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Synthesis of cylopalladated anils of benzoylferrocene via transmetallation reaction of mercurated ferrocenylketimines with Li_2PdCl_4 or by direct cyclopalladation reaction of ferrocenylketimines

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Abstract

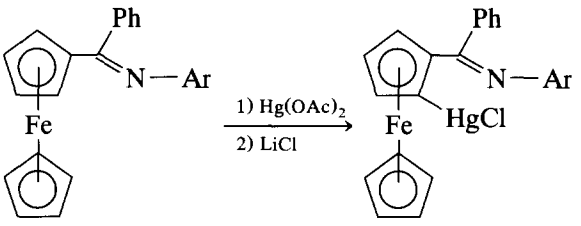
A series of cyclopalladated anils of benzoylferrocene with the general formula $[Pd\overline{\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CPh{=}NAr)\}}Cl(PPh_3)]$ (Ar = a variety of substituted phenyls and β = napthyl) were synthesized by transmetallation reaction of the corresponding cyclomercurated derivatives $[HgCl\overline{\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CPh{=}NAr)\}}]$ with lithium tetrachloropalladate or by direct cyclopalladation reaction of the corresponding ferrocenylketimines $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CPh{=}NAr)]$, followed by the treatment of the resulting products with triphenylphosphine. The composition and the structure of the metallocycles were characterized by elemental analysis, IR, ^1H NMR and two-dimensional NOESY spectra. Some spectral features of these complexes were also discussed.

Keywords: Palladium; Iron; Mercury; Cyclopalladation; Transmetallation; Ferrocene

1. Introduction

The chemistry of cyclometallated complexes is undoubtedly one of the most advanced areas of modern organometallic chemistry and has been well reviewed by several workers [1]. Since the first example of cyclopalladated metallocene was reported by Alper [2] in 1974, there has been considerable interest in the syntheses of cyclometallated ferrocene derivatives containing coordinating groups, especially nitrogen donor ligands, by direct cyclometallation with transition metals such as palladium and platinum. Most of the documented researches involving nitrogen donor ligands has focused on *N,N'*-dimethylaminomethylferrocene [3], 2-pyridylferrocene [4] and their analogues [1,5], while there are a few reports on the other ligands [6]. More recently, the cyclomercuration and the cyclopalladation of some ferrocenylimines have been reported by López's and our laboratory. It was found that the reactions occur predominantly at the *ortho* position of the substituted cyclopentadienyl (p) ring to afford the corresponding cyclomercurated and cyclopalladated derivatives respectively [7,8].

It is note worthy that the mercuration of anils of benzoylferrocene **1** gives the corresponding orthomercurated products **2** in high chemical regioselectivities and yields, and provides a convenient route to synthesizing 1,2-disubstituted ferrocenes [8c]. We have also



1 **2**

reported that mercurated Schiff bases can be used as the transmetallating reagents for the synthesis of other organometallic compounds [9]. In order to gain further insight into transmetallation and cyclopalladation reactions, in the present work, we describe the synthesis of cyclopalladated anils of benzoylferrocene via transmetallation reaction of the mercurated ferrocenylketimines

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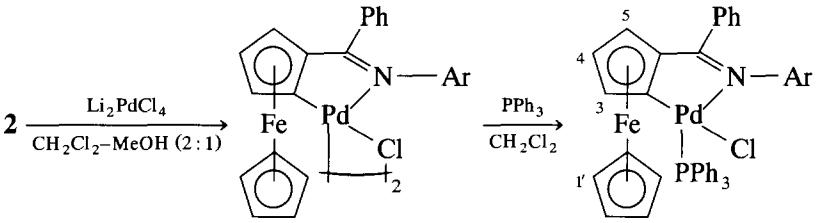
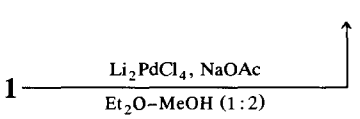




Ar = *p*-$CH_3OC_6H_4$(**a**), *p*-$CH_3C_6H_4$(**b**), C_6H_5(**c**), *p*-ClC_6H_4(**d**), *p*-BrC_6H_4(**e**), *p*-IC_6H_4(**f**), *m*-$CH_3C_6H_4$(**g**), *m*-ClC_6H_4(**h**) *m*-BrC_6H_e(**i**), *m*-$NO_2C_6H_4$(**j**), *o*-ClC_6H_e(**k**), *β*-naphthyl(**l**).

