# How the Substitution Faraway from NHCs Affects the Structural Features and Catalytic Activity of Dicarbene Dipalladium Complexes

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**Abstract.** A series of  $[PdPyCl_2]_2(di-NHC)$  complexes were prepared (di-NHC are two 1-(2,6-dimethylphenyl)imidazolidene molecules bridged by an aliphatic  $-(CH_2)_n$ - linker (n = 3, 4, 5, 6, and 10)). All complexes were fully characterized by NMR spectroscopy and elemental analyses. The crystal structures of four complexes (n = 3, 4, 5 and 6) were determined by X-ray diffraction. The influence of the distant methyl group on the structural features and catalytic activity with increasing of length of linker was investigated by comparing the results of these 2,6-dimethylphenyl palladium complexes with those of

# their known mesityl analogues. X-ray studies show the distant methyl substitution has big impact on the structure feature of the complexes with the shorter linker between two NHC (ethylene and propylene), but has a little or no effect on that of the complexes with longer linker (butylene and hexylene). Catalytic results of the arylation of styrene show that the remote substitute has big effect on the regioselectivity of the product in all complexes with shorter and longer linkers, but has a limited effect on the yield.

# Introduction

Over the past few decades, the transition metal complexes of N-heterocyclic carbenes (NHCs) have attracted considerable attention due to their structural variety, easy access, and stability toward heat, moisture and air.<sup>[1]</sup> In the family of N-heterocyclic carbenes, a large number of bidentate bis-NHC ligands and their many complexes have been studied. In these ligands, a pair of NHC moieties are connected by either an aliphatic linker, such as alkyl<sup>[2]</sup> and ether chain,<sup>[3]</sup> or aromatic linker, such as phenyl<sup>[4]</sup> and pyridyl chain.<sup>[5]</sup> Three types of metal complexes are mainly formed (Scheme 1), which are related to the flexibility and size of the linkers, steric hindrance of N substitutes of the NHC, and types of NHC rings. Among the bis-NHC ligands, di-NHCs with an aliphatic  $-(CH_2)_{\mu}$ linker are the first ones to be prepared.<sup>[6]</sup> The easy preparation of this type of ligand has allowed a controlled study of their coordination to metals by modifying the length of the linker.

We have prepared a series of di-NHC dipalladium complexes of the type III with different  $-(CH_2)_n$  bridges and different N-substitutes on NHC; and investigated the influence of the bridging linker and N-substitutes on the structure and cata-

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Scheme 1. The conformations of NHC metal complexes.

lytic reactivity of the Pd complexes.<sup>[7]</sup> In previous study, we also found that 4-substitution on phenyl, which is quite far away from NHC ring has some effect on the structure and catalytic reactivity of complexes with ethylene bridged linker (Scheme 2). For example, 2,6-dimethylphenyl complex 1a adopts a cis configuration with a torsion angle of -88.28° involving backbone atoms of N1-C1-C4-N2, however, the mesityl complex 1b adopts a trans configuration with 179.59° of torsion angle (Figure 1).<sup>[7a,7c]</sup> Furthermore, in the catalytic arylation of styrene with bromobenzene under the same reaction conditions, 1a gave 93% yield with 11:1 of E/Z ratio of the product, whilst 1b gave 96% yield with an E/Z ratio of 22:1. To further understand how the faraway substitution from NHC affects the structure and catalytic activity of palladium complexes with increasing of the length of bridge, we synthesized a new series of 2,6-dimethylphenyl palladium complexes with  $-(CH_2)_n$  bridges (n = 3-6 and 10; **2a-6a**). In the paper, we investigated their solid-state structures and catalytic activities in arylation reactions, and compared the results with those of their known mesityl analogues (2b-6b).

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**1**a

Figure 1. Crystal structures of complexes 1a and 1b.



Scheme 2. Di-NHC dipalladium complexes.

