

Synthesis, characterization and structure of cyclopalladated ferrocenyketimines

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Received 2 February 1994; in revised form 23 March 1994

Abstract

The reactions of ferrocenyketimines $C_5H_5FeC_5H_4C(CH_3)=NAr$ (Ar = a variety of substituted phenyls, 1-naphthyl and 2-naphthyl) with lithium tetrachloropalladate (II) in the presence of sodium acetate in methanol for about 20 h at room temperature and the treatment of the resulting products with triphenylphosphine lead to the five-membered cyclopalladated derivatives $[PdCl \{C_5H_5FeC_5H_3C(CH_3)=NAr\} (PPh_3)]$. The structures of these metallocycles have been confirmed by IR and ¹H NMR spectroscopies, and further by X-ray crystal structure determination of $[PdCl \{C_5H_5FeC_5H_3C(CH_3)=N(C_6H_4-4-Cl)\} (PPh_3)]$. The palladium atom shows the four-coordinate structure typical of palladium complex, and the Pd–N distance is 2.135 Å. The ¹H NMR spectra of $[PdCl \{C_5H_5FeC_5H_3C(CH_3)=NAr\} (PPh_3)]$ (Ar = C₆H₄-2-Cl and 1-naphthyl) show that both compounds exist as a mixture of two isomers.

Keywords: Iron; Palladium; Cyclometallation; Ferrocene; Imine

1. Introduction

Cyclometallation reactions have been widely used to synthesize new organometallic compounds by activation of C–H bonds [1]. The first example of intramolecular *ortho*-palladation of metallocene was reported by Alper in 1974, showing that thiopivaloylferrocene was readily palladated by treatment with equimolar sodium tetrachloropalladate(II) to afford the cyclopalladated derivative [2]. Since then, there has been considerable interest in the cyclometallation of ferrocene derivatives containing coordinating groups, especially nitrogen-donor ligands, by transition metals such as palladium and platinum. Most of the documented research involving nitrogen-donor ligands has focused on (dimethylaminomethyl) ferrocene [3] and 2-pyridylferrocene [4] and their analogues [1,5], while there are few reports on the other ligands [6]. Although the cyclometallation

reactions of numerous imines have been extensively studied, none involve cyclometallation of ferrocenyimines by transition metals [1,7].

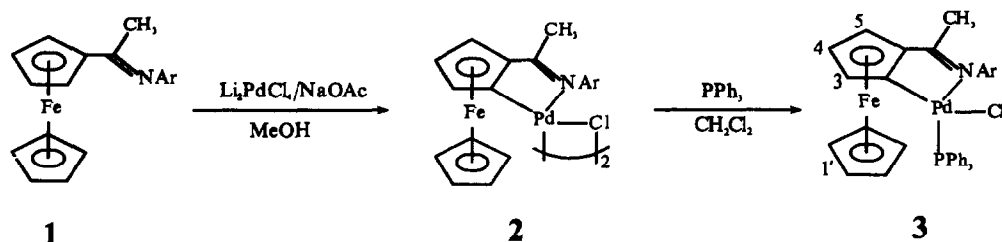
This paper reports the syntheses, structures and properties of cyclopalladated ferrocenyketimines, which represent the first example of transition metal cyclometallated ferrocenyimines.

2. Results and discussion

2.1. Cyclopalladation reaction

Duff and Shaw et al. have previously shown that acetate ion promotes internal metallation reactions [8]. Sokolov and Reutov et al. further demonstrated that acetate ion not only serves as an acid binding agent consuming the hydrogen chloride liberated in the reaction, but participates in the formation of the reaction transition state as well [9]. As expected, we found that ferrocenyketimine (1c) underwent palladation readily

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Ar = *p*-CH₃OC₆H₄ (**a**), *p*-CH₃C₆H₄ (**b**), C₆H₅ (**c**), *p*-ClC₆H₄ (**d**), *p*-BrC₆H₄ (**e**),
p-IC₆H₄ (**f**), *p*-NO₂C₆H₄ (**g**), *m*-CH₃C₆H₄ (**h**), *m*-Cl C₆H₄ (**i**), *m*-BrC₆H₄ (**j**),
m-NO₂C₆H₄ (**k**), *o*-ClC₆H₄ (**l**), 1-naphthyl (**m**), 2-naphthyl (**n**).

Table 1
The yields, analytical data and melting points for the compounds **3**

Compound	Yield ^a (%)	M.P. (°C)	Analytical data ^b		
			C	H	N
3a ^f	90	205–207 ^c	58.03(57.83)	4.52(4.40)	1.90(1.80)
3b	80	238–240 ^d	61.64(61.60)	4.44(4.61)	2.27(1.94)
3c ^g	81	155–157 ^c	56.30(56.16)	3.90(4.20)	1.86(1.77)
3d	78	245–247 ^d	57.98(58.29)	4.20(4.08)	2.04(1.89)
3e	74	> 270 ^e	54.91(55.06)	3.65(3.85)	1.63(1.78)
3f	34	> 270 ^e	51.72(51.96)	3.46(3.63)	1.81(1.68)
3g	65	> 270 ^e	57.37(57.55)	3.87(4.02)	3.84(3.73)
3h ^g	78	165–170 ^c	56.50(56.68)	4.25(4.38)	1.92(1.74)
3i ^g	66	165–168 ^c	53.60(53.82)	3.63(3.90)	1.91(1.70)
3j ^g	60	165–170 ^c	50.88(51.07)	3.52(3.71)	1.88(1.61)
3k	72	> 270 ^e	57.46(57.55)	3.73(4.02)	3.82(3.73)
3l ^a	65	160–165 ^c	53.71(53.82)	3.69(3.90)	1.86(1.70)
3m ^g	21	176–180 ^c	58.40(58.53)	4.40(4.19)	1.74(1.66)
3n	61	> 270 ^e	63.38(63.52)	4.36(4.40)	1.97(1.85)

