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Synthesis, structure and catalytic activity of dicarbene dipalladium complexes with different alkane bridge

Jianfeng Zhao [a], Long Yang [a], Kaiqi Ge [a], Qian Chen [a], Yongzhong Zhuang [a], Changsheng Cao [a,*], Yanhui Shi [a,b,*]

[a] College of Chemistry and Chemical Engineering and Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, Xuzhou Normal University, Xuzhou, Jiangsu, 221116, PR China
[b] State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, 210093, PR China

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ABSTRACT

A series of di-NHC dipalladium complexes $Pd_2LPy_2Cl_4$ ($L = L^{C3}, L^{C5}, L^{C6}$ and L^{C10}) with alkyl bridges of different chain lengths were prepared. The molecular structures of $Pd_2L^{C3}Py_2Cl_4$ (**1**) and $Pd_2L^{C6}Py_2Cl_4$ (**3**) were determined by X-ray diffraction studies. The influence of the different bridges on the structure and reactivity of the complexes was studied. The structure of complex **3** consists of two pseudo-square-planar subunits in a *trans* configuration, however complex **1** shows an X configuration due to π–π stacking of both imidazole rings and pyridine rings. The catalytic activity of the new binuclear palladium complexes was successfully tested in the Mizoroki–Heck reaction of styrene with aryl bromides. The length of the bridged ligands had some effect on the yield and regioselectivity of the products.

The chemistry of transition-metal complexes containing N-heterocyclic carbenes (NHCs) has been extensively studied, and a large number of compounds have been reported [1–5]. Owing to their wide application as potentially useful catalysts in organic synthesis, the chemistry of palladium-NHC complexes has become an area of great interest and has been extensively studied [6–8]. In particular, those bearing dicarbene ligands have received much attention mainly due to the higher stability to heat and air, and their improved catalytic performances. Over the last years, several chelating palladium complexes with alkane-bridged bidentate carbenes have been reported [9–15]. However, bimetallic palladium complexes in which the bidentate ligand bridges the two metal centers are scarce [16–18]. The design and synthesis of binuclear complexes with di-NHC are of considerable interest because the adjacent metals can function in a synergic manner in their interactions with substrate molecules [19]. We have been interested in the chemistry of bimetallic di-NHC complexes concentrated on *homo*dinuclear and *hetero*dinuclear complexes. We report here the synthesis and structure of a series of di-NHC dipalladium complexes bridged by different alkyl chain, diagrammed in Scheme 1.

The synthesis of di-NHC dipalladium complexes **1**–**4** was achieved by refluxing of the corresponding imidazolium salt, with palladium chloride in presence of K_2CO_3 in pyridine in moderate yield, according to literature procedure [20]. The novel dicarbene ligands, e.g. bisimidazolium dichlorides and palladium complexes were fully characterized by NMR spectroscopy and gave satisfactory elemental analyses [21–23]. The complexes are air and moisture stable and can be stored at air atmosphere in solid state for more than 6 months without any noticeable decomposition.

The proton signal of NC*H*N of imidazolium chlorides (from 10.15 ppm to 10.52 ppm) was absent in the ^1H NMR of palladium complexes, confirming carbene generation. In addition, ^{13}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*carbene resonance shifted downfield relative to that of the imidazolium N*C*HN peak of the starting ligand precursor (ca. 140 ppm).

Single crystals for the solid-state structure determinations of **1** and **3** could be obtained by slow evaporation of a dichloromethane (DCM) saturated solution. The molecular structures of **1** and **3** were determined by means of X-ray diffraction studies [24]. The molecular diagrams of **1** and **3** are shown in Figs. 1 and 2 and selected crystallographic data are shown in Table 1. The structure of complex **1** consists of two pseudo-square-planar subunits in a *cis* configuration bridged with propylene, while the structure of complex **3** consists of two pseudo-square-planar subunits in a *trans* configuration bridged with hexylene. Two complexes show slightly distorted square-planar geometries around two palladium centers, which are surrounded by imidazolylidene, two chloro ligands in a *trans* configuration, and a pyridine. The $Pd\text{-}C_{carbene}$ distance is 1.957(12) Å and 1.971(14) Å for **1** and 1.984(7) Å for **3** (Table 2), similar to that shown by other palladium-related species [25,26]. The $Pd\text{-}N_{pyridine}$ distance in complex **1** [2.115(11) Å and 2.062(14) Å], **3** [2.106(6) Å] is comparable to that of its related saturated mono-palladium carbene analogs [26]. All other distances and angles lie in the expected range (Table 2).

