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Cyclopalladated ferrocenylimine complexes with dicyclohexylphosphinobiphenyl ligands: Synthesis, crystal structures and their use as highly efficient catalysts for Suzuki reaction of aryl chlorides

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Abstract

Two air, moisture and thermally stable cyclopalladated ferrocenylimine complexes with monophosphinobiphenyl ligands **4** and **5** have been easily synthesized. Their detailed structures are determined by single crystal X-ray analysis. Palladacycle **4** is found to be an *anti*, *trans*-complex, while **5** is a *syn*, *trans*-complex in the solid state. The two complexes could effectively catalyze the Suzuki reaction of aryl chlorides and phenylboronic acid with catalytic loadings of 0.0001–0.05 mol% in the presence of Cs_2CO_3 as base in dioxane at 100 °C, affording the coupled products in excellent yields.

Keywords: Cyclopalladated ferrocenylimine complex; Dicyclohexylphosphinobiphenyl ligand; Crystal structure; Suzuki reaction; Aryl chloride

1. Introduction

Cyclopalladated compounds or palladacycles containing at least one Pd–C bond intramolecularly stabilized by at least one donor atom are one of the most developed and studied classes of organopalladium derivatives, primarily due to their easy synthetic accessibility, structural versatility and intriguing applications in organic synthesis, organometallic catalysis, and new molecular materials [1–6]. On the other hand, palladium-catalyzed Suzuki reaction of aryl halides with arylboronic acids has become an extremely powerful tool in organic synthesis for the formation of C–C bonds [7–12]. Since the first report on the use of palladacycle for the Suzuki reaction by Herrmann and co-workers [13], a wide variety of known and new palladacycles derived from the cyclopalladation of phosphines, phosphites, phosphinites, amines, imines, oximes or thioethers have been successfully used in this C–C coupling reaction [1–6]. However, only a few palladacycles have proved to be efficient for the activation of notoriously unreactive aryl chlorides under relatively mild reaction conditions [14–26]. The best results were obtained with palladacycles modified with *N*-heterocyclic carbenes (2 mol% catalytic loadings, r.t.) [16,17] or bulky, electron-rich alkylphosphine ligands [18–26].

During the past decades we have extensively studied the cyclometalation including cyclopalladation of ferrocenylimine ligands [27–29]. Some of the obtained cyclopalladated ferrocenylimine complexes have been applied to the Suzuki reaction [30–35]. Among them, tricyclohexylphosphine (PCy_3) containing palladacycles (**1**, Scheme 1) were found to be very effective for the coupling of both activated and deactivated aryl chlorides [34,35]. Furthermore, we have recently demonstrated that a cyclopalladated ferrocenylimine complex with dicyclohexylphosphinobiphenyl ligand **2** is highly active for the amination of aryl chlorides in water (Scheme 1) [36]. These precatalysts combine the stability imparted by a palladacycle framework with the high activity commonly associated with alkylphosphine ligands. In view of these findings, we prepared

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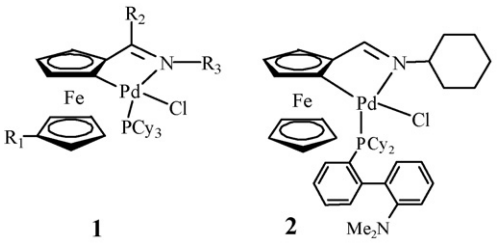


R_1 = H; R_2 = H; R_3 = ^{i}Pr (**a**),
R_1 = H; R_2 = CH_3; R_3 = *p*-CH_3-C_6H_4 (**b**),
R_1 = H; R_2 = H; R_3 = Cy (**c**),
R_1 = H; R_2 = CH_3; R_3 = *p*-OEt-C_6H_4 (**d**),
R_1 = H; R_2 = CH_3; R_3 = *p*-Br-C_6H_4 (**e**),
R_1 = H; R_2 = CH_3; R_3 = *p*-Cl-C_6H_4(**f**),
R_1 = H; R_2 = CH_3; R_3 = *o*-Cl-C_6H_4 (**g**),
R_1 = CHO; R_2 = H; R_3 = Cy (**h**).