2 or by the direct cyclopalladation reaction of the ferrocenylketimine **1**.

2. Results and discussion

2.1. Synthesis of cyclopalladated Schiff bases 4 via transmetallation reaction of mercurated derivatives 2

As one of the routes to the synthesis of cyclopalladated derivatives **4**, the mercurated anils of benzoylferrocene **2** were used as the transmetallating reagents to react with lithium tetrachloropalladate (II). When **2a–2l** were treated with Li_2PdCl_4 in 2:1 CH_2Cl_2:MeOH mixed solvent at room temperature, the initially clear red solution became dark and a violet solid precipitated with stirring. This solid can be assigned to binuclear complexes **3** of palladium. Because of their poor solubility in all common organic solvents, they were subjected to a bridge-splitting reaction with the ligand triphenylphosphine to produce the monomeric triphenylphosphine derivatives **4**, with overall yields of 45–84%. The results of the reactions were summarized in Table 1.

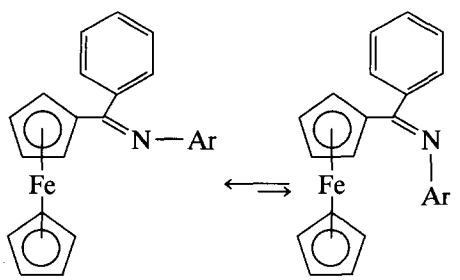
Table 1
Yields of **4a–4l** and isomer ratios for **1a–1l**

Ar	Yield (%) of **4**		*trans-to-cis* ratio for **1** [c]
	T [a]	D [b]	
a	70	45	8.1
b	84	56	6.5
c	75	33	6.5
d	69	20	7.8
e	70	53	8.6
f	82	38	6.9
g	48	24	5.8
h	77	50	7.0
i	65	37	6.3
j	45	20	8.2
k	57	55	9.0
l	80	15	

[a] Yields based on mercurated anils of benzoylferrocene via transmetallation reaction.
[b] Yields based on the anils of benzoylferrocene by direct palladation.
[c] Determined by ^1H NMR in $CDCl_3$.

2.2. Synthesis of cyclopalladated Schiff bases 4 by direct cyclopalladation of ferrocenylimines

As mentioned in the introduction, the synthesis of cyclopalladated ferrocenylketimines can be achieved by direct cyclopalladation of ferrocenylketimines with Li_2PdCl_4 followed by treatment with PPh_3 [8d]. In order to compare with the procedure for the synthesis of cyclopalladated ferrocenylketimines **4** via transmetallation, a direct metallation pathway was also applied. The cyclopalladation of ferrocenylketimines **1** with Li_2PdCl_4 was conducted in 2:1 methanol:ethyl ether mixed solvent at room temperature for 20 h. The result of the reaction and the subsequent treatment with PPh_3 were the same as those described in the transmetallation reaction. The yields of monomeric triphenylphosphine derivatives **4** were presented in Table 1. It was found that the yields of the cyclopalladated compounds **4** by direct cyclopalladation were usually lower than those obtained by transmetallation procedure, particularly in the case of cyclopalladation of **1l** (only 15% yield). It should be noticed that the yields of cyclopalladated Schiff base derivatives of acetylferrocene are usually higher than those in the present study [8d]. This is probably because an NMR study on the behavior of anils of benzoylferrocene **1** indicated the presence of a mixture of *trans* and *cis* isomers in the solution [8c] and only the *trans* isomer may be the reactive species.



trans-**1** *cis*-**1**

Table 2
IR of C=N stretching frequencies (cm^{-1}) for compounds **1**, **2** and **4**

	a	b	c	d	e	f	g	h	i	j	k	l
1 [a]	1614	1616	1600	1616	1616	1614	1616	1614	1614	1604	1608	1610
2 [a]	1604	1590	1590	1590	1590	1590	1590	1580	1580	1584	1595	1586
4	1554	1532	1532	1532	1534	1541	1542	1542	1542	1521	1552	1541

[a] The data cited from reference [8c].