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* Corresponding authors at: College of Chemistry and Chemical Engineering and Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, Xuzhou Normal University, Xuzhou, Jiangsu, 221116, PR China. Fax: +86 516 83500349.
E-mail address: yhshi_2000@126.com (Y. Shi).

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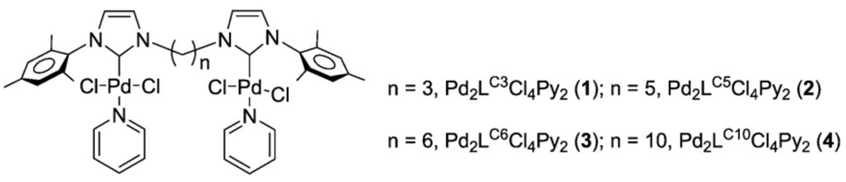

Scheme 1. di-NHC dipalladium complexes (**1**–**4**) with different alkyl bridge lengths.

Owing to the rotational freedom in the alkyl linking groups between the dicarbene of these bidentate ligands, two pseudo-square-planar subunits around palladium centers of the complexes tend to adopt a *trans* arrangement, in which the subunits are quite widely spaced in order to minimize steric repulsions between the metal coordination spheres. The complex **3** indeed adopts the *trans* configuration having two pyridine ligands far away. Both the dihedral angles in complex **3** between two intramolecular imidazole rings and two pyridine rings are 0°, meaning they are parallel to each other. However, complex **1** adopts a surprising X configuration. Two intramolecular pyridines are almost parallel with 109.88° of torsion angle involving the backbone atoms N1–C1–C4–N2, and two intramolecular imidazole rings have a 32.83° of torsion angle. It is the face-to-face π–π stacking that causes the unique structure of complex **1** as well. There are two types of π–π stacking exiting in this structure. One is face-to-face π–π stacking between two intramolecular imidazole rings; the other is face-to-face π–π stacking between two intermolecular pyridines. The distance of the centers of the two intramolecular imidazolylidene is 3.986 Å and the shortest atom distance is 3.308 Å. Two adjacent intermolecular pyridines are parallel to each other with a distance of 3.641 Å. The bond lengths of Pd–C in all the complexes are equivalent within the margin of error. The same applies to the bonds of palladium nitrogen and palladium chloride.

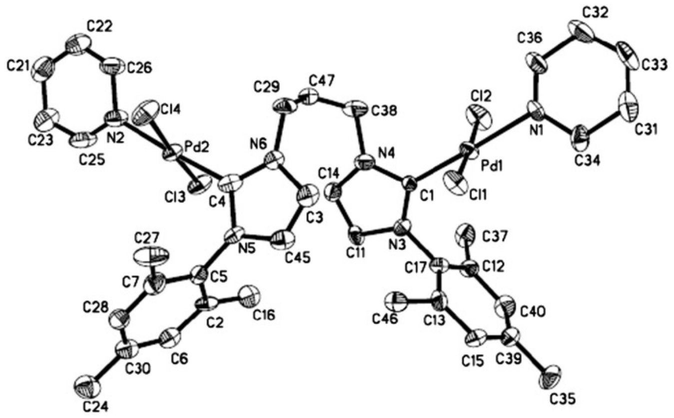

Fig. 1. ORTEP structure of complex **1** (n = 3) with the probability ellipsoids drawn at the 30% level. Hydrogen atoms have been omitted for clarity.