Scheme 1. Cyclopalladated ferrocenylimine complexes with alkylphosphine ligands which showed high activities in the Suzuki reaction and amination of aryl chlorides.

two new cyclopalladated ferrocenylimine complexes **4** and **5** (Scheme 2), analogues of **2**, and examined their catalytic activities in the Suzuki reaction of aryl chlorides. The two complexes were found to be much more active than complexes of type **1** for the Suzuki reaction. Interestingly, complex **4** adopts an *anti*, *trans*-geometry, while **5** reveals a *syn*, *trans*-geometry in the solid state.

2. Experimental

2.1. Materials and methods

The chloride-bridged palladacyclic dimer **3** [37] was prepared according to published procedure. All other chemicals were used as purchased. Solvents were dried and freshly distilled prior to use. Suzuki reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. Melting points were measured using a WC-1 microscopic apparatus and were uncorrected. Elemental analyses of the products were obtained from a Thermo Flash EA 1112 elemental analyzer. IR spectra were collected on a Bruker VECTOR22 spectrophotometer in KBr pellets. ^{1}H, ^{31}P{^{1}H}NMR spectra were recorded on a Bruker DPX-400 spectrometer in $CDCl_3$ with TMS as an internal standard for ^{1}H NMR and 85% H_3PO_4 as external standard for ^{31}P{^{1}H}NMR. High-resolution mass spectra were measured on a Waters Q-Tof Micro^{TM} spectrometer.

2.2. Synthesis of the complexes *4* and *5*

A solution of chloride-bridged palladacyclic dimer **3** (0.1 mmol) and 2-(dicyclohexylphosphanyl)biphenyl (DCPB) or 2-dicyclohexylphosphanyl-2′-(*N*,*N*-dimethylamino)biphenyl (DCPAB) (0.22 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 30 min. The solvent was evaporated and the product was separated by passing through a short silica gel column with CH_2Cl_2 or CH_2Cl_2/ethyl acetate (1:1, v/v) as eluent. The first band was collected and afforded complex **4** or **5** after the evaporation of the solvent.

2.2.1. *[PdCl{[(η^5-C_5H_5)]Fe[(η^5-C_5H_3)-C(CH_3)=NC_6H_4-2-Cl]}(DCPB)] (4)*

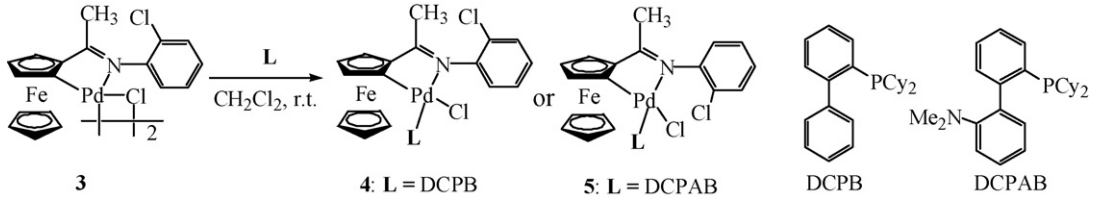
Complex **4** was obtained as red solids (yield 85%). mp 207–210 °C. Anal Calcd. for $C_{42}H_{46}Cl_2FeNPPd{\cdot}CH_2Cl_2$: C, 56.51; H, 5.29; N, 1.53%. Found: C, 56.82; H, 5.01; N, 1.86. IR (KBr, cm^{-1}): 2926, 2851, 1579 (C=N), 1461, 1365, 1321, 1223, 1122, 1002, 873, 766. ^{1}H NMR spectrum of complex **4** was more complicated than expected. It was difficult to identify the signals of different isomer and the ratio of the isomers could not be calculated consequently. ^{31}P{^{1}H}NMR (162 MHz, $CDCl_3$): δ 60.38. HRMS (ESI) $C_{42}H_{46}ClFeNPPd$: Calcd for [M–Cl]$^+$: 792.1441, found: 792.1445.

2.2.2. *[PdCl{[(η^5-C_5H_5)]Fe[(η^5-C_5H_3)-C(CH_3)=NC_6H_4-2-Cl]}(DCPAB)] (5)*

Complex **5** was obtained as red solids (yield 69%). mp 206–209 °C. Anal Calcd. for $C_{44}H_{51}Cl_2FeN_2PPd$: C, 60.60; H, 5.89; N, 3.21%. Found: C, 60.82; H, 6.02; N, 3.36. IR (KBr, cm^{-1}): 2926, 2851, 1574 (C=N), 1460, 1364, 1316, 1121, 1054, 1002, 875, 762. ^{1}H NMR spectrum of complex **5** was also more complicated than expected. It was difficult to identify the signals of different isomer and the ratio of the isomers could not be calculated consequently. ^{31}P{^{1}H}NMR (162 MHz, $CDCl_3$): δ 67.34, 66.37, 65.25. HRMS (ESI) $C_{44}H_{51}ClFeN_2PPd$: Calcd for [M–Cl]$^+$: 835.1863, found: 835.1876.

