

Efficient Suzuki coupling of aryl chlorides catalyzed by tricyclohexylphosphine adducts of cyclopalladated ferrocenylimines

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Abstract

The air and moisture stable tricyclohexylphosphine (PCy₃) adducts of dimeric cyclopalladated ferrocenylimines **5** and **6** have been easily synthesized and successfully used in palladium-catalyzed Suzuki cross-coupling of aryl chlorides. Using 0.1 mol% of **6** in the presence of 2 equivalent of Cs₂CO₃ as base in dioxane at 100 °C provided coupled products in excellent yields in the reaction of non-activated and deactivated aryl chlorides with phenylboronic acid. For activated chlorides such as 4-chloronitrobenzene and 4-chloroacetophenone, the catalyst loadings could be lowered to 0.01 mol% without loss of activity.
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Keywords: Suzuki coupling; Cyclopalladated ferrocenylimines; Tricyclohexylphosphine adducts; Aryl chlorides; Phenylboronic acid

1. Introduction

Palladium-catalyzed reactions are widely used in organic synthesis for formation of carbon–carbon and carbon–heteroatom bonds [1]. The Suzuki reaction of aryl halides/triflates with boronic acids has been one of the most widely studied owing to its applicability and the low toxicity of the reagents [2]. There is currently much interest in development of catalysts that can activate aryl chlorides since these substrates are cheaper and more readily available than the corresponding bromides and iodides [3]. Substantial progress has been made by using catalysts with bulky, electron-rich phosphines [2–7] and *N*-heterocyclic carbenes [2,3,8]. Moreover, palladacyclic catalysts are amongst the most active catalysts for forming carbon–carbon and carbon–heteroatom bonds [2b,3b,7c,8c–9]. A large number of phosphorus, nitrogen or sulfur based palladacycles derived from phosphines, phosphites, phosphinites, amines, imines,

oximes or thioethers have been synthesized and used in the Suzuki reaction. The advantages of such palladacyclic catalysts include their ease of synthesis, facile modification and convenience of handling (insensitivity to air or moisture). Most of the palladacycles show considerable activity with activated aryl chlorides but only limited activity with deactivated substrates [3b]. It was recently reported, however, that isolated or in situ formed secondary [10] or tertiary phosphine [11] adducts (L = HP(*t*Bu)₂, HPCy₂ or PCy₃, PtBu₃, e.g.) of dimeric phosphorus- or nitrogen-containing palladacycles (Fig. 1) efficiently promote the Suzuki coupling of both activated and deactivated aryl chlorides.

Our work had focused on cyclometallation of ferrocenylimines and applications of these systems [12]. We have found that cyclopalladated ferrocenylimines **4** are effective for the Heck reaction [13] and the dimerization of arylmercurials [14]. They also showed good activity in the Suzuki coupling reaction of aryl iodides and bromides. In contrast, only activated aryl chlorides gave good results [15]. We thought it interesting to study whether the activity of palladacycles **4** with aryl

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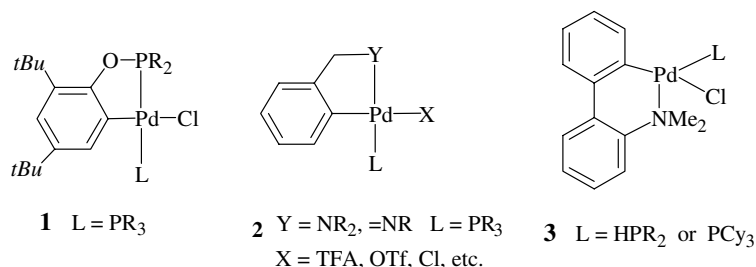
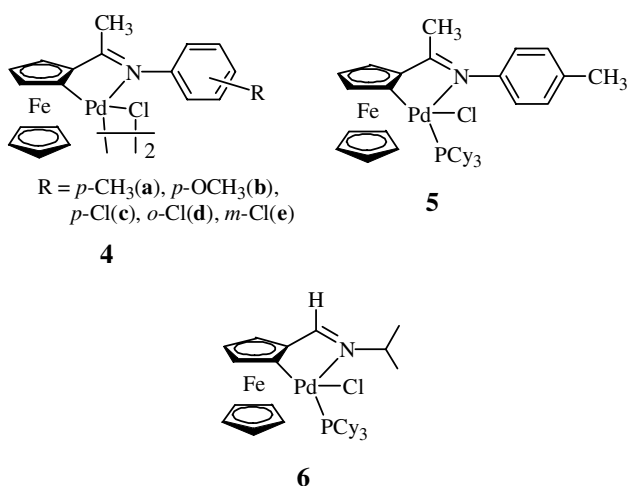


