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Piperazine- and DABCO-bridged dinuclear *N*-heterocyclic carbene palladium complexes: synthesis, structure and application to Hiyama coupling reaction

Haozhen Wang and Jin Yang*

Four dinuclear *N*-heterocyclic carbene (NHC) palladium complexes were prepared by reaction of imidazolinium salts, $PdCl_2$ and bridging ligands (piperazine and DABCO) in one pot or by direct cleavage of the chloro-bridged dimeric compounds $[Pd(\mu\text{-}Cl)(Cl)(NHC)]_2$ with bridging ligands. All of the complexes were fully characterized using ^1H NMR, ^{13}C NMR, high-resolution mass and infrared spectroscopies, elemental analysis and single-crystal X-ray diffraction. The catalytic activities of the obtained palladium catalysts towards Hiyama coupling of aryl chlorides with phenyltrimethoxysilane were investigated and the results showed that the dinuclear palladium complexes were considerably active for the coupling reaction. Copyright © 2016 John Wiley & Sons, Ltd.

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Keywords: *N*-heterocyclic carbene; palladium; dinuclear complexes; Hiyama coupling

Introduction

Since the first successful isolation of a stable carbene by Arguengo *et al.* in 1991, *N*-heterocyclic carbenes (NHCs) and their palladium complexes have attracted considerable attention due to their high catalytic activity in organic transformations including C–C and C–N coupling reactions.[1,2] One of the most efficient NHC–Pd catalysts is $(NHC)PdCl_2$(3-chloropyridine) (Pd-PEPPSI-(NHC), PEPPSI = pyridine, enhanced, precatalyst, preparation, stabilization and initiation), which was first reported by Organ's group in 2006.[3] In a typical NHC–Pd-catalyzed C–C coupling reaction, the role of NHC has been recognized as a strong electron donor assisting initial reduction and oxidative addition, and the steric bulkiness increasing the rate of reductive elimination. However, the bulky NHC ligand may also hinder the coordination of the substrate to the metal center, thus decreasing the catalytic activity.[4] In order to improve the activity of NHC–Pd complexes, an external hemilabile donor is incorporated to the Pd center. In Pd-PEPPSI-(NHC) catalyst, 3-chloropyridine allows for efficient stabilization of the NHC–Pd, while in the catalytic process the Pd center could lose the additional donor, opening up free coordination site for incoming substrate. Following the success of Pd-PEPPSI-(NHC) in Pd-catalyzed coupling reactions, a series of modified NHC–Pd complexes have been developed and applied in organic reactions.[5] Although the catalytic activity of NHC–Pd is mainly dependent on the electronic property and steric hindrance of NHC, the ancillary ligands also play an important role in the catalytic process. For example, Organ and co-workers reported that $(NHC)PdCl_2$(pyridine) were more active than their 3-chloropyridine analogues, due to either a higher dissociation rate of pyridine or a higher tendency to re-coordinate to [(NHC)Pd(0)] species.[6] Based on this, other types of N-donors have received attention and been introduced into the coordination with NHC–Pd complexes, including triethylamine,[7] diethylamine,[8] 1-methylimidazole,[9] 2-phenyl-4,5-dihydrooxazole,[10] morpholine,[11] 2-phenylimidazole,[12] acetonitrile,[13] benzoxazole (benzothiazole),[14] (iso)quinoline,[15] 1-methylpyrazole (1-methylindazole),[16] etc. All of them have shown promising catalytic activity in organic transformations.

Despite the excellent progress made so far in mononuclear NHC–Pd complexes, the properties of bridging ligand-stabilized dinuclear complexes are less studied. A suitable bridging ligand could effectively conjoin two NHC–Pd units to form a dinuclear complex and provide a model to test the catalytic activity of multi-metallic catalytic sites.[17] We have recently reported pyrazine- and DABCO-bridged dinuclear NHC–Pd complexes based on unsaturated imidazol-2-ylidene ligands as well as their application in the Hiyama coupling reaction.[17] Encouraged by the results mentioned above and also in continuation of our efforts in the development of NHC–Pd complexes, herein we present facile synthesis and characterization of dinuclear NHC–Pd complexes based on saturated imidazolidin-2-ylidene ligands through reaction of imidazolinium salt, $PdCl_2$ and bridging ligands (piperazine and DABCO) in one pot with a simple tandem procedure. Furthermore, the dinuclear NHC–Pd complexes could also be

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obtained by direct cleavage of $[Pd(\mu\text{-Cl})(Cl)(NHC)]_2$ with piperazine or DABCO (Scheme 1). The application of the resulting dinuclear complexes in Hiyama coupling reactions of aryl chlorides with phenyltrimethoxysilane was investigated.