The palladium-catalyzed arylation of olefins (Mizoroki–Heck reaction) has found wide application in organic synthesis. The activity of complexes **1**–**4** in the catalytic arylation of styrene was tested in order to elucidate the influence of the ligands. The alkyl bromides with different electronic properties e.g. phenyl bromide, *p*-methoxyphenyl bromide, and *p*-flourophenyl bromide were chosen in the reactions. The reactions were conducted in a vial in the presence of catalytic amounts of palladium catalysts **1**–**4** and K_2CO_3 in a mixture of aryl bromide and styrene [27], and the results were given in Table 3. From the results, it can be seen that the complexes of **1**–**4** are good catalysts with almost 100% conversion yield for the arylation of olefins with different alkyl halides. For the arylation of styrene with phenyl bromide, the highest yield of product (93%) with 25:1 and 23:1 of A to B ratio was detected with **1** and **3** as catalyst (Table 3, entries 1 and 3), however, the highest of A to B ratio (29:1) of product in 89% yield was obtained with **2** (Table 3, entry 2). For the reactions with phenyl bromide substituted with electron donating group (*p*-OMe), complex **1** gave the highest yield of 95%, and the best regioselectivity of A to B of 17:1 (Table 3, entry 5). For the reactions with phenyl bromide substituted with electron withdrawing group (*p*-F), the highest yield of 93% and A to B ratio of 20:1 was observed with complex **3** (Table 3, entry 11), whereas the lowest yield and A to B ratio was detected with **4** (Table 3, entry 12). Therefore, complexes **1** (with 3 carbon of linker) and **3** (with 6 carbon of linker) generally gave the high yield and good regioselectivity, whereas complex **4** (with 10 carbon of linker) gave the poor yield. However, the difference of catalytic performance for these complexes is not significant. In order to elutriate if a synergic manner exists in these new bimetallic palladium complex, mono-palladium complex *trans*-[1,3-bis(2,4,6-trimethylphenyl)imidazole-2-ylidene]PdCl$_2$(pyridine) [26] was prepared and its catalytic performance was tested in the above reactions. With the mono-palladium complex, 85% yield with 27:1 of A:B in 100% of conversion was detected in the reaction of phenyl bromide. In addition, 89% yield with 20:1 of A:B in 100% of conversion was detected in the reaction of *p*-methoxyphenyl bromide, and 90% yield with 21:1 of A:B in 98% of conversion was detected in the reaction of *p*-flourophenyl bromide. From the results, it can be seen that the catalytic performance of this mono-palladium is very much like those of complex **4** (with 10 carbon of linker). The possible reason for this is that the very long linkage between two Pd units in **4** makes them work freely and look like two mono-palladium complexes. Therefore, there is no synergic function in complex **4**, but probably there is a weak function in complexes **1** and **3**.

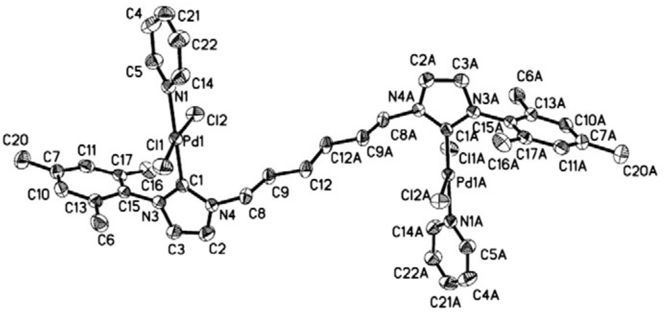

Fig. 2. ORTEP structure of complex **3** (n = 6) with the probability ellipsoids drawn at the 30% level. Hydrogen atoms have been omitted for clarity.

Table 1
Selected crystallographic data for complexes **1** and **3**.

