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2-(1-Aryliminoethyl)cycloheptapyridylpalladium complexes: Synthesis, characterization and the use in the Heck-reaction

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ABSTRACT

A series of 2-(1-aryliminoethyl)cycloheptapyridine derivatives (**L1**–**L7**) were prepared in good yield by the condensation reaction of 2-acetylcycloheptapyridine with various anilines, and then reacted with $PdCl_2(CH_3CN)_2$ in dichloromethane to form the respective palladium(II) complexes (**C1**–**C7**). All organic and palladium compounds were characterized by FT-IR and NMR spectroscopy, as well as by elemental analysis. The molecular structures of the complexes **C4**, **C5** and **C7** were determined by single crystal X-ray diffraction studies and revealed distorted square geometries at each palladium center via the coordination of two nitrogen atoms and two chlorides. All palladium complexes exhibited good activity in the Heck cross-coupling reaction between bromoarenes and styrene, and the catalytic systems possessed high thermal stability.

1. Introduction

The Heck reaction has remained an effective methodology in carbon–carbon bond formation over the past four decades [1], as highlighted by the numerous review articles and book chapters [2–6]. Indeed, such coupling reactions have been widely used to synthesize fine chemicals, drug intermediates, natural products, bioactive compounds, UV absorbers, antioxidants by the chemical industry. [7–11] This wide application is made possible because the Heck reaction is commonly used under mild conditions and can tolerate various functional groups [12,13]. In regard to the palladium complexes used for carbon-coupling reactions, the electronic and steric influence of the substituents is more significant in the Heck reaction [14–16] than for the Sonogashira–Hagihara [17,18], or Suzuki–Miyaura [19–22] reactions. Recently, attempts have been made to employ non-phosphine ligands by using various nitrogen-based heterocyclic compounds [23–25], and a number of palladium complexes have been prepared using bi-dentate *N*,*N*-ligands such as diimine [26], dipyridine [27–32] and hydrazone [33] derivatives. However, despite the successful deployment of iminopyridylpalladium complex pre-catalysts for olefin polymerization [34–37] as well as their biological interest [38], such palladium complexes have not been well explored for the Heck reaction [39,40]. With this in mind, a new series of heterocyclic compounds has been used as ligands in palladium complexes, which were then screened in the Heck reaction. In particular, 2-(1-aryliminoethyl)cycloheptapyridine derivatives (**L1**–**L7**) and their palladium(II) complexes (**C1**–**C7**) have been synthesized herein and fully characterized. The trial of these palladium complexes in ethylene polymerization revealed low activity, fortunately though high activities have been observed for these palladium complexes in the Heck cross-coupling reaction of aryl halides with olefins. Herein, the synthesis and characterization of 2-(1-aryliminoethyl)cycloheptapyridine derivatives (**L1**–**L7**) and their palladium(II) complexes (**C1**–**C7**) are reported and are discussed along with their use in the Heck cross-coupling reaction.

2. Results and discussion

2.1. Synthesis and characterization of the ligands and complexes

The synthesis of 2-acetylcycloheptapyridine was achieved in high yield using the Stille coupling reaction [41] of 2-chlorocycloheptapyridine with tributyl(1-ethoxyvinyl)tin (Scheme 1). Further condensation reactions of 2-acetyl-cycloheptapyridine with various anilines in toluene afforded the corresponding 2-(1-aryliminoethyl)cycloheptapyridine derivatives (**L1**–**L7**) in moderate to good isolated yield (57–80%). Further reaction of the 2-(1-aryliminoethyl) cycloheptapyridine derivatives (**L1**–**L7**) with $PdCl_2(CH_3CN)_2$ in dichloromethane afforded the title complexes, 2-(1-aryliminoethyl)cycloheptapyridylpalladium complexes (**C1**–**C7**, Scheme 1). All

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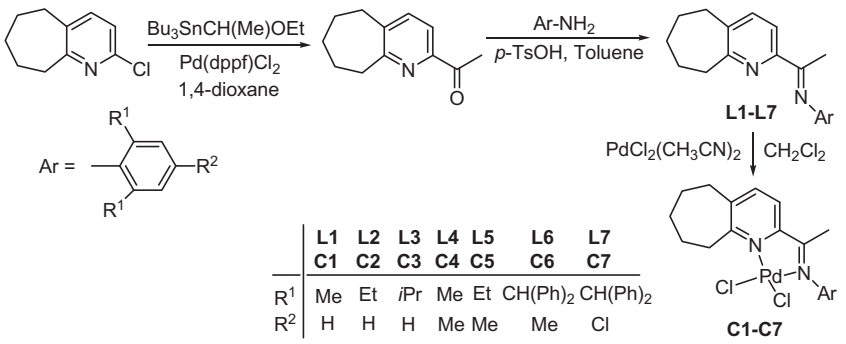


Scheme 1. Synthetic procedure.

the organic compounds and complexes were fully characterized by FT-IR and NMR spectroscopic measurements and by elemental analysis. According to their FT-IR spectra, the *v*C=N stretching frequencies have been shifted to higher field at about 1580 cm^{-1} and with a slightly weaker intensity for the coordinated palladium complexes in the comparison to 1641–1645 cm^{-1} for the corresponding organic compounds, consistent with previous observations for related palladium species [42]. In the ^{13}C NMR measurements, the δ C=N groups in the palladium complexes are shifted to lower field, for example 178.0 ppm for **C2** versus 167.3 ppm for **L2**, indicating strong coordination between the N_{imino} and Pd centers [43]. Moreover, the molecular structures of the palladium complexes **C4**, **C5** and **C7** have been confirmed by single crystal X-ray diffraction studies.

2.2. Crystal and molecular structures

Single crystals of the complexes **C4**, **C5** and **C7** were individually obtained by slow diffusion of diethyl ether into their dichloromethane solutions at ambient temperature. All the palladium complexes **C4**, **C5** and **C7** revealed a distorted square planar geometry at palladium, with the metal coordinated by two nitrogen atoms of the chelating ligand and two chlorides. The molecular structures are shown in the Figs. 1–3, with selected bond lengths and angles tabulated in Table 1. According to the data in Table 1, all three palladium complexes showed similar square planar geometry around the palladium center. The phenyl planes linked on the imino-group are almost perpendicular to the coordination plane Pd1, N1 and N2 with slight differences of the dihedral angles at 82.63° in **C4**, 87.33° in **C5** and 86.86° in **C7**, respectively. However, the influence of the substituents could be significantly observed when considering their bulk. For example, assigning two coordination planes as one of Pd1, N1 and N2 atoms and the other as the Pd1, Cl1, and Cl2

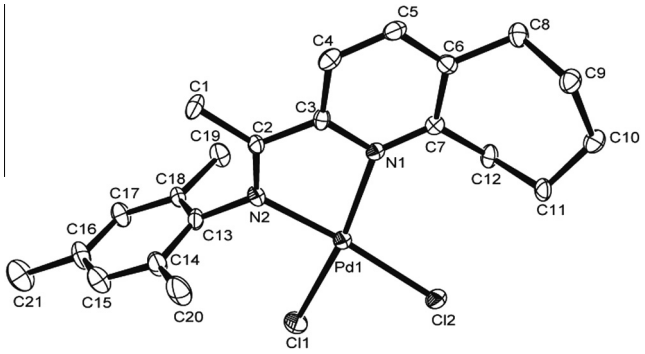


Fig. 1. ORTEP drawing of **C4**. Thermal ellipsoids are shown at the 30 % probability level. Hydrogen atoms have been omitted for clarity.