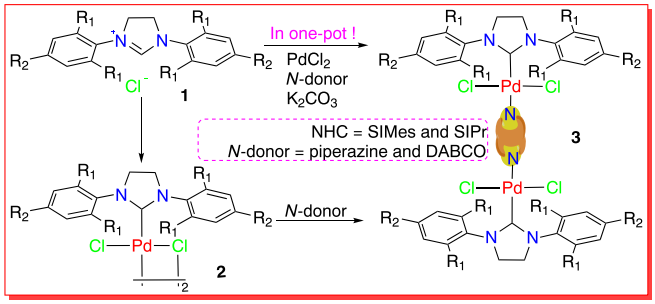
Results and Discussion

Synthesis and Characterization of NHC–Pd Complexes

According to the method reported in the literature,[17] the synthesis of the dinuclear NHC–Pd complexes is easily done in one pot from imidazolinium salts, $PdCl_2$ and bridging ligands (piperazine and DABCO) in tetrahydrofuran (THF) at reflux. The expected dinuclear complexes **3a**–**3d** are isolated in good yields (74–82%) after purification. In addition, the imidazolinium salts can be converted to chloro-bridged dimeric compounds $[Pd(\mu\text{-Cl})(Cl)(NHC)]_2$ under mild conditions, and $[Pd(\mu\text{-Cl})(Cl)(NHC)]_2$ are then readily cleaved with piperazine or DABCO to provide the dinuclear complexes **3a**–**3d** in excellent yields (90–95%). All complexes are isolated as yellow, air-stable solids and fully characterized using ^1H NMR and ^{13}C NMR spectroscopy, high-resolution mass spectrometry (HR-MS), elemental analysis, Fourier transform infrared (FT-IR) spectroscopy and X-ray crystallography. The formation of the dinuclear complexes is evident from the distinctive stoichiometric proton signal resonances of the NHCs with bridging ligands. In addition, the chemical shifts of the diagnostic Pd–$C_{carbene}$ peaks which appear in the range 184.6–187.9 ppm in ^{13}C NMR spectra are compared with the ^{13}C NMR signals of $C_{carbene}$ in NHC–Pd analogues. Moreover, their formation is confirmed by HR-MS analysis where exclusive signals are observed for their respective $[M + H]^+$ fragments.

Crystal Structures

The X-ray analysis of single crystals reveals the structure of the obtained complexes. The five-membered ring topology of the saturated NHCs varies prominently for different complexes with the absolute values of the N–C–C–N dihedral angles being in the range 13.02–22.64°. The crystal analysis of **3a**–**3d** shows dinuclear structures with N-donors bridging across two NHC–Pd units. As shown in Figs 1 and 2, complexes **3a** and **3b** have similar compositions and structures, each Pd center being surrounded by an imidazolidene, a nitrogen atom from piperazine, and two chloro ligands in a slightly distorted square planar geometry. The two $PdCNCl_2$ coordination planes, which adopt coplanar arrangements, are oriented approximately perpendicularly to the carbene ring planes with dihedral angles of 71.81° and 69.01°, respectively. The piperazine with chair conformation combines two NHC–Pd units



Scheme 1. Overview the preparation of the dinuclear NHC–Pd complexes **3a**–**3d**.