# **Results and Discussion**

## Synthesis and Characterization of the di-NHC Dipalladium Complexes (2a-6a)

The synthesis of di-NHC dipalladium complexes 2a-6a was achieved by refluxing of the corresponding imidazolium chloride with palladium chloride in the presence of K<sub>2</sub>CO<sub>3</sub> in pyridine in good yield (Scheme 3). The palladium complexes were fully characterized by NMR spectroscopy and gave satisfactory elemental analyses. The complexes are air- and moisture stable and can be stored in an air atmosphere in solid state for more than 6 months without any noticeable decomposition. The proton signal of NCHC of imidazolium chlorides (ca. 10 ppm) was absent in the <sup>1</sup>H NMR of palladium complexes, confirming carbene generation. In addition, <sup>13</sup>C NMR provides direct evidence of the metalation of the ligand, as seen by the signal at ca. 150 ppm, which is assigned to the Pd-C resonance



Scheme 3. Synthesis of complexes 2a-6a.

shifted downfield relative to that of the imidazolium NCHN peak of the starting ligand precursors (ca. 137 ppm).<sup>[8]</sup>

### Solid State Structures of the Palladium Complexes

The molecular structures of 2a-5a were determined by means of X-ray diffraction studies. The molecular diagrams of 2a–5a are shown in Figure 2, Figure 3, Figure 4, and Figure 5.



Figure 2. ORTEP structure of complex 2a (n = 3) with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity.



Figure 3. ORTEP structure of complex 3a (n = 4) with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity.



Figure 4. ORTEP structure of complex 4a (n = 5) with the probability ellipsoids drawn at the 30% level. Hydrogen atoms and solvent are omitted for clarity.

Selected bond lengths and angles are given in Table 1. All complexes show slightly distorted square-planar arrangements around two central palladium atoms, which are surrounded by imidazolylidene, two chloro ligands in a *trans* configuration, and a pyridine. Interestingly, the structure of complexes **2a** and **3a** with shorter bridge (n = 3, 4) consists of two pseudo-square-planar subunits in a *cis* configuration, however, the structure of complexes **4a** and **5a** with longer bridge (n = 5, 6) consists of two subunits in a *trans* configuration. All bond lengths and angles lie in the expected ranges (Table 1). The bond lengths of Pd–C<sub>carbene</sub> and Pd–N<sub>pyridine</sub> in these com-



Figure 5. ORTEP structure of complex 5a (n = 6) with the probability ellipsoids drawn at the 30% level. Hydrogen atoms and solvent are omitted for clarity.

plexes are similar and comparable to those shown in their mesityl analogues. The distance of Pd(1)–Pd(2) in a molecule was supposed to increase with the increasing the length of linker between two NHCs. However, the distance in complex **2a** with propylene linker is 6.569 Å, whilst it is 4.816 Å in **3a** with butylene linker. The shortness of the Pd–Pd distance in **3a** is due to a face-to-face  $\pi$ – $\pi$  stacking between two pyridines, which pulls the two central palladium atoms much closer.

The structure feature of 2a with a propylene bridge is very different from its methyl-substituted analogue 2b. For 2a, the dihedral angle of two imidazole and pyridine rings is  $61.05^{\circ}$ 

Table 1. Selected bond lengths /Å and angles /° for complexes 2a-5a.