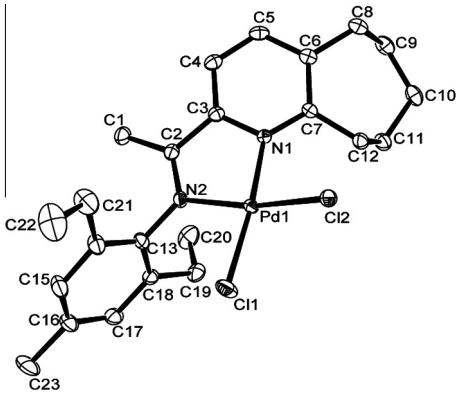


Fig. 2. ORTEP drawing of **C5**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.

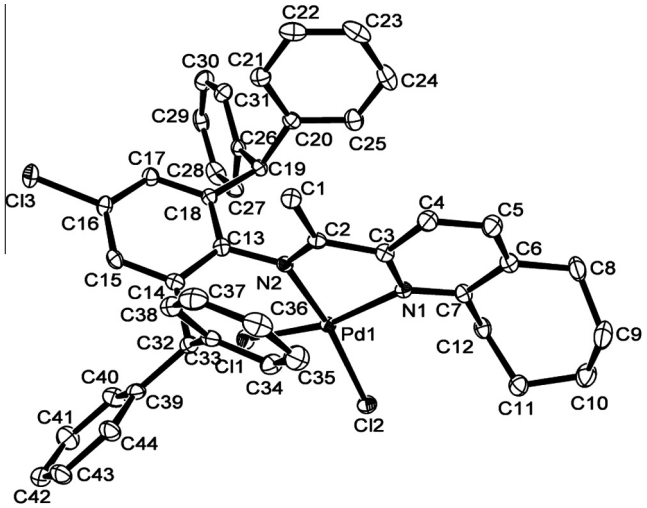


Fig. 3. ORTEP drawing of **C7**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.

atoms, their dihedral angles are 9.80° in **C4**, 12.94° in **C5** and 15.39° in **C7**, indicating the larger dihedral angle is caused by the space demands of the bulky substituents within the ligands used. The C=N double-bond character is revealed by the N2–C2 lengths at 1.290 Å in **C4**, 1.293 Å in **C5** and 1.292 Å in **C7**; the Pd–N_{imino} bond lengths are shorter than the Pd–$N_{pyridyl}$ bonds, as illustrated by the stronger Pd–N_{imino} (2.028(6) in **C4**, 2.032(3) in **C5** and 2.025(3) Å in **C7**) versus Pd–$N_{pyridyl}$ (2.118(6) in **C4**, 2.059(3) in **C5** and 2.108(2) Å in **C7**), respectively; *i.e.* weaker coordination occurred between the palladium with an sp^2-nitrogen within the

Table 1
Selected bond lengths (Å) and angles (°) for the complexes **C4**, **C5** and **C7**.

	C4	C5	C7
Bond lengths			
Pd(1)–N(1)	2.118(6)	2.059(3)	2.108(2)
Pd(1)–N(2)	2.028(6)	2.032(3)	2.025(3)
Pd(1)–Cl(1)	2.262(2)	2.2654(10)	2.2755(8)
Pd(1)–Cl(2)	2.307(2)	2.3065(9)	2.3044(8)
N(1)–C(3)	1.385(9)	1.370(4)	1.377(4)
N(1)–C(7)	1.321(9)	1.336(4)	1.350(4)
N(2)–C(2)	1.290(10)	1.293(4)	1.292(4)
N(2)–C(13)	1.444(10)	1.437(4)	1.443(4)
Bond angles			
N(1)–Pd(1)–N(2)	79.7(2)	79.77(11)	80.22(10)
N(1)–Pd(1)–Cl(1)	171.68(17)	173.64(8)	167.53(6)
N(1)–Pd(1)–Cl(2)	101.64(17)	96.81(8)	102.33(7)
N(2)–Pd (1)–Cl(1)	92.52(19)	93.93(9)	91.22(7)
N(2)–Pd(1)–Cl(2)	170.71(19)	166.69(8)	167.73(7)
Cl(1)–Pd(1)–Cl(2)	86.53(8)	89.51(4)	87.96(3)

conjugated aryl ring. The Pd–Cl lengths in the complexes **C4**, **C5** and **C7** exhibit typical bond lengths [43,44].

2.3. Catalytic behavior

Initially, complexes **C1**–**C7** were screened in ethylene polymerization, however results were poor and so the focus of our screening program switched to the Heck coupling reaction. Complex **C5** was used to optimize the reaction conditions for the typical Heck reaction of bromobenzene and styrene (affording 1,2-diphenylethene), including variation of solvent and base used. By employing a slight excess (1.2 equivalent) of styrene and 1.1 equivalent of base to bromobenzene in the presence of a catalytic amount ([Pd]/[bromobenzene] = 4×10^{-5}) of **C5** and different solvents, the conversion of bromobenzene was monitored and the results are tabulated in Table 2. Inspired by the literature [45], *N*,*N*-dimethylacetamide (DMA) appears to be the preferred solvent and was used to select a suitable base (entries 1–10, Table 2). Illustrated by the observations in entries 1 and 2 with the base sodium carbonate, the current system preferred elevated reaction temperatures; trace amounts of bromobenzene were converted over 24 h at 120 °C (entry 1), while 71% of bromobenzene was converted over 24 h at 150 °C (entry 2). On varying the base (entries 2–10), the catalytic system with $NaHCO_3$ was found to exhibit 92% bromobenzene conversion (entry 10). On optimizing the influence of solvent (entries 10–17), *N*,*N*-dimethylformamide (DMF) was found to be the best choice (entry 14). It is necessary to conduct the reaction over 24 h (entry 10) due to the relatively low conversion rates (entry 18). Moreover, it proved possible to reduce the amount of the palladium catalyst used (entry 19) by about a half, whilst still maintaining high efficiency (entry 14).