^a Calculated on the basis of the starting ferrocenylketimines. ^b Calculated values in parentheses. ^c Melts with gas evolution. ^d Melts with decomposition. ^e Decomposes without melting. ^f Contained 0.5 CH₂Cl₂ per molecule. ^g Contained one CH₂Cl₂ per molecule.

Table 2
The IR absorption frequencies (cm⁻¹) for the compounds **3** ^a

Compound	1100–1000 rule	917 rule ^b	C=N ^b	δ (C–H) ^c	PPh ₃	
3a	1095, 997	918 (900)	1566 (1623)	816	740	691
					1241 (C–O–C)	
3b	1096, 997	917 (900)	1569 (1624)	816	740	688
3c	1096, 998	920 (897)	1574 (1634)	817	748	688
3d	1094, 1000	917 (898)	1570 (1623)	820	740	690
3e	1094, 1000	917 (897)	1570 (1623)	819	740	689
3f	1095, 1000	917 (900)	1566 (1623)	818	738	689
3g	1100, 1000	918 (900)	1569 (1632)	820	748	690
					1510, 1340 (NO ₂)	
3h	1098, 998	932 (915)	1574 (1624)	810	740	690
3i	1096, 998	923 (905)	1569 (1624)	820	740	688
3j	1097, 998	920 (902)	1570 (1624)	820	733	688
3k	1095, 998	934 (920)	1570 (1638)	820	740	688
					1520, 1344 (NO ₂)	
3l	1097, 998	918 (900)	1570 (1627)	820	740	690
3m	1095, 998	917 (900)	1570 (1626)	810	740	690
3n	1095, 997	920 (904)	1569 (1631)	816	738	688

^a KBr pellets. ^b Values in parentheses are for the corresponding free ligands **1**. ^c Values for the ferrocene Cp rings.

when treated with mole equivalents of lithium tetrachloropalladate(II) and sodium acetate in methanol-ethyl ether for 20 h at room temperature, and the resulting precipitates were isolated as a red crystalline solid, which is insoluble in all common organic solvents, and which can be assigned to a binuclear complex of palladium **2c**. Since the solid readily underwent a bridge-splitting reaction with ligand triphenylphosphine to produce quantitatively the monomeric triphenylphosphine derivative **3c** (overall yield 80%), which is a typical reaction of a chlorine-bridged binuclear complex of palladium [3,4]. In contrast, the reaction of **1c** with lithium tetrachloropalladate(II) in the absence of sodium acetate yielded a smaller amount of brown solid, which was treated with triphenylphosphine to afford cyclopalladated compound **3c** in only 30% overall yield, as well as a considerable amount of the dichlorobis (triphenylphosphine) palladium(II).

The other cyclopalladated compounds **3** were also synthesized by a procedure similar to that for **3c** in the presence of sodium acetate. All the new compounds **3** are air stable crystals. The yields, analytical data and

melting points or decomposition temperatures of the compounds are shown in Table 1. The main IR data for the compounds **3** are summarized in Table 2 and the ^1H NMR data in Table 3.

2.2. Spectral properties of cyclopalladated compounds

The IR spectra of **3a–n** showed absorption bands at 1000 and 1100 cm^{-1} , which are indicative of an unsubstituted cyclopentadienyl ring [10]. Rosenblum and Howells have previously suggested that the IR spectra may serve to define the structures of homoannularly-disubstituted ferrocene derivatives; the 1, 2-isomer possesses one band near 917 cm^{-1} [11]. All compounds **3** exhibited absorptions near 917 cm^{-1} characteristic of homoannularly 1, 2-disubstituted ferrocene derivatives, as expected. Furthermore, a careful comparison of the IR spectra of free ligands **1** with those of the cyclometallated compounds **3** indicated that the 917 cm^{-1} band might be regarded as a result of the shift to high energy of the bands near 900 cm^{-1} for **1** when the cyclopalladation occurred to produce **3**, since the 900

