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Synthesis, Structure, and Reactivity of Dicarbene Dipalladium Complexes

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Keywords: Dinuclear complexes; Palladium; N-Heterocyclic carbene; Cystral structure; Heck reaction

Abstract. A series of imidazole-based and benzimidazole-based di-NHC dipalladium complexes with alkyl bridges of different chain lengths were prepared. All complexes were fully characterized by NMR spectroscopy and elemental analyses. The crystal structures of three complexes were determined by X-ray diffraction. X-ray studies show the length of linker effects the solid structure of these complexes and π–π stacking plays an important role for the configuration of NHC-Pd-Py subunits. The activity of NHC-palladium complexes was investigated in the mono- and double-Heck reactions, and the imidazole-based palladium complex bearing the shortest ethylene bridge shows the best activity and selectivity in both reactions.

Introduction

Palladium-catalyzed C–C or C–*X* (*X* = N, S, O etc.) cross coupling reaction is one of the most important classes of organometallic reactions[1] and finds wide applications in pharmaceuticals, fine chemicals, and natural products.[2] Among the various coupling reactions, the Mizoroki–Heck reaction is one of the most powerful methods for C–C bond formation.[3] This reaction can be accomplished with a great number of palladium catalyst precursors under various reaction conditions.[4] Among these palladium sources, Pd-NHC (N-heterocyclic carbenes) have emerged as favorites, particularly due to their unique properties including their facile synthesis, their insensitivity to air and moisture, their thermal stability and their tunability of steric and electronic properties.[5] Over the last years, the chemistry of palladium-NHC complexes has become an area of great interest and has been extensively studied.[6] In particular, those bearing N-heterocyclic dicarbene ligands have received much attention mainly due to the higher stability to heat and air as a result of the chelate effect, and their improved catalytic performances. Many chelating bidentate NHC-palladium complexes have been reported,[7] comparing to which, bimetallic palladium complexes with the bidentate NHC ligand bridged the two central metal atoms are relatively fewer.[8] Besides palladium complexes, other bimetallic complexes with bridging NHC ligands such as Au, Cu, Ag, Re, Ru, and Pt were reported.[8d–8i] The design and synthesis of dinuclear complexes with di-NHC are of considerable interest because the adjacent metals could function in a synergic manner in their interactions with substrate molecules.[9] Furthermore, the heterodimetallic complexes provide the possibility for one-pot multiple catalytic transformations.[9b] We were interested in the chemistry of bimetallic di-NHC complexes concentrated on *homo*dinuclear and *hetero*dinuclear complexes, and we studied the relationship of the structure and catalytic reactivity. In our previous study, we investigated the influence of the different substituents on NHC and different bridges between aryl-substituted imidazole-based di-NHC on the structure and reactivity.[10] To extend our work, we prepared a series of dipalladium complexes bearing alkyl (*tert*-butyl) substituted imidazole-based and benzimidazole-based di-NHC ligands bridged by different alkyl chain and investigated the influence of spacer lengths and electronic effect of NHC on solid structure and on the mono and double Heck reactions.

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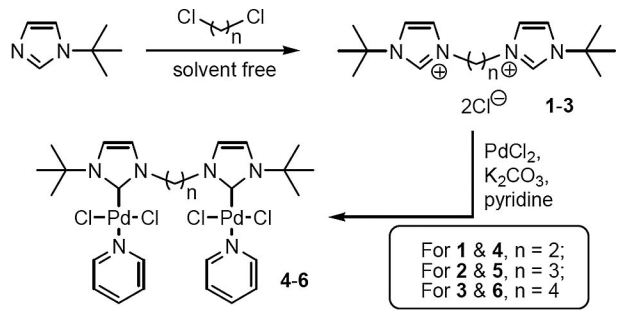
Results and Discussion

Synthesis of Imidazolium Salts

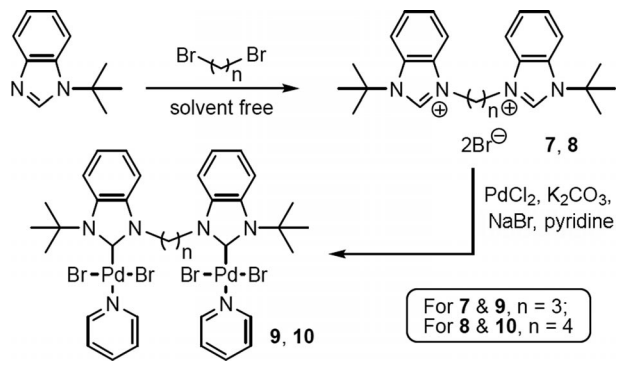
1-(*tert*-Butyl)imidazole was synthesized according to a literature procedure,[11] and 1-(*tert*-butyl)benzimidazole was prepared by substitution reaction of benzimidazole with *tert*-butyl bromide in basic conditions.[12] The bisimidazolium dichlorides **1**–**3** were prepared by the reaction of 1-*tert*-butylimidazole and the corresponding dichloroalkanes under neat conditions. The bisbenzimidazolium dibromides **7** and **8** were prepared by the reaction of 1-*tert*-butylbenzimidazole and the corresponding dibromoalkanes in 1,4-dioxane. The product identities were confirmed by ^{1}H and ^{13}C NMR and elemental analysis.