Distance	2a	3a	Angle	2a	3a
Pd(1)–C(1)	1.968(5)	1.969(3)	Cl(1)–Pd(1)–Cl(2)	174.95(6)	176.27(4)
Pd(1)-Cl(1)	2.3048(17)	2.3084(10)	C(1)-Pd(1)-N(1)	177.4(2)	178.77(13)
Pd(1)-Cl(2)	2.3075(16)	2.2949(10)	C(4) - Pd(2) - N(2)	174.8(2)	
Pd(1) - N(1)	2.136(5)	2.097(3)	Cl(3)-Pd(2)-Cl(4)	179.00(6)	
C(1)–N(4)	1.356(7)	1.348(4)	N(4)-C(1)-N(3)	105.7(5)	105.6(3)
C(1)–N(3)	1.340(7)	1.347(4)	N(6)-C(4)-N(12)	105.0(5)	
Pd(2)-C(4)	1.963(5)		N(4)-C(1)-Pd(1)	128.8(4)	126.7(2)
Pd(2)–Cl(3)	2.2893(17)		N(3)-C(1)-Pd(1)	125.3(4)	127.6(3)
Pd(2)-Cl(4)	2.3131(17)		N(6)-C(4)-Pd(2)	124.8(4)	
Pd(2)–N(2)	2.093(4)		N(12)-C(4)-Pd(2)	129.9(4)	
C(4)–N(6)	1.345(7)		Imidazole dihedral angle a)	61.05	49.63
C(4)–N(12)	1.358(7)		Pyridine dihedral angle b)	35.89	9.62
Pd(1)-Pd(2)	6.569	4.816	Torsion angle <sup>c)</sup>	-22.62	29.49
Distance	4a	5a	Angle	4a	5a
Pd(1)-C(21)	1.974(6)	1.963(3)	Cl(1)–Pd(1)–Cl(2)	177.61(6)	174.14(4)
Pd(1)-Cl(1)	2.3034(16)	2.2990(10)	C(21)-Pd(1)-N(1)	179.2(2)	176.93(11)
Pd(1)-Cl(2)	2.2915(15)	2.2919(10)	N(4)-C(21)-N(3)	105.7(5)	105.3(3)
Pd(1)-N(1)	2.102(5)	2.102(3)	Cl(3)-Pd(2)-Cl(4)	174.82(8)	
C(21)–N(3)	1.338(7)	1.347(4)	C(29)-Pd(2)-N(2)	178.2(2)	
C(21)–N(4)	1.353(7)	1.350(4)	N(5)-C(29)-N(6)	104.4(4)	
Pd(2)-C(29)	1.960(5)		N(3)-C(21)-Pd(1)	127.1(4)	128.2(2)
Pd(2)–Cl(3)	2.2927(18)		N(4)-C(21)-Pd(1)	127.1(4)	126.5(2)
Pd(2)-Cl(4)	2.3013(17)		N(5)-C(29)-Pd(2)	129.9(4)	
Pd(2)–N(2)	2.111(5)		N(6)-C(29)-Pd(2)	125.7(4)	
C(29)–N(5)	1.333(7)		Imidazole dihedral angle <sup>a)</sup>	37.08	0.00
C(29)–N(6)	1.362(7)		Pyridine dihedral angle b)	55.26	0.00
Pd(1)-Pd(2)	8.233	11.325	Torsion angle <sup>c)</sup>	158.25	180.00

a) Imidazole dihedral angle = angle between LS planes of imidazole rings. b) Pyridine dihedral angle = angle between LS planes of pyridine rings. c) Torsion angle = torsion angle involving the backbone atoms N(pyridine)-C(carbene)-N(pyridine).

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and 35.89°, respectively. However, the dihedral angle decreases to 32.83° and 0.44° for 2b, respectively. In addition, the two NHC-Pd-Py subunits adopt the cis configuration with  $-22.62^{\circ}$  of torsion angle involving of the backbone atoms N(pyridine)-C(carbene)-N(pyridine) in 2a, whilst two subunits adopt a surprising X-shaped configuration with 109.88° in **2b**.<sup>[7b]</sup> The reason for the different configuration of these two complexes is due to different face-to-face  $\pi$ - $\pi$  stacking involving in the two complexes. In 2a, there is a strong  $\pi$ - $\pi$  stacking in two intermolecular pyridine rings with 3.458 Å (N1-C72) of the shortest atom-to-atom distance and 3.467 Å of the distance of the centers of the two pyridine rings (Figure 6). However, the  $\pi$ - $\pi$  stacking exits in two intramolecular imidazole rings and two intermolecular pyridines in **2b**.<sup>[7b]</sup> The different steric effect due to the substitution might be the reason for the different  $\pi$ - $\pi$  stacking ability in complexes 2a and 2b.