Fig. 1. Examples of adducts resulting from the corresponding dimeric palladacycles with phosphines.

chlorides could be enhanced with the corresponding tricyclohexylphosphine adduct **5**. Novel palladacycle **6** was also prepared for comparison. The results of this study are presented below.



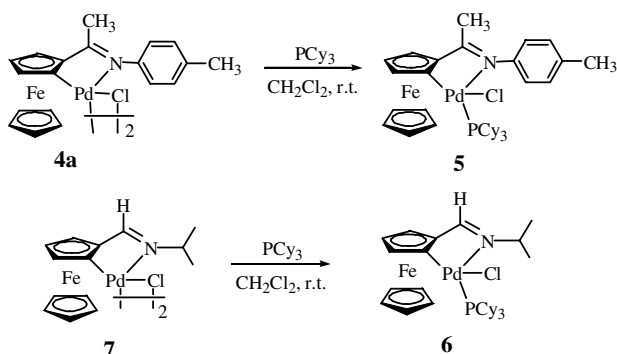
ladium in CH_2Cl_2 at room temperature produced the corresponding tricyclohexylphosphine adduct **5** or **6** as red crystals after recrystallization from CH_2Cl_2 –petroleum ether in 53.4% and 57.0% yield, respectively. Both **5** and **6** are air and moisture stable both in the solid state and in solution.

The new compounds **5** and **6** were characterized by 1H NMR, IR and high resolution mass spectrometry. The structure of **5** was determined by X-ray single crystal analysis. The molecule is shown in Fig. 2. Crystallographic and data collection parameters for $\mathbf{5} \cdot CH_2Cl_2$ are summarized in Table 1. Selected bond length (Å) and angles ($^\circ$) are given in Table 2. As depicted in Fig. 2, the palladium adopts an approximately square planar configuration defined by the P, N, Cl(1) and C(6) atoms. The N–Pd–C(6) bond angle ($80.5(2)^\circ$) is essentially identical to the corresponding values in PPh_3 adducts of cyclopalladated ferrocenylimines **4** [16,17]. The coor-

2. Results and discussion

2.1. Synthesis and characterization of complexes **5** and **6**

The reaction of chloride-bridged palladacyclic dimers **4a** or **7** (Scheme 1) with 1.2 equivalent of PCy_3 per pal-



Scheme 1.

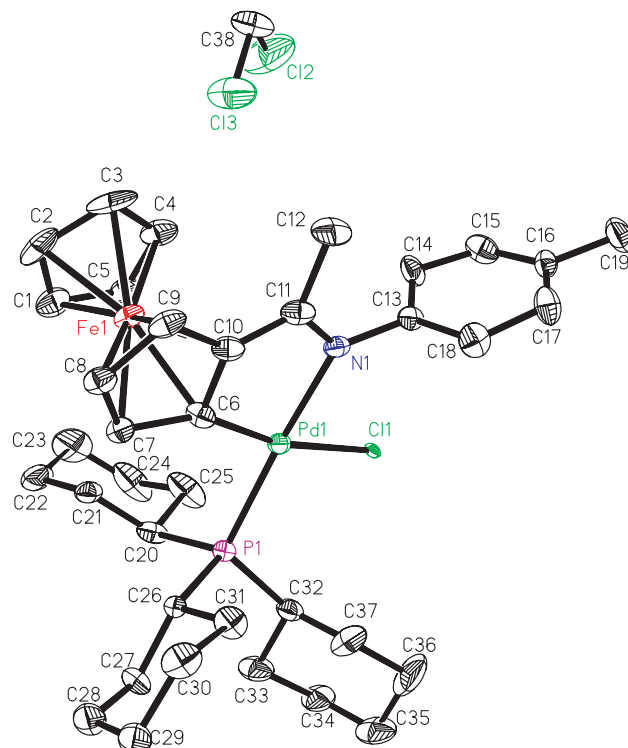
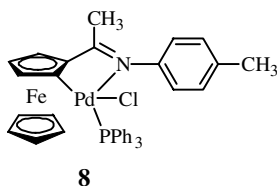