Table 3
 ^1H NMR data for cyclometallated ferrocenylketimines **3**^a

Compound	CH_3	3	4	5	1'	Ar-H		PPh ₃ -H		
3a	2.07s	3.35d (2.4)	4.09t (2.6)	4.43d (2.6)	3.90s	6.86d (9.0)	6.94d (8.7)	7.35–7.37, 7.72–7.76(m)		
3b	2.06s	3.35d (1.7)	4.09t (2.4)	4.43d (2.4)	3.91s	6.89d (7.8)	7.13d (8.0)	7.35–7.37, 7.72–7.76(m)		
3c	2.06s	3.37d (1.5)	4.11t (2.4)	4.45d (2.4)	3.92s	7.00d (7.4)	7.15t (7.5)	7.34–7.37, 7.72–7.76(m) ^b		
3d	2.06s	3.39d (2.4)	4.13t (2.6)	4.45d (2.5)	3.90s	6.94d (8.4)	7.30d (8.0)	7.36–7.38, 7.72–7.76(m)		
3e	2.06s	3.39d (2.4)	4.13t (2.5)	4.45d (2.4)	3.90s	6.89d (8.4)	7.44d (8.4)	7.36–7.38, 7.71–7.75(m)		
3f	2.06s	3.39d (2.4)	4.13t (2.4)	4.45d (2.4)	3.89s	6.77d (8.3)	7.63d (8.4)	7.35–7.37, 7.71–7.75(m)		
3g	2.09s	3.46d (2.4)	4.20t (2.4)	4.49d (2.3)	3.92s	7.15d (9.0)	8.23d (9.0)	7.36–7.42, 7.70–7.74(m)		
3h	2.06s	3.37d (2.4)	4.09t (2.4)	4.44d (2.0)	3.91s	6.80bs (7.4)	6.95d (8.1)	7.22t (8.1)	7.35–7.38, 7.71–7.75(m) ^b	
3i	2.08s	3.41d (2.4)	4.14t (2.5)	4.46d (2.0)	3.91s	6.92d (8.4)	7.00s (8.4)	7.13d (8.4)	7.27t (8.4)	7.36–7.38, 7.71–7.75(m)
3j	2.08s	3.41d (2.4)	4.14t (2.5)	4.46d (2.5)	3.90s	6.96d (8.1)	7.14s (8.5)	7.21t (8.1)	7.28d (8.1)	7.36–7.38, 7.70–7.74(m)
3k	2.11s	3.47d (2.2)	4.19t (2.4)	4.49d (2.5)	3.92s	7.51t (8.0)	7.83s (8.0)	8.03d (8.0)	7.37–7.41, 7.71–7.75(m) ^b	
3l	2.05s	3.30d (2.4)	4.14m	4.47m	4.01s	6.96d (8.3)	7.11t (8.4)	7.22t (8.3)	7.10–7.40, 7.71–7.75(m) ^b	
	2.06s	3.37d (2.4)	4.14m	4.47m	3.93s	7.09d (8.3)	7.11t (8.4)	7.28t (8.3)	7.10–7.40, 7.71–7.75(m) ^b	
3m	1.94s	3.42d (2.4)	4.16t (2.4)	4.48d (2.5)	3.99s	7.18d (7.1)	7.83d (8.0)	7.95d (7.8)	7.31–7.56, 7.67–7.85(m) ^b	
	1.97s	3.38d (2.4)	4.18t (2.4)	4.50d (2.5)	4.06s	7.03d (7.1)	7.83d (8.0)	8.26d (8.0)	7.31–7.56, 7.67–7.85(m) ^b	
3n	2.09s	3.41d (2.4)	4.13t (2.4)	4.47d (2.0)	3.95s	7.22d (7.5)			7.35–7.40, 7.73–7.77(m) ^b	

^a Chemical shifts in ppm relative to the solvent CHCl_3 (δ 7.24); coupling constants in Hz in parentheses.

^b Partial proton signals for the N-phenyl rings contained in the multiplets.

cm^{-1} bands for **1** disappear without exception in the IR spectra of the corresponding cyclopalladated compounds **3**. The C=N absorptions of **3** are shifted to lower wavelengths by ca. 50 cm^{-1} in comparison with the corresponding frequencies of **1**, indicating that nitrogen is coordinated to palladium through its lone pair [7a,12]. The strong absorptions at ca. 740 and 690 cm^{-1} observed in compounds **3**, a feature of the mono-substituted benzene ring, are assigned to the $\delta(\text{CH})$ of PPh_3 . These IR features are in good agreement with the proposed structures for the compounds **3**.

The compounds **3** are easily soluble in methylene chloride or chloroform, thus offering the possibility of characterizing them by ^1H NMR techniques. The ^1H NMR spectra of the compounds **3** were completely consistent with a 1,2-structure for the compounds. Additionally, it was found in their ^1H NMR spectra that one CH_2Cl_2 per molecule is contained in the compounds **3c**, **3h–j**, **3l** and **3n** in which there is no substituent present in the *para*-position of the N-phenyl ring. For example, the ^1H NMR spectrum of **3c** exhibited the expected AMX system of multiplets for the three different protons on the substituted Cp ring with a triplet at δ 4.11 integrating for the proton 4, and two doublets at δ 3.37 and δ 4.45 for the protons 3 and 5, respectively. The singlet at δ 3.92 is for the five protons of the unsubstituted Cp ring, at δ 5.28 for the protons of the solvent methylene chloride contained in the compound, at δ 2.06 for the protons of the α methyl, a doublet at δ 7.00 and a triplet at δ 7.15 for the protons on the N-phenyl ring, and two complex

multiplets at ca. δ 7.36 and δ 7.74 for the fifteen protons of the P-phenyl rings and two protons of the N-phenyl ring. In comparison with the starting materials **1** [13], the proton signals for Cp rings in the compounds **3** are shifted to high fields, and moreover, the proton 3 adjacent to the palladium atom appears at the highest field. This must be caused by a ring current effect of a phosphine phenyl ring, also consistent with a *cis* arrangement of the phosphine and the metallated Cp ring and thus a *trans* disposition of phosphorus and nitrogen atoms. On the other hand, we have shown clearly [14] that in the 2-chloromercurated ferrocenylimines, a chloromercurio group in Cp ring shields the proton α to this group to a greater extent than the proton β to it, and it can be considered that the palladium atom in the compounds **3** might have a similar effect, thus also leading to the upfield shift of the proton 3.