Therefore the ratio of *trans-to-cis* will be one of the important factors which influences the cyclopalladation. A careful examination of the *trans-to-cis* ratio of ferrocenylketimines **1** in $CDCl_3$ at room temperature by NMR demonstrated that the values of the *trans-to-cis* ratio range from 9.0 to 5.8. In general, the ferrocenylimines possessing higher values of the *trans-to-cis* ratio gave the cyclopalladated products with higher yields and conversely, those having lower *trans-to-cis* ratios as shown in Table 1 gave the corresponding cyclopalladated derivatives with lower yields with the exception of **1a**, **1b**, **1d** and **1j**. Accordingly, we tentatively suggest that it is the transformation of ferrocenylimines from *trans*-**1** to *cis*-**1** in some cases which reduces the reaction rate of the cyclopalladation to give the products **4**, because of the decrease in the concentration of the reactive species.

2.3. Spectral properties of cyclopalladated products 4

The IR spectral features of **4** are similar to those described in our previous paper on cyclopalladation of Schiff bases [8d]. The absorption bands at 1000 cm^{-1} are indicative of an unsubstituted cyclopentadienyl ring [8a]. As shown in Table 2, the C=N absorptions of **4** are shifted to lower energy by 56–84 cm^{-1} in comparison with those of the corresponding ferrocenylketimines, indicating that nitrogen is coordinated to palladium through its lone pair electrons [8d]. The IR spectra of the corresponding mercurated ferrocenylketamines **2** showed only about 20 cm^{-1} lower energy shifts of C=N absorption compared with unmercurated parent compounds **1** [8c]. By comparison of the values of lower energy shifts of C=N absorption in mercurated and palladated ferrocenylketimines, it can be concluded that the intramolecular N → Pd coordination in palladated products **4** is much stronger than the intramolecular N → Hg coordination in the mercurated derivatives **2**. The strong absorptions at about 745 cm^{-1} and 695 cm^{-1} observed in **4**, being the feature of monosubstituted phenyl ring, are assigned to the δ(CH) of PPh_3.

The ^1H NMR spectra of **4** were completely consistent as expected with the homoannularly 1,2-disubstituted structures. Two-dimensional NOESY (Fig. 1) was also measured for **4c** to assign unambiguously the doublets at 4.20 ppm and 3.51 ppm. It was confirmed that the downfield doublet at 4.20 ppm corresponds to the proton 5, owing to the appearance of the negative cross-peak representing the nuclear overhauser effect (NOE) between proton 5 and the protons of the C-phenyl