Synthesis and Characterization of NHC-Palladium Complexes (4–6, 9, and 10)

The synthesis of $(CH_2)_n$-linked (n = 2–4) imidazole-based di-NHC dipalladium complexes **4–6** was achieved by the procedure shown in Scheme 1. The reaction of **1–3** with one equiv. $PdCl_2$ in pyridine in the presence of K_2CO_3 as a base afforded complexes **4–6** in good yield. The synthesis of benzimidazole-based di-NHC dipalladium complexes **9** and **10** was similar to that of **4–6**, except that NaBr as bromide ion provider must be added to the reaction (Scheme 2). The completed exchange of chloride to bromide was detected with a large excess of NaBr. Unfortunately, the effort to make ethylene-bridged dipalladium complexes bearing the benzimidazole-based NHC ligand failed. Only $PdCl_2Py_2$ was formed and most of 1,1-di-*tert*-butyl-3,3-(1,3-ethylene)bisbenzimidazolium dibromides were recovered in this reaction, no matter if we increased the reaction temperature and reaction time. All of these complexes were characterized by NMR spectroscopy and gave satisfactory elemental analyses. The complexes are air and moisture stable and can be stored at air atmosphere for more than 6 months without any noticeable decomposition.



Scheme 1. Synthesis of compounds **1–6**.



Scheme 2. Synthesis of compounds **7–10**.

The proton signal of NC*H*N from the imidazolium salts was absent in the ^{1}H NMR of palladium complexes, confirming carbene generation. In addition, the ^{13}C NMR of palladium complexes provide direct evidence of the metalation of the ligand, as seen by the signal at ca. 151.4 to 158.2 ppm, which is assigned to the Pd–$C_{carbene}$. The resonance of carbene carbon in these C4–C5 unsaturated palladium complexes is significantly upfield compared to that in those C4–C5 saturated complexes (ca. 183 ppm),[13] which means that the carbene in unsaturated complexes is more electron rich than that in their saturated analogues.

The molecular structures of **4**, **6**, and **9** were determined by means of X-ray diffraction studies. The molecular diagrams of **4**, **6**, and **9** are shown in Figure 1, Figure 2, and Figure 3, respectively, and selected bond lengths and angles are given below the Figures. Interestingly, the solid-state structures of these complexes are very different. Complexes **4** and **6** show slightly distorted square-planar arrangements around two central palladium atoms, which are surrounded by imidazolylidene, two chloro ligands in a *trans* configuration, and one pyridine. In complex **4**, two pseudo-square-planar subunits bridged with ethylene are in a *cis* configuration with a torsion angle of –75.77° involving the backbone atoms N6–C1–C17–N1, however two subunits in **6**, bridged with butylenes, are in a *cis* configuration with a torsion angle of –28.50° involving the backbone atoms N1–C1–C1A–N1A. That means the two NHC-Pd-Py subunits in **4** are nearly perpendicular to each other, whereas they are nearly parallel to each other in **6**. The different environment in these two complexes is possibly due to different π–π stacking caused by different length of linker. For example, there is a face-to-face π–π stacking between two intramolecular imidzaole rings in **4**. The shortest atom-to-atom distance of two imidazole rings is 2.824 Å (e.g. distance of N3–N4) and the distance of centroids of the rings is 4.236 Å. However, there is a face-to-face π–π stacking between two intramolecular pyridine rings in **6**. The shortest atom-to-atom distance of two pyridine rings is 3.359 Å (e.g. distance of C10–C10A) and the distance of centroids of the rings is 3.678 Å.