Under the optimized conditions, 1.2 equivalents of styrene and 1.1 equivalents of $NaHCO_3$ to bromobenzene with the [Pd]/[bromobenzene] at 2×10^{-5} at 150 °C for 24 h in DMF, all palladium complexes were explored for the Heck coupling reaction (Table 3). In general, similar activities were observed, however, slight differences were revealed such that there was a trend for bulky substituents to cause lower activities for their palladium catalysts: Me (for **C1**) > Et (for **C2**) > *i*-Pr (for **C3**) (entries 1–3). With an additional methyl group present for the ligands in **C4** and **C5**, better catalytic activities were achieved because of higher solubility (entries 4 and 5). However, the complexes **C6** and **C7** bearing ligands with bulky benzhydryl-substituents also showed high activities, for which the slight difference is attributed to the *para*-substituted methyl (entry 6) or chloride (entry7).

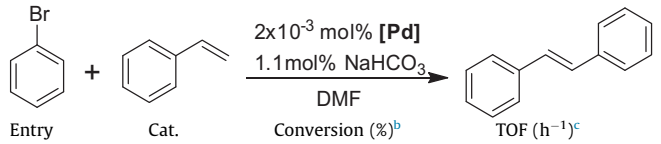
The Heck reaction with various aryl halides was explored using the complex **C5**, and results are summarized in Table 4; indicating the possibility for all bromoarenes. It appeared that electron withdrawing *para*-substituents on the bromoarenes enhanced the

Table 2
Optimization of bromobenzene and styrene using complex **C5**.[a]

Entry	Base	Solvent	Temp (°C)	Time (h)	Conversion (%)[b]	TOF (h^{-1})[c]
1	Na_2CO_3	DMA	120	24	trace	–
2	Na_2CO_3	DMA	150	24	71	740
3	K_2CO_3	DMA	150	24	73	760
4	NaOAc	DMA	150	24	55	570
5	NaOH	DMA	150	24	65	670
6	Et_3N	DMA	150	24	trace	–
7	Na_3PO_4	DMA	150	24	trace	–
8	NaF	DMA	150	24	trace	–
9	CaF_2	DMA	150	24	trace	–
10	$NaHCO_3$	DMA	150	24	92	960
11	$NaHCO_3$	toluene	110	24	trace	–
12	$NaHCO_3$	1,4-dioxane	100	24	trace	–
13	$NaHCO_3$	DMA/H_2O[d]	150	24	78	810
14	$NaHCO_3$	DMF	150	24	99	1030
15	$NaHCO_3$	DMF/H_2O[d]	150	24	93	970
16	$NaHCO_3$	CH_3CN	80	24	trace	–
17	$NaHCO_3$	THF	60	24	trace	–
18	$NaHCO_3$	DMF	150	12	77	1600
19[e]	$NaHCO_3$	DMF	150	24	97	2020

[a] Reaction conditions: 2.0 mmol bromobenzene, 2.4 mmol styrene, 2.2 mmol base, 8×10^{-8} mol **C5**, 4.0 mL solvent.
[b] Determined by GC.
[c] TOF: mol bromobenzene/mol Pd h.
[d] Mixture of proportion (10:1).
[e] 4×10^{-8} mol **C5** was used.

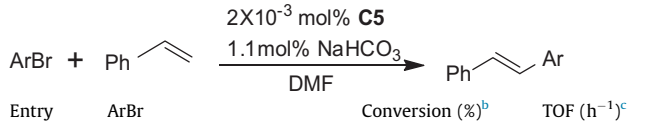
Table 3
Heck reaction of bromobenzene and styrene by **C1**–**C7**.[a]

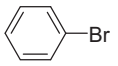
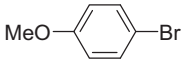
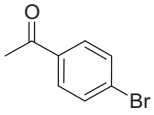
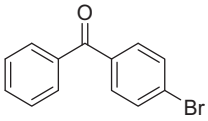
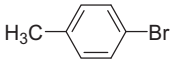
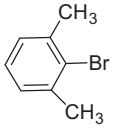
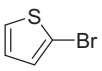


Entry	Cat.	Conversion (%)[b]	TOF (h^{-1})[c]
1	C1	92	1920
2	C2	89	1850
3	C3	87	1810
4	C4	95	1980
5	C5	97	2020
6	C6	97	2020
7	C7	95	1980

[a] Reaction conditions: 2.0 mmol bromobenzene, 2.4 mmol styrene, 2.2 mmol $NaHCO_3$, 4.0 mL DMF, 150 °C, 24 h.
[b] Determined by GC.
[c] TOF: mol bromobenzene/mol Pd h.

Table 4
Heck reaction of aryl bromides and styrene using complex **C5**.[a]



Entry	ArBr	Conversion (%)[b]	TOF (h^{-1})[c]
1		97	2020
2		97	2020
3		99	2060
4		88	1830
5		92	1920
6		33	690
7		54	1120

[a] Reaction conditions: 2.0 mmol ArBr, 2.4 mmol styrene, 2.2 mmol Na_2CO_3, 4.0 mL DMF 150 °C, 24 h.
[b] Determined by GC.
[c] TOF: mol ArBr/mol Pd h.

coupling reactions (entries 1–3); meanwhile methyl-substituents on the bromoarenes deactivated the reaction (entries 1, 5, and 6); *ortho*-methyl substituents exhibited a negative effect due to sterics, which is consistent to previous literature results [46]. A lower activity was observed for 2-bromothiophene (entries 7), and trace conversion of 2-bromobenzenamine and 4-bromoaniline were achieved; this is tentatively attributed to the potential coordination of their functional groups (amine and sulfur atom) to the palladium species. All products were isolated and their identity confirmed by ^1H and ^{13}C NMR spectroscopy by comparison with literature data [47–49].

3. Conclusions

The newly designed 2-acetylcycloheptapyridine was effectively synthesized by using the Stille coupling reaction of 2-chlorocycloheptapyridine and tributyl(1-ethoxyvinyl)tin. A series of 2-(1-aryliminoethyl)cycloheptapyridine derivatives were achievable through the condensation reactions between 2-acetylcycloheptapyridine and various aniline derivatives. The 2-(1-aryliminoethyl)cycloheptapyridine derivatives acted as bi-dentate ligands on coordination with $PdCl_2(CH_3CN)_2$. The dichloropalladium complexes revealed a distorted square geometry at palladium *via* coordination with two nitrogen atoms and two chlorides. All palladium complexes showed good catalytic activities for the Heck coupling between bromoarenes and styrene, and the catalytic systems possessed high thermal stability.