It is noteworthy that, as shown in Fig. 1, the ^1H NMR spectra of **3l** and **3m** indicated that both the compounds exist as a mixture of two isomers, but attempts to separate the two isomers by column chromatography and fractional recrystallization have been unsuccessful. It is, therefore, difficult unequivocally to define the structures of the isomers. Even so, it is our belief that this isomerism must be in relation to the *ortho*-substitution in the N-phenyl ring, and it is likely that the free rotation of the N-phenyl ring about the C–N bond will be blocked due to the steric hindrance between the *ortho*-substituents and α methyl as well as the chlorine bonded to the palladium, consequently,

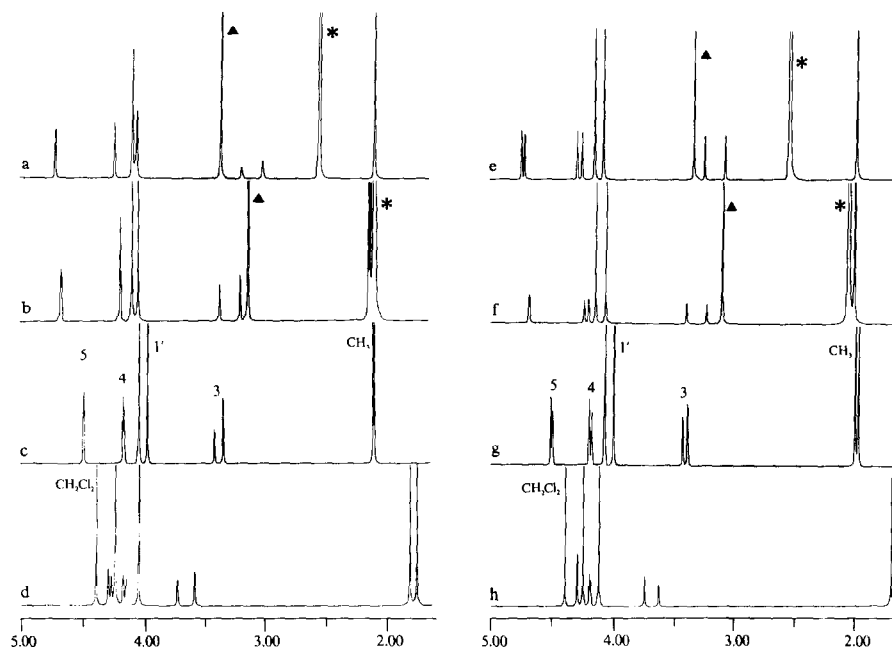
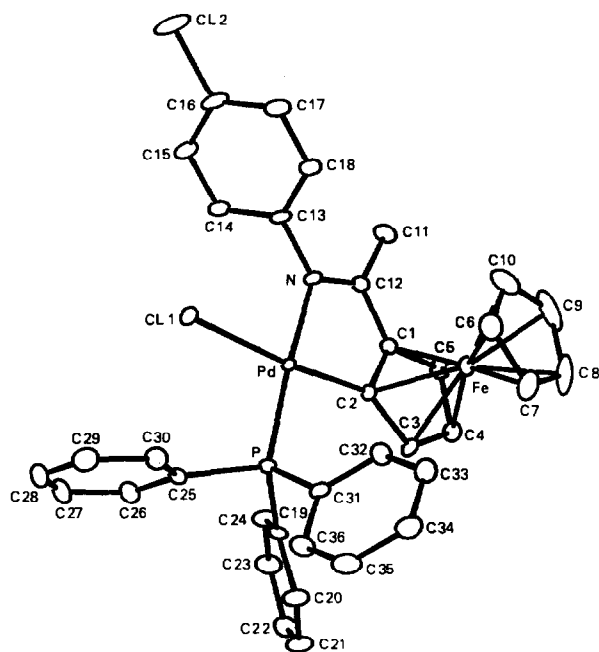


Fig. 1. Partial ^1H NMR spectra of **3l** in $\text{DMSO}-d_6$ (a), CD_3COCD_3 (b), CDCl_3 (c) and C_6D_6 (d) and **3m** in $\text{DMSO}-d_6$ (e), CD_3COCD_3 (f), CDCl_3 (g) and C_6D_6 (h), using TMS as internal standard. * Solvent peaks. ▲ Water peaks.

Fig. 2. Molecular structure of **3d**.

resulting in two isomers, i.e. an *anti* arrangement of the *ortho*-substituents and ferrocene moiety and a *syn* arrangement.