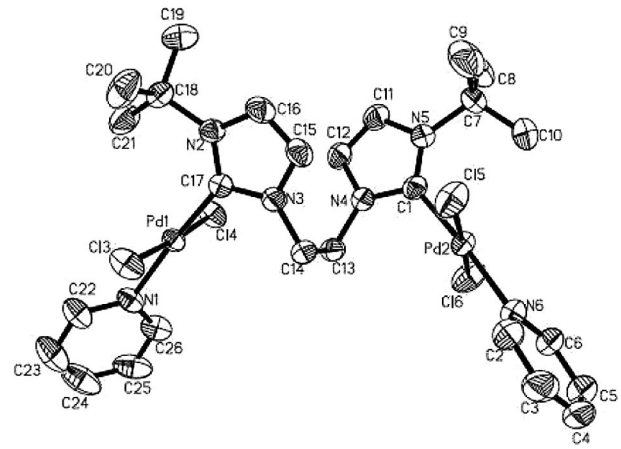


Figure 1. ORTEP structure of complex **4** with the probability ellipsoids drawn at the 50% level. Hydrogen atoms are omitted for clarity. Selected bond lengths /Å and angles /°: Pd1–C17 1.968(4), Pd1–N1 2.100(3), Pd1–Cl3 2.3138(11), Pd1–Cl4 2.3188(10), C17–Pd1–N1 175.46(14), C17–Pd1–Cl3 88.58(11), N1–Pd1–Cl3 90.76(9), C17–Pd1–Cl4 90.17(11), N1–Pd1–Cl4 90.74(9), Cl3–Pd1–Cl4 176.44(4); Pd2–C1 1.961(4), Pd2–N6 2.124(4), Pd2–Cl6 2.2970(12), Pd2–Cl5 2.3261(11), C1–Pd2–N6 175.52(15), C1–Pd2–Cl6 85.60(11), N6–Pd2–Cl6 92.23(11), C1–Pd2–Cl5 90.17(11), N6–Pd2–Cl5 91.99(11), Cl6–Pd2–Cl5 175.76(4).

Owing to the rotational freedom in the alkyl linking groups and lack of stronger intramolecular interaction in complex **9**, the two NHC-Pd-Py subunits are in *trans* configuration and are almost parallel to each other with a torsion angle of

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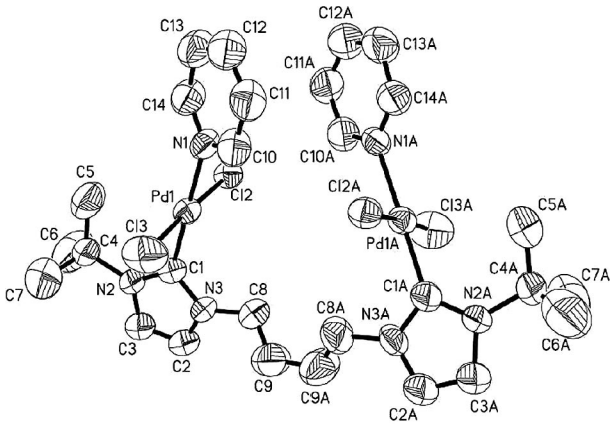


Figure 2. ORTEP structure of complex **6** with the probability ellipsoids drawn at the 50 % level. Hydrogen atoms are omitted for clarity. Selected bond lengths /Å and angles /°: Pd1–C1 1.956(9), Pd1–N1 2.095(7), Pd1–Cl1 2.311(2), Pd1–Cl2 2.301(2), C1–Pd1–N1 179.2(3), C1–Pd1–Cl2 88.6(3), N1–Pd1–Cl2 91.1(2), C1–Pd1–Cl1 90.1(3), N1–Pd1–Cl1 90.2(2), Cl2–Pd1–Cl1 177.07(10).

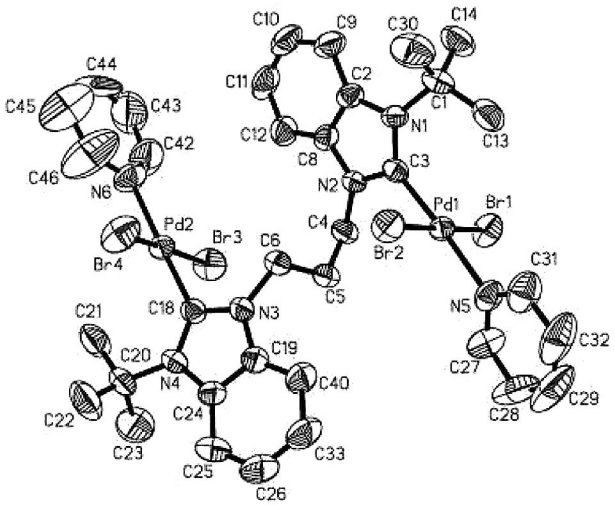


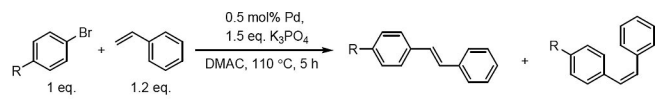
Figure 3. ORTEP structure of complex **9** with the probability ellipsoids drawn at the 50 % level. Hydrogen atoms are omitted for clarity. Selected bond lengths /Å and angles /°: C3–Pd1 1.969(4), Pd1–N5 2.090(4), Br1–Pd1 2.4396(9), Br2–Pd1 2.4498(9), C3–Pd1–N5 176.82(18), C3–Pd1–Br1 90.23(11), N5–Pd1–Br1 91.48(10), C3–Pd1–Br2 88.34(11), N5–Pd1–Br2 89.91(10), Br1–Pd1–Br2 178.26(2); Pd2–C18 1.966(4), N6–Pd2 2.227(18), Pd2–Br4 2.4268(8), Pd2–Br3 2.4510(9), C18–Pd2–N6 173.4(5), C18–Pd2–Br4 84.69(12), N6–Pd2–Br4 96.5(4), C18–Pd2–Br3 87.96(12), N6–Pd2–Br3 90.2(4), Br4–Pd2–Br3 171.30(2).