4. Experimental

4.1. General procedure and materials

All manipulations of moisture-sensitive compounds were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Melting points were determined using a digital electrothermal apparatus without calibration. NMR spectra were recorded on a Bruker DMX 400 MHz instrument at ambient temperature using TMS as an internal standard; δ values are given in ppm and J values in Hz. The IR spectra were obtained on a Perkin Elmer FT-IR 2000 spectrophotometer by using the KBr disc in the range of 4000–400 cm^{-1}. Elemental analysis was carried out using a Flash EA 1112 microanalyzer. Conversions were determined by CP-3800 GC.

4.2. Syntheses and characterization

4.2.1. Synthesis of 2-acetyl-cycloheptapyridine

2-Chloro-cycloheptapyridine (0.1 mol, 18.1 g), tributyl(1-ethoxyvinyl)tin (0.11 mol, 40.0 g), $Pd(dppf)Cl_2$ (3 mmol, 2.22 g), and 250 mL of chlorobenzene were added into a 500 mL three-necked flask. The mixture was refluxed for 12 h under N_2, and then cooled to room temperature. The solution was washed with KF solution (0.3 M, 100 mL × 3) and 100 mL of 10% aqueous HCl. The resultant solution was neutralized by aqua ammonia and extracted with dichloromethane. The organic layer was collected and dried over anhydrous Na_2SO_4, and then concentrated *in vacuo* to afford the crude product. The residue was purified by silica gel chromatography to afford 2-acetyl-cycloheptapyridine (15.7 g, yield 83%) as a white solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 8.0 Hz, 1H, Py–*H*,) 7.46 (d, J = 7.6 Hz, 1H, Py–*H*), 3.08 (t, J = 5.6 Hz, 2H, CH_2), 2.81 (t, J = 4.0 Hz, 2H, CH_2), 2.68 (s, 3H, CH_3), 1.86–1.90 (m, 2H, CH_2), 1.66–1.71 (m, 4H, 2 × CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.6, 162. 8, 150.8, 142.5, 137.0, 119.6, 39.5, 35.5, 32.5, 27.8, 26.6, 25.8.

4.2.2. Synthesis of 2-(1-(2,6-dimethylphenylimino)ethyl)cycloheptapyridine (*L1*)

2,6-Dimethylaniline (0.24 g, 2.0 mmol) was added to a solution of 2-acetyl-cycloheptapyridine (0.19 g, 1.0 mmol) with a catalytic amount of *p*-toluenesulfonic acid (0.02 g, 0.1 mmol) in 30 mL of toluene. The mixture was stirred at reflux temperature for 6 h. The solvent was evaporated under reduced pressure, and the residue was subsequently purified by silica gel chromatography to afford the light yellow solid (0.21 g, 72%). Mp: 82–83 °C. FT-IR (KBr, cm^{-1}): 2921 (s), 2850 (m), 2361 (s), 2336 (w), 1643 (s), 1569 (m), 1463 (w), 1437 (s), 1358 (m), 1304 (w), 1254 (w), 1191 (m), 1161 (w), 1116 (s), 1085 (m), 1035 (w), 955 (m), 853 (w), 810 (w), 754

Table 5
Crystal data and structure refinements for **C4**, **C5** and **C7**.

	C4	C5	C7
Empirical formula	$C_{21}H_{26}Cl_2N_2Pd$	$C_{23}H_{30}Cl_2N_2Pd$	$C_{44}H_{39}Cl_3N_2Pd$
Crystal color	brown	brown	brown
Formula weight	483.74	511.79	808.52
T (K)	173 (2)	173 (2)	173 (2)
λ (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2(1)/n$	$P2(1)/c$	$P2(1)2(1)2(1)$
a (Å)	18.573(4)	9.3545(19)	11.965(2)
b (Å)	11.581(2)	7.9698(16)	17.221(3)
c (Å)	20.647(4)	30.667(6)	17.751(4)
α (°)	90	90	90
β (°)	110.77(3)	97.00(3)	90
γ (°)	90	90	90
V (Å^3)	4152.4(14)	2269.3(8)	3657.4(13)
Z	8	4	4
D_{calc} (mg m^{-3})	1.548	1.498	1.468
μ (mm^{-1})	1.158	1.064	0.762
F(000)	1968	1048	1656
Cryst size (mm)	0.26 × 0.19 × 0.07	0.44 × 0.40 × 0.20	0.39 × 0.31 × 0.16
θ (°)	1.27–27.48	2.68–27.48	2.63–27.50
Limiting indices	$-21 \leqslant h \leqslant 24$, $-15 \leqslant k \leqslant 15$, $-26 \leqslant l \leqslant 18$	$-11 \leqslant h \leqslant 12$, $-10 \leqslant k \leqslant 10$, $-39 \leqslant l \leqslant 39$	$-15 \leqslant h \leqslant 12$, $-13 \leqslant k \leqslant 22$, $-23 \leqslant l \leqslant 15$
No. of reflections collected	29370	15021	13153
No. unique reflections (R_{int})	9467 (0.0653)	5113 (0.0371)	8167 (0.0295)
Completeness to θ (%)	99.5	98.3	99.0
Abs corr	none	none	none
Data/restraints/params	9467/0/469	5113/0/253	8167/0/451
Goodness of fit (GOF) on F^2	1.074	0.954	1.073
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0715$, $wR_2 = 0.1775$	$R_1 = 0.0426$, $wR_2 = 0.1360$	$R_1 = 0.0362$, $wR_2 = 0.0844$
R indices (all data)	$R_1 = 0.0901$, $wR_2 = 0.2205$	$R_1 = 0.0473$, $wR_2 = 0.1455$	$R_1 = 0.0377$, $wR_2 = 0.0856$
Largest difference in peak and hole (e Å^{-3})	1.112 and −1.059	1.063 and −0.706	0.774 and −0.717

(s), 712 (w), 686 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J = 8.0 Hz, 1H, Py–*H*), 7.47 (d, J = 7.6 Hz, 1H, Py–*H*), 7.05 (d, J = 7.6 Hz, 2*H*, 2 × Ar–*H*), 6.90 (t, J = 7.6 Hz, 1H, Ar–*H*), 3.10 (t, J = 5.6 Hz, 2H, C*H*$_2$), 2.84 (t, J = 5.6 Hz, 2H, C*H*$_2$), 2.16 (s, 3H, C*H*$_3$), 2.03 (s, 6H, 2 × C*H*$_3$), 1.92–1.88 (m, 2H, C*H*$_2$), 1.75–1.70 (m, 4H, 2 × C*H*$_2$). ^{13}C NMR (100 MHz; $CDCl_3$): δ 167.6, 162.2, 153.3, 149.1, 139.7, 137.1, 136.9, 128.0, 127.8, 125.6, 118.8, 39.7, 35.3, 32.7, 28.0, 26.7, 18.0, 16.7. *Anal.* Calc. for $C_{20}H_{24}N_2$ (292): C, 82.15; H, 8.27; N, 9.58. Found: C, 82.20; H, 8.36; N, 9.52%.

