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ISOMERISM OF THE CYCLOPALLADATED FERROCENYLKETIMINES

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Abstract—Five new cyclopalladated ferrocenylketimines with the general formula $[\mathrm{PdCl}(\eta^5\text{-}C_5H_5)\mathrm{Fe}(\eta^5\text{-}C_5H_3\mathrm{CMe{=}NC_6H_4R})(\mathrm{PPh_3})]$(R = 2-OMe **3a**, 2-OEt **3b**, 2-Me **3c**, 2-Br **3d**, 2,4,6-trimethyl **3e**) have been synthesized and characterized to be mixtures of *anti* and *syn* isomers in solution except for **3e**. It was confirmed that the cause of this isomerism is that the free rotation around the C—N bond is hindered. Attempts to synthesize ferrocenylketimines in which R = 2,6-dichloro, 2,6-dibromo, 2,4,6-tribromo failed to yield new products, but only obtained the condensation product of two molecules of acetylferrocene. Copyright © 1996 Elsevier Science Ltd

During our studies on the cyclopalladation reaction of ferrocenylketimines[1] we have found that there exists a mixture of two isomers in the case of cyclopalladated products $[\mathrm{PdCl}(\eta^5\text{-}C_5H_5)\mathrm{Fe}(\eta^5\text{-}C_5H_3\mathrm{CMe{=}NAr})(\mathrm{PPh_3})]$ (Ar = C_6H_4-2-Cl or α-naphthyl) (Fig. 1), and assumed that the isomerism may be in relation to the *ortho*-substitution in the N-phenyl ring. It is our belief that the steric hindrance between the *ortho*-substituent in the N-phenyl ring and α-methyl group as well as the chlorine atom bonded to the palladium block the free rotation of the N-phenyl ring about the C—N bond, resulting in two isomers, i.e. an *anti* arrangement of the *ortho*-substituent and the ferrocenyl moiety and a *syn* arrangement. However, we still cannot exclude another isomerism in which there may be a *trans* or a *cis* orientation of the phosphine group versus the N atom, resulting in two isomers.

In order to clarify which one of the two effects described above is the genuine factor, we continued our work in this aspect, and designed and synthesized ferrocenylketimines containing an *ortho*-substituent in the N-phenyl ring and their corresponding cyclopalladated products **3a**–**3e**.

RESULTS AND DISCUSSION

Syntheses

The preparation of the imines was carried out by condensation of acetylferrocene and the corresponding amines in the presence of freshly activated Al_2O_3.[2] All attempts to prepare Schiff bases from acetylferrocene with 2-nitroaniline, 2,6-dichloroaniline, 2,6-dibromoaniline, 2,4,6-tribromoaniline, respectively, failed to yield new imines even with long reaction periods (*ca* 4–6 days) and daily additions of a small amount of amine to force the displacement of the equilibria. In the case of 2-nitroaniline, acetylferrocene was recovered from the reaction mixture; this result may be related to the strong electron-withdrawing effect

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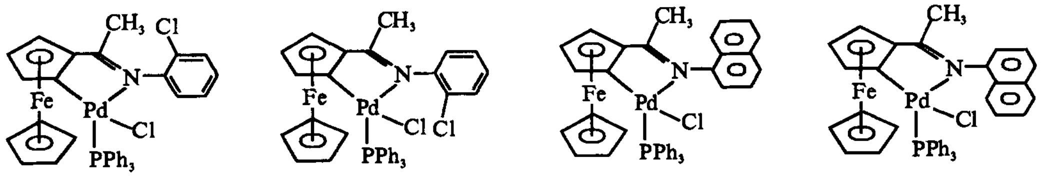
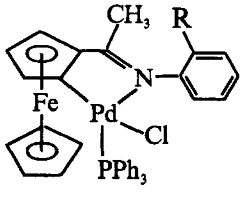


anti *syn* *anti* *syn*

Fig. 1. The two isomers of the cyclopalladated ferrocenylketimines.