179.88° involving the backbone atoms N5–C3–C18–N6. Complex **9** shows slightly distorted square-planar arrangement around two central palladium atoms as well, which are surrounded by benzoimidazolylidene, two bromo ligands in a *trans* configuration, and one pyridine. The bond lengths of Pd–C are equivalent within the margin of error in these complexes. The same applies to the bonds of palladium nitrogen, palladium chloride, and palladium bromide. The Pd–$C_{carbene}$ distances are 1.968(4) Å and 1.961(4) Å for **4**; 1.956(9) Å for **6**; 1.969(4) Å and 1.966(4) Å for **9**, similar to that shown by other palladium-related species.[13] The Pd–$N_{pyridine}$ distances in complex **4** [2.100(3) Å and 2.124(4) Å], **6** [2.095(7) Å], and **9** [2.090(4) Å and 2.227(18) Å] are comparable to that of its related palladium carbene analogues,[14] however, the distance of Pd2–N6 in complex **9** is off the expected range due to the disorder of the pyridine ring. All other distances and angles lie in the expected range.

Catalytic Activity for Mizoroki–Heck Cross-Coupling Reaction

To evaluate the catalytic activity of **4**–**6**, **9**, and **10** in the mono-Heck cross-coupling, we performed the reaction of bromobenzene and 4-chloro bromobenzene with styrene in the presence of K_3PO_4 as base at 110 °C for 5 h with 0.5 mol% catalyst loading in an argon atmosphere. The results in Table 1 show that complex **4** is the one that provides the best activity and selectivity in both reactions, whereas, the other complexes show relatively low activity and poor selectivity. For example, 84 % yield of the monoarylation product with 12:1 of *E*/*Z* ratio was observed in the reaction of bromobenzene catalyzed by **4**, meanwhile, 93 % yield with 18:1 of *E*/*Z* ratio was observed in the reaction of 4-chloro bromobenzene. In addition, the better activity and selectivity over *E*/*Z* isomer of the imidazole-based NHC complex than that of its analogous benzimidazole-based NHC complex with the same spacer were observed.

Table 1. Monoarylation of styrene catalyzed by palladium complexes.

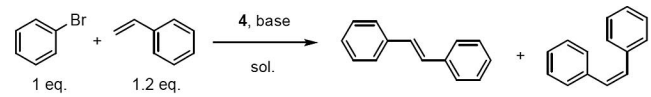


Entry[a]	Pd cat.	R	Yield[b]	E/Z
1	**4**	H	84	18:1
2	**5**	H	73	14:1
3	**6**	H	74	15:1
4	**9**	H	61	9.5:1
5	**10**	H	64	13:1
6	**4**	Cl	93	12:1
7	**5**	Cl	88	11:1
8	**6**	Cl	66	7.6:1
9	**9**	Cl	72	11:1
10	**10**	Cl	56	3:1

a) Reaction conditions: aryl bromide (1 mmol), styrene (1.2 mmol), and K_3PO_4 (1.5 mmol) in DMAC (1 mL). b) Isolated yield.

Further experiments were performed to investigate the effect of different solvents, bases, catalyst loadings, and temperatures with catalyst **4** (Table 2). The results show that among the bases employed, K_3PO_4 is the most suitable base. The relatively low yield was detected with other bases, like K_2CO_3, NaOAc, $NaHCO_3$, whereas the lowest yield (38 %) was observed with the organic base Et_3N. Furthermore, DMAC is the best solvent tested, and a relatively low yield was observed in 1,4-dioxane, DMF, and toluene. Only 30 % yield was observed in THF as solvent. The yield was decreased with less catalyst

Table 2. Monoarylation of styrene catalyzed by complex **4** under different conditions.



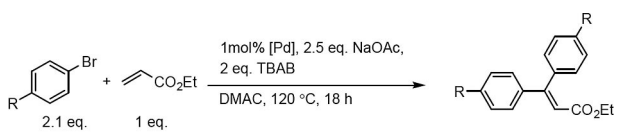
Entry[a]	Catalyst loading (mol%)	base	solvent	Temp (°C)	Time (h)	Yield[b]	E/Z
1	0.5	K_3PO_4	DMAC	110	5	84	18:1
2	0.5	K_2CO_3	DMAC	110	5	73	18:1
3	0.5	NaOAc	DMAC	110	5	67	18:1
4	0.5	Et_3N	DMAC	110	5	38	18:1
5	0.5	$NaHCO_3$	DMAC	110	5	69	18:1
6	0.5	K_3PO_4	1,4-dioxane	110	5	77	18:1
7	0.5	K_3PO_4	toluene	110	5	74	18:1
8	0.5	K_3PO_4	DMF	110	5	72	18:1
9	0.5	K_3PO_4	THF	110	5	30	18:1
10	0.3	K_3PO_4	DMAC	110	5	73	18:1
11	0.1	K_3PO_4	DMAC	110	5	71	18:1
12	0.05	K_3PO_4	DMAC	110	5	68	18:1
13	0.5	K_3PO_4	DMAC	100	4	52	18:1
14	0.5	K_3PO_4	DMAC	110	4	69	18:1
15	0.5	K_3PO_4	DMAC	120	4	83	18:1