4.2.3. Synthesis of 2-(1-(2,6-diethylphenylimino)ethyl)cycloheptapyridine (*L2*)

Using the same procedure as for the synthesis of **L1**, **L2** was obtained as a light yellow oil (0.24 g, 75%). FT-IR (KBr, cm^{-1}): 2964 (w), 2925 (s), 2851 (s), 1644 (s), 1589 (w), 1569 (m), 1458 (s), 1400 (w), 1363 (s), 1306 (m), 1280 (w), 1255 (w), 1192 (s), 1160 (w), 1118 (s), 1074 (w), 958 (m), 869 (w), 851 (w), 823 (w), 803 (w), 767 (s), 695 (s), 664 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 7.6 Hz, 1H, Py–*H*), 7.50 (d, J = 8.0 Hz, 1H, Py–*H*), 7.14 (d, J = 7.6 Hz, 2H, 2 × Ar–*H*), 7.05 (t, J = 7.6 Hz, 1H, Ar–*H*), 3.15 (t, J = 4.2 Hz, 2H, C*H*$_2$), 2.86 (t, J = 4.0 Hz, 2H, C*H*$_2$), 2.52–2.44 (m, 4H, 2 × C*H*$_2$), 2.24 (s, 3H, C*H*$_3$), 1.95–1.91 (m, 2H, C*H*$_2$), 1.79–1.74 (m, 4H, 2 × C*H*$_2$), 1.18 (t, J = 7.4 Hz, 6H, 2 × C*H*$_3$). ^{13}C NMR (100 MHz; $CDCl_3$): δ 167.3, 162.2, 153.3, 148.2, 139.7, 137.1, 137.0, 131.4, 125.9, 123.2, 118.8, 39.7, 35.4, 32.7, 28.0, 26.7, 24.7, 17.1, 13.8, 13.7. *Anal.* Calc. for $C_{22}H_{28}N_2$ (320): C, 82.45; H, 8.81; N, 8.74. Found: C, 82.50; H, 8.75; N, 8.56%.

4.2.4. Synthesis of 2-(1-(2,6-diisopropylphenylimino)ethyl)cycloheptapyridine (*L3*)

Using the same procedure as for the synthesis of **L1**, **L3** was obtained as a light yellow solid (0.28 g, 80%). Mp: 108–109 °C. FT-IR (KBr, cm^{-1}): 2956 (w), 2924 (s), 2855 (w), 2361 (s), 2336 (w), 1645 (s), 1570 (m), 1460 (s), 1436 (s), 1381 (w), 1363 (w), 1324 (w), 1309 (m), 1280 (w), 1242 (w), 1190 (s), 1160 (w), 1120 (s), 1077 (w), 956 (w), 931 (w), 860 (w), 820 (m), 761 (s), 697 (m), 669 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 8.0 Hz, 1H, Py–*H*,) 7.49 (d, J = 7.6 Hz, 1H, Py–*H*), 7.16 (d, J = 0.8 Hz, 2H, 2 × Ar–*H*), 7.07 (t, J = 8.4 Hz, 1H, Ar–*H*), 3.11 (t, J = 5.6 Hz, 2H, C*H*$_2$), 2.85 (t, J = 3.6 Hz, 2H, C*H*$_2$), 2.78–2.73 (m, 2H, 2 × C*H*), 2.20 (s, 3H, C*H*$_3$), 1.92–1.89 (m, 2H, C*H*$_2$), 1.78–1.70 (m, 4H, 2 × C*H*$_2$), 1.15 (d, J = 7.6 Hz, 12H, 4 × C*H*$_3$). ^{13}C NMR (100 MHz; $CDCl_3$): δ 167.3, 162.2, 153.3, 146.9, 139.6, 137.1, 136.0, 123.4, 123.0, 118.8, 39.7, 35.4, 32.7, 28.3, 28.0, 26.7, 23.4, 23.1, 17.4. *Anal.* Calc. for $C_{24}H_{32}N_2$ (348): C, 82.71; H, 9.25; N, 8.04. Found: C, 82.64; H, 9.25; N, 8.01%.

4.2.5. Synthesis of 2-(1-(2,4,6-trimethylphenylimino)ethyl)cycloheptapyridine (*L4*)

Using the same procedure as for the synthesis of **L1**, **L4** was obtained as a light yellow solid (0.22 g, 72%). Mp: 92–93 °C. FT-IR (KBr, cm^{-1}): 2925 (s), 2851 (w), 2361 (s), 2335 (w), 1642 (s), 1571 (m), 1478 (w), 1441 (s), 1403 (w), 1359 (s), 1306 (w), 1278 (w), 1216 (s), 1191 (m), 1146 (w), 1119 (s), 1074 (w), 1033 (w), 1011 (w), 957 (m), 930 (w), 852 (s), 827 (w), 787 (m), 712 (w), 687 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 8.0 Hz, 1H, Py–*H*,) 7.47 (d, J = 8.0 Hz, 1H, Py–*H*), 6.87 (s, 2H, 2 × Ar–*H*), 3.10 (t, J = 4.0 Hz, 2H, C*H*$_2$), 2.83 (t, J = 4.0 Hz, 2H, C*H*$_2$), 2.28 (s, 3H, C*H*$_3$), 2.16 (s, 3H, C*H*$_3$), 1.99 (s, 6H, 2 × C*H*$_3$), 1.92–1.88 (m, 2H, C*H*$_2$), 1.76–1.69 (m, 4H, 2 × C*H*$_2$). ^{13}C NMR (100 MHz; $CDCl_3$): δ 167.9, 162.2, 153.4, 146.6, 139.6, 137.1, 136.9, 131.9, 128.6, 125.5, 118.8, 39.7, 35.4, 32.7, 28.0, 26.7, 20.8, 18.0, 16.7. *Anal.* Calc. for $C_{21}H_{26}N_2$ (306): C, 82.31; H, 8.55; N, 9.14. Found: C, 82.00; H, 8.52; N, 9.26%.