The 2D EXSY spectrum was measured for **3m**, no cross peak representing the chemical exchange between the isomers being found, and the ^1H NMR spectrum of **3m** recorded at 60°C showed no obvious change compared with that at 20°C . These results indicated that the energy required for free rotation is quite high.

The ^1H NMR spectra of the compounds **3l** and **3m** in different solvents (C_6D_6 , CDCl_3 , CD_3COCD_3 and $\text{DMSO}-d_6$) have been recorded in order to define the

effect of solvent on the spectra of the two compounds. The result indicated that, as shown in Fig. 1, with the increase of the coordinating ability of the solvents, the signals of protons **3** shift towards high field, and those of protons **5** towards low field. In contrast, the signals of the protons **1'**, **4** and those of α methyls show no obvious dependence on the solvents except benzene, which causes upfield shift of the protons of α methyl and downfield shift of the protons **1'**. It can also be seen that the differences between the chemical shifts of corresponding protons for each pair of isomers of **3l** and **3m** change with the solvents used. A possible explanation for the observed solvent effect is that the coordination to palladium of the solvent containing the coordinating atom should be expected to disturb the influence of the palladium on the electron distribution in the Cp rings, especially the substituted ring, thus leading to electron redistribution which may cause the solvent effects. In addition, specific orientation of the solvents, especially benzene, by interaction with **3l** and **3m** should be taken into account for the interpretation of the effect.

2.3. X-ray crystal structure of **3d**

The single crystal structure of $[\text{PdCl}\{\text{C}_5\text{H}_5\text{FeC}_5\text{H}_3\text{C}(\text{CH}_3)=\text{N}(\text{C}_6\text{H}_4-4\text{-Cl})\}(\text{PPh}_3)]$ (**3d**) was determined. The structure is shown in Fig. 2, and atomic coordinates and equivalent isotropic temperature factors in Table 4. Selected bond lengths and angles are listed in Tables 5 and 6.

The structure determined is completely consistent with that proposed for the compounds **3**, which has been supported by the spectral data. The substituted Cp ring was palladated in one *ortho*-position, resulting in a five-membered metallocycle. The palladium atom

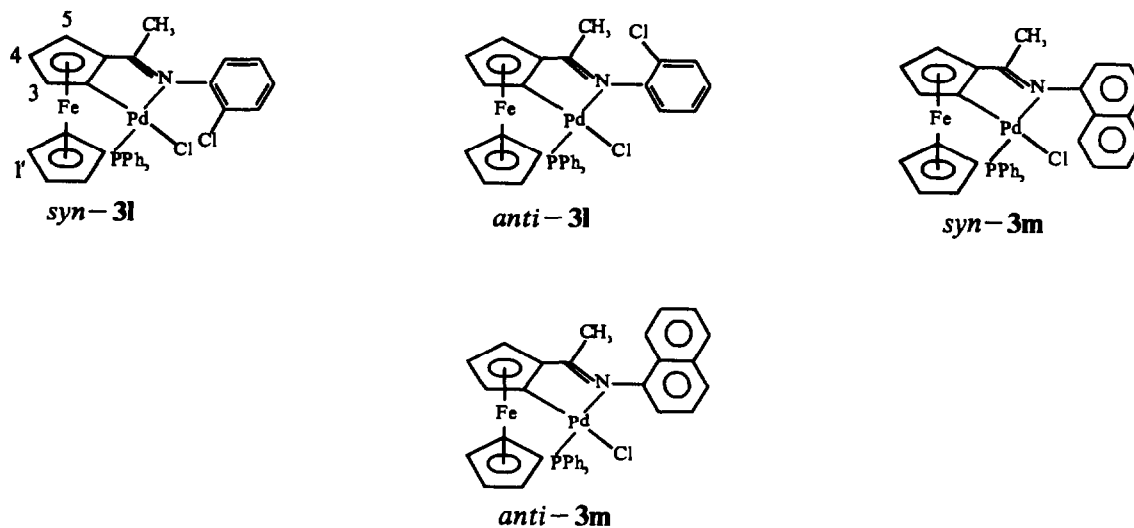


Table 4
Final positional parameters for C₃₆H₃₀ClFeNPPd (3d)