a) Reaction conditions: phenyl bromide (1 mmol), styrene (1.2 mmol), and base (1.5 mmol) in solvent (1 mL). b) Isolated yield.

loading insignificantly and 68 % of yield was still tested with 0.05 mol-% of **4**. The good yield can be reached with either longer reaction time or higher reaction temperature. Form all the results showed herein, the *tert*-butyl-substituted imidazole-based NHC complex **4** bridged by ethylene was an effective mono-Heck reaction precatalyst, and good yield and selectivity was achieved in the shorter reaction time compared to the reported aryl-substituted imidazole-based NHC complexes.[10]

As some β,β-diaryl acrylates are valuable intermediates for the synthesis of natural products and pharmaceuticals, the development of an efficient catalyst for double coupling reaction of terminal acrylates would be of significant utility. We tried a one-pot synthesis of β,β-diaryl acrylates by the reaction of ethyl acrylate with bromobenzene and 4-chloro bromobenzene with higher catalyst loading (1 mol-%) in presence of NaOAc as base and TBAB as additive at 120 °C for 18 h (Table 3). To our delight, all complexes **4**–**10** allowed to form trisubstiuted olefins 2,2-diaryl acrylates in moderate to good yield, and no formation of 1,2-diaryl acrylates were observed in the reaction. Among these complexes, complex **4** is also the one that provides the best activity. For example, 88 % of diarylation product was obtained with bromobenzene, and 87 % product was achieved with chloro bromobenzene. However, mainly monoarylation product was formed in the reaction catalyzed by $Pd(OAc)_2$ and $PdCl_2$ under the same reaction conditions, only less than 10 % of diarylation product was observed. The activity of the imidazole-based complex is comparable to that of its analogous benzimidazole-based complex with the same spacer in most of tested reactions.

Table 3. Diarylation of ethyl acrylate catalyzed by palladium complexes.



Entry[a]	Pd cat.	R	Yield[b]
1	**4**	H	88
2	**5**	H	80
3	**6**	H	54
4	**9**	H	78
5	**10**	H	74
6	$Pd(OAc)_2$	H	5
7	$PdCl_2$	H	10
8	**4**	Cl	87
9	**5**	Cl	73
10	**6**	Cl	69
11	**7**	Cl	79
12	**8**	Cl	67

a) Reaction conditions: aryl bromide (2.1 mmol), ethyl acrylate (1 mmol), TBAB (2 mmol), and NaOAc (2.5 mmol) in DMAC (1 mL). b) Isolated yield.

From the catalytic results, we can see that in these complexes the length of the bridge plays a role in the catalytic

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activity. Complex **4** with the shortest bridge (ethylene group) between two NHCs gives the best result for both reactions. The reason for this might be that the two palladium atoms in complex **4** could function in a synergic manner in some way due to the short spacer, however, the two palladium atoms in complex **6** with a butylene bridge are too far away to have any synergic function due to the long spacer.

Conclusions

We have synthesized and characterized a series of highly stable di-NHC di-palladium complexes with different $(CH_2)_n$-linker. X-ray studies show that the length of linker affects the solid structure of these complexes and π–π stacking plays an important role for the configuration of NHC-Pd-Py subunits. The catalytic studies show that the length of linker affects the catalytic activity of these complexes as well. Imidazole-based complex **4** bearing the shortest ethylene bridge appears good activity and selectivity in both mono- and double-Heck coupling reactions.

Experimental Section

Materials and General Procedures: *Tert*-butyl imidazole,[11] imidazolium chloride (**1**), and complex **4** were prepared according to reported procedures.[10] Although *tert*-butyl benzimidazole was a known compound, the synthetic procedure was not available in literature. Therefore, the procedure was reported herein, and benzimidazole was synthesized by the procedure given as followed. All operations were performed in an inert atmosphere of argon using standard Schlenk-line or glovebox techniques. DMAC and pyridine were distilled from calcium hydride in an argon atmosphere. Potassium carbonate was ground to a fine powder prior to use. All other reagents were commercially available and were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker DPX 400 MHz spectrometer at room temperature and referenced to the residual signals of the solvent. Elemental analyses were performed with a EuroVektor Euro EA-300 elemental analyzer. GC-MS was performed with an Agilent 6890–5973N system with electron ionization (EI) mass spectrometry.