Fig. 2. Molecular structure of $\mathbf{5} \cdot CH_2Cl_2$.

dinated PCy₃ is *trans* to the imino nitrogen with a P–Pd–N angle of 172.25(14)°. The Pd–C(6) (2.019(6) Å), Pd–N (2.170(5) Å) and Pd–P (2.2833(16) Å) bond lengths in **5** are longer than those of **8** (1.998(3) Å, 2.136(3) Å, 2.2371(10) Å, respectively) [17] possibly due to the steric bulk of the PCy₃ ligand.

**8**

2.2. Suzuki coupling reaction

Initially, a quick survey of solvents, including dioxane, toluene and THF, with phenyl chloride and phenylboronic acid as the coupling partners (using 0.1 mol% of **6** and Cs₂CO₃ as the base) revealed that dioxane gave the fastest reaction (data not shown). We further investigated the effect of the base in the same reaction (Table 3), examining K₂CO₃, Cs₂CO₃, K₃PO₄, KF · 2H₂O and *t*-BuONa. It was found that Cs₂CO₃

Table 1

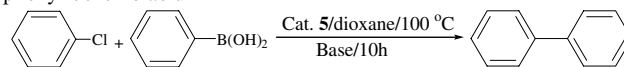
Crystallographic and data collection parameters for 5 · CH ₂ Cl ₂	
Empirical formula	C ₃₇ H ₅₁ ClFeNPPd · CH ₂ Cl ₂
Formula weight	823.38
Temperature (K)	291(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2 ₁ 2 ₁ 1
Unit cell dimensions	
<i>a</i> (Å)	12.003(2)
<i>b</i> (Å)	15.614(3)
<i>c</i> (Å)	20.924(4)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å ³)	3921.8(14)
<i>Z</i>	4
Calculated density (Mg/m ³)	1.395
Absorption coefficient (mm ⁻¹)	1.100
<i>F</i> (000)	1704
Crystal size (mm)	0.20 × 0.18 × 0.17
Theta range for data collection (°)	1.63–25.00
Index ranges	–14 ≤ <i>h</i> ≤ 14, 0 ≤ <i>k</i> ≤ 18, –24 ≤ <i>l</i> ≤ 24
Reflections collected/unique [<i>R</i> _(int)]	11 325/6429 [0.0433]
Completeness to 2 θ = 25.00	96.2%
Absorption correction	None
Maximum and minimum transmission	0.8351 and 0.8100
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	6429/0/413
Goodness-of-fit on <i>F</i> ²	1.008
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0461, <i>wR</i> ₂ = 0.0973
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0669, <i>wR</i> ₂ = 0.1036
Absolute structure parameter	0.50(3)
Extinction coefficient	0.00057(16)
Largest difference peak and hole (e Å ⁻³)	0.631 and –0.384