Atom	x	y	z	B(Å ²)
Pd	0.32635(4)	0.05736(3)	0.22155(3)	1.703(8)
Fe	0.03925(9)	-0.05083(8)	0.24634(7)	2.77(2)
Cl(1)	0.5643(1)	0.0282(1)	0.2110(1)	3.04(3)
Cl(2)	0.7914(2)	-0.4510(2)	-0.0504(2)	6.84(6)
P	0.3297(1)	0.2305(1)	0.3392(1)	1.95(3)
N	0.2984(5)	-0.0983(4)	0.1053(4)	2.4(1)
C(1)	0.0667(6)	-0.0220(5)	0.1282(5)	2.5(1)
C(2)	0.1225(5)	0.0640(5)	0.2117(4)	2.3(1)
C(3)	0.0032(6)	0.1333(6)	0.2554(5)	3.0(1)
C(4)	-0.1213(6)	0.0906(6)	0.1977(5)	3.4(2)
C(5)	-0.0843(6)	-0.0068(6)	0.1181(5)	3.1(2)
C(6)	0.1914(8)	-0.1514(7)	0.3410(5)	4.4(2)
C(7)	0.0760(8)	-0.0745(7)	0.3831(5)	4.8(2)
C(8)	-0.0540(8)	-0.1064(8)	0.3200(7)	6.9(2)
C(9)	-0.015(1)	-0.2037(7)	0.2399(7)	7.5(2)
C(10)	0.139(1)	-0.2305(7)	0.2572(7)	6.2(3)
C(11)	0.1226(7)	-0.2166(6)	-0.0028(5)	3.5(2)
C(12)	0.1688(6)	-0.1142(5)	0.0760(4)	2.5(1)
C(13)	0.4149(6)	-0.1867(5)	0.0631(4)	2.4(1)
C(14)	0.4654(7)	-0.1568(5)	0.0021(5)	3.0(1)
C(15)	0.5816(7)	-0.2402(6)	-0.0348(5)	3.6(2)
C(16)	0.6426(7)	-0.3480(6)	-0.0071(5)	3.8(2)
C(17)	0.5945(8)	-0.3791(6)	0.0553(5)	3.6(2)
C(18)	0.4780(7)	-0.2966(5)	0.0912(5)	3.0(2)
C(19)	0.1678(6)	0.3562(5)	0.3182(4)	2.3(1)
C(20)	0.1161(8)	0.4480(6)	0.3932(5)	3.6(2)
C(21)	-0.0039(8)	0.5441(6)	0.3726(6)	4.1(2)
C(22)	-0.0730(7)	0.5502(6)	0.2784(6)	3.9(2)
C(23)	-0.0250(8)	0.4593(6)	0.2020(5)	3.8(2)
C(24)	0.0953(7)	0.3631(6)	0.2235(5)	3.2(2)
C(25)	0.4784(6)	0.2938(5)	0.3522(5)	2.6(1)
C(26)	0.4598(7)	0.3679(6)	0.2919(5)	3.9(2)
C(27)	0.5777(8)	0.4028(6)	0.2916(6)	5.2(2)
C(28)	0.7106(7)	0.3675(6)	0.3536(7)	5.7(2)
C(29)	0.7294(8)	0.2964(7)	0.4131(7)	5.5(2)
C(30)	0.6138(7)	0.2571(6)	0.4121(6)	4.0(2)
C(31)	0.3522(6)	0.2142(5)	0.4594(4)	2.4(1)
C(32)	0.3230(7)	0.1144(6)	0.4695(5)	3.2(2)
C(33)	0.3392(8)	0.0984(6)	0.5606(5)	3.9(2)
C(34)	0.3841(8)	0.1831(6)	0.6434(5)	3.7(2)
C(35)	0.4137(8)	0.2819(6)	0.6341(5)	3.9(2)
C(36)	0.3983(7)	0.2993(6)	0.5447(5)	3.1(2)

is coordinated to P, N, Cl(1) and C(2), showing the four-coordinate structure typical of the palladium complexes. The angles between adjacent atoms in the coordination sphere lie in the region of 79.9° for NPdC(2), and 94.8° for C(2)PdP. The phosphine molecule and the imino nitrogen adopt a *trans* arrangement with an angle PPdN of 173.8°, as indicated by the ¹H NMR features of the compounds 3. Due to the coordination between the palladium and the nitrogen atoms, the angles C(2)C(1)C(12) and C(1)C(2)Pd are decreased to 117.8° and 112.1°, respectively, when compared with the normal value of 126°, and the angles C(1)C(12)N and PdNC(12) are 113.8° and 115.3°, respectively, also smaller than 120°, the value required for the sp² hybridization state. The Pd–ligand distances are similar

Table 5
Selected bond distances (Å) for 3d

Pd–Cl(1)	2.3600(9)	C(8)–C(9)	1.44(1)
Pd–P	2.2569(9)	C(9)–C(10)	1.43(2)
Pd–N	2.135(3)	C(11)–C(12)	1.491(6)
Pd–C(2)	1.991(4)	Cl(2)–C(16)	1.753(4)
Fe–C(1)	2.026(5)	C(13)–C(14)	1.367(6)
Fe–C(2)	2.095(4)	C(13)–C(18)	1.384(6)
Fe–C(3)	2.076(4)	C(14)–C(15)	1.399(6)
Fe–C(4)	2.042(5)	C(15)–C(16)	1.359(7)
Fe–C(5)	2.035(5)	C(16)–C(17)	1.376(8)
Fe–C(6)	2.052(5)	C(17)–C(18)	1.392(6)
Fe–C(7)	2.052(6)	C(19)–C(20)	1.399(6)
Fe–C(8)	2.030(6)	C(19)–C(24)	1.381(6)
Fe–C(9)	2.050(6)	C(20)–C(21)	1.385(7)
Fe–C(10)	2.076(6)	C(21)–C(22)	1.366(8)
P–C(19)	1.823(4)	C(22)–C(23)	1.395(8)
P–C(25)	1.833(4)	C(23)–C(24)	1.390(6)
P–C(31)	1.806(4)	C(25)–C(26)	1.386(7)
N–C(12)	1.296(5)	C(25)–C(30)	1.379(7)
N–C(13)	1.458(5)	C(26)–C(27)	1.392(8)
C(1)–C(2)	1.434(6)	C(27)–C(28)	1.37(1)
C(1)–C(5)	1.435(5)	C(28)–C(29)	1.35(1)
C(1)–C(12)	1.450(6)	C(29)–C(30)	1.393(7)
C(2)–C(3)	1.435(5)	C(31)–C(32)	1.387(6)
C(3)–C(4)	1.426(6)	C(31)–C(36)	1.411(6)
C(4)–C(5)	1.426(7)	C(32)–C(33)	1.386(7)
C(6)–C(7)	1.410(8)	C(33)–C(34)	1.385(7)
C(6)–C(10)	1.379(9)	C(34)–C(35)	1.373(8)
C(7)–C(8)	1.43(1)	C(35)–C(36)	1.370(7)