Complex	1	3
Formula	$C_{37} H_{44} Cl_4 N_6 Pd_2$	$C_{40} H_{48} Cl_4 N_6 Pd_2$
Formula weight	927.38	967.44
Temperature of measurement (K)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	Cc	P2(1)/c
Unit cell dimensions		
a (Å)	16.4050(6)	9.7607(4)
b (Å)	21.5136(5)	28.3574(14)
c (Å)	13.2164(3)	8.8148(3)
α (°)	90.00	90.00
β (°)	120.963(2)	101.689(3)
γ (°)	90.00	90.00
Volume ($Å^3$)	3999.8(2)	2389.23(17)
Z	4	2
Crystal size (mm)	0.50 × 0.40 × 0.20	0.30 × 0.22 × 0.20
F(000)	1872	980
Theta range for data collection (°)	1.73–28.28	1.44–28.42
Goodness-of-fit on F_2	1.088	1.000
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0332$	$R_1 = 0.0766$
	$wR_2 = 0.0817$	$wR_2 = 0.2624$
R indices (all data)	$R_1 = 0.0500$	$R_1 = 0.1095$
	$wR_2 = 0.0953$	$wR_2 = 0.2981$

Table 2
Selected Bond Lengths and angles for complexes **1** and **3.**

Distance (Å)	1	3
C1–Pd1	1.957(12)	1.984(7)
N1–Pd1	2.115(11)	2.106(6)
Pd1–Cl1	2.297(5)	2.316(2)
Pd1–Cl2	2.303(5)	2.308(2)
Angle (°)		
C1–Pd1–N1	177.9(5)	178.0(3)
C1–Pd1–Cl1	89.9(4)	90.0(2)
C1–Pd1–Cl2	90.2(4)	88.7(2)
N1–Pd1–Cl1	91.4(3)	91.91(19)
N1–Pd1–Cl2	88.3(3)	89.46(19)
[a]Imidazole dihedral angle	32.83	0
[b]Pyridine dihedral angle	0.44	0
[c]Torsion angle	109.88	167.63

[a] Imidazole dihedral angle = angle between LS planes: one through the C1 imidazole ring; one through C4 imidazole ring.

[b] Pyridine dihedral angle = angle between LS plans of pyridine.

[c] Torsion angle = torsion angle involving the backbone atoms N1–C1–C4–N2.

We have synthesized a series of dicarbene dipalladium complexes with different length of linker. X-ray diffraction studies showed that the two pseudo-square-planar subunits around palladium centers of the complex **3** with longer linking group (hexylene bridge) adopt the *trans* configuration. However, complex **1** adopts an X configuration due to the face-to-face π–π stacking. The new binuclear complexes were successfully tested in the catalytic Mizoroki–Heck reaction of styrene with alkyl bromide. The complexes of **1**–**4** showed good catalysts for the arylation of olefins.

Acknowledgements

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Appendix A. Supplementary material

CCDC-870507 and CCDC-870508 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge form The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK or Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

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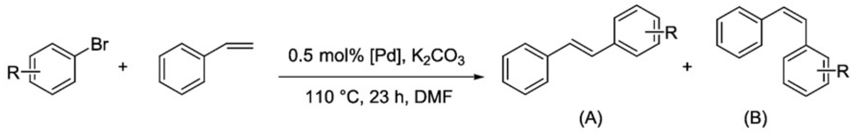
Table 3
Results of the Mizoroki–Heck reaction.



Entry	Catalyst	R	Conversion (%)[a]	Yield (%)[a]	A:B ratio[a]
1	**1**	H	100	93	25:1
2	**2**	H	97	89	29:1
3	**3**	H	100	93	23:1
4	**4**	H	100	89	23:1
5	**1**	*p*-OMe	100	95	17:1
6	**2**	*p*-OMe	100	90	5:1
7	**3**	*p*-OMe	100	91	11:1
8	**4**	*p*-OMe	95	87	12:1
9	**1**	*p*-F	100	93	19.:1
10	**2**	*p*-F	100	91	20:1
11	**3**	*p*-F	100	93	20:1
12	**4**	*p*-F	100	89	15:1

[a] Determined by GC using dodecane as internal standard.

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[21] General procedures: All manipulations were carried out using standard Schlenk techniques. Solvents were purified and degassed by standard procedures. 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. ^{1}H and ^{13}C spectra were recorded on a Bruker AV 400 MHz spectrometer at room temperature and referenced to the residual signals of the solvent. GC-MS was performed on an Agilent 6890–5973 N system with electron ionization (EI) mass spectrometry. Elemental analyses were performed on a EuroVektor Euro EA-300 elemental analyzer.