Table 2

Selected bond lengths (Å) and angles (°) for 5 · CH ₂ Cl ₂	
Pd(1)–C(6)	2.019(6)
Pd(1)–P(1)	2.2833(16)
Pd(1)–Cl(1)	2.530(3)
N(1)–C(13)	1.444(8)
C(10)–C(11)	1.441(10)
Pd(1)–N(1)	2.170(5)
Pd(1)–Cl(1')	2.426(3)
N(1)–C(11)	1.299(8)
C(6)–C(10)	1.441(9)
C(6)–Pd(1)–N(1)	80.5(2)
N(1)–Pd(1)–P(1)	172.25(14)
P(1)–Pd(1)–Cl(1')	93.38(10)
P(1)–Pd(1)–Cl(1)	92.29(8)
C(11)–N(1)–Pd(1)	114.0(4)
C(6)–Pd(1)–P(1)	96.81(18)
N(1)–Pd(1)–Cl(1')	89.56(17)
N(1)–Pd(1)–Cl(1)	91.76(16)
Cl(1')–Pd(1)–Cl(1)	9.41(11)
N(1)–C(11)–C(10)	114.7(6)

Table 3

Influence of base on the Suzuki coupling of phenyl chloride with phenyl boronic acid



Entry	Base	% Yield ^a
1	K ₂ CO ₃	24.2 (20.2)
2	Cs ₂ CO ₃	76.4 (66.2)
3	K ₃ PO ₄	38.7 (35.0)
4	KF · 2H ₂ O	35.6 (32.5)
5	<i>t</i> -BuONa	13.9 (12.6)

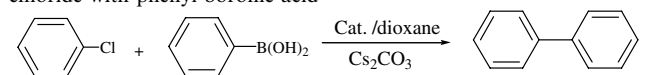
Reaction conditions: catalyst **5** (0.1 mol%), PhCl (1 mmol), PhB(OH)₂ (1.5 mmol), base (2 mmol), dioxane (6 mL), 100 °C, 10 h.

^a Determined by GC (undecane standard), based on PhCl, average of two runs. Yields in parentheses refer to isolated yields, average of two runs.

was much better than others (with 0.1 mol% **5**, 100 °C, 10 h, GC yield was 76.4%). Therefore, Cs₂CO₃ was ultimately chosen as the base for this system.

With the appropriate solvent (dioxane) and base (Cs₂CO₃) in hand, the relative activities of several palladacycles (Table 4) for the same model reaction were then studied. When the reaction was carried out at 100 °C for 10 h, both **5** and **6** exhibited high activity with catalyst loadings as low as 0.1 mol%. Catalyst **6** was slightly more active (76.4% versus 82.6% GC yield, respectively, entries 1 and 2), while dimeric complex **4a** and the corresponding PPh₃ adduct **8** were almost inactive under the same reaction conditions (entries 3 and 4). The notably high efficiency of **5** and **6** (relative to **4a** and **8**) is attributed to electronic effects of the coordinated PCy₃, suggesting that PCy₃ participates in the catalytic cycles. The isolated yield of biphenyl could reach 100% by prolonging the reaction time from 10 to 15 h (entry 5). The reaction also proceeded well when the

Table 4
Relative activities of palladacycles for the Suzuki coupling of phenyl chloride with phenyl boronic acid



Entry	Catalyst (mol%)	T (°C)	Time (h)	% Yield ^a
1	5 (0.1)	100	10	76.4 (66.2)
2	6 (0.1)	100	10	82.6 (76.1)
3	4a (0.1)	100	10	1.1
4	8 (0.1)	100	10	0.8
5	6 (0.1)	100	15	100 (100)
6	5 (1.0)	80	5	96.1
7	6 (1.0)	60	5	<1
8	6 (0.05)	100	20	(66.2)
9	6 (0.01)	100	15	28.3 (25.9)

Reaction conditions: PhCl (1 mmol), PhB(OH)₂ (1.5 mmol), Cs₂CO₃ (2 mmol), dioxane (6 mL).