2.3. Suzuki reaction

A Schlenk tube was charged with the appropriate aryl halide, phenylboronic acid and base under nitrogen. The required amount of the catalyst stock solution and additional solvent were



Scheme 2. Preparation of complexes **4** and **5**.

Table 1
Crystallographic data and structure refinement for complexes **4**·CH_2Cl_2 and **5**·$(H_2O)_{0.5}$

Compound	**4**·CH_2Cl_2	**5**·$(H_2O)_{0.5}$
Elemental formula	$C_{43}H_{48}Cl_4FeNPPd$	$C_{44}H_{52}Cl_2FeN_2O_{0.50}PPd$
Formula weight	913.84	881.00
Crystal system	Triclinic	Monoclinic
Space group	*P*-1	*P*21*n*
a/Å	11.764 (2)	10.098 (2)
b/Å	12.417 (3)	19.020 (4)
c/Å	14.599 (3)	21.267 (4)
α/°	97.57 (3)	90
β/°	92.06 (3)	96.72 (3)
γ/°	100.06 (3)	90
V/Å^3	2077.6 (7)	4056.6 (14)
D_c/g cm^{-3}	1.461	1.443
Z	2	4
Crystal size/mm	0.20 × 0.18 × 0.18	0.20 × 0.18 × 0.17
F(0 0 0)	936	1820
μ/mm^{-1}	1.109	1.007
GOF (on F^2)	1.031	1.061
Data/restraints/parameters	6591/0/461	6838/2/460
R_1, wR_2 [$I > 2\sigma(I)$][a]	0.0417, 0.1046	0.0710, 0.1803

[a] $R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$, $wR_2 = [\sum (F_0^2 - F_c^2)^2 / \sum w(F_0^2)^2]^{1/2}$.

added to obtain a total volume of 3 mL. The reaction mixture was heated at 100 °C for 12–24 h, and then allowed to cool. The reaction mixture was extracted three times with dichloromethane, and the combined organic layers were washed with water, dried ($MgSO_4$), and evaporated to dryness. The products were isolated by flash chromatography on silica gel, and analyzed by ^{1}H NMR.

2.4. Single crystal X-ray structure determination

Intensity data of the complexes **4**·CH_2Cl_2 and **5**·$(H_2O)_{0.5}$ were measured on a Rigaku-Raxis-IV X-ray diffractometer using graphite-monochromated Mo Ka radiation (λ = 0.71073 Å) at 291(2) K. All data were collected using the *ω*–2*θ* scan technique and corrected for Lorenz-polarization effects. The two structures were solved by direct methods and expanded using Fourier techniques. All non-hydrogen atoms were described anisotropically, hydrogen atoms were included but not refined. The full-matrix least-squares calculations on F^2 were applied on the final refinement. Their raw data were corrected and the structures were solved using the SHELXL-97 program [38]. **CCDC** reference numbers 611597 and 613292 for **4**·CH_2Cl_2 and **5**·$(H_2O)_{0.5}$, respectively. Details of crystal structure determination of **4**·CH_2Cl_2 and **5**·$(H_2O)_{0.5}$ are summarized in Table 1.