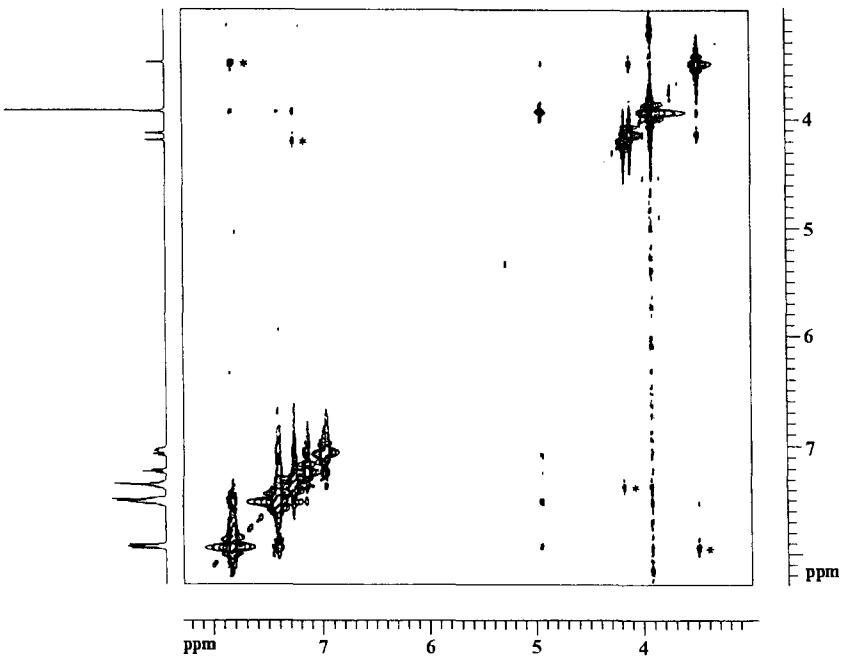


Fig. 1. 2D NOESY spectrum of **4c** *, NOE peaks.

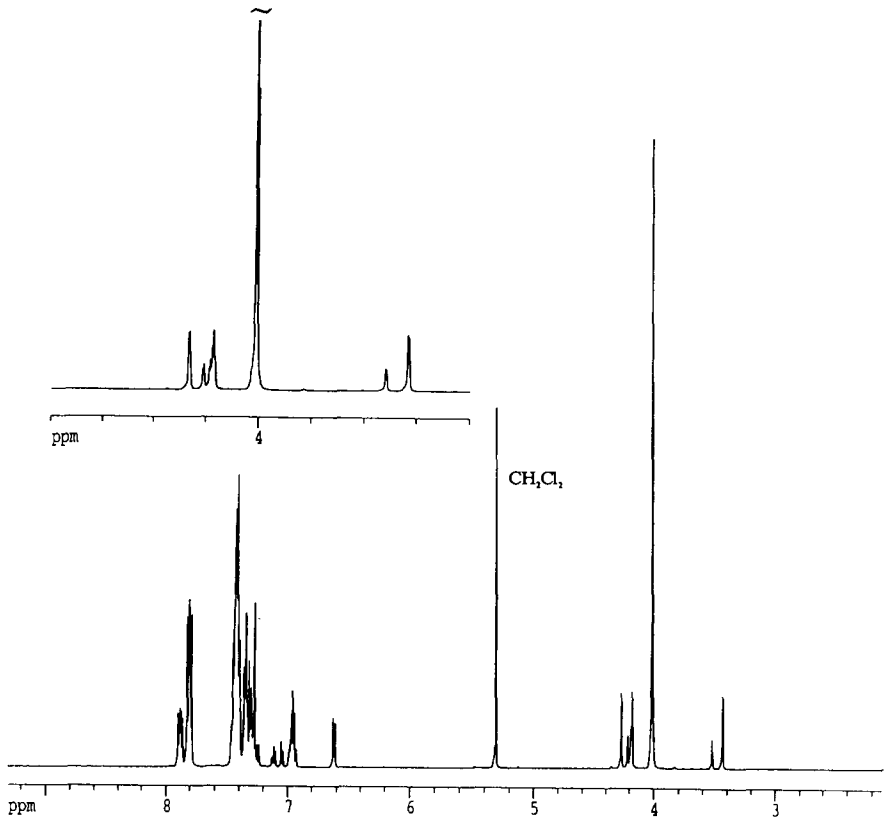
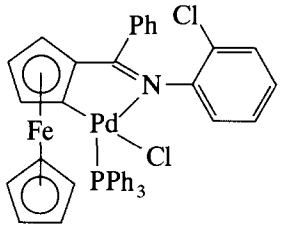


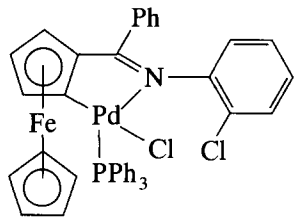
Fig. 2. ^{1}H NMR spectrum of **4k**.