[22] General procedures for the synthesis of ligands [H2L2]Cl2.Mesitylimidazole (4 mmol, 0.745 g) and dichloroalkane (2 mmol) were heated to 110 °C for 4–5 h in a 10 mL of pressure tube. After the completion of the reaction, the solid was dissolved in DCM (2.5 mL) and precipitated out with diethyl ether (10 mL) to give product as a white powder.$[H_2L^{C3}{}_2]Cl_2$: Yield:81%. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 10.15 (s, 2H, NC*H*N), 8.67 (s, 2H, NC*H*), 7.08 (s, 2H, NC*H*), 7.00 (s, 4H, Ar–*H*), 4.96 (t, 4H, CH_2), 3.18 (m, 2H, CH_2), 2.35 (s, 6H,CH_3), 1.92 (s, 12H, CH_3).$[H_2L^{C5}]Cl_2$: Yield: 79% (0.811 g). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 10.50 (s, 2H, NC*H*N), 8.70 (s, 2H, NC*H*), 7.07 (s, 2H, NC*H*), 6.97 (s, 4H, Ar–*H*), 4.79 (t, $J=7.6$ Hz, 4H, NCH_2), 2.31 (s, 6H, CH_3), 2.04 (s, 12H, CH_3), 1.90 (m, 4H, CH_2), 1.64 (m, 2H, CH_2). ^{13}C NMR (CDCl$_3$, 100 MHz): 140.8, 137.8, 134.0, 130.8, 129.6, 124.6, 122.5, 48.8, 28.8, 21.6, 20.9, 17.4. Anal. Calc. for $C_{29}H_{38}Cl_2N_4$ (513.54 g/mol): C, 67.82; H, 7.46; N, 10.91. Found: C, 67.55; H, 7.32; N, 11.36%.$[H_2L^{C5}]Cl_2$: Yield: 79% (0.811 g). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 10.50 (s, 2H, NC*H*N), 8.70 (s, 2H, NC*H*), 7.07 (s, 2H, NC*H*), 6.97 (s, 4H, Ar–*H*), 4.79 (t, $J=7.6$ Hz, 4H, NCH_2), 2.31 (s, 6H, CH_3), 2.04 (s, 12H, CH_3), 1.90 (m, 4H, CH_2), 1.64 (m, 2H, CH_2). ^{13}C NMR (CDCl$_3$, 100 MHz): 140.8, 137.8, 134.0, 130.8, 129.6, 124.6, 122.5, 48.8, 28.8, 21.6, 20.9, 17.4. Anal. Calc. for $C_{29}H_{38}Cl_2N_4$ (513.54 g/mol): C, 67.82; H, 7.46; N, 10.91. Found: C, 67.55; H, 7.32; N, 11.36%.$[H_2L^{C6}]Cl_2$: Yield: 64% (0.675 g). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 10.37 (s, 2H, NC*H*N), 8.47 (s, 2H, NC*H*), 7.11 (s, 2H, NC*H*), 6.96 (s, 4H, Ar–H), 4.70 (m, 4H, NCH_2), 2.31 (s, 6H, CH_3), 2.15 (m, 8H, CH$_2$), 2.03 (s, 12H, CH_3).^{13}C NMR (CDCl$_3$, 100 MHz): 140.8, 137.7, 134.0, 130.7, 129.6, 124.2, 122.8, 49.4, 29.2, 24.1, 20.9, 17.3. Anal. Calc. for $C_{30}H_{40}Cl_2N_4$ (527.57 g/mol): C, 68.30; H, 7.64; N, 10.62. Found: C, 67.98; H, 7.33; N, 10.85%.$[H_2L^{C6}]Cl_2$: Yield: 64% (0.675 g). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 10.37 (s, 2H, NC*H*N), 8.47 (s, 2H, NC*H*), 7.11 (s, 2H, NC*H*), 6.96 (s, 4H, Ar–H), 4.70 (m, 4H, NCH_2), 2.31 (s, 6H, CH_3), 2.15 (m, 8H, CH$_2$), 2.03 (s, 12H, CH_3).^{13}C NMR (CDCl$_3$, 100 MHz): 140.8, 137.7, 134.0, 130.7, 129.6, 124.2, 122.8, 49.4, 29.2, 24.1, 20.9, 17.3. Anal. Calc. for $C_{30}H_{40}Cl_2N_4$ (527.57 g/mol): C, 68.30; H, 7.64; N, 10.62. Found: C, 67.98; H, 7.33; N, 10.85%.$[H_2L^{C10}]Cl_2$: Yield: 66% (0.771 g). ^{1}H NMR (CDCl$_3$, 400 MHz): 10.52 (s, 2H, NC*H*N), 8.17 (s, 2H, NC*H*), 7.18 (s, 2H, NC*H*), 6.94 (s, 4H, Ar–*H*), 4.66 (m, 4H, NCH_2), 2.29 (s, 6H, CH_3), 2.02 (s, 12H, CH_3; 4H, CH_2), 1.25–1.35 (m, 12H, CH_2). ^{13}C NMR (CDCl$_3$, 100 MHz): 141.1, 140.5, 138.6, 134.2, 130.9, 129.8, 123.1, 50.0, 30.2, 28.5, 28.0, 25.6, 21.1, 17.6. Anal. Calc. for $C_{34}H_{48}Cl_2N_4$ (583.68 g/mol): C, 69.96; H, 8.29; N, 9.60. Found: C, 69.35; H, 8.04; N, 10.01%.