4.2.6. Synthesis of 2-(1-(2,6-diethyl-4-methylphenylimino)ethyl)cycloheptapyridine (*L5*)

Using the same procedure as for the synthesis of **L1**, **L5** was obtained as a light yellow solid (0.26 g, 78%). Mp: 78–79 °C. FT-IR (KBr, cm^{-1}): 2967 (w), 2923 (s), 2852 (w), 2361 (s), 2336 (w),

1641 (s), 1570 (m), 1461 (s), 1441 (s), 1359 (s), 1306 (w), 1209 (w), 1191 (m), 1146 (w), 1119 (s), 1075 (m), 955 (m), 885 (w), 858 (s), 825 (w), 805 (w), 783 (w), 692 (w), 669 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 8.0 Hz, 1H, Py–*H*), 7.47 (d, J = 8.0 Hz, 1H, Py–*H*), 6.91 (s, 2H, 2 × Ar–*H*), 3.10 (t, J = 5.6 Hz, 2H, C*H*$_2$), 2.83 (t, J = 4.0 Hz, 2H, C*H*$_2$), 2.38–2.28 (m, 4H, 2 × C*H*$_2$), 2.34 (s, 3H, C*H*$_3$), 2.17 (s, 3H, C*H*$_3$), 1.93–1.88 (m, 2H, C*H*$_2$), 1.76–1.70 (m, 4H, 2 × C*H*$_2$), 1.11 (t, J = 7.6 Hz, 6H, 2 × C*H*$_3$). ^{13}C NMR (100 MHz; $CDCl_3$): δ 167.5, 162.1, 153.4, 145.6, 137.1, 136.9, 132.2, 131.3, 126.7, 118.7, 39.7, 35.4, 32.7, 28.0, 24.6, 21.1, 17.0, 14.2, 13.9. *Anal.* Calc. for $C_{23}H_{30}N_2$ (334): C, 82.59; H, 9.04; N, 8.37. Found: C, 83.07; H, 8.96; N, 8.16%.

4.2.7. Synthesis of 2-(1-(2,6-dibenzhydryl-4-methylphenylimino)ethyl)cycloheptapyridine (*L6*)

Using the same procedure as for the synthesis of **L1**, **L6** was obtained as a light yellow solid (0.35 g, 57%). Mp: 210–211 °C. FT-IR (KBr, cm^{-1}): 2919 (s), 2849 (w), 1641 (s), 1600 (w), 1571 (m), 1493 (m), 1445 (s), 1361 (w), 1309 (w), 1240 (m), 1213 (w), 1193 (w), 1121 (m), 1075 (w), 1029 (w), 853 (w), 827 (w), 770 (s), 746 (m), 697 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.0 Hz, 1H, Py–*H*), 7.43 (d, J = 7.6 Hz, 1H, Py–*H*), 7.36–6.92 (m, 20H, 20 × Ar–*H*), 6.78 (s, 2H, 2 × Ar–*H*), 5.40 (s, 2H, 2 × C*H*), 3.11 (t, J = 4.8 Hz, 2H, C*H*$_2$), 2.87 (t, J = 4.8 Hz, 2H, C*H*$_2$), 2.24 (s, 3H, C*H*$_3$), 1.98–1.94 (m, 2H, C*H*$_2$), 1.78–1.72 (m, 4H, 2 × C*H*$_2$), 1.22 (s, 3H, C*H*$_3$). ^{13}C NMR (100 MHz; $CDCl_3$): δ 162.0, 153.2, 146.6, 144.0, 143.0, 139.3, 136.7, 132.5, 131.4 130.1, 129.7, 128.7, 128.4, 128.1, 126.2, 126.1, 118.9, 52.1, 39.7, 35.4, 32.7, 28.1, 26.8, 21.5, 17.3. *Anal.* Calc. for $C_{45}H_{42}N_2$ (610): C, 88.48; H, 6.93; N, 4.59. Found: C, 88.47; H, 7.07; N, 4.38%.

4.2.8. Synthesis of 2-(1-(2,6-dibenzhydryl-4-chlorophenylimino)ethyl)cycloheptapyridine (*L7*)

Using the same procedure as for the synthesis of **L1**, **L7** was obtained as a light yellow solid (0.40 g, 63%). Mp: 212–213 °C. FT-IR (KBr, cm^{-1}): 2921 (s), 2848 (w), 1642 (s), 1570 (m), 1493 (m), 1441 (s), 1365 (w), 1309 (w), 1260 (m), 1182 (s), 1121 (m), 1075 (m), 1027 (s), 955 (w), 926 (w), 889 (w), 862 (w), 792 (w), 770 (w), 743 (w), 696 (s), 659 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J = 8.0 Hz, 1H, Py–*H*), 7.36 (d, J = 8.0 Hz, 1H, Py–*H*), 7.25–6.98 (m, 20H, 20 × Ar–*H*), 6.83 (s, 2H, 2 × Ar–*H*), 5.26 (s, 2H, 2 × C*H*), 3.02 (t, J = 5.4 Hz, 2H, C*H*$_2$), 2.81 (t, J = 5.2 Hz, 2H, C*H*$_2$), 1.91–1.87 (m, 2H, C*H*$_2$), 1.72–1.67 (m, 4H, 2 × C*H*$_2$), 1.08 (s, 3H, C*H*$_3$). ^{13}C NMR (100 MHz; $CDCl_3$): δ170.7, 162.1, 152.7, 147.5, 143.0, 142.0, 139.6, 136.7, 134.7, 129.9, 129.5, 128.5, 128.3, 128.0, 127.8, 126.5, 126.4, 118.9, 52.0, 39.6, 35.4, 32.7, 28.0, 26.7, 17.3. *Anal.* Calc. for $C_{44}H_{39}ClN_2$ (631): C, 83.54; H, 6.20; N, 4.53. Found: C, 83.08; H, 6.34; N, 4.33%.

4.2.9. Synthesis of 2-(1-(2,6-dimethylphenylimino)ethyl)cycloheptapyridyl palladium(II) chloride (*C1*)

The ligand **L1** (0.14 g, 0.48 mmol) and $PdCl_2(CH_3CN)_2$ (0.10 g, 0.40 mmol) were dissolved in 8 mL dichloromethane. The reaction mixture was stirred for 20 h. The reaction volume was reduced to about 1 mL by removing the solvent *in vacuo*, and then 15 mL ether was poured into the mixture to precipitate the complex. After stirring for 1 h, the yellow precipitate was collected by filtration, washed with diethyl ether (3 × 10 mL), and dried at room temperature to afford the yellow solid (0.16 g, 85%). FT-IR (KBr, cm^{-1}): 2919 (s), 2855 (w), 1609 (s), 1581 (s), 1466 (m), 1442 (m), 1402 (s), 1373 (w), 1334 (s), 1317 (w), 1288 (w), 1243 (w), 1207 (s), 1160 (w), 1095 (m), 1034 (w), 849 (m), 828 (s), 795 (s), 731 (m), 661 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 7.6 Hz, 1H, Py–*H*), 7.60 (d, J = 7.6 Hz, 1H, Py–*H*), 7.16 (t, J = 4.2 Hz, 1H, Ar–*H*), 7.09 (d, J = 7.2 Hz, 2H, 2 × Ar–*H*), 3.78 (t, J = 5.6 Hz, 2H, C*H*$_2$), 2.95 (t, J = 5.4 Hz, 2H, C*H*$_2$), 2.32(s, 6H, 2 × C*H*$_3$), 2.14 (s, 3H, C*H*$_3$), 1.90–1.85 (m, 4H, 2 × C*H*$_2$), 1.77–1.74 (m, 2H, C*H*$_2$). ^{13}C NMR (100 MHz; CD_2Cl_2): δ 178.8, 171.5, 153.5, 147.2, 143.9, 139.8, 130.3, 128.0, 127.5, 125.2, 40.4, 36.1, 31.7, 27.9, 27.6, 18.4, 18.4. *Anal.* Calc. for $C_{20}H_{24}Cl_2N_2Pd$ (469): C, 51.14; H, 5.15; N, 5.96. Found: C, 51.12; H, 5.21; N, 6.14%.