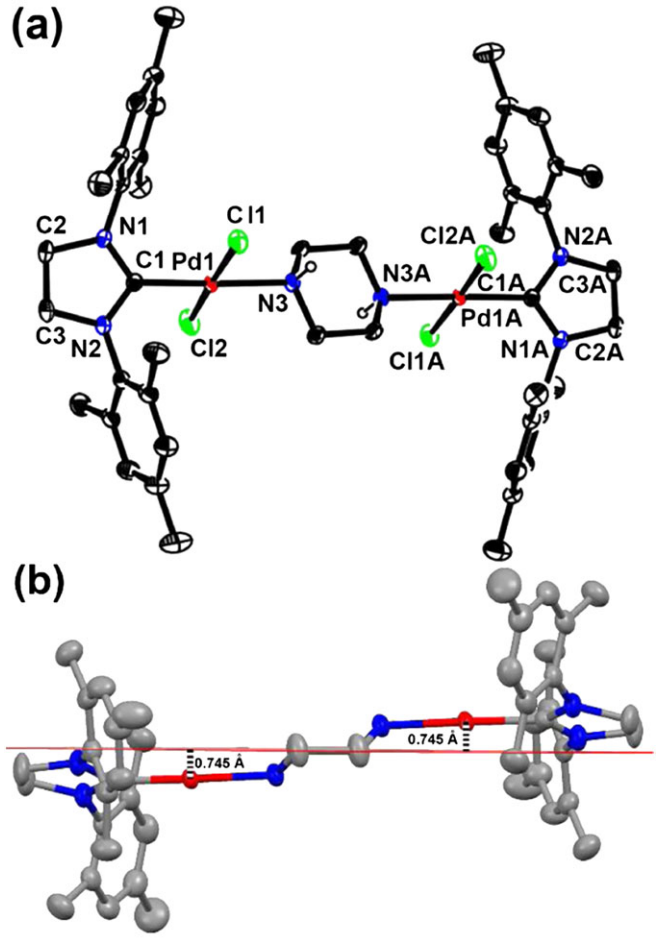


Figure 1. (a) ORTEP diagram of **3a** with thermal displacement parameters drawn at 30% probability. Hydrogen atoms and solvent molecules (CH_2Cl_2) have been omitted for clarity. Symmetry codes: A, $1 - x$, $1 - y$, $2 - z$. (b) Perspective view of **3a** showing the distance between the Pd atoms and the plane defined by the carbon atoms of piperazine.

and the Pd centers out of the plane defined by the carbon atoms of piperazine with distances of 0.745 and 0.573 Å, respectively. As usual in NHC-bearing complexes, Pd–$C_{carbene}$ distances fall in the range of a single bond (1.965(2) Å for **3a** and 1.964(6) Å for **3b**), which are slightly shorter than in the typical Pd-PEPPSI-(NHC) (1.990(3) Å for SIPr-$PdCl_2$(3-chloropyridine)].[7] The Pd–N bonds amounting to 2.125(2)–2.126(7) Å are in the range similar to that found for other N-donor-stabilized NHC–Pd analogues. The crystal structures of **3c** and **3d** (Figs 3 and 4) confirm dinuclear structures which are bridged by DABCO. All of the Pd centers possess square planar geometries and the NHC ligands occupy the *trans* position to DABCO. The dihedral angles between the $PdCNCl_2$ coordination planes and carbene rings range from 71.07° to 75.21°, being slightly larger than those in **3a** and **3b**. The Pd–$C_{carbene}$ bonds (about 1.97 Å) are slightly longer than those in **3a** and **3b**, but are slightly shorter than in SIPr-$PdCl_2$-(3-chloropyridine). The Pd–N bond lengths around the Pd centers are similar and compare well to those of related NHC–Pd complexes with N-donors.

Hiyama Coupling of Phenyltrimethoxysilane with Aryl Chlorides

As one of the most convenient methods to create C–C bonds, Hiyama coupling has been widely applied in organic synthesis.