3. Results and discussion

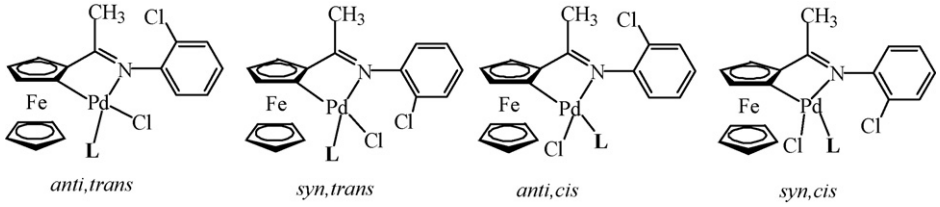
3.1. Synthesis and characterization

The preparation of complexes **4** and **5** is given in Scheme 2. Bridge-splitting reaction of palladacyclic dimer **3** with 2-(dicyclohexylphosphanyl)biphenyl (DCPB) or 2-dicyclohexylphosphanyl-2′-(*N*,*N*-dimethylamino)biphenyl (DCPAB) in CH_2Cl_2 at room temperature readily afforded the corresponding monomer **4** or **5** in good yields. The two complexes are air, moisture and thermally stable both in the solid state and in solution. They are very soluble in chloroform, dichloromethane and acetone, but insoluble in petroleum ether and *n*-hexane.

Complexes **4** and **5** were characterized by elemental analysis, IR, ^{1}H, ^{31}P{^{1}H}NMR and HRMS (ESI). The IR spectrum of the free ferrocenylimine showed an intense sharp band for C=N stretching at 1627 cm^{-1} [37]. For complexes **4** and **5**, this band shifted to lower energy (1579 and 1574 cm^{-1}, respectively), indicating that the imino nitrogen atom was coordinated to palladium through its lone pair. The ^{1}H NMR spectra of **4** and **5** exhibited more signals than expected, suggesting the existence of isomers in solution. Similar phenomenon was found in the ^{1}H NMR spectra of complex **1g** [35] and other monomeric cyclopalladated ferrocenylimine complexes which all had an *ortho*-substituent in the *N*-phenyl ring [37,39]. The cause of this isomerism might be that the free rotation of the *N*-phenyl ring around N–C(Ar) bond was blocked by the steric hindrance, resulting in an *anti* arrangement of the *ortho*-substituent and ferrocenyl moiety and a *syn* arrangement (Scheme 3). In addition, the appearance of only one singlet at δ 60.4 ppm for complex **4** and three singlets at δ 67.3, 66.4 and 65.3 ppm, respectively for complex **5** in their ^{31}P NMR spectra implied the possibility of other isomerisms such as the *trans* or *cis*-disposition of the coordinated phosphine ligand to the imino nitrogen. In the high resolution mass spectra of complexes **4** and **5**, the most intense peak was found at *m*/*z* 792.1445 and 835.1876, respectively which was attributed to [M–Cl]$^+$. The [M]$^+$ peak was not observed. Since the above analytical and spectroscopic date gave limited structural information, we have attempted to obtain single crystals of the two complexes by recrystallization from CH_2Cl_2/petroleum ether solution at room temperature.

3.2. Crystal structures

Single crystal X-ray analysis clearly confirmed formation of the expected complexes **4** and **5**. Interestingly, **4**·CH_2Cl_2 adopts



Scheme 3. Possible isomers of complexes **4** and **5**.