**Figure 6.**  $\pi$ - $\pi$  stacking between two pyridine rings in complex 2a.

The molecular arrangements in solid-state structure of 3a and **3b** with butylene linker are guite similar. For **3a**, the dihedral angle of two imidazole and pyridine rings is 49.64° and 9.62°, respectively, and the two NHC-Pd-Py subunits adopt a cis configuration with 29.49° of torsion angle involving of the backbone atoms N(pyridine)-C(carbene)-C(carbene)-N(pyridine). For 3b, the dihedral angle of two imidazole and pyridine rings is respectively 48.52° and 17.40°, and the two NHC-Pd-Py subunits adopt the cis configuration with 32.17° of torsion angle. The face-to-face  $\pi$ - $\pi$  stacking between two intramolecular and intermolecular pyridines is the reason for this special configuration in these two complexes. In 3a, the shortest distance between two intramolecular and intermolecular pyridines is 3.364 Å (N1–C8A) and 3.356 Å (N1–C17A), respectively. The distance of the centers of the two intramolecular and intermolecular pyridine rings is 3.601 Å and 3.562 Å, respectively (Figure 7).

For **4a** with pentylene linker, the two subunits adopt a *trans* configuration with 158.25° of torsion angle, and the dihedral angle of two imidazole and pyridine rings is 37.08° and 55.26°, respectively. Unfortunately, the qualified crystal of **4b** is not available for comparison. The molecular arrangement of complexes **5a** and **5b** are the same, with *trans* configuration and parallel pyridine and imidazole rings. Therefore, the 4-substitute far from NHC has big impact on the solid-state structure of the complexes with shorter linker between two NHC (ethyl-



**Figure 7.**  $\pi$ - $\pi$  stacking among pyridine rings in complex **3a**.

ene and propylene), has a little or no effect on that of the complexes with longer linker (butylene and hexylene).

# Catalytic Activity for Mizoroki-Heck Cross-coupling Reaction

The palladium-catalyzed arylation of olefins has found wide application in organic synthesis. The activity of complexes **2a**– **6a** in the catalytic arylation of styrene was tested in order to elucidate the influence of the ligands. The reactions were conducted in a vial in the presence of 0.5 mol% of palladium catalysts **2a–6a** and K<sub>2</sub>CO<sub>3</sub> in a mixture of bromobenzene and styrene in an argon atmosphere. The results are given in Table 2. From the results, we can see the complexes of **2a–6a** 

Table 2. Results of the arylation of styrene with bromobenzene.

$\bigcirc$	+ Br	0.5 mol%	[Pd], K <sub>2</sub> CO <sub>3</sub>	, <sup>†</sup> R	
Entry <sup>a)</sup>	Catalyst	R	Conversion <sup>a)</sup> /%	Yield <sup>a)</sup> /%	<i>E/Z</i> ratio <sup>b)</sup>
1	2a	Н	100	95	17:1
2	3a	Н	100	93	16:1
3	4a	Н	100	95	12:1
4	5a	Н	100	92	15:1
5	6a	Н	100	94	16:1
6	2a	p-OMe	98	91	6:1
7	3a	p-OMe	100	93	5:1
8	<b>4</b> a	p-OMe	100	95	10:1
9	5a	<i>p</i> -OMe	100	94	9:1
10	6a	p-OMe	100	96	10:1
11	2a	p-F	100	95	11:1
12	3a	p-F	96	90	17:1
13	4a	p-F	100	93	14:1
14	5a	p-F	97	90	16:1
15	6a	p-F	92	89	15:1
16	2a	o-OMe	54	40	19:1
17	3a	o-OMe	65	63	4:1
18	<b>4</b> a	o-OMe	46	44	2:1
19	5a	o-OMe	47	39	20:1
20	6a	o-OMe	56	49	3:1

a) Reaction conditions: 0.5 mmol of aryl bromide, 0.6 mmol of styrene, and 0.75 mmol of  $K_2CO_3$  in 1 mL of DMF. b) Determined by GC using dodecane as internal standard.

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have shown good catalysis for the arylation of olefins with less hindered bromobenzene with both electron-withdrawing and electron-donating substitutes. However, only moderate yields were obtained with more hindered *o*-methoxy bromobenzene. The length of the bridged ligands has limited effect on the yield and regioselectivity of the products and it is hard to rationalize the effect on the current stage.