to those found in other palladated compounds. The Pd–N distance of 2.135 Å is comparable with the values found in compounds with a Pd–N bond (ca. 2.0 Å), suggesting the formation of a Pd–N bond in compound 3d.

Table 6
Selected bond angles (deg) for 4d

Cl(1)–Pd–P	93.47(3)	C(14)–C(13)–C(18)	121.6(4)
Cl(1)–Pd–N	91.93(9)	C(13)–C(14)–C(15)	119.2(5)
Cl(1)–Pd–C(2)	171.5(1)	C(14)–C(15)–C(16)	118.8(4)
P–Pd–N	173.78(9)	C(15)–C(16)–C(17)	122.8(4)
P–Pd–C(2)	94.8(1)	C(16)–C(17)–C(18)	118.4(4)
N–Pd–C(2)	79.9(1)	C(13)–C(18)–C(17)	119.1(4)
C(2)–C(1)–C(5)	110.7(4)	Cl(2)–C(16)–C(15)	119.0(4)
C(1)–C(2)–C(3)	106.0(3)	Cl(2)–C(16)–C(17)	118.3(4)
C(2)–C(3)–C(4)	108.2(4)	C(19)–P–C(25)	103.6(2)
C(3)–C(4)–C(5)	109.8(4)	C(19)–P–C(31)	105.8(2)
C(1)–C(5)–C(4)	105.3(4)	C(25)–P–C(31)	104.4(2)
C(7)–C(6)–C(10)	109.5(6)	P–C(19)–C(20)	123.3(3)
C(6)–C(7)–C(8)	106.8(6)	P–C(19)–C(24)	118.3(3)
C(7)–C(8)–C(9)	108.3(6)	P–C(25)–C(26)	119.2(4)
C(8)–C(9)–C(10)	106.0(6)	P–C(25)–C(30)	121.1(4)
C(6)–C(10)–C(9)	109.4(6)	P–C(31)–C(32)	119.3(3)
C(2)–C(1)–C(12)	117.8(3)	P–C(31)–C(36)	122.8(3)
C(5)–C(1)–C(12)	131.2(4)	C(12)–N–C(13)	120.4(3)
N–C(12)–C(1)	113.8(3)	Pd–N–C(12)	115.3(1)
N–C(12)–C(11)	125.5(4)	Pd–N–C(13)	124.3(1)
C(1)–C(12)–C(11)	120.7(4)	Pd–P–C(25)	112.9(1)
N–C(13)–C(14)	119.7(4)	Pd–P–C(19)	114.3(1)
N–C(13)–C(18)	118.6(4)	Pd–P–C(31)	114.8(1)
Pd–C(2)–C(1)	112.1(2)	Pd–C(2)–C(3)	141.7(2)

The ferrocene moiety has planar Cp rings which are not completely parallel, with interplanar angle 7.04° . The distances Fe–Cp rings are 1.655 and 1.660 Å for the substituted and unsubstituted rings, respectively. The Fe–C distances are in the range 2.026 Å to 2.095 Å, means 2.055 and 2.052 Å for the substituted ring and the other ring, respectively. The Cp ring bond lengths average 1.431 and 1.418 Å for the substituted ring and the other one, respectively. Interestingly, the N–aryl ring forms a dihedral angle of 76.0° with the plane C(1)C(11)C(12)NC(13) and this has been attributed to steric interaction between the aryl and α methyl as well as the chlorine bonded to the palladium. In addition, n - π conjugation between the π -electrons in the ring and n -electrons in the imino nitrogen atom also favours this orientation. In contrast, the palladated Cp ring forms a dihedral angle of only 8.4° with the plane, indicating that the electrons in the Cp ring can be delocalized over a larger skeleton than those in the N–aryl ring. The dihedral angle between the Cp ring and the N–aryl ring is 82.1° .

3. Experimental details

3.1. Materials and instruments

Melting points were determined on a WC-1 microscopic apparatus and are uncorrected. ^1H NMR spectra were recorded using a Bruker ARX 500 spectrometer, in chloroform-*d*, and all J values are in Hz. IR spectra were recorded on a Shimadzu IR 435 spectrophotometer. Elemental analyses were determined with a Carlo Erba 1106 Elemental Analyzer, and some of the palladium complexes crystallized as solvates from methylene chloride and the analytical data for these crystalline compounds are calculated on the basis of the quantity of methylene chloride observed in individual samples by ^1H NMR measurements. Chromatographic work was carried out on a short column packed with dry silica gel under reduced pressure.