Synthesis of 1-(*tert*-Butyl)-1H-benzimidazole: Benzimidazole (1.181 g, 10 mmol), butyl bromide (3.425 g, 25 mmol), triethylamine (2.023 g, 20 mmol), and toluene (14 mL) were added into a pressure tube, and the mixture was heated at 120 °C for 48 h with stirring. After the mixture was cooled to room temperature, it was filtered through a plug of Celite and washed with DCM. The volatile was removed under vacuum, and the residue was purified by chromatography with DCM/ethanol = 8:1 to give the product as a yellow liquid (0.71 g, 41 %). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.02 (s, 1 H), 7.83–7.81 (m, 1 H), 7.65–7.63 (m, 1 H), 7.27–7.25 (m, 2 H), 1.76 (s, 9 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 145.0, 140.3, 132.6, 121.9, 121.3, 120.3, 112.9, 55.8, 29.0.

Synthesis of 1,1-Di-*tert*-butyl-3,3-(1,3-propylene)bisimidazolium Dichlorides (2): The synthesis of **2** was carried out in a similar way as that described for **1**, but 1,3-dichloropropane (0.224 g, 2 mmol) was used instead of 1,2-dichloroethane. Yield: 86 % (0.62 g), white solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 10.44 (s, 2 H, NC*H*N), 8.29 (s, 2 H, NC*H*), 7.25 (s, 2 H, NC*H*), 4.70 (t, *J* = 7.6 Hz, 4 H, CH_2), 2.97 (m, 2 H, CH_2), 1.68 (s, 18 H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 135.2, 123.8, 119.2, 59.9, 46.7, 31.0, 29.9. $C_{17}H_{30}Cl_2N_4$ (361.35 g·mol^{-1}): calcd. C 56.50; H 8.73; N 15.50 %; found: C 56.29; H 8.64; N 15.73 %.

Synthesis of 1,1-Di-*tert*-butyl-3,3-(1,4-butylene)bisimidazolium Dichlorides (3): The synthesis of **3** was carried out in a similar way as that described for **1**, but 1,3-dichlorobutane (0.254 g, 2 mmol) was used instead of 1,2-dichloroethane. Yield: 83 % (0.62 g), white solid. **^{1}H NMR** (400 MHz, D_2O): δ = 8.85 (s, 2 H, NC*H*N), 7.64 (s, 2 H, NC*H*), 7.46 (s, 2 H, NC*H*), 4.19 (s, 4 H, CH_2), 1.86 (s, 4 H, CH_2), 1.59(s, 18 H, CH_3). **^{13}C NMR** (100 MHz, D_2O-DMSO): δ = 134.2, 122.8, 120.9, 60.4, 49.3, 29.4, 26.9. $C_{18}H_{32}Cl_2N_4$ (375.38 g·mol^{-1}): calcd. C 57.59; H 8.59; N 14.93 %; found: C 57.33; H 8.46; N 15.11 %.

Synthesis of Complex 5: The synthesis of **5** was carried out in a similar way as that described for **4**, but **2** (0.361 g, 1 mmol) was used instead of **1**. Yield: 90 % (0.72 g), yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 9.00 (d, *J* = 5.2 Hz, 4 H, Py-*H*), 7.77 (t, *J* = 7.2 Hz, 2 H, Py-*H*), 7.36 (t, *J* = 6.8 Hz, 4 H, Py-*H*), 7.32 (s, 2 H, NC*H*), 6.95(s, 2 H, NC*H*), 5.01 (t, *J* = 6.4 Hz, 4 H, CH_2), 3.29–3.22 (m, 2 H, CH_2), 2.08 (s, 18 H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 151.4, 145.1, 138.0, 124.6, 122.2, 120.1, 59.0, 50.2, 32.2, 29.8. $C_{26}H_{36}Cl_4N_6Pd_2$ (801.28 g·mol^{-1}): calcd. C 40.47; H 4.78; N 10.49 %; found: C 40.25; H 4.63; N 10.61 %.

Synthesis of Complex 6: The synthesis of **6** was carried out in a similar way as that described for **4**, but **3** (0.374 g, 1 mmol) was used instead of **1**. Yield: 96 % (0.78 g), yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 9.00 (d, *J* = 5.2 Hz, 4 H, Py-*H*), 7.73 (t, *J* = 6.4 Hz, 2 H, Py-*H*), 7.34 (t, *J* = 6.8 Hz, 4 H, Py-*H*), 7.07 (s, 4 H, NC*H*), 4.95 (s, 4 H, CH_2), 2.37 (s, 4 H, CH_2), 2.09 (s, 18 H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 151.5, 145.6, 137.9, 124.6, 121.4, 120.4, 59.1, 51.7, 32.2, 27.2. $C_{28}H_{40}Cl_4N_6Pd_2$ (815.31 g·mol^{-1}): calcd. C 41.25; H 4.95; N 10.31 %; found: C 41.02; H 4.79; N 10.48 %. Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of toluene into DCM saturated solution at room temperature.