^a Determined by GC (undecane standard), based on PhCl, average of two runs. Yields in parentheses refer to isolated yields, average of two runs.

reaction temperature was decreased from 100 to 80 °C when 1 mol% of **5** was used for 5 h (96.1% GC yield, entry 6). Further decrease in temperature to 60 °C, however, led to loss of the activity of the catalyst (entry 7). In terms of reduction of catalyst loading, palladacycle **6** was still efficient at 0.05 mol% level (entry 8), although at 0.01 mol% it gave biphenyl product in only 25.9% isolated yield (entry 9).

The scope of the Suzuki coupling was investigated by varying the aryl chloride under the optimized reaction conditions (Cs₂CO₃, dioxane, 100 °C) (Table 5). A variety of electronically and structurally diverse aryl chlorides including 3-chloropyridine could be cross-coupled very efficiently with phenylboronic acid. *ortho*-Substituents were tolerated and even the very sterically hindered 2-chloro-*m*-xylene provided the biaryl product in 98.7% isolated yield using 0.1 mol% of **6** (entries 1–4). A strongly electron-donating group such as methoxy led to a certain drop in isolated yield under the same reaction conditions (88.1%, entry 5). For activated chlorides such as 4-chloronitrobenzene and 4-chloroacetophenone, the catalyst loadings could be lowered to 0.01 mol% without loss of activity (entries 8–10). Coupling of heteroaryl chlorides with phenylboronic acid with this catalyst system was also studied. In case of 2-chloropyridine, using only 0.01 mol% of **6** afforded the corresponding product in 74.6% isolated yield (entry 11). For 3-chloropyridine only 22.7% yield was obtained under the low catalyst loading conditions as those of 2-chloropyridine (entry 12), but the yield was improved to 62.1% in the presence of 0.1 mol% of **6** (entry 14). Finally, 2-chlorothiophene was found to be a poor coupling partner in this system giving only 24.4% yield with 0.1 mol% of **6** (entry 15).

In summary, we have demonstrated that novel, simple PCy₃ adducts of cyclopalladated ferrocenylimines **5**

and **6** are efficient catalysts for the Suzuki coupling of aryl chlorides with phenylboronic acid. A diverse array of aryl chlorides, including sterically hindered, electronically deactivated and some heteroaryl chlorides, have been successfully coupled using this system. Applications involving these adducts in other palladium-catalyzed reactions are currently under investigation in our laboratory.

3. Experimental

3.1. General


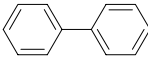

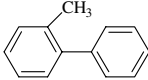
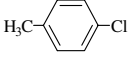
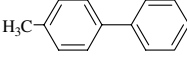
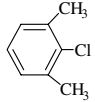
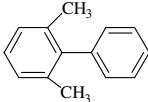

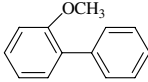
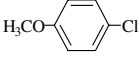
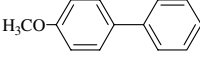
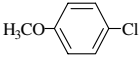
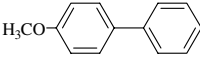
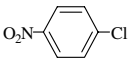
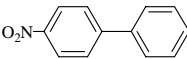
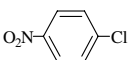
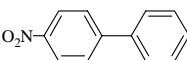
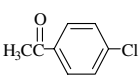
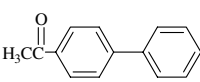

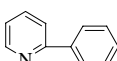

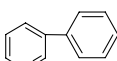

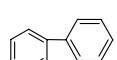

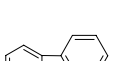

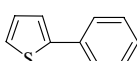
All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. 1,4-Dioxane was dried over sodium benzophenone and distilled under nitrogen prior to use. The chloride-bridged palladacyclic dimer **4a**, **7** [13a] and PCy₃ [18] were prepared according to published procedures. All other chemicals were used as purchased. Melting points were measured using a WC-1 microscopic apparatus and were uncorrected. IR spectra were collected on a Bruker VEC-TOR22 spectrophotometer in KBr pellets. ¹H and ³¹P{¹H} NMR spectra were recorded on a Bruker DPX-400 spectrometer in CDCl₃ with TMS as an internal standard. GC analysis was performed on Agilent 4890D gas chromatograph. High-resolution mass spectra were measured on a Waters Q-ToF Micro™ spectrometer.