[23] General procedures for the synthesis of palladium complexes Pd2L2Cl4(C5H5N) 2.To a mixture of bisimidazolium dichloride (3.0 mmol), PdCl$_2$ (1.069 g, 6.0 mmol), and K$_2$CO$_3$ (8.293 g, 60 mmol) in a 50 mL round bottom flask was added 10.5 mL of pyridine. 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 / ether.$Pd_2L^{C3}{}_2Cl_4(C_5H_5N)_2$ (**1**): Yield: 77 % (2.142 g). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.81 (m, 4H, Py–*H*), 7.70 (m, 2H, NC*H*), 7.54 (m, 2H, Py–*H*), 7.32–7.23 (m, 4H, Py–*H*), 7.02 (s, 4H, Ar–*H*), 6.81 (m, 2H, NC*H*), 4.95 (m, 4H, NCH_2), 3.40 (m, 2H, CH_2), 2.36 (s, 6H, CH_3), 2.29 (s, 6H, CH_3), 2.25 (s, 6H, CH_3),. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 152.5 (Pd–NCN), 151.9, 151.2 (Pd–NCN), 139.1, 137.8, 137.7, 137.6, 136.3, 136.1, 136.0, 134.7, 129.2, 124.5, 124.2, 124.0, 123.0, 122.9, 49.7, 49.5, 49.3, 30.5, 30.4, 30.3, 21.08, 19.9, 19.6, 19.1, 18.9. Anal. Calc. for $C_{37}H_{42}Cl_4N_6Pd_2$ (925.42 g/mol): C, 48.02; H, 4.57; N, 9.08. Found: C, 48.62; H, 4.25; N, 9.31%.$Pd_2L^{C5}Cl_4(C_5H_5N)_2$ (**2**): Yield: 78% (2.231 g). ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta=8.79$ (m, 4H, Py–*H*), 7.66 (m, 2H, Py–*H*), 7.24–7.22 (m, 2H, NC*H*; 4H, Py–*H*), 7.00 (s, 4H, Ar–*H*), 6.78 (s, 2H, NC*H*), 4.81 (t, $J=6.8$Hz, 4H, NCH_2), 2.42 (m, 4H, CH_2), 2.35 (s, 6H, CH_3), 2.23 (s, 12H, CH_3), 1.68 (m, 2H, CH_2). ^{13}C NMR (CDCl$_3$, 100 MHz): $\delta=151.4$, 150.0 (Pd–NCN), 139.1, 137.7, 136.3, 134.9, 129.2, 124.2, 123.8, 122.3, 51.0, 29.8, 23.3, 21.1, 19.0. Anal. Calc. for $C_{39}H_{46}Cl_4N_6Pd_2$ (953.47 g/mol): C, 49.13; H, 4.86; N, 8.81. Found: C, 48.86; H, 4.51; N, 9.07%.$Pd_2L^{C6}Cl_4(C_5H_5N)_2$ (**3**): Yield: 56 % (1.625 g). ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta=8.77$ (m, 4H, Py–*H*), 7.63 (m, 2H, Py–*H*), 7.22 (m, 4H, Py–*H*), 7.17 (m, 2H, NC*H*), 6.99 (s, 4H, Ar–*H*), 6.82 (m, 2H, NC*H*), 4.74 (t, $J=7.6$Hz, 4H, NCH_2), 2.34 (s, 6H, CH_3), 2.27 (m, 4H, CH_2), 2.23 (s, 12H, CH_3), 1.68 (m, 4H, CH_2). ^{13}C NMR (CDCl$_3$, 100 mHz): $\delta=151.2$, 149.9 (Pd–NCN), 139.0, 137.7, 136.3, 134.9, 129.1, 124.2, 123.9, 121.9, 51.2, 30.1, 25.9, 21.1, 18.9. Anal. Calc. for $C_{40}H_{48}Cl_4N_6Pd_2$ (967.50 g/mol): C, 49.66; H, 5.00; N, 8.69. Found: C, 49.12; H, 4.71; N, 9.24%.$Pd_2L^{C10}Cl_4(C_5H_5N)_2$ (**4**): Yield: 77% (2.365 g). ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta=8.77$ (m, 4H, Py–*H*), 7.65 (m, 2H, Py–*H*), 7.23 (m, 4H, Py–*H*), 7.12 (m, 2H, NC*H*), 7.00 (s, 4H, Ar–*H*), 6.85 (m, 2H, NC*H*), 4.72 (t, $J=7.6$Hz, 4H, NCH_2), 2.35 (s, 6H, CH_3), 2.25 (s, 12H, CH_3), 2.17 (m, 4H, CH_2), 1.50–1.36 (m, 12H, CH_2). ^{13}C NMR (CDCl$_3$, 100 MHz): $\delta=151.3$, 150.0 (Pd–NCN), 139.0, 137.7, 136.3, 134.9, 129.1, 124.1, 123.8, 121.6, 51.4, 30.5, 29.3, 29.1, 26.6, 21.1, 18.9. Anal. Calc. for $C_{44}H_{56}Cl_4N_6Pd_2$ (1023.61 g/mol): C, 51.63; H, 5.51; N, 8.21. Found: C, 51.96; H, 5.32; N, 8.44%.