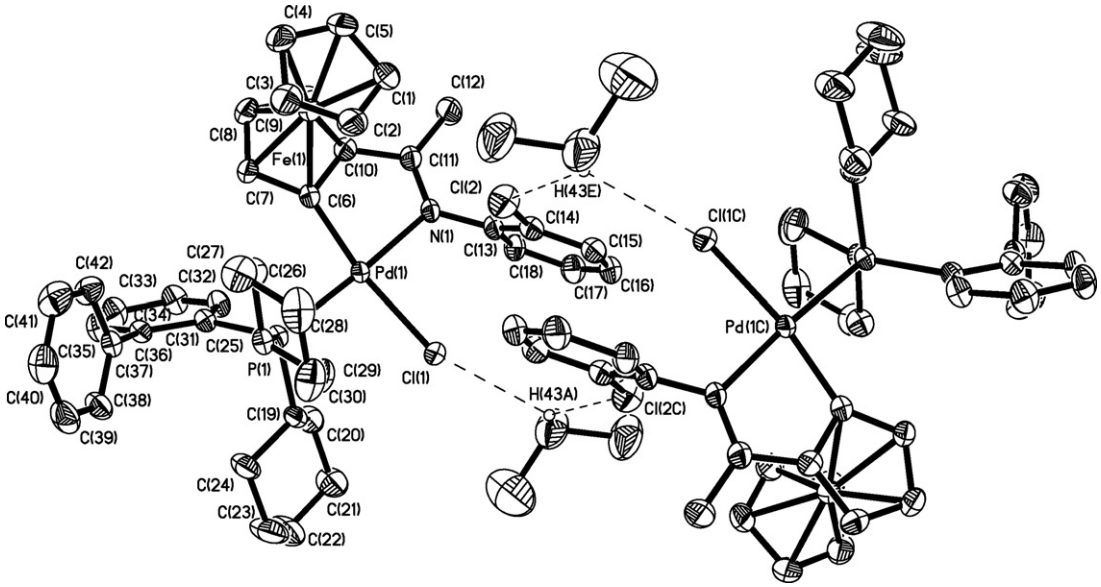


Fig. 1. The dimeric structure of complex **4**·CH_2Cl_2 showing the hydrogen bonds. Non-hydrogen bonding H atoms are omitted for clarity.

an *anti*, *trans*-, while complex **5**·$(H_2O)_{0.5}$ reveals a *syn*, *trans*-geometry in the solid state. The result undoubtedly proved the existence of *anti*- and *syn*-isomerism. The molecules are shown in Figs. 1–3 (displacement ellipsoids are drawn at the 30% probability level). Selected bond (Å) and angles (°) are listed in Table 2.

The Pd atom in each complex is in a slightly distorted square-planar environment bonded to the phosphorus atom, the chlorine atom, the nitrogen and C6 atoms of the ferrocenylimine. The deviations of the Pd atoms from the planes are 0.0506 and 0.1567 Å for complexes **4**·CH_2Cl_2 and **5**·$(H_2O)_{0.5}$, respectively. In each structure, the two Cp rings are almost parallel with dihedral angles of 1.6° and 3.1°, respectively. The Pd–P (2.2696(11) and 2.2652(18) Å) bond lengths of two complexes are slightly shorter than that of the related PCy_3-complex **1g** [35] [2.2797(13) Å].

Fig. 1 shows that Complex **4**·CH_2Cl_2 exists as a dimer in the crystal due to two types of intermolecular hydrogen bonds. One hydrogen bond is between the chlorine atom and the adjacent C–H group of dichloromethane [Cl(1)···

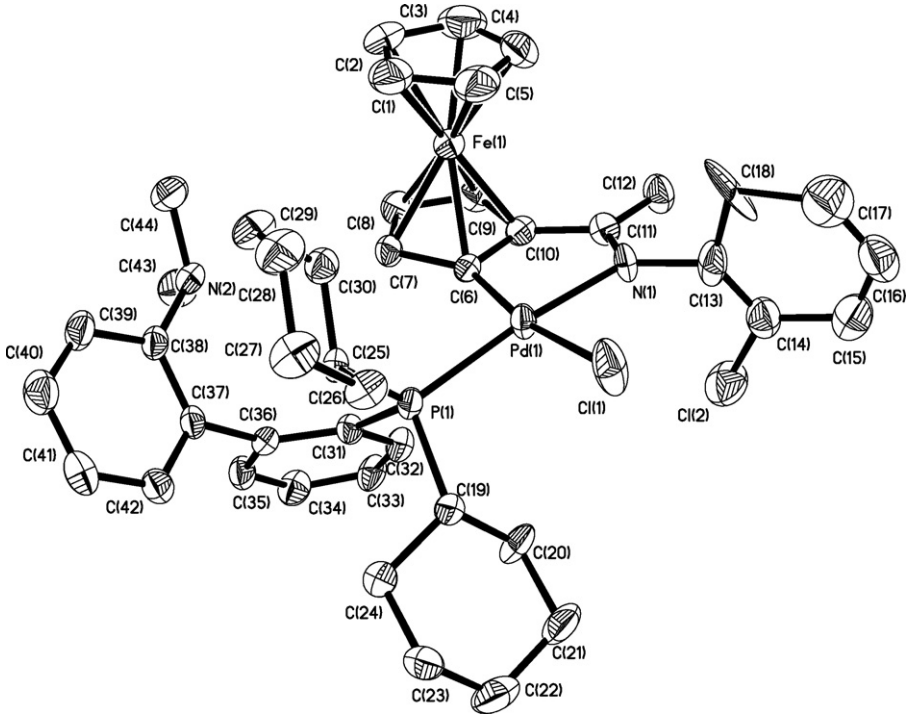


Fig. 2. Molecular structure of complex **5**·$(H_2O)_{0.5}$. Hydrogen atoms and O are omitted for clarity.