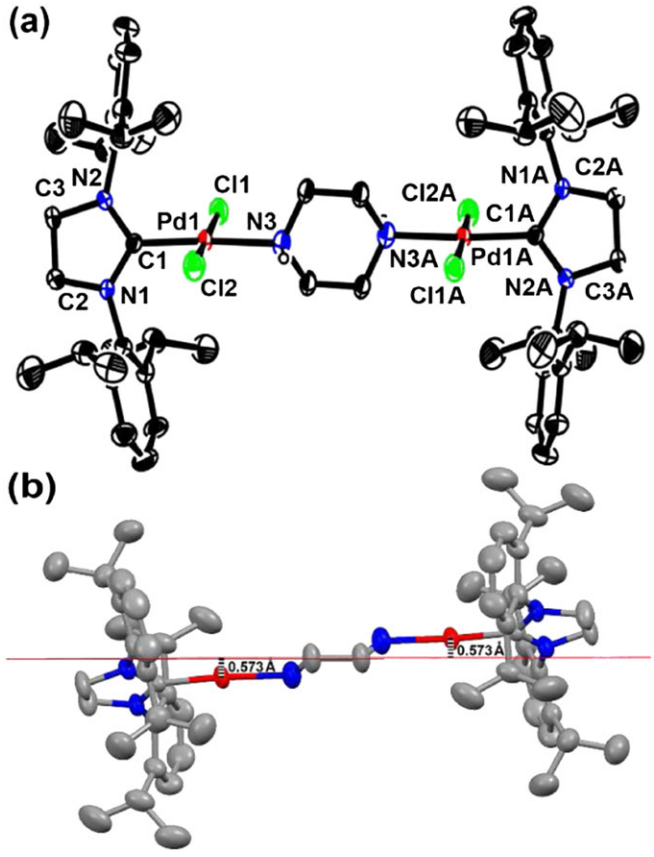


Figure 2. (a) ORTEP diagram of **3b** with thermal displacement parameters drawn at 30% probability. Hydrogen atoms and solvent molecules (CH_2Cl_2) have been omitted for clarity. Symmetry codes: A, $2-x, -y, 2-z$. (b) Perspective view of **3b** showing the distance between the Pd atoms and the plane defined by the carbon atoms of piperazine.

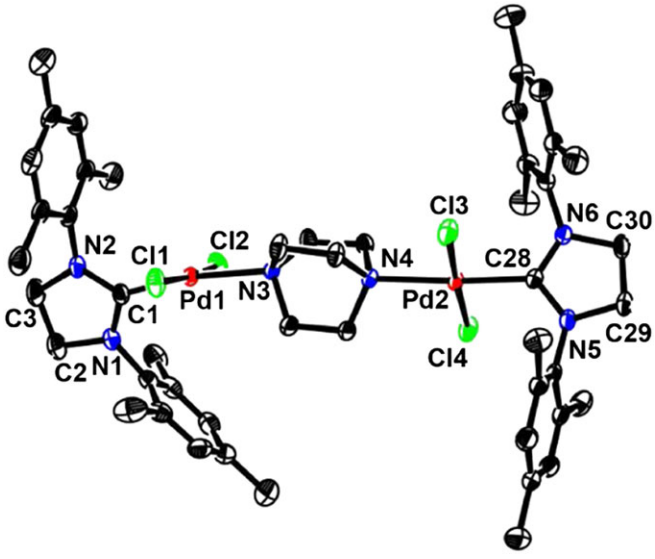


Figure 3. ORTEP diagram of **3c** with thermal displacement parameters drawn at 30% probability. Hydrogen atoms and solvent molecules (CH_2Cl_2) have been omitted for clarity.

Generally, aryl iodides and bromides have been extensively used in the reaction; the application of aryl chlorides has recently attracted much attention because of their low cost and wide availability.[18] Moreover, only a handful of examples of Hiyama coupling-based NHC–Pd catalysts have been reported.[19] To test the catalytic properties of **3a**–**3d**, the coupling of 4-chloroanisole with phenyltrimethoxysilane was chosen as a model reaction (Table 1, entries 1–4). It is found that in the presence of 0.25 mol% of the complexes with *n*-Bu_4NF as the base in toluene at 110°C, the corresponding biaryl product is isolated in high yield after 8 h. However, a reduction in the catalyst loading from 0.25 to 0.125 mol% leads to decreased yields (entries 5–6). Complexes **3b** and **3d** show higher catalytic activities than **3a** and **3c**. The different yields among **3a**–**3d** are possible due to the different steric hindrance of the NHC ligands. The sterically bulky ligand (*N*,*N*′-bis(2,6-di(isopropyl)phenyl)imidazolidin-2-ylidene) displays a higher conversion to product.