3.2. Synthesis of tricyclohexylphosphine adducts **5** and **6**

A solution of chloride-bridged palladacyclic dimer **4a** (0.084 g, 0.092 mmol) and PCy₃ (0.061 g, 0.22 mmol) in dichloromethane (10 mL) was stirred at room temperature for 30 min. The solution was filtered through Celite and evaporated to dryness. The crude product was recrystallized from dichloromethane–petroleum ether to afford red crystals of **5** (0.081 g, 53.4%); m.p. 163–165 °C. IR (KBr pellet): 3434, 2926, 2852, 1626, 1582, 1508, 1451, 1108, 1006 cm⁻¹. ¹H NMR (CDCl₃): δ 1.27 (m, 9H, PCy₃), 1.76 (m, 15H, PCy₃), 1.98 (s, 3H, CH₃), 2.05 (m, 6H, PCy₃), 2.33 (m, 3H, CH₃), 2.54 (m, 3H, PCy₃), 4.26 (s, 5H, C₅H₅), 4.47 (m, 2H, C₅H₅), 4.54 (m, 1H, C₅H₅), 5.30 (s, 2H, CH₂Cl₂), 6.81 (m, 2H, Ar-H), 7.15 (m, 2H, Ar-H). ³¹P{¹H} NMR (CDCl₃): δ 46.78, 48.24. HRMS (positive ESI) calc. for C₃₇H₅₁ClFeNPPd: 737.1832, found: 737.1840.

Adduct **6** was prepared by a similar procedure: Dimer **7** (0.086 g, 0.11 mmol) reacted with PCy₃ (0.073 g, 0.26 mmol) in DCM to produce 0.084 g (57.0%) of **6** as red crystals after recrystallization from CH₂Cl₂–petroleum ether; m.p. 199–201 °C. IR (KBr pellet): 3442, 2928, 2852, 1611, 1449, 1302, 1171, 1117, 1002 cm⁻¹. ¹H NMR (CDCl₃): δ 1.32 (m, 15H, PCy₃), CH(CH₃)₂, 1.78 (m, 15H, PCy₃), 2.07 (m, 6H, PCy₃),

Table 5
Suzuki coupling of aryl chlorides with phenyl boronic acid

Entry	Aryl halide	Catalyst (mol%)	Time (h)	Product	% Yield ^a
1		6 (0.1)	15		100
2		6 (0.1)	15		100
3		6 (0.1)	15		100
4		6 (0.1)	15		98.7
5		6 (0.1)	15		88.1
6		6 (0.5)	12		93.5
7		5 (0.5)	12		87.4
8		6 (0.1)	10		100
9		6 (0.01)	10		93.6
10		6 (0.01)	10		98.7
11		6 (0.01)	15		74.6
12		6 (0.01)	15		22.7
13		6 (0.05)	15		55.4
14		6 (0.1)	15		62.1
15		6 (0.1)	15		24.4

Reaction conditions: ArCl (1 mmol), PhB(OH)₂ (1.5 mmol), Cs₂CO₃ (2 mmol), dioxane (6 mL), 100 °C.

^a Isolated yields, based on ArCl, average of two runs.

2.54 (m, 3H, PCy₃), 4.21 (s, 5H, C₅H₅), 4.41 (m, 2H, C₅H₃), 4.53 (m, 1H, C₅H₃), 4.81 (m, 1H, CHMe₂), 8.09 (m, 1H, N=CH). ³¹P{¹H} NMR (CDCl₃): δ 45.57, 46.92. HRMS (positive ESI) calc. for C₃₂H₄₉ClFeNPPd: 675.1675, found: 675.1670.