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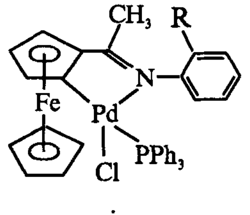
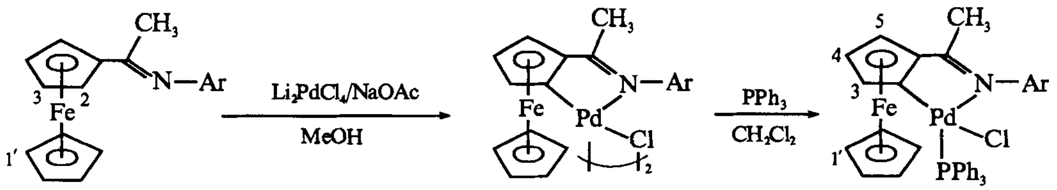


cis



1 **2** **3**

Ar = 2-OMe (**a**), 2-OEt (**b**), 2-Me (**c**), 2-Br (**d**), 2,4,6-trimethyl (**e**).

of the nitro group in the N-phenyl ring, which can decrease the reactivity of the amine. Interestingly, in the other cases the condensation product of two molecules of acetylferrocene was obtained quantitatively. No ferrocenylketimines could be detected, which may be ascribed to the large bulk in the 2,6-position of the N-phenyl ring, resulting in the condensation reaction with amines being more difficult.

The cyclopalladation reaction was carried out according to our previous procedure.[1] When **1a–e** were treated with a stoichiometric amount of Li_2PdCl_4 and anhydrous sodium acetate in methanol at room temperature, the initially clear red solution became dark and the red solid precipitated with stirring. This solid can be assigned to binuclear complexes of palladium, because of their poor solubility, except **2e** (R = 2,4,6-trimethyl), in all common organic solvents, they were subjected to a bridge-splitting reaction with the ligand triphenylphosphine to produce the monomeric triphenylphosphine derivatives **3**. Evidence of the cleavage of the Pd—N bond was not observed in any case, even when a large excess of phosphine (up to four-fold molar ratio) was used, showing that for these cyclopalladated complexes, the Pd—N bond is very unreactive.

Special attention should be paid to the R = 2,4,6-trimethyl case, in which the red solid obtained is very soluble in common solvents such as chloroform, dichloromethane and benzene. A TLC examination of this solid showed two bands: the band possessing a higher R_f value was shown to be a binuclear complex by IR and elemental analyses, and the band possessing a lower R_f value was proved to be a bis-adduct of the type $[PdCl_2L_2]$, because a large yellow precipitate was produced when it was treated with PPh_3, which can be assigned to $(PPh_3)_2PdCl_2$ by comparison of its IR spectrum with that of an authentic sample and elemental analyses.

Characterization of ferrocenylketimines and their cyclopalladated complexes

The compounds obtained are orange–red crystals or powders at room temperature; in all cases the elemental analyses were consistent with the proposed formula (Table 1). The ferrocenylketimines **1** and the monomeric complexes **3** are very soluble in chloroform, dichloromethane, acetone, benzene and toluene, but insoluble in petroleum ether and n-hexane.

The IR spectra of the free imines show an intense sharp band in the range 1620–1640 cm^{-1}; for the cyclopalladated complexes this band shifted to lower wavenumbers by *ca* 50 cm^{-1} compared with the corresponding frequencies of **1**, indicating that the nitrogen atom is coordinated to palladium through its lone pair.[3,4] 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 δ(CH) of PPh_3. These IR features are in good agreement with the proposed structures for compounds **3**.

The ^1H NMR can well support our conclusion. If the reason for the isomerism is the free rotation around the hindered C—N bond, then all the compounds **3a–d** which contain an ortho-substituent in the N-phenyl ring will exist as two isomers in solution. On the other hand, compound **3e** will not exist as two isomers because the *anti* and the *syn* configurations are the same in this case. If **3e** still exists as two isomers, then it may be attributed to the formation of the *trans* and *cis* orientation of the phosphine group *versus* the nitrogen atom. The ^1H NMR spectra showed all compounds **3a–d** exist as two isomers, the ratios ranging from 1.58 : 1 to 3.45 : 1, whereas **3e** only exists in one form (see Fig. 2). Therefore, we concluded that the isomerism is caused by the former factor. The ^1H NMR spectrum (Table 2), for example, one isomer of **3a**, exhibited the expected AMX system protons on the substituted Cp ring with a triplet at δ 4.10 integrating for the proton 4, and two doublets at δ 3.33 and δ 4.43 for the protons 3 and 5, respectively.[1] The singlet at δ 4.00 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 2.04 for the protons of the methyl and δ 3.93 for the protons of the methoxy group.

It should be noted that the 2D EXSY spectrum measured for $[\overline{PdCl(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CMe{=}N}\,Ar)PPh_3)]$ (Ar = α-naphthyl) in our previous study[1] showed "no cross peak representing the chemical exchange between the isomers being found, and the ^1H NMR spectrum of the compound recorded at 60°C showed no obvious change compared with that at 20°C. These results indicate that the energy required for free rotation is quite high".