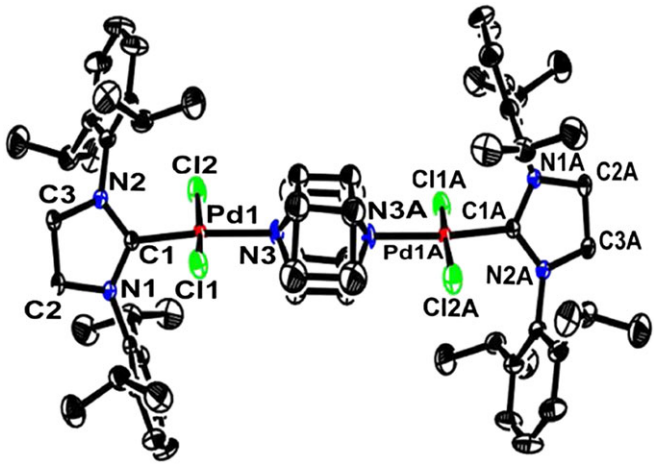
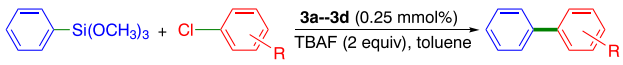


Figure 4. ORTEP diagram of **3d** with thermal displacement parameters drawn at 30% probability. Hydrogen atoms have been omitted for clarity. Symmetry codes: A, $1-x, 1-y, -z$.

Then some other aryl chlorides were subjected to the reaction according to the conditions described above. Generally, most of the coupling reactions proceed efficiently to provide the biaryl products in good yields. Substrates with electron-withdrawing group such as nitro group (entries 7–10) and acetyl group (entries 11–14) are easily coupled with phenyltrimethoxysilane. In addition, 3-chloroanisole and 2-chloroanisole are also tolerated under these conditions and moderate to good yields are achieved. For other aryl chlorides, chlorobenzene and 4-chlorotoluene were tolerated in this condition and moderate yields were obtained.

Finally, a comparison of the catalytic activities between the complexes **3c** and **3d** and some well-defined NHC–Pd complexes was investigated. Under the same conditions, the coupling of phenyltrimethoxysilane with 4-chloroanisole was carried out. As evident from Table 2, the catalytic activities of the dinuclear complexes **3c** and **3d** are similar to those of the unsaturated analogues $[(IMes)PdCl_2]_2(\mu\text{-DABCO})$ and $[(IPr)PdCl_2]_2(\mu\text{-DABCO})$ and slightly better than that of the dimer $[Pd(\mu\text{-Cl})(Cl)(SIPr)]_2$. But compared with the mononuclear PEPPSI catalysts $(IPr)PdCl_2$(3-chloropyridine) and $(SIPr)PdCl_2$(3-chloropyridine), the dinuclear complexes do not display outstanding superiority in catalyst amount and reaction activity under the same amount of metal loading. The reason may be that the distance between the two palladium centers is so large that the dinuclear complexes cannot form effective cooperative interactions. Other factors such as the stability of complexes also have an influence on the catalytic activity.

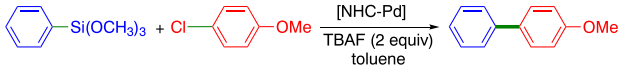
Table 1. Hiyama coupling of aryl chlorides with phenyltrimethoxysilane catalyzed by **3a–3d**[a]



Entry	Catalyst	Aryl chloride	Yield (%)[b]
1	**3a**	R = 4-OMe	78
2	**3b**	R = 4-OMe	85
3	**3c**	R = 4-OMe	80
4	**3d**	R = 4-OMe	85
5[c]	**3b**	R = 4-OMe	45
6[c]	**3d**	R = 4-OMe	36
7	**3a**	R = 4-NO_2	82
8	**3b**	R = 4-NO_2	88
9	**3c**	R = 4-NO_2	80
10	**3d**	R = 4-NO_2	87
11	**3a**	R = 4-$COCH_3$	83
12	**3b**	R = 4-$COCH_3$	85
13	**3c**	R = 4-$COCH_3$	85
14	**3d**	R = 4-$COCH_3$	87
15	**3a**	R = 3-OMe	75
16	**3b**	R = 3-OMe	80
17	**3c**	R = 3-OMe	78
18	**3d**	R = 3-OMe	83
19	**3a**	R = 2-OMe	70
20	**3b**	R = 2-OMe	75
21	**3c**	R = 2-OMe	68
22	**3d**	R = 2-OMe	77
23	**3a**	R = H	62
24	**3b**	R = H	70
25	**3c**	R = H	65
26	**3d**	R = H	72
27	**3a**	R = 4-CH_3	63
28	**3b**	R = 4-CH_3	72
29	**3c**	R = 4-CH_3	68
30	**3d**	R = 4-CH_3	68