3.3. General procedure for the coupling reactions

A Schlenk tube was charged with the appropriate aryl chloride (1.0 mmol), phenyl boronic acid (0.183 g, 1.5 mmol) and base (2.0 mmol) under nitrogen. The catalyst was introduced as a dioxane solution (0.001 mmol/mL) via syringe, and additional dioxane was added to obtain a total volume of 6 mL. The reaction mixture was then placed in an oil bath and heated at 60–100 °C for a certain time, cooled and quenched with water. The organic layer was separated and the aqueous layer was extracted with dichloromethane, then the combined organic layers were washed with water, dried over MgSO₄, filtered, and the solvent was removed on a rotary evaporator. The residue was analyzed by GC (dissolved in dioxane, undecane as internal standard) or purified by column chromatography on silica gel (the purified products were identified by comparison of melting points with the literature values [19] or by ¹H NMR spectra).

2,6-Dimethylbiphenyl. Colorless oil. ¹H NMR (CDCl₃): δ 2.02 (s, 3H, CH₃), 2.03 (s, 3H, CH₃), 7.12 (m, 5H, Ar-H), 7.32 (m, 1H, Ar-H), 7.39 (m, 2H, Ar-H).

2-Methoxybiphenyl. Colorless oil. ¹H NMR (CDCl₃): δ 3.81 (s, 3H, OCH₃), 6.98 (m, 1H, Ar-H), 7.03 (t, *J* = 7.6 Hz, 1H, Ar-H), 7.32 (m, 3H, Ar-H), 7.40 (t, *J* = 7.6 Hz, 2H, Ar-H), 7.52 (d, *J* = 7.2 Hz, 2H, Ar-H).

2-Phenylpyridine. Colorless oil. ¹H NMR (CDCl₃): δ 7.24 (m, 1H, Py-H), 7.46 (m, 3H, Ar-H), 7.74 (m, 2H, Py-H), 8.00 (d, *J* = 7.2 Hz, 2H, Ar-H), 8.70 (d, *J* = 4.4 Hz, 1H, Py-H).

3-Phenylpyridine. Colorless oil. ¹H NMR (CDCl₃): δ 7.45 (m, 4H, Py-H, Ar-H), 7.59 (d, *J* = 7.4 Hz, 2H, Ar-H), 7.90 (d, *J* = 7.8 Hz, 1H, Py-H), 8.60 (s, 1H, Py-H), 8.86 (s, 1H, Py-H).

2-Methylbiphenyl. Colorless oil. ¹H NMR (CDCl₃): δ 2.27 (s, 3H, CH₃), 7.25 (m, 4H, Ar-H), 7.33 (m, 3H, Ar-H), 7.40 (m, 2H, Ar-H).

2-Phenylthiophene. White solid; m.p. 39–41 °C (lit. 40–41 °C). ¹H NMR (CDCl₃): δ 7.09 (t, *J* = 4.2 Hz, 1H, C₄H₃S), 7.29 (m, 3H, C₄H₃S, Ar-H), 7.38 (t, *J* = 7.6 Hz, 2H, Ar-H), 7.62 (d, *J* = 7.6 Hz, 2H, Ar-H).

4-Methoxybiphenyl. White solid; m.p. 88–90 °C (lit. 91–92 °C).

4-Methylbiphenyl. White solid; m.p. 47–49 °C (lit. 48–50 °C).

4-Acetylbiphenyl. White solid; m.p. 117–119 °C (lit. 116–118 °C).

4-Nitrobiphenyl. White solid; m.p. 113–115 °C (lit. 112–114 °C).

3.4. Structure determination

Crystals of **5** were obtained by recrystallization from CH₂Cl₂–petroleum ether solution at 0 °C. A single crystal suitable for X-ray analysis was mounted on a glass fiber. All measurements were made on a Rigaku-IV imaging plate area detector with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The data were corrected for Lorentz and polarization factors. The structure was solved by direct methods [20] and expanded using Fourier techniques and refined by full-matrix least-squares methods. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included but not refined. All calculations were performed using the TEXSAN [21] crystallographic software package of Molecular Structure corporation.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 262129. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk or on the web www: <http://www.ccdc.cam.ac.uk>.

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