EXPERIMENTAL

General

Melting points were determined on a WC-1 microscope 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 using silica gel packed dry column under reduced pressure.

Materials and syntheses

Acetylferrocene and the amines were obtained from commercial sources and used as received. All the solvents were dried and distilled before use. The ferrocenylketimines **1**[2] and the cyclopalladated

Table 1. Elemental analyses, melting points and IR data [ν(C=N)] for compounds **3**

			Elemental analysis				
		Yield[b]	%C	%H	%N		
Compound	Empirical formula	(%)	Calc. (Found)	Calc. (Found)	Calc. (Found)	M.pt	IR(C=N)
3a	$C_{37}H_{33}ClFeNOPPd$[a]	78	55.6(55.7)	4.3(4.3)	1.7(1.8)	157–159	1580
3b	$C_{38}H_{35}ClFeNOPPd$	69	60.8(60.8)	4.7(4.7)	1.9(2.2)	209–210[c]	1578
3c	$C_{37}H_{33}ClFeNPPd$	80	61.7(62.0)	4.6(4.8)	1.9(2.2)	202–204[c]	1570
3d	$C_{36}H_{30}BrClFeNPPd$[a]	71	51.1(50.7)	3.7(3.7)	1.6(1.8)	154–158	1570
3e	$C_{39}H_{37}ClFeNPPd$[a]	41	57.7(57.4)	4.7(4.6)	1.7(1.8)	139–140	1575

[a] Contained one CH_2Cl_2 per molecule.

[b] Calculated on the basis of the starting ferrocenylketimines.

[c] Melts with decomposition.

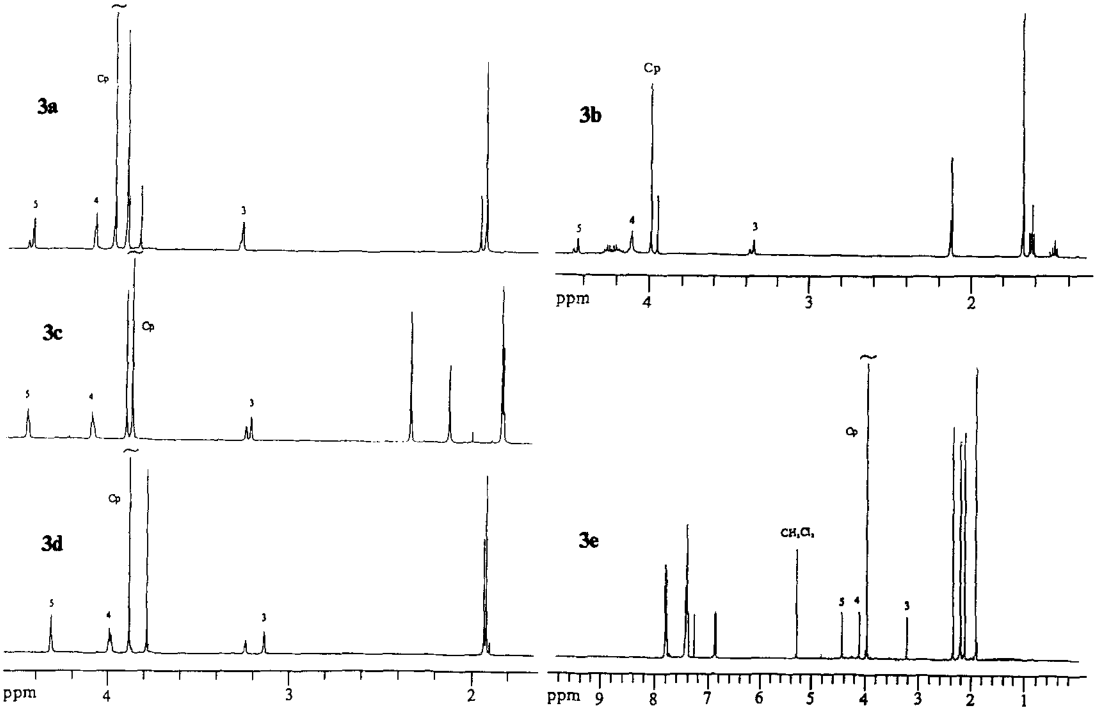


Fig. 2. ^{1}H NMR spectra of compounds **3a**–**3e**.