[24] Preliminary examination and data collection were carried out on a Rigaku Mercury CCD device at the window of a sealed X-ray tube with graphite-monochromated Mo Kα radiation. Absorption correction was performed by SADABS program. All the structures were solved by directed methods using the SHELXS-97 program and refined by full-matrix least squares techniques on F^2.

[25] L. Ray, S. Barman, M.M. Shaikh, P. Ghosh, Highly convenient amine-free Sonogashira coupling in air in a polar mixed aqueous medium by trans- and cis-[(NHC)$_2$-PdX$_2$] (X = Cl, Br) complexes of N/O-functionalized N-heterocyclic carbenes, Chem. Eur. J. 14 (2008) 6646–6655.

[26] C. Dash, M.M. Shaikh, P. Ghosh, Fluoride-free Hiyama and copper- and amine-Free Sonogashira coupling in air in a mixed aqueous medium by a series of PEPPSI-themed precatalysts, Eur. J. Inorg. Chem. 12 (2009) 1608–1618.

[27] Mizoroki–Heck reaction of styrene. An oven-dried 4 mL vial containing a stirrer bar was charged with aryl bromide (1 mmol), catalyst (0.5 mol%) and K$_2$CO$_3$ (207.4 mg, 1.5 mmol) in the glove box and sealed with a cap containing a POFE septum. DMF (1 mL) and styrene (140 μL, 1.2 mmol) were injected sequentially. The mixture was stirred at 110 °C for 23 h.