Synthesis of 1,1-Di-*tert*-butyl-3,3-(1,3-propylene)bisbenzimidazolium Dibromides (7): A mixture of 1-(tert-butyl)benzimidazole (0.696 g, 4 mmol), 1,3-dibromopropane (0.403 g, 2 mmol), and 1,4-dioxane (3 mL) was put in a pressure tube with a magnetic bar. The reaction was heated at 110 °C for 12 h. After the mixture was cooled to room temperature, it was washed with diethyl ether (10 mL) with ultrasonication for 20 min. The solid was filtered and washed with diethyl ether (10 mL) to give the product as a white solid. Yield: 92 % (1.0 g). **^{1}H NMR** (400 MHz, D_2O): δ = 9.25 (s, 2 H, NC*H*N), 8.04 (d, *J* = 8.0 Hz, 2 H, Ph-*H*), 7.90 (d, *J* = 8.0 Hz, 2 H, Ph-*H*), 7.71–7.63 (m, 4 H, Ph-*H*), 3.31 (s, 4 H, CH_2), 2.97–2.91 (m, 2 H, CH_2), 1.55 (s, 18 H, CH_3). **^{13}C NMR** (100 MHz, D_2O-DMSO): δ = 139.8, 132.7, 130.6, 127.8, 127.5, 117.3, 113.7, 67.2, 61.9, 45.7, 28.5. $C_{25}H_{34}Br_2N_4$ (550.37 g·mol^{-1}): calcd. C 54.56; H 6.23; N 10.18 %; found: C 54.45; H 6.11; N 10.29 %.

Synthesis of 1,1-Di-*tert*-butyl-3,3-(1,3-butylene)bisbenzimidazolium Dibromides (8): The synthesis of **8** was carried out in a similar way as that described for **7**, but 1,4-dibromobutane (0.431 g, 2 mmol) was used instead of 1,3-dibromopropane. Yield: 86 % (0.97 g), white solid. **^{1}H NMR** (400 MHz, D_2O): δ = 9.24 (s, 2 H, NC*H*N), 8.02 (d, *J* = 8.4 Hz, 2 H, Ph-*H*), 7.60 (d, *J* = 8.4 Hz, 2 H, Ph-*H*), 7.53–7.49 (m, 2 H, Ph-*H*), 7.45–7.41 (m, 2 H, Ph-*H*), 4.46 (s, 4 H, CH_2), 1.92 (s, 4 H, CH_2), 1.75 (s, 18 H, CH_3). **^{13}C NMR** (100 MHz, D_2O-DMSO): δ = 140.0, 132.4, 131.0, 127.2, 127.1, 117.0, 113.5, 61.8, 46.9, 28.7, 25.3. $C_{26}H_{36}Br_2N_4$ (560.40 g·mol^{-1}): calcd. C 55.33; H 6.43; N 9.93 %; found: C 55.17; H 6.34; N 10.05 %.

Synthesis of Complex 9: To an oven-dried solution of **7** (0.548 g, 1 mmol) in toluene (25 mL), $PdCl_2$ (0.354 g, 2.0 mmol), and K_2CO_3 (2.763 g, 20 mmol) and NaBr (2.057 g, 20 mmol), pyridine (10 mL) was injected through a septum in an argon atmosphere. The reaction mixture was stirred at 80 °C for 12 h. After cooling to room temperature, the mixture was filtered through a plug of Celite and washed by DCM. After the volatile was removed in a vacuum, the solid was recrystallized by DCM/diethyl ether to give **9** as a yellow solid. Yield: 91 % (0.98 g). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 9.12 (d, J = 4.8 Hz, 4 H, Py-*H*), 7.83–7.75 (m, 4 H, Py-*H*), 7.67 (d, J = 8.0 Hz, 2 H, Py-*H*), 7.40 (t, J = 6.8 Hz, 4 H, Ph-*H*), 7.19–7.16 (m, 4 H, Ph-*H*), 5.57 (t, J = 8.0 Hz, 4 H, CH_2), 3.16 (m, 2 H, CH_2), 2.36 (s, 18 H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 158.2, 152.9, 138.0, 134.9, 134.5, 124.9, 123.2, 122.3, 114.5, 111.7, 60.3, 48.5, 31.6, 28.0. $C_{35}H_{42}Br_4N_6Pd_2$ (1079.20 g·mol^{-1}): calcd. C 38.95; H 3.92; N 7.79 %; found: C 38.81; H 3.83; N 7.85 %. Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of toluene into DCM saturated solution at room temperature.