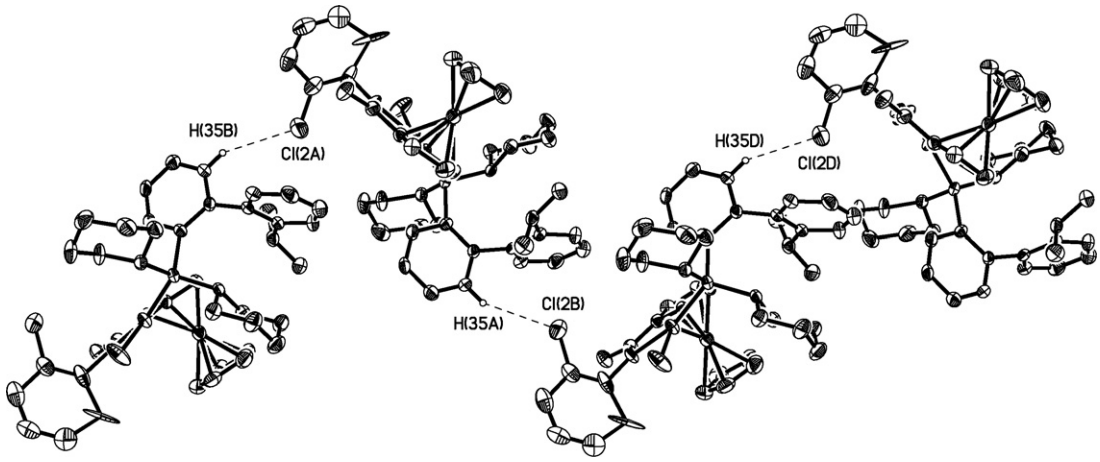


Fig. 3. One-dimensional zigzag chain structure of complex **5**·$(H_2O)_{0.5}$ showing the hydrogen bonds. Non-hydrogen bonding H atoms and O are omitted for clarity.

Table 2
Selected bond lengths (Å) and angles (°) for **4**·CH_2Cl_2 and **5**·$(H_2O)_{0.5}$

Compound	**4**·CH_2Cl_2	**5**·$(H_2O)_{0.5}$
Pd(1)—C(6)	1.990 (4)	1.976 (6)
Pd(1)—N(1)	2.148 (3)	2.169 (5)
Pd(1)—P(1)	2.2696 (11)	2.2652 (18)
Pd(1)—Cl(1)	2.3793 (14)	2.407 (2)
N(1)—C(11)	1.292 (5)	1.299 (8)
C(6)—Pd(1)—N(1)	79.95 (14)	79.2 (2)
C(6)—Pd(1)—P(1)	96.35 (11)	93.57 (19)
N(1)—Pd(1)—P(1)	174.07 (10)	164.93 (17)
C(6)—Pd(1)—Cl(1)	171.03 (11)	169.7 (2)
N(1)—Pd(1)—Cl(1)	91.27 (10)	94.12 (16)
P(1)—Pd(1)—Cl(1)	92.55 (5)	94.69 (7)
C(11)—N(1)—Pd(1)	115.1 (3)	114.5 (4)

H(43A) = Cl(1C)···H(43E) = 2.868 Å]. The other hydrogen bond is between the chlorine atom in benzene ring and the adjacent C–H group of dichloromethane [Cl(2)···H(43E) = Cl(2C)···H(43A) = 2.796 Å]. This is different from that of **1g**, in which chlorine atom in benzene ring does not participate in hydrogen bonding [35]. For complex **5**·$(H_2O)_{0.5}$, it has a one-dimensional zigzag chain structure formed by the hydrogen bonds [Cl(2A)···H(35B) = Cl(2B)···H(35A) = 2.908 Å] between the chlorine atom in benzene ring and the adjacent C–H group of DCPAB ligand (Fig. 3).

