHFP, 0.05 M). The scan rates were 30–150 mV/s. Oxygen was purged from the one-compartment cell before each electrochemical run.

Based upon the X-ray single crystal structural analysis for ligand **1** and complex **2**, calculations of the extended hückel charge of ligand **1** and complex **2** have been carried out using a personal computer with the GAUSSIAN03 program package. The B3LYP density function and the 6-31G basis set were used for the molecular geometry optimization of ligand **1** and complex **2** [17].

2.2. Synthesis

2.2.1. Synthesis of the N-(diferrocenylmethylene)aniline ligand 1

FcCOFc (199 mg, 0.5 mmol, 1 equiv.) and $PhNH_2$ (0.2 mL, 2 mmol, 4 equiv.) were dissolved in toluene (20 mL), then the red reaction mixture that formed was cooled to 0 °C. $TiCl_4$ (0.2 mL, 1.8 mmol) in toluene (10 mL) was dropped into the reactive system, and the resulting red reaction mixture was stirred for 15 min at 0 °C. The reaction temperature was increased to room temperature and the stirring was continued for 3 h. The red reaction mixture was then poured into water (100 mL, 0 °C) and the red mixture was extracted 3 times with dichloromethane. The combined organic phases were dried using anhydrous $MgSO_4$ for 2 h, the solvent was removed under reduced pressure and the residue was subjected to silica gel column chromatography. Elution with a mixture of petroleum ether, dichloromethane and ethyl acetate (2:11:1, V/V) afforded the raw Schiff base product ($Fc_2C = NPh$). Orange crystals of the Schiff base N-(diferrocenylmethylene)aniline (**1**) were obtained by a hexane/dichloromethane recrystallizing technique.

Table 1
Summary of crystallographic data for ligand **1** and complex **2**.

	1	2
Formula	$C_{27}H_{23}Fe_2N$	$C_{96}H_{86}Cl_8Fe_4N_2OP_2Pd_2$
Formula weight	473.16	2065.41
T (K)	296(2)	293(2)
λ (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	15.584(2)	11.8928(17)
b (Å)	7.4101(10)	18.4465(10)
c (Å)	20.406(2)	20.2775(10)
α (°)	90	90
β (°)	117.190(8)	96.0830(10)
γ (°)	90	90
V (Å^3)	2096.1(4)	4423.4(7)
Z	4	2
ρ_{Calcd} (g cm^{-3})	1.499	1.551
Absorbed coefficient (mm^{-1})	1.398	1.363
F(000)	976	2092
θ (°)	2.04–25.01	2.20–27.50
Reflections collected	17391	32486
Unique	3696	9796
Completeness to θ (%)	99.9	96.3
$T_{max.}$ and $T_{min.}$	0.932 and 0.920	0.761 and 0.754
Goodness-of-fit (GOF) on F^2	1.033	0.998
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0247$, $wR_2 = 0.0653$	$R_1 = 0.0721$, $wR_2 = 0.1998$
R indices (all data)	$R_1 = 0.0275$, $wR_2 = 0.0673$	$R_1 = 0.0877$, $wR_2 = 0.2268$

*N-(diferrocenylmethylene)aniline (**1**):* 323 mg (yield, 68%). M.p.: 157–159 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.70–7.01 (m, 5H, Ph), 4.13–5.23 (m, 18H, 2Fc); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 166.20 (1C, C=N), 153.33 (1C, Ph), 128.99, 122.17, 116.39 (5C, Ph), 84.41 (1C, Cp), 71.88, 70.48, 70.04, 70.02, 69.75, 69.27 (19C, 2Fc); FT-IR (KBr disk, cm^{-1}): 3093, 3054 (ν_{C-H}, Cp, Ph), 1587 ($\nu_{C=N}$), 1462, 1392 ($\nu_{C=C}$, Ph, Cp), 1104, 996 (δ_{CH}, Cp), 820 (γ_{CH}, Cp); ESI-MS (CH_2Cl_2, *m/z*): 473 (M^+); *Anal.* Calc. for $C_{27}H_{23}NFe_2$: C, 68.54; H, 4.90; N, 2.96. Found: C, 68.12; H, 4.81; N, 2.92%.