Table 2. ^{1}H NMR data for cyclopalladated ferrocenylketimines **3**[a] (in the range 1.00–5.00 ppm)

Compound	1′	3	4	5	Others				Ratio
3a	4.00s	3.33d (1.9)	4.10t (2.25)	4.43d (2.35)	2.04s	3.93s			3.45 : 1
	3.94s	3.34d (2.1)	4.10t (2.25)	4.46d (2.35)	2.07s	3.86s			
3b	3.98s	3.32d (2.15)	4.10m	4.44d (2.3)	2.07s	1.54t (6.95)	4.17dd (6.95)		2.73 : 1
	3.94s	3.35d (2.15)	4.10m	4.46d (2.3)	2.08s	1.39t (6.95)	4.25dd (6.95)		
3c	3.93s	3.32d (1.8)	4.13m	4.47d (2.6)	2.03s	2.50s			1.65 : 1
	3.96s	3.35d (1.9)	4.13m	4.46d (2.6)	2.02s	2.29s			
3d	4.04s	3.28d (2.35)	4.14m	4.47m	2.02s				1.58 : 1
	3.93s	3.38d (2.4)	4.14m	4.47m	2.04s				
3e	3.97s	3.22d (2.3)	4.10t (2.3)	4.43d (2.35)	1.92s	2.15s	2.25s	2.36s	

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

complex **3** (new compounds) were prepared as described previously.[1] The compounds **3** were obtained as red or yellow powders, needles or prisms. The elemental analyses, melting points and IR data for compounds **3** are presented in Table 1, while ^{1}H NMR data are presented in Table 2. The compounds **1d** and **1e** are new ferrocenylketimines and were characterized as follows:

1d. Red rods, yield 75%, m.pt 106–108°C. IR

(KBr pellets): 1625, 1105, 1000, 820, 760 cm^{-1}. ^{1}H NMR: δ 2.03 (s, 3H, CH_3), 4.27 (s, 5H, C_5H_5), 4.43 (t, 2H, $J = 1.85$ Hz, H-3), 4.81 (t, 2H, $J = 1.85$ Hz, H-2), 6.71–7.56 (m, 4H, Ar-H). Found: C, 56.3; H, 4.1; N, 3.7. Calc. for $C_{18}H_{16}BrFeN$: C, 56.6; H, 4.2; N, 3.7%.

1e. Red needles, yield 83%, m.pt 123–124°C. IR (KBr pellets): 1630, 1102, 1000, 818 cm^{-1}. ^{1}H NMR: δ 1.91 (s, 3H, CH_3), 2.01 (s, 6H, CH_3), 2.25 (s, 3H, CH_3), 4.21 (s, 5H, C_5H_5), 4.40 (t, 2H, $J = 1.85$ Hz, H-3), 4.81 (t, 2H, $J = 1.85$ Hz, H-2), 6.78 (s, 1H, Ar-H), 6.83 (s, 1H, Ar-H). Found: C, 73.2; H, 6.6; N, 4.5. Calc. for $C_{21}H_{23}FeN$: C, 73.1; H, 6.7; N, 4.1%.

$[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CMe{=}NC_6H_2\text{-}2,4,6\text{-}trimethyl)\}(\mu\text{-}Cl)]_2$ (**2e**). A solution of lithium tetrachloropalladate(II) (0.26 g, 1 mmol), anhydrous sodium acetate (0.08 g, 1 mmol) and **1e** (0.35 g, 1 mmol) in methanol (30 cm^3) was stirred for *ca* 20 h at room temperature. This solution was filtered and the filtrate was evaporated *in vacuo* to a minimum amount, then subjected to a short dry column of silica gel, eluted with methylene chloride. The first band was collected to afford the μ-chloro-bridged complex **2e** after the evaporation of the solvent and recrystallized from methylene chloride–petroleum ether (60–90°C).

2e. Red crystals, yield 57%. m.pt > 184°C (dec.) IR: 1562, 1469, 815 cm^{-1}. ^{1}H NMR: δ 1.55 (s, 6H, CH_3), 1.80–2.33 (m, 18H, Ar-CH_3), 3.54 (s, 2H, H-3), 4.23 (m, 2H, H-4), 4.36 (s, 5H, C_5H_5), 4.56 (s, 5H, C_5H_5), 4.80 (s, 2H, H-5), 6.66 (m, 2H, Ar-H), 7.25 (m, 2H, Ar-H). Found: C, 51.6; H, 4.4; N, 2.7. Calc. for $C_{42}H_{44}Cl_2Fe_2N_2Pd_2$: C, 51.9; H, 4.6; N, 2.9%.

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