3.3. Catalysis

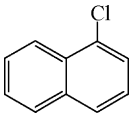
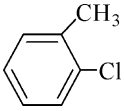
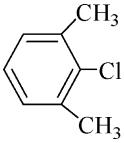
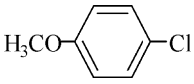
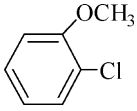
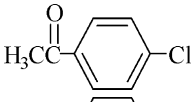
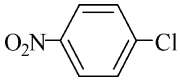
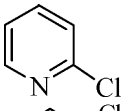
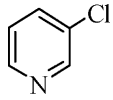
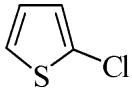
In 1998, Buchwald et al. reported monodentatephosphine ligand with biphenyl backbone and its application to room-temperature Suzuki couplings and amination of aryl chlorides [40]. Later more ligands of this type were easily synthesized by a one-pot procedure [41,42] and were found to be excellent supporting ligands for the palladium-catalyzed carbon–carbon [43–48] or carbon–heteroatom bond-forming reactions under mild reaction conditions [49–53]. Based on these results and in connection with our experience in palladacylic precatalysts for coupling reactions [30–36], we were interested to see whether the obtained cyclopalladated ferrocenylimine complexes with

Table 3
Suzuki coupling of aryl halides with phenylboronic acid catalyzed by **4** and **5**[a]

Entry	Aryl halide	Catalyst (mol%)	Solvent	Base	Temp. (°C)	Time (h)	%Yield[b]
1	4-Chlorotoluene	**Pd/L** (0.05/0.1)	Toluene	K_3PO_4	100	25	93[c]
2	4-Chlorotoluene	**4** (0.05)	Toluene	K_3PO_4	100	24	95[d]
3	4-Chlorotoluene	**5** (0.05)	Toluene	K_3PO_4	100	24	100[d]
4	2-Bromo-m-xylene	**4** (0.5)	Toluene	KF	r.t.	24	33[e]
5	Bromobenzene	**4** (0.5)	Toluene	KF	r.t.	12	34[e]
6	Chlorobenzene	**4** (0.05)	Dioxane	Cs_2CO_3	100	12	91
7	Chlorobenzene	**5** (0.01)	Dioxane	Cs_2CO_3	100	12	29
8	Chlorobenzene	**5** (0.05)	Dioxane	Cs_2CO_3	100	12	95
9	4-Chlorotoluene	**4** (0.01)	Dioxane	K_3PO_4	100	24	25
10	4-Chlorotoluene	**5** (0.01)	Dioxane	K_3PO_4	100	24	27
11	4-Chlorotoluene	**5** (0.05)	Dioxane	K_3PO_4	100	12	38
12	4-Chlorotoluene	**5** (0.05)	Dioxane	Cs_2CO_3	100	12	93

[a] Reaction conditions: ArX (0.5 mmol), $PhB(OH)_2$ (0.6 mmol), base (0.75 mmol), solvent (3 mL).
[b] Isolated yields, average of two runs.
[c] Data from Ref. [43]. $Pd(OAc)_2$/DCPB Cat., ArCl (1.0 equiv.), $PhB(OH)_2$ (1.5 equiv.), K_3PO_4 (2.0 equiv.).
[d] $PhB(OH)_2$ (0.75 mmol), K_3PO_4 (1.0 mmol).
[e] $PhB(OH)_2$ (0.75 mmol), KF(1.5 mmol).

Table 4
Suzuki coupling of aryl chlorides with phenylboronic acid catalyzed by **5**[a]

Entry	Aryl chloride	Catalyst (mol%)	Time (h)	%Yield[b]
1		5 (0.05)	12	96
2		5 (0.05)	12	91
3		5 (0.05)	16	90
4		5 (0.05)	16	98
5		5 (0.05)	16	94
6		5 (0.01)	12	97
7		5 (0.01)	12	100
8		5 (0.001)	12	97
9		5 (0.0001)	12/16	80/91
10		5 (0.01)	12	97
11		5 (0.01)	12	92
12		5 (0.01)	12	70

[a] Reaction conditions: ArCl (0.5 mmol), $PhB(OH)_2$ (0.6 mmol), Cs_2CO_3 (0.75 mmol), dioxane (3 mL), 100 °C.
[b] Isolated yields, average of two runs.

monophosphinobiphenyl ligands **4** and **5** were also highly active for the Suzuki reaction of aryl chlorides.