ring. Accordingly, the upfield doublet at 3.51 ppm represents the resonance of proton 3 because of the appearance of the NOE cross-peak between the proton 3 and the protons of the triphenylphosphine. In comparison with the starting materials **1** [8c], the proton signals for Cp rings in **4** are shifted to higher fields and in particular, the proton 3 adjacent to the palladium atom appears at the highest field. This phenomenon is similar to the case of cyclopalladated [1-(arylimino) ethyl]ferrocenes [8d] and can be attributed to the ring current effect of a phosphine phenyl ring. As a result, it is a reasonable that the arrangement of the phosphine and the metallated Cp ring is *cis* and the disposition of phosphine and nitrogen atoms is *trans*. The protons of phosphine phenyl ring, *N*-phenyl ring and unsubstituted Cp ring in **4** resonate at similar positions to those found in our previous papers [8d]. However, the signal of proton 5 in **4** shows a significant upfield shift (about 0.30 ppm) compared with that of the corresponding proton in cyclopalladated [~-(arylimino) ethyl]ferrocenes [8d]. This result is probably caused by the non-coplanarity between the C-phenyl ring and substituted Cp ring [8c,10], which increase the shielding effect of phenyl ring on proton 5.

It is note worthy that, as shown in Fig. 2, the ^{1}H NMR spectrum of **4k** indicated that there exist two isomers in $CDCl_3$ solution, which is similar to the case of compounds [Pd{(η^5-C_5H_5)Fe(η^5-C_5H_3CMe=NAr)}-Cl(PPh_3)](Ar= *o*-ClC_6H_4, α-naphthyl) [8d]. To the best of our knowledge, this phenomenon must be related to the *ortho* substitution in the *N*–phenyl ring, and it is likely that the free rotation of the *N*–phenyl about the C–N bond will be blocked owing to the steric hindrance between the *ortho* substitutent and the *C*–phenyl as well as the chlorine bonded to the palladium, consequently resulting in two isomers, i.e. an *anti* arrangement of the *ortho* substituents and ferrocene moiety and a *syn* arrangement of them. This conclusion is consistent with that reported by Bosque et al. [7c].



anti-**4k**



syn-**4k**

3. Experimental details

3.1. Materials and instruments

Melting points were measured on a WC-1 microscopic apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker ARX 500 spectrometer,

using $CDCl_3$ as the solvent and tetramethylsilane as an internal standard. IR spectra were recorded on a Perkin–Elmer FTIR 1750 spectrophotometer. Elemental analyses were determined with a Carlo Erba 1106 elemental analyser. Chromatographic work was carried out using 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 ligand ferrocenylketimines **1** and the corresponding cyclomercurated derivatives **2** were prepared according to the published procedure [7c].

3.2. General procedure for the transmetallation of 2

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 equivalent mole of mercurated ferrocenylketimines **2** in 15 ml of dichloromethane/methanol (2:1 v/v), the resulting red solution was stirred at room temperature for about 20 h. The initially clear red solution became dark and a violet solid precipitated. The solid was filtered and washed with methanol; then without further purification it was treated with PPh_3 (0.39 g, 1.5 mmol) in 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. After evaporation of the solvent, the residue was recrystallized from dichloromethane–petroleum ether (60–90°C) to give **4** with the yields shown in Table 1.

3.3. General procedure for cyclopalladation of 1

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 molar equivalents of NaOAc and ferrocenylketimines **1** in 30 ml of methanol:ethyl ether (2:1 = v/v); the resulting red solution was stirred at room temperature for 20 h and then the precipitated solid was filtered. Treatment of the solid was carried out following the procedure described above. The yields for the formation of **4** by cyclopalladation were summarized in Table 1.