A lithium tetrachloropalladate(II) solution in methanol (0.1 M) was prepared by stirring two equivalents of anhydrous lithium chloride and one equivalent of anhydrous palladium chloride in methanol until a homogeneous solution was formed. The ligands ferrocenylketimines **1** were prepared according to the published procedure [13]. The compound **1h** is a new ferrocenylketimine and was characterized as follows:

1h: Orange yellow platelets, yield 60%, m.p. 100 – 102°C . Anal. Found: C, 71.78; H, 6.01; N, 4.63. $\text{C}_{19}\text{H}_{19}\text{FeN}$ calc.: C, 71.96; H, 5.73; N, 4.42%. IR (KBr): 1624, 1100, 950, 822 cm^{-1} . ^1H NMR (CDCl_3): δ 2.10 (s, 3H, CH_3), 2.35 (s, 3H, Ar– CH_3), 4.22 (s, 5H, C_5H_5), 4.43 (bs, 2H, H-3), 4.81 (bs, 2H, H-2), 6.55 (d, 1H, $J = 7.4$, H α to N), 6.59 (s, 1H, H α to N and CH_3), 6.88 (d,

1H, $J = 7.4$, H α to CH_3), 7.21 (t, 1H, $J = 7.5$, H β to N and CH_3).

3.2. General procedure for the cyclopalladation

A solution of lithium tetrachloropalladate(II) in 10 ml of methanol (0.26 g of Li_2PdCl_4 , 1 mmol) was added to a solution of mole equivalents of NaOAc and ferrocenylimines **1** in 30 ml of methanol or methanol-ethyl ether ($v/v = 2:1$), the resulting red solution was stirred at room temperature for about 20 h and then filtered, and the solid obtained without further purification was treated with PPh_3 (0.39 g, 1.5 mmol) in CH_2Cl_2 at room temperature for 0.5 h and then filtered. The filtrate was concentrated in vacuo and then recrystallized from CH_2Cl_2 -petroleum ether (60 – 90°C) to produce cyclopalladated compounds **3**. A rapid chromatographic process on silica gel was used only when necessary. The cyclopalladated ferrocenylketimines **3** were obtained as red or deep red platelets, needles, prisms or rods.

3.3. Reaction of **1c** with lithium tetrachloropalladate(II) in the absence of sodium acetate

A solution of 0.13 g lithium tetrachloropalladate(II) (0.5 mmol) and 0.15 g of **1c** (0.5 mmol) in 30 ml of methanol was stirred for about 20 h and then filtered, and 0.13 g brown solid was obtained. The solid was treated with PPh_3 (0.09 g) in CH_2Cl_2 at room temperature for 0.5 h and then filtered, and 0.07 g of pale yellow powder was obtained, m.p. 260°C , which can be assigned to $(\text{PPh}_3)_2\text{PdCl}_2$ by comparison of its IR spectrum with that of an authentic sample and the elemental analysis, found: C, 61.91; H, 4.37. $\text{C}_{36}\text{H}_{30}\text{Cl}_2\text{P}_2\text{Pd}$ calc.: C, 61.65; H, 4.28%. The filtrate was concentrated in vacuo and the residue was recrystallized from CH_2Cl_2 -petroleum ether (60 – 90°C), to give 0.12 g of **3c**, 30% overall yield.

3.4. X-ray crystal structure determination for **3d**

Crystal data: $\text{C}_{36}\text{H}_{30}\text{Cl}_2\text{FeNPPd}$, $M_r = 740.77$, triclinic, $P\bar{1}$ (No. 2), $a = 10.100(1)$, $b = 11.976(1)$, $c = 14.980(1)$ Å, $\alpha = 108.51(1)$, $\beta = 109.22(1)$, $\gamma = 70.88(1)^\circ$, $V = 1564.9$ Å³, $Z = 2$, $D_c = 1.572$ g cm^{-3} , $F(000) = 748$, $\lambda = 1.5418$ Å, $\mu(\text{Cu K}\alpha) = 107.98$ cm^{-1} .

Data collection: A crystal suitable for X-ray structure analysis ($0.18 \times 0.10 \times 0.10$ mm) was mounted on an Enraf-Nonius CAD-4 diffractometer. Intensities were collected with graphite monochromated Cu $K\alpha$ radiation, using the ω -scan technique, 5534 reflections were measured in the range $1 \leq \theta \leq 65^\circ$, 4844 of which had $I > 3\sigma(I)$ and were used in all calculations. The intensities of the standard reflections monitored at regular intervals showed no crystal decomposition over

the data collection period. Data were corrected for Lorentz and polarization effects. An empirical absorption correction on the basis of ψ scans was applied.

Structure solution and refinement: The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares methods. Hydrogen atoms were included in calculated positions. The final R factor was 0.052 ($R_w = 0.060$) for all observed reflections. The residual electron density in final difference synthesis was $1.069 \text{ e}/\text{\AA}^3$ near the palladium atom. Computations were carried out with the Enraf-Nonius SDP program package [15] on a PDP 11/44 computer.

Supplementary material available: Full tables of bond lengths and angles, hydrogen coordinates, thermal parameters and structure factors are available from the authors.

Acknowledgements

We are grateful to the National Natural Science Foundation of China and the Natural Science Foundation of Henan Province for financial support of this work.

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