4.2.10. Synthesis of 2-(1-(2,6-diethylphenylimino)ethyl)cycloheptapyridyl palladium(II) chloride (*C2*)

Using the above procedure for **C1**, **C2** was isolated as a yellow solid in 84% yield. FT-IR (KBr, cm^{-1}): 2922 (s), 2855 (w), 1610 (w), 1585 (s), 1437 (s), 1405 (m), 1369 (m), 1329 (m), 1289 (m), 1245 (m), 1201 (s), 1142 (w), 1097 (w), 1065 (w), 952 (m), 842 (w), 810 (s), 777 (s), 730 (w), 661 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 7.2 Hz, 1H, Py–*H*), 7.71 (d, J = 7.6 Hz, 1H, Py–*H*), 7.28 (t, J = 7.6 Hz, 1H, Ar–*H*), 7.15 (d, J = 7.2 Hz, 2H, 2 × Ar–*H*), 3.76 (t, J = 4.2 Hz, 2H, C*H*$_2$), 2.95 (t, J = 4.0 Hz, 2H, C*H*$_2$), 2.90–2.83 (m, 2H, C*H*$_2$), 2.50–2.44 (m, 2H, C*H*$_2$), 2.14 (s, 3H, C*H*$_3$), 1.90–1.85 (m, 4H, 2 × C*H*$_2$), 1.77–1.73 (m, 2H, C*H*$_2$), 1.29 (t, J = 7.4 Hz, 6H, 2 × C*H*$_3$). ^{13}C NMR (100 MHz; $CDCl_3$): δ 178.0, 171.7, 153.3, 146.9, 142.6, 139.5, 135.1, 127.9, 125.4, 124.6, 40.5, 36.1, 31.6, 27.6, 27.5, 24.3, 18.8, 13.2. *Anal.* Calc. for $C_{22}H_{28}Cl_2N_2Pd$ (497): C, 53.08; H, 5.67; N, 5.63. Found: C, 52.98; H, 5.77; N, 5.49%.

4.2.11. Synthesis of 2-(1-(2,6-diisopropylphenylimino)ethyl)cycloheptapyridyl palladium(II) chloride (*C3*)

Using the procedure for **C1**, **C3** was isolated as a yellow solid in 82% yield. FT-IR (KBr, cm^{-1}): 2957 (w), 2921 (s), 2861 (w), 1609 (w), 1584 (s), 1440 (s), 1404 (m), 1363 (m), 1321 (m), 1292 (w), 1249 (w), 1198 (w), 1180 (w), 1098 (w), 1057 (w), 957 (m), 830 (w), 800 (s), 773 (s), 726 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 8.0 Hz, 1H, Py–*H*,), 7.60 (d, J = 8.0 Hz, 1H, Py–*H*), 7.32 (t, J = 7.8 Hz, 1H, Ar–*H*), 7.19 (d, J = 8.0 Hz, 2H, 2 × Ar–*H*), 3.78 (t, 2H, C*H*$_2$), 3.20–3.13 (m, 2H, 2 × C*H*), 2.96 (t, J = 5.4 Hz, 2H, C*H*$_2$) 2.16 (s, 3H, C*H*$_3$), 1.91–1.87 (m, 4H, 2 × C*H*$_2$), 1.78–1.75 (m, 2H, C*H*$_2$), 1.44 (d, J = 6.8 Hz, 6H, 2 × C*H*$_3$), 1.11 (d, J = 7.2 Hz, 6H, 2 × C*H*$_3$). ^{13}C NMR (100 MHz; CD_2Cl_2): δ 178.7, 171.7, 153.5, 147.4, 141.2, 140.5, 139.5, 128.3, 124.9, 123.7, 40.2, 36.2, 31.7, 28.9, 27.9, 27.6, 23.7, 23.6, 19.8. *Anal.* Calc. for $C_{24}H_{32}Cl_2N_2Pd$ (525): C, 54.82; H, 6.13; N, 5.33. Found: C, 54.52; H, 5.99; N, 5.05%.

4.2.12. Synthesis of 2-(1-(2,4,6-trimethylphenylimino)ethyl)cycloheptapyridyl palladium(II) chloride (*C4*)

Using the procedure for **C1**, **C4** was isolated as a yellow solid in 85% yield. FT-IR (KBr, cm^{-1}): 2910 (s), 2850 (w), 1609 (w), 1584 (s), 1437 (s), 1403 (m), 1372 (w), 1323 (m), 1292 (m), 1247 (w), 1213 (w), 1122 (w), 1096 (w), 1031 (w), 957 (s), 856 (s), 838 (s), 732 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 5.4 Hz, 1H, Py–*H*,), 7.56 (d, J = 5.4 Hz, 1H, Py–*H*), 6.95 (s, 2H, 2 × Ar–*H*), 3.10 (t, J = 4.0 Hz, 2H, C*H*$_2$), 2.83 (t, J = 4.0 Hz, 2H, C*H*$_2$), 2.28 (s, 3H, C*H*$_3$), 2.16 (s, 3H, C*H*$_3$), 1.99 (s, 6H, 2 × C*H*$_3$), 1.92–1.87 (m, 2H, C*H*$_2$), 1.74–1.70 (m, 4H, 2 × C*H*$_2$). ^{13}C NMR (100 MHz; CD_2Cl_2): δ 179.1, 171.9, 154.0, 147.5, 142.0, 140.0, 137.8, 130.4, 129.1, 125.3, 40.8, 36.5, 32.1, 28.3, 28.0, 21.3, 18.7, 18.7. *Anal.* Calc. for $C_{21}H_{26}Cl_2N_2Pd$ (483): C, 52.14; H, 5.42; N, 5.79. Found: C, 52.07; H, 5.37; N, 5.48%.