3.3.1. $[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CPh{=}NC_6H_4OMe\text{-}4)\}Cl(PPh_3)]$ (4a)

Dark-violet needles; melting point (m.p.), above 236°C (decomposition). Anal. Found: C, 62.97; H, 4.37; N, 2.25. $C_{42}H_{35}ClFeNOPPd$ Calc.: C, 63.19; H, 4.42; N, 1.75%. IR (KBr pellet): ν 1544, 1246, 1099, 1000, 834, 740, 702 cm^{-1}. ^1H NMR: δ 3.48 (d, 1H, $J = 2.3$ Hz, H-3), 3.69 (s, 3H, OCH_3), 3.93 (s, 5H, C_5H_5), 4.11 (t, 1H, $J = 2.25$ Hz, H-4), 4.18 (d, 1H, $J = 2.0$ Hz, H-5), 6.66 (d, 2H, $J = 8.8$ Hz, N–Ar–H), 6.87 (d, 2H, $J = 8.8$ Hz, N–Ar–H), 7.27 (m, 5H, C–Ph–H), 7.40–7.44, 7.80–7.84 (m, 15H, PPh_3–H) ppm.

3.3.2. $[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CPh{=}NC_6H_4Me\text{-}4)\}Cl(PPh_3)]$ (4b)

Dark-violet needles; m.p., above 240°C (decomposition). Anal. Found: C, 65.06; H, 4.53; N, 2.11. $C_{42}H_{35}ClFeNPPd$ Calc.: C, 64.48; H, 4.51; N, 1.79%. IR (KBr pellet): ν 1532, 1100, 1003, 820, 745, 692 cm^{-1}. ^1H NMR: δ 2.20 (s, 3H, CH_3), 3.48 (d, 1H, $J = 2.4$ Hz, H-3), 3.94 (s, 5H, C_5H_5), 4.11 (t, 1H, $J = 2.4$ Hz, H-4), 4.17 (d, 1H, $J = 2.45$ Hz, H-5), 6.85 (d, 2H, $J = 8.0$ Hz, N–Ar–H), 6.93 (d, 2H, $J = 8.0$ Hz, N–Ar–H), 7.27 (m, 5H, C–Ph–H), 7.40–7.42, 7.80–7.84 (m, 15H, PPh_3-H) ppm.

3.3.3. $[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CPh{=}NC_6H_5)\}Cl(PPh_3)]$ (4c)

Dark-violet needles; m.p., 255–257°C (decomposition). Anal. Found: C, 64.62; H, 4.52; N, 2.16. $C_{41}H_{33}ClFeNPPd$ Calc.: C, 64.09; H, 4.33; N, 1.82%. IR (KBr pellet): ν 1532, 1097, 1002, 824, 756, 696 cm^{-1}. ^1H NMR: δ 3.51 (d, 1H, $J = 2.1$ Hz, H-3), 3.94 (s, 5H, C_5H_5), 4.14 (t, 1H, $J = 2.35$ Hz, H-4), 4.20 (d, 1H, $J = 2.3$ Hz, H-5), 6.95 (m, 3H, N–Ar–H), 7.13 (m, 2H, N–Ar–H), 7.27 (m, 5H, C–Ph–H), 7.39–7.44, 7.80–7.84 (m, 15H, PPh_3–H) ppm.

3.3.4. $[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CPh{=}NC_6H_4Cl\text{-}4)\}Cl(PPh_3)]$ (4d)

Dark-violet rods; m.p., 219–221°C (decomposition). Anal. Found: C, 59.39; H, 4.00; N, 1.85. $C_{41}H_{32}Cl_2FeNPPd \cdot \frac{1}{2} CH_2Cl_2$ Calc.: C, 58.97; H, 3.94; N, 1.66%. IR (KBr pellet): 1536, 1094, 1006, 826, 740, 702 cm^{-1}. ^1H NMR: δ 3.53 (d, 1H, $J = 2.2$ Hz, H-3), 3.93 (s, 5H, C_5H_5), 4.16 (t, 1H, $J = 2.3$ Hz, H-4), 4.20 (d, 1H, $J = 2.3$ Hz, H-5), 5.30 (s, 1H, CH_2Cl_2), 6.89 (d, 2H, $J = 8.8$ Hz, N–Ar–H), 7.09 (d, 2H, $J = 8.8$ Hz, N–Ar–H), 7.27 (m, 5H, C–Ph–H), 7.39–7.44, 7.79–7.83 (m, 15H, PPh_3–H) ppm.