Compared to their mesityl analogues 2b-6b, the reaction catalyzed by complexes 2a-6a generally provided the similar yield but poor regioselectivity in all complexes whether the linker is shorter or longer. For example, complex 2b with shorter propylene linker gave 93% of yield with 25:1 of E/Z ratio of product in the reaction of bromobenzene with styrene (95% with 17:1 for p-methoxy bromobenzene and 93% with 19:1 for *p*-fluoro bromobenzene),<sup>[7b]</sup> whereas, **2a** gave 95% yield with 17:1 ratio in the reaction of bromobenzene (91% with 6:1 for bromobenzene and 95% with 11:1 for p-fluoro bromobenzene). Furthermore, complex 5b with longer decylene linker gave 93% of yield with 23:1 of E/Z ratio of product in the reaction of bromobenzene with styrene (91% with 11:1 for p-methoxy bromobenzene and 93% with 20:1 for p-fluoro bromobenzene),<sup>[7b]</sup> whereas, 5a gave 92% yield with 15:1 ratio in the reaction of bromobenzene (94% with 9:1 for bromobenzene and 90% with 16:1 for p-fluoro bromobenzene). The reason for the good regioselectivity of mesityl Pd complexes is not very clear on current stage, probably due to the combinative electronic and steric effects.

Further experiments to investigate the effect of different solvents, bases, and catalyst loadings with catalyst **5a** were performed (Table 3). The results show that among the bases employed,  $K_2CO_3$  is the most suitable base. The relatively low yield was detected with other bases, like  $Cs_2CO_3$  and  $K_3PO_4$ , whereas no product was observed with organic base DMAP. Furthermore, DMF is the best solvent tested, and relatively low yield was observed in 1,4-dioxane, DMSO, and toluene.

 Table 3. Arylation of styrene catalyzed by 5a under different conditions.



a) Reaction conditions: 0.5 mmol of phenylbromide, 0.6 mmol of styrene, and 0.75 mmol of base in 1 mL of solvent. b) Determined by GC using dodecane as internal standard.

The yield was decreased with less catalyst loading insignificantly, and 13% of yield was found with 0.2 mol% of **5a**.

# Conclusions

A series of bi-palladium dicarbene complexes **2a–6a** with different length of linker was synthesized. The solid-state structures of **2a–5a** and the catalytic activities of **2a–6a** were studied. The influence of the 4-methyl-group of phenyl on the structural features and catalytic activities of **these** complexes was investigated by comparing the results of **2a–6a** with those of their known mesityl analogues **2b–6b**. X-ray studies show that the distant substitute has big impact on the structural features of the complexes with the shorter linker between two NHC (ethylene and propylene), but has a little or no effect on that of the complexes with longer linker (butylene and hexylene). Catalytic results of arylation of styrene show that the distant substitute has great effect on the regioselectivity of the product in all complexes with shorter and longer linkers, but has limited effect on the yield.

# **Experimental Section**

**Materials and General Procedures:** All manipulations were carried out using standard Schlenk techniques. Solvents were purified and degassed by standard procedures. The corresponding imidazolium chlorides were prepared according to the previous method.<sup>[8]</sup> Pyridine was distilled from calcium hydride under argon atmosphere. Potassium carbonate was ground to a fine powder prior to use. All other chemicals were obtained from common suppliers and used without further purification. <sup>1</sup>H and <sup>13</sup>C spectra were recorded with a Bruker AV 400 MHz spectrometer at room temperature and referenced to the residual signals of the solvent. GC-MS was performed with an Agilent 6890-5973N system with electron ionization (EI) mass spectrometry. Elemental analyses were performed with an EuroVektor Euro EA-300 elemental analyzer.