We first evaluated the effectiveness of palladacycles **4** and **5** for the coupling of 4-chlorotoluene with phenylboronic acid under the same reaction conditions that Buchwald reported [43]. The two palladacycles were found to be slightly more active than Buchwald's $Pd(OAc)_2$/DCPB catalytic system producing the coupled products in excellent yields (Table 3, entries 1–3). Furthermore, the use of palladacyclic precatalysts had the advantage of not needing excess of ligand. While for Buchwald's catalytic systems, L/Pd ratios of 2/1 were usually employed. Since mixtures of $Pd(OAc)_2$ and DCPB or DCPAB were demonstrated to be able to efficiently catalyze the room-temperature Suzuki coupling of aryl bromides [43] and chlorides [40] with 1–2 mol% Pd, we next investigated room-temperature Suzuki coupling of aryl bromides in the presence of 0.5 mol% of complex **4** to further compare the two catalytic systems. Disappointingly, the best isolated yield of the product was only 33% for very sterically hindered 2-bromo-m-xylene (entry 4). In the case of relatively reactive bromobenzene, high yield could not be obtained, either (entry 5). The results indicated that palladacyclic precatalyst with DCPB was inferior to $Pd(OAc)_2$/DCPB for room-temperature Suzuki couplings although it was highly active at elevated temperatures. A possible reason was that lower temperature did not favor the cleavage of stable palladacycles [Pd(II)] to form catalytically active Pd(0) species.

We have previously shown that PCy_3-cyclopalladated ferrocenylimine complexes **1** are efficient catalysts for the coupling of aryl chloride with phenylboronic acid. In a typical experiment, using 0.1 mol% of catalyst in the presence of Cs_2CO_3 as base in dioxane at 100 °C for 12 h provided coupled prod-

ucts in excellent yields [34,35]. Under these reaction conditions, cyclopalladated ferrocenylimine complexes with monophosphinobiphenyl ligands **4** and **5** displayed higher catalytic efficiency than complexes of type **1**. For example, chlorobenzene and 4-chlorotoluene were efficiently converted to the corresponding biaryls with a catalytic loading as low as 0.05 mol% (entries 6–8,12). In addition, Cs_2CO_3 was found to be a more effective base than K_3PO_4 in dioxane (entries 9–12).

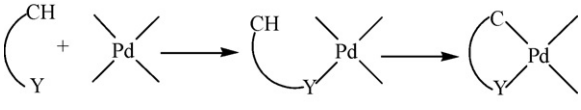
The following experiments further proved that complexes **4** and **5** were much more active than PCy_3-cyclopalladated ferrocenylimine complexes **1** for the couplings of a variety of electronically and structurally diverse aryl chlorides with phenylboronic acid (Table 4). Similar to the results of chlorobenzene and 4-chlorotoluene, excellent yield (96%) was also obtained in the case of chloronaphthalene with a catalytic loading of 0.05 mol% (entry 1). *Ortho*-substituents were tolerated and even the very sterically hindered 2-chloro-m-xylene could provide the biaryl product in a 90% isolated yield by prolonging the reaction time from 12 to 16 h (entries 2–3). Reactions of electron-rich aryl chlorides such as 4- and 2-chloroanisoles also gave very high yields after 16 h (98 and 94%, respectively, entries 4–5). For electron-deficient aryl chlorides such as 4-chloroacetophenone and 4-chloronitrobenzene, they could be coupled very efficiently with a catalytic loading as low as 0.01 mol% (entries 6–7). The catalytic loadings could be further lowered to 0.0001 mol% without loss of activity (entries 8–9). Finally, couplings of heteroaryl chlorides with phenylboronic acid were studied. In case of 2-chloropyridine, using only 0.01 mol% of **5** afforded the product in a 97% yield and the result was slightly better than that of 3-chloropyridine (entries 10–11). 2-Chlorothiophene could provide a 70% yield under the same reaction conditions (entry 12). While for complexes of type **1**, a catalytic loading of 0.1 mol% was needed to get high yields. Even so, 2-chlorothiophene only gave a 23% yield [34,35].

4. Conclusion

Two stable cyclopalladated ferrocenylimine complexes with monophosphinobiphenyl ligands **4** and **5** were easily synthesized and structurally characterized. Single crystal X-ray analysis confirmed the *anti*, *trans*-structure of palladacycle **4** as well as the *syn*, *trans*-structure of **5** in the solid state. The two complexes were found to be highly efficient for the Suzuki reaction of a variety of aryl chlorides.

Definition of field-specific term

The cyclopalladation reaction, also termed orthopalladation, is a chemical process involving chelation-controlled regioselective C–H bond activation of a ligand with palladating reagent to form new Pd–C bond as well as palladacycle.



Y= NR_2, SR, =NR, PR_2, etc

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