3.3.5. $[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CPh{=}NC_6H_4Br\text{-}4)\}Cl(PPh_3)$ (4e)

Dark-violet needles; m.p., 229.5–231.5°C (decomposition). Anal. Found: C, 57.79; H, 3.78; N, 2.23. $C_{41}H_{32}BrClFeNPPd$ Calc.: C, 58.13; H, 3.81; N, 1.65%. IR (KBr pellet): ν 1534, 1098, 1011, 825, 745, 693 cm^{-1}. ^1H NMR: δ 3.54 (d, 1H, $J = 2.3$ Hz, H-3), 3.93 (s, 5H, C_5H_5), 4.16 (t, 1H, $J = 2.3$ Hz, H-4), 4.20 (d, 1H, $J = 2.15$ Hz, H-5), 6.83 (d, 2H, $J = 8.6$ Hz, N–Ar–H), 7.25–7.39 (m, 7H, N–Ar–H and C–Ph–H), 7.41–7.44, 7.79–7.83 (m, 15H, PPh_3–H) ppm.

3.3.6. $[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CPh{=}NC_6H_4I\text{-}4)\}Cl(PPh_3)]$ (4f)

Dark-violet needles; m.p., above 240°C (decomposition). Anal. Found: C, 55.38; H, 3.63; N, 1.83. $C_{41}H_{32}ClIFeNPPd$ Calc.: C, 55.07; H, 3.61; N, 1.57%. IR (KBr pellet): ν 1541, 1098, 1002, 821, 745, 694 cm^{-1}. ^1H

NMR: δ 3.54 (d, 1H, $J = 2.4$ Hz, H-3), 3.93 (s, 5H, C_5H_5), 4.16 (t, 1H, $J = 2.35$ Hz, H-4), 4.20 (d, 1H, $J = 2.45$ Hz, H-5), 6.71 (d, 2H, $J = 8.0$ Hz, N–Ar–H), 7.26–7.39 (m, 7H, N–Ar–H and C–Ph–H), 7.41–7.45, 7.80–7.84 (m, 15H, PPh_3–H) ppm.

3.3.7. [Pd{(η^5-C_5H_5)Fe(η^5-C_5H_3CPh=NC_6H_4Me-3)}Cl(PPh_3)] (4g)

Dark-violet needles; m.p., above 223°C (decomposition). Anal. Found: C, 64.56; H, 4.53; N, 1.64. $C_{42}H_{35}$ClFeNPPd Calc.: C, 64.48; H, 4.51; N, 1.79%. IR (KBr pellet): ν 1542, 1098, 1000, 819, 749, 695 cm^{-1}. ^1H NMR: δ 2.20 (s, 3H, CH_3), 3.52 (d, 1H, $J = 2.35$ Hz, H-3), 3.93 (s, 5H, C_5H_5), 4.12 (t, 1H, $J = 2.4$ Hz, H-4), 4.19 (d, 1H, $J = 2.3$ Hz, H-5), 6.76–7.00 (m, 4H, N–Ar–H), 7.27 (m, 5H, C–Ph–H), 7.40–7.44, 7.79–7.83 (m, 15H, PPh_3–H) ppm.

3.3.8. [Pd{(η^5-C_5H_5)Fe(η^5-C_5H_3CPh=NC_6H_4Cl-3)}Cl(PPh_3)] (4h)

Dark-violet needles; m.p., above 245°C (decomposition). Anal. Found: C, 61.28; H, 4.03; N, 1.74. $C_{41}H_{32}Cl_2$FeNPPd Calc.: C, 61.34; H, 4.02; N, 1.74%. IR (KBr pellet): ν 1542, 1097, 1000, 819, 743, 698 cm^{-1}. ^1H NMR: δ 3.56 (s, 1H, H-3), 3.93 (s, 5H, C_5H_5), 4.17 (s, 1H, H-4), 4.21 (s, 1H, H-5), 6.93–7.39 (m, 9H, N–Ar–H and C–Ph–H), 7.40–7.45, 7.79–7.83 (m, 15H, PPh_3–H) ppm.