2.2.2. Synthesis of the diferrocenylimine cyclopalladated complex 2

$Fc_2C = NPh$ (189 mg, 0.4 mmol, 1 equiv.), NaOAc (33 mg, 0.4 mmol, 1 equiv.) and Li_2PdCl_4 (4 mL, 0.4 mmol, 0.1 M, 1 equiv.) were dissolved in methanol (20 mL), and the reaction mixture was stirred for 27 h at room temperature. The reaction was stopped after a great deal of a red solid was deposited. The reaction

Table 2
Selected bond lengths (Å) and angles (°) for ligand **1** and complex **2**.

1			
C(5)—N(1)	1.2876(19)	C(5)—C(6)	1.486(2)
C(5)—C(16)	1.480(2)	C(4)—N(1)	1.409(2)
N(1)—C(5)—C(16)	114.21(13)	C(27)—C(4)—N(1)	122.10(15)
N(1)—C(5)—C(6)	125.18(14)	C(3)—C(4)—N(1)	118.48(16)
C(16)—C(5)—C(6)	120.61(12)	C(10)—C(6)—C(5)	126.31(14)
C(20)—C(16)—C(5)	123.32(13)	C(7)—C(6)—C(5)	127.38(13)
C(17)—C(16)—C(5)	129.81(13)	C(5)—N(1)—C(4)	123.26(13)
2			
Pd(1)—N(1)	2.124(4)	C(15)—C(11)	1.449(7)
Pd(1)—P(4)	2.2576(13)	N(1)—C(45)	1.310(6)
Pd(1)—C(15)	1.995(5)	C(45)—C(11)	1.463(6)
Pd(1)—Cl(1)	2.3900(12)	C(45)—C(1)	1.471(7)
C(15)—Pd(1)—N(1)	79.83(18)	N(1)—Pd(1)—P(4)	173.22(11)
C(15)—Pd(1)—P(4)	93.86(14)	C(45)—N(1)—Pd(1)	116.3(3)
C(45)—N(1)—C(39)	120.3(4)	C(39)—N(1)—Pd(1)	122.2(3)
N(1)—C(45)—C(11)	112.9(4)	C(11)—C(45)—C(1)	122.4(4)
N(1)—C(45)—C(1)	124.7(4)	C(11)—C(15)—Pd(1)	112.9(3)
C(15)—C(11)—C(45)	117.4(4)	Pd(1)—C(15)—Fe(2)	120.9(2)

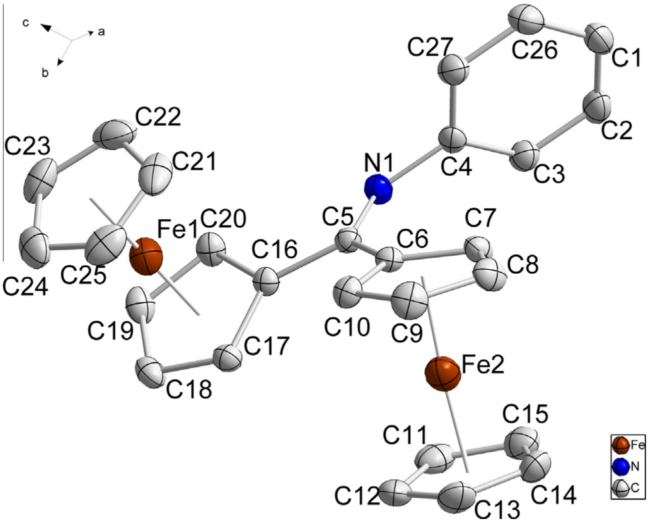

Fig. 1. Molecular structure of ligand **1**. The H atoms have been omitted for clarity.