Synthesis of Complex 10: The synthesis of **10** was carried out in the same way as that described for **9**, but **8** (0.562 g, 1 mmol) was used instead of **7**. Yield: 90 % (0.99 g). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 9.06 (d, J = 5.2 Hz, 4 H, Py-*H*), 7.72–7.67 (m, 4 H, Py-*H*), 7.53–7.51 (m, 2 H, Py-*H*), 7.34–7.30 (m, 4 H, Ph-*H*), 7.23–7.19 (m, 4 H, Ph-*H*), 5.35 (s, 4 H, CH_2), 2.63 (s, 4 H, CH_2), 2.37 (s, 18 H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 152.9, 152.4, 137.7, 135.2, 134.4, 124.8, 122.9, 122.1, 114.8, 110.9, 60.2, 49.9, 31.6, 26.2. $C_{36}H_{44}Br_4N_6Pd_2$ (1093.23 g·mol^{-1}): calcd. C 39.55; H 4.06; N 7.69 %; found: C 39.42; H 4.01; N 7.74 %.

Procedure for the Mono-Heck Coupling Reaction: In a typical run, a 5 mL vial equipped with a magnetic bar was charged with a mixture of aryl bromide (1 mmol), styrene (1.2 mmol), Pd catalyst (0.005 mmol), K_3PO_4 (1.5 mmol), and 1 mL of DMAC in an argon atmosphere. The reaction was heated at 110 °C for 5 h. Afterwards the mixture was cooled to room temperature and brine was added into it. The resulting mixture was extracted with ethyl acetate for 3 times, and the crude was obtained by removing volatile. The product was purified by flash column chromatography on silica gel.

Procedure for the Double-Heck Coupling Reaction: In a typical run, a 5 mL vial equipped with a magnetic bar was charged with a mixture of aryl bromide (2.1 mmol), ethyl acrylate (1 mmol), Pd catalyst (0.01 mmol), TBAB (2 mmol), NaOAc (2.5 mmol), and 1 mL of DMAC in an argon atmosphere. The reaction was heated at 120 °C for 18 h. Afterwards the mixture was cooled to room temperature and brine was added into it. The resulting mixture was extracted with ethyl acetate for 3 times, and the crude was obtained by removing volatile. The product was purified by flash column chromatography on silica gel.

X-ray Crystallography: Intensity data were collected with a Rigaku Mercury CCD area detector in ω scan mode by using Mo-K_α radiation (λ = 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.[15] 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 crystallographic data for compounds **4**, **6**, and **9** are shown in Table 4. Crystals of complex **4** suitable for X-ray diffraction analysis were obtained by slow evaporation of a DCM saturated solution at room temperature.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic

Table 4. Crystallographic data for complexes **4**, **6**, and **9**.

	4	**6**	**9**
Expirical formula	$C_{26}H_{36}Cl_4N_6Pd_2$	$C_{28}H_{40}Cl_4N_6Pd_2$	$C_{35}H_{42}Br_4N_6Pd_2$
Formula weight	787.21	815.26	1079.19
Temperature /K	296(2)	293(2)	293(2)
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/c$	*Pbcn*	$P2_1/c$
Crystal size /mm	0.49 × 0.42 × 0.37	0.49 × 0.42 × 0.37	0.21 × 0.18 × 0.16
a /Å	24.4190(14)	20.917(3)	18.713(4)
b /Å	9.0757(5)	12.3705(19)	12.173(2)
c /Å	14.2019(8)	13.6330(16)	18.251(4)
α /°	90.00	90.00	90.00
β /°	93.421(2)	90.00	106.41(3)
γ /°	90.00	90.00	90.00
V /Å^3	3141.8(3)	3527.6(8)	3988.1(14)
Z	4	4	4
D_{calcd} ./mg·cm^{-3}	1.664	1.535	1.797
Absorption coefficient /mm^{-1}	1.551	1.349	4.941
F(000)	1576	1640	2104
θ range /°	0.84–25.20	1.91–25.20	3.22–25.40
Reflections collected / unique	35615 / 5642 [*R*(int) = 0.0266]	9146 / 3097 [*R*(int) = 0.0455]	31790 / 7338 [*R*(int) = 0.0425]
Data / restrains / parameteres	5642 / 0 / 343	3097 / 211 / 181	7338 / 24 / 479
Goodness-of-fit on F_2	1.087	1.008	1.033
Final *R* indices [$I>2\sigma$ (*I*)]	R_1 = 0.0261	R_1 = 0.0597	R_1 = 0.0333
	wR_2 = 0.0997	wR_2 = 0.1784	wR_2 = 0.0740
R indices (all data)	R_1 = 0.0354	R_1 = 0.0794	R_1 = 0.0499
	wR_2 = 0.1282	wR_2 = 0.1932	wR_2 = 0.798

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-892532 (**4**), CCDC-892533 (**6**), and CCDC-892534 (**9**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

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