3.3.9. [Pd{(η^5-C_5H_5)Fe(η^5-C_5H_3CPh=NC_6H_4Br-3)}Cl(PPh_3)] (4i)

Dark-violet needles; m.p., above 230°C (decomposition). Anal. Found: C, 57.98; H, 3.74; N, 1.97. $C_{41}H_{32}$BrClFeNPPd Calc.: C, 58.13; H, 3.81; N, 1.65%. IR (KBr pellet): 1542, 1100, 1002, 821, 742, 700 cm^{-1}. ^1H NMR: δ 3.57 (d, 1H, $J = 1.7$ Hz, H-3), 3.91 (s, 5H, C_5H_5), 4.17 (t, 1H, $J = 2.45$ Hz, H-4), 4.21 (d, 1H, $J = 2.45$ Hz, H-5), 6.92–7.39 (m, 9H, N–Ar–H and C–Ph–H), 7.41–7.45, 7.79–7.83 (m, 15H, PPh_3–H) ppm.

3.3.10. [Pd{(η^5-C_5H_5)Fe(η^5-C_5H_3CPh=N$C_6H_4NO_2$-3)}Cl(PPh_3)] (4j)

Dark-violet plates; m.p., above 260°C (decomposition). Anal. Found: C, 60.58; H, 4.06; N, 3.30. $C_{41}H_{32}$ClFeN_2O_2PPd Calc.: C, 60.55; H, 3.97; N, 3.44%. IR (KBr pellet): ν 1349, 1521, 1098, 1001, 821, 750, 695 cm^{-1}. ^1H NMR: δ 3.62 (d, 1H, $J = 2.3$ Hz, H-3), 3.95 (s, 5H, C_5H_5), 4.23 (t, 1H, $J = 2.3$ Hz, H-4), 4.25 (d, 1H, $J = 1.85$ Hz, H-5), 7.26–7.83 (m, 24H, N–Ar–H, C–Ph–H and PPh_3–H) ppm.

3.3.11. [Pd{(η^5-C_5H_5)Fe(η^5-C_5H_3CPh=NC_6H_4Cl-2)}Cl(PPh_3)] (4k)

Brown needles; m.p., 221–222°C (decomposition). Anal. Found: C, 57.07; H, 3.87; N, 1.77. $C_{41}H_{32}Cl_2$FeNPPd · CH_2Cl_2 Calc.: C, 56.82; H, 3.80; N, 1.58%. IR (KBr pellet): ν 1552, 1103, 1000, 821, 741, 693 cm^{-1}. ^1H NMR: δ 3.43, 3.51 (d, 1H, $J = 2.35$ Hz, H-3), 4.01, 4.00 (s, 5H, C_5H_5), 4.18 (m, 1H, H-4), 4.26, 4.21 (d, 1H, $J = 2.35$ Hz, H-5), 5.30 (s, 2H, CH_2Cl_2), 6.60–7.81 (m, 24H, N–Ar–H, C–Ph–H and PPh_3–H) ppm. The ratio of the two isomers is 2.6 : 1.

3.3.12. [Pd{(η^5-C_5H_5)Fe(η^5-C_5H_3CPh=Nnaphthyl-2)}Cl(PPh_3)] (4l)

Dark-violet needles; m.p., above 244°C (decomposition). Anal. Found: C, 66.18; H, 4.34; N, 2.10. $C_{45}H_{35}$ClFeNPPd Calc.: C, 66.04; H, 4.31; N, 1.71%. IR (KBr pellet): ν 1541, 1098, 1002, 818, 747, 698 cm^{-1}. ^1H NMR: δ 3.56 (d, 1H, $J = 2.35$ Hz, H-3), 3.99 (s, 5H, C_5H_5), 4.16 (t, 1H, $J = 2.3$ Hz, H-4), 4.23 (d, 1H, $J = 2.1$ Hz, H-5), 7.26–7.84 (m, 27H, N–Ar–H, and C–Ph–H and PPh_3–H) ppm.

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