Representative Procedure for the Synthesis of Complex 2a: To a mixture of 1,1'-bis(2,6-dimethylphenyl)-3,3'-(1,3-propanediyl)bisimidazolium dichloride (1.372 g, 3.0 mmol), PdCl<sub>2</sub> (1.069 g, 6.0 mmol), and K<sub>2</sub>CO<sub>3</sub> (8.292 g, 60 mmol) in a 50 mL round-bottomed flask was added pyridine (35.5 mL). The reaction mixture was heated at 85 °C for 18 h, after which time the mixture was filtered through Celite and washed with DCM. The solvent was removed under vacuum, and the crude was washed by diethyl ether (15 mL). The pure compound was obtained as yellow solid by recrystallization with DCM / diethyl ether in 64% yield. (1.723 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 8.79 (d, J = 5.6 Hz, 4 H, Py-H), 7.70 (t, J = 7.6 Hz, 2 H, Py-H), 7.56 (d, J = 1.2 Hz, 2 H, NCH), 7.35-7.21 (m, 6 H, Ar-H, 4 H, Py-H), 6.82 (d, 2 H, J = 1.6 Hz, NCH), 4.97 (t, J = 6.8 Hz, 4 H, NCH<sub>2</sub>), 3.45 (quin, J = 7.2 Hz, 2 H,  $CH_2$ ), 2.30 (s, 12 H,  $CH_3$ ). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 151.3, 150.1, 137.9, 137.3, 136.7, 129.4, 128.5, 124.3, 123.8, 123.1, 49.4, 30.7, 19.1.  $C_{35}H_{38}Cl_4N_6Pd_2$  (897.37 g·mol<sup>-1</sup>): calcd. C 46.85; H 4.27; N 9.37 %; found: C 46.27; H 3.79; N 9.89 %.

Synthesis of Complex 3a: The complex was synthesized by a similar procedure as described for 2a using 1,1'-bis(2,6-dimethylphenyl)-3,3'-(1,4-butanediyl)bisimidazolium dichloride (1.414 g, 3 mmol) instead of 1,1'-bis(2,6-dimethylphenyl)-3,3'-(1,3-propanediyl)bisimidazolium dichloride. Yield: 78 % (2.133 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta =$ 



8.78 (d, J = 5.2 Hz, 4 H, Py-H), 7.66 (t, J = 7.6 Hz, 2 H, Py-H), 7.35–7.20 (m, 2 H, NCH, 6 H, Ar-H, 4 H, Py-H), 6.88 (d, J = 1.2 Hz, NCH), 4.93 (t, J = 5.6 Hz, 4 H, NC $H_2$ ), 2.48 (quin, J = 7.2 Hz, 4 H, C $H_2$ ), 2.30 (s,12 H, C $H_3$ ). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 151.4$ , 150.2, 137.7, 137.3, 136.7, 129.4, 128.4, 124.2, 123.9, 122.2, 50.8, 27.3, 19.0. C<sub>36</sub>H<sub>40</sub>Cl<sub>4</sub>N<sub>6</sub>Pd<sub>2</sub> (911.40 g·mol<sup>-1</sup>): calcd. C 47.44; H 4.42; N 9.22 %; found: C 47.04; H 4.11; N 9.67 %.

**Synthesis of Complex 4a:** The complex was synthesized by a similar procedure as described for **2a** using 1,1'-bis(2,6-dimethylphenyl)-3,3'-(1,5-pentanediyl)bisimidazolium dichloride (1.456 g, 3 mmol) instead of 1,1'-bis(2,6-dimethylphenyl)-3,3'-(1,3-propanediyl)bisimidazolium dichloride. Yield: 69% (1.916 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 8.77 (d, J = 5.2 Hz, 4 H, Py-H), 7.67 (t, J = 7.2 Hz, 2 H, Py-H), 7.34–7.20 (m, 2 H, NCH, 6 H, Ar-H, 4 H, Py-H), 6.81 (d, J = 2.0 Hz, 2 H, NCH), 4.83 (t, J = 7.2 Hz, 4 H, NCH<sub>2</sub>), 2.43 (quin, J = 7.2 Hz, 4 H, CH<sub>2</sub>), 2.28 (s, 12 H, CH<sub>3</sub>), 1.69 (quin, J = 7.0 Hz, 2 H, CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 151.3, 150.1, 137.7, 137.4, 136.8, 129.3, 128.5, 124.2, 123.6, 122.3, 51.0, 29.8, 23.3, 19.1. C<sub>37</sub>H<sub>42</sub>Cl<sub>4</sub>N<sub>6</sub>Pd<sub>2</sub> (925.42 g·mol<sup>-1</sup>): calcd. C 48.02; H 4.57; N 9.08%; found: C 47.78; H 4.23; N 9.38%.