4.2.13. Synthesis of 2-(1-(2,6-diethyl-4-methylphenylimino)ethyl)cycloheptapyridyl palladium(II) chloride (*C5*)

Using the procedure for **C1**, **C5** was isolated as a yellow solid in 84% yield. FT-IR (KBr, cm^{-1}): 2963 (w), 2913 (s), 2852 (m), 1606 (w), 1579 (s), 1456 (s), 1404 (s), 1371 (m), 1326 (m), 1291 (m), 1246 (w), 1198 (s), 1097 (w), 1065 (w), 1000 (w), 955 (s), 856

(s), 832 (s), 736 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 7.6 Hz, 1H, Py–*H*,) 7.57 (d, J = 8.0 Hz, 1H, Py–*H*), 6.94 (s, 2H, 2 × Ar–*H*), 3.77 (t, J = 5.6 Hz, 2H, CH_2), 2.95 (t, J = 4.0 Hz, 2H, CH_2), 2.86–2.80 (m, 2H, CH_2), 2.46–2.41 (m, 2H, CH_2), 2.32 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 1.88–1.83 (m, 4H, 2 × CH_2), 1.77–1.74 (m, 2H, CH_2), 1.26 (t, J = 7.6 Hz, 6H, 2 × CH_3). ^{13}C NMR (100 MHz; $CDCl_3$): δ 178.7, 171.3, 153.3, 146.7, 140.3, 139.8, 137.3, 134.9, 126.1, 125.1, 40.4, 36.1, 31.6, 27.6, 27.4, 24.2, 21.5, 18.9, 13.3. *Anal.* Calc. for $C_{23}H_{30}Cl_2N_2Pd$ (511): C, 53.97; H, 5.91; N, 5.47. Found: C, 53.78; H, 5.66; N, 5.19%.

4.2.14. Synthesis of 2-(1-(2,6-dibenzhydryl-4-methylphenylimino)ethyl)cyclohepta-pyridylpalladium(II) chloride (**C6**)

By using the procedure for **C1**, **C6** was isolated as a yellow solid in 90% yield. FT-IR (KBr, cm^{-1}): 3024 (w), 2918 (s), 2852 (w), 1602 (w), 1578 (m), 1494 (m), 1445 (s), 1405 (m), 1327 (m), 1293 (w), 1249 (w), 1190 (m), 1077 (w), 1030 (w), 749 (m), 699 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, J = 7.6 Hz, 1H, Py–*H*), 7.34–7.05 (m, 20H, 20 × Ar–*H*), 6.87 (s, 2H, 2 × Ar–*H*), 6.61 (d, J = 7.6 Hz, 1H, Py–*H*), 6.23 (s, 2H, 2 × C*H*), 3.92 (t, J = 4.8 Hz, 2H, CH_2), 2.96 (t, J = 4.8 Hz, 2H, CH_2), 2.14 (s, 3H, CH_3), 1.91–1.87 (m, 4H, 2 × CH_2), 1.79–1.76 (m, 2H, CH_2), −0.21 (s, 3H, CH_3). ^{13}C NMR (100 MHz; CD_2Cl_2): δ 182.3, 171.4, 153.2, 147.1, 142.8, 140.8, 140.7, 139.2, 137.1, 130.2, 129.6, 128.9, 128.6, 128.0, 126.7, 126.3, 123.7, 52.3, 40.1, 36.0, 31.6, 27.8, 27.5, 21.3, 18.1. *Anal.* Calc. for $C_{45}H_{42}Cl_2N_2Pd$ (788): C, 68.58; H, 5.37; N, 3.55. Found: C, 68.20; H, 5.20; N, 3.50%.

4.2.15. Synthesis of 2-(1-(2,6-dibenzhydryl-4-chlorophenylimino)ethyl)cyclohepta pyridyl palladium(II) chloride (**C7**)

By using the procedure for **C1**, **C7** was isolated as a yellow solid in 89% yield. FT-IR (KBr, cm^{-1}): 3024(w), 2920 (s), 2853 (m), 1577 (s), 1494 (s), 1435 (s), 1407 (m), 1328 (w), 1294 (m), 1247 (w), 1193 (s), 1106 (w), 1077 (m), 744 (s), 698 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J = 7.0 Hz, 1H, Py–*H*), 7.32–7.08 (m, 20H, 20 × Ar–*H*), 6.87 (s, 2H, 2 × Ar–*H*), 6.62 (d, J = 8.0 Hz, 1H, Py–*H*), 6.24 (s, 2H, 2 × C*H*), 3.91 (t, J = 4.8 Hz, 2H, CH_2), 2.97 (t, J = 4.8 Hz, 2*H*, CH_2), 1.92–1.88 (m, 4H, 2 × CH_2), 1.79–1.76 (m, 2H, CH_2), −0.22 (s, 3H, CH_3). ^{13}C NMR (100 MHz; CD_2Cl_2): δ 171.8, 153.0, 147.6, 142.0, 141.7, 140.0, 139.6, 139.4, 133.1, 130.3, 129.6, 129.0, 129.0, 128.4, 127.2, 126.9, 124.1, 52.5, 40.2, 36.2, 31.7, 27.9, 27.6, 18.4. *Anal.* Calc. for $C_{44}H_{39}Cl_3N_2Pd$ (808): C, 65.36; H, 4.86; N, 3.46. Found: C, 64.88; H, 4.78; N, 3.24%.

4.3. Heck reaction

General procedure for the Heck reaction of bromobenzene with styrene in the presence of palladium complex: as a typical procedure, the example uses **C5** as in entry 14 of Table 2. A 50 ml oven-dried Schlenk flask was charged under nitrogen with 2.0 mmol bromobenzene (210 μl, 313 mg), 2.4 mmol styrene (280 μl, 254 mg), anhydrous 2.2 mmol $NaHCO_3$ (185 mg) and 4.0 ml DMF. A 100 μl solution of 4 μmol complex **C5** in 5 ml DMF was added via syringe to the above solution, and then the reactor was sealed and placed in a 150 °C oil bath, and stirred for 24 h. After cooling to room temperature, the mixture was diluted with EtOAc and water. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel using a mixture of petroleum ether and ethyl acetate.

4.4. X-ray crystallographic studies

Single crystals of complexes **C4**, **C5** and **C7** suitable for X-ray diffraction were grown by slow diffusion of diethyl ether into dichloromethane solutions at room temperature. X-ray studies were carried out on a Rigaku Saturn724 + CCD with graphite-monochromatic Mo Kα radiation (λ = 0.71073 Å) at 173(2) K; cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package [50]. Details of the X-ray structure determinations and refinements are provided in Table 5.

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Appendix A. Supplementary material

CCDC 945889–945891 contain the supplementary crystallographic data for palladium complexes **C4**, **C5** and **C7**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2013.08.008.

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