[a]Reaction conditions: aryl chloride (0.50 mmol), phenyltrimethoxysilane (0.60 mmol), Pd complex (0.00125 mmol), *n*-Bu_4NF (1.0 mmol) in toluene (2.0 ml) at 110°C for 8 h.
[b]Isolated yield.
[c]0.125 mol% of [Pd] catalyst was used.

Table 2. Hiyama coupling of 4-chloroanisole with phenyltrimethoxysilane catalyzed by NHC–Pd catalysts[a]



Entry	Catalyst	Pd complex (%)	Yield (%)[b]
1	**3c**	0.25	80
2	**3d**	0.25	85
3	[(IMes)$PdCl_2]_2$(μ-DABCO)	0.25	78
4	[(IPr)$PdCl_2]_2$(μ-DABCO)	0.25	84
5	(IPr)$PdCl_2$(3-chloropyridine)	0.5	86
6	(SIPr)$PdCl_2$(3-chloropyridine)	0.5	88
7	[Pd(μ-Cl)(Cl)(SIPr)]$_2$	0.25	68

[a]Reaction conditions: aryl chloride (0.50 mmol), phenyltrimethoxysilane (0.60 mmol), Pd complex (0.25–0.5 mol%), *n*-Bu_4NF (1.0 mmol) in toluene (2.0 ml) at 110°C for 8 h.
[b]Isolated yield.

Conclusions

In summary, four new dinuclear NHC–Pd complexes bridged by piperazine or DABCO have been conveniently synthesized and fully characterized. These complexes have been utilized as catalysts for Hiyama coupling of aryl chlorides with phenyltrimethoxysilane to produce biaryl products. The results demonstrate that these complexes show good catalytic activity and tolerance to various chemical functions. Further modification of the NHC–Pd complexes and their application are in progress in our laboratory.

Experimental

General Remarks

The chemicals were purchased from commercial suppliers and were used without purification prior to use unless otherwise indicated. NMR spectra were recorded at 400 MHz (for ^{1}H NMR) and 100 MHz (for ^{13}C NMR) with a Bruker Avance 400 NMR spectrometer. ^{1}H NMR and ^{13}C NMR spectroscopy was performed with samples in $CDCl_3$ with tetramethylsilane as an internal standard. HR-MS was conducted with an Agilent 6550 iFunnel Q-TOF MS system. FT-IR spectra were recorded with a Bruker IFS 120HR spectrometer using KBr discs. The C, H and N analyses were performed with a Vario EL III Elementar. Flash column chromatography was carried out using 300–400 mesh silica gel. The chloro-bridged dimeric compounds [Pd(μ-Cl)(Cl)(NHC)]$_2$ were prepared according to the literature.[20]

General Procedure for Synthesis of Complexes 3a–3d

Procedure 1

A mixture of imidazolinium chloride (0.24 mmol), $PdCl_2$ (0.2 mmol), K_2CO_3 (0.3 mmol) and piperazine or DABCO (0.12 mmol) was stirred in anhydrous THF (10.0 mL) under reflux for 12 h. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel (hexane–CH_2Cl_2) to afford the corresponding dinuclear NHC–Pd complexes **3a**–**3d** as yellow solids.

Procedure 2

A mixture of dimeric compound [Pd(μ-Cl)(Cl)(NHC)]$_2$ (0.10 mmol) and the bridging ligand (piperazine or DABCO) (0.10 mmol) was dissolved in CH_2Cl_2 (10.0 ml) and stirred at room temperature for 12 h. The reaction mixture was then filtered over Celite and the solvent was reduced under reduced pressure. The resulting residue was washed with ether