**Synthesis of Complex 5a:** The complex was synthesized by a similar procedure as described for **2a** using 1,1'-bis(2,6-dimethylphenyl)-3,3'-(1,6-hexanediyl)bisimidazolium dichloride (1.498 g, 3 mmol) instead of 1,1'-bis(2,6-dimethylphenyl)-3,3'-(1,3-propanediyl)bisimidazolium dichloride. Yield: 69% (1.945 g). <sup>1</sup>**H NMR** (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 8.76 (d, J = 5.2 Hz, 4 H, Py-H), 7.65 (t, J = 7.2 Hz, 2 H, Py-H), 7.33–7.19 (m, 2 H, NCH, 6 H, Ar-H, 4 H, Py-H), 6.86 (d, J = 1.6 Hz, 2 H, NCH), 4.75 (t, J = 7.2 Hz, 4 H, NCH<sub>2</sub>), 2.29 (m, 12 H, CH<sub>3</sub>, 4 H, CH<sub>2</sub>), 1.70 (quin, J = 7.2 Hz, 4 H, CH<sub>2</sub>), <sup>13</sup>**C NMR** (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 151.3, 150.1, 137.7, 137.4, 136.8, 129.3, 128.4, 124.2, 123.7, 122.0, 51.2, 30.1, 26.0, 19.0. C<sub>38</sub>H<sub>44</sub>Cl<sub>4</sub>N<sub>6</sub>Pd<sub>2</sub> (939.45 g·mol<sup>-1</sup>): calcd. C 48.0258; H 4.72; N 8.95%; found: C 48.41; H 4.56; N 9.32%.

**Synthesis of Complex 6a:** The complex was synthesized by a similar procedure as described for **2a** using 1,1'-bis(2,6-dimethylphenyl)-3,3'-

Table 4.	Crystallographic	data for	complexes	2a-5a
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(1,10-decanediyl)bisimidazolium dichloride (1.667 g, 3 mmol) instead of 1,1'-bis(2,6-dimethylphenyl)-3,3'-(1,3-propanediyl)bisimidazolium dichloride. Yield: 87% (2.598 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 8.75 (d, J = 5.2 Hz, 4 H, Py-H), 7.66 (d, J = 7.6 Hz, 2 H, Py-H), 7.33–7.19 (m, 2 H, NCH, 4 H, Ar-H, 4 H, Py-H), 7.14 (d, J = 1.6 Hz, 2 H, Ar-H), 6.88 (d, J = 2.0 Hz, 2 H, NCH), 4.74 (d, J = 7.6 Hz, 4 H, NCH<sub>2</sub>), 2.29 (s, 12 H, CH<sub>3</sub>), 2.19 (quin, J = 7.2 Hz, 4 H, CH<sub>2</sub>), 1.48 (m, 8 H, CH<sub>2</sub>), 1.37 (quin, J = 7.2 Hz, 4 H, CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 151.3, 150.2, 137.7, 137.4, 136.8, 129.3, 128.4, 124.2, 123.7, 121.7, 51.5, 30.5, 29.3, 29.1, 26.6, 19.0. C<sub>42</sub>H<sub>52</sub>Cl<sub>4</sub>N<sub>6</sub>Pd<sub>2</sub> (995.55 g·mol<sup>-1</sup>): calcd. C 50.67; H 5.26; N 8.44%; found: C 50.35; H 4.96; N 8.83%.

**Procedure for the Heck Coupling Reaction:** An oven-dried 4 mL vials containing a stirrer bar was charged with aryl bromide (0.50 mmol), catalyst (0.5 mol%), and K<sub>2</sub>CO<sub>3</sub> (103.7 mg, 0.75 mmol) in the glove box and sealed with a cap containing a PTFE septum. DMF (1 mL) and styrene (70  $\mu$ L, 0.60 mmol) were injected sequentially. The mixture was stirred at 110 °C for 23 h. Yield was determined by GC using dodecane as internal standard.

**X-ray Crystallography:** Intensity data were collected with a Rigaku Mercury CCD area detector in  $\omega$  scan mode by using Mo- $K_{\alpha}$  radiation ( $\lambda = 0.71075$  Å). The diffracted intensities were corrected for Lorentz polarization effects and empirical absorption corrections. Details of the intensity data collection and crystal data are given by full-matrix least-squares procedures based on  $F^{2,[9]}$  All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms in these complexes were all generated geometrically (C–H bond lengths fixed at 0.95 Å), assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All the hydrogen atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement. The structure was solved by directed methods using the SHELXS-97 program and absorption correction was performed by SADABS program. Selected crystallo-graphic data are shown in Table 4. Crystals suitable of complexes **2a**-

	2a	3a	4a	5a
Empirical formula	C35H38Cl4N6Pd2	$C_{36}H_{40}Cl_4N_6Pd_2$	$C_{38}H_{44}Cl_6N_6Pd_2$	$C_{40}H_{48}Cl_8N_6Pd_2$
Formula weight	897.35	911.34	1010.29	1109.24
Temperature /K	293(2)	293(2)	298(2)	298(2)
Crystal system	orthorhombic	monoclinic	triclinic	monoclinic
Space group	Pbca	C2/c	P1	P21/c
Crystal size /mm	$0.30 \times 0.20 \times 0.10$	$0.55 \times 0.40 \times 0.33$	$0.40 \times 0.30 \times 0.20$	$0.40 \times 0.30 \times 0.20$
a /Å	16.3672(13)	20.079(2)	11.7805(4)	13.0124(15)
b /Å	13.4879(12)	22.699(4)	15.2507(5)	13.5202(16)
c /Å	34.333(4)	14.3096(18)	15.3214(5)	14.5259(17)
a /°	90	90	90.156(2)	90
β /°	90	132.956(7)	103.480(2)	112.232(2)
γ /°	90	90	105.546(2)	90
V/Å <sup>3</sup>	7579.3(13)	4773.3(11)	2572.64(15)	2365.6(5)
Z	8	4	2	2
$D_{\rm calcd}$ /mg·cm <sup>-3</sup>	1.573	1.268	1.304	1.557
Absorption coefficient /mm <sup>-1</sup>	1.264	1.005	1.039	1.247
F(000)	3600	1832	1016	1116
$\theta$ range /°	1.72 to 25.01°	1.79 to 28.32°	2.02 to 25.00°	1.69 to 25.00°
Reflections collected / unique	19586 / 5848	8255 / 5254	38229 / 9003	27130 / 4149
Data / restrains / parameters	5848 / 0 / 424	5254 / 0 / 217	9003 / 29 / 466	3314/0/210
Goodness-of-fit on $F_2$	1.184	1.082	1.028	1.286
Final R indices $[I \ge 2\sigma (I)]$	$R_1 = 0.0402$	$R_1 = 0.0515$	$R_1 = 0.0552$	$R_1 = 0.0290$
	$wR_2 = 0.0917$	$wR_2 = 0.1835$	$wR_2 = 0.1729$	$wR_2 = 0.0820$
R indices (all data)	$R_1 = 0.0579$	$R_1 = 0.0775$	$R_1 = 0.0686$	$R_1 = 0.0342$
	$wR_2 = 0.1064$	$wR_2 = 0.2258$	$wR_2 = 0.1913$	$wR_2 = 0.1049$

**5a** for X-ray diffraction analysis were obtained by slow evaporation of a saturated DCM solution at room temperature.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-948181 (**3a**), CCDC-948182 (**4a**), and CCDC-948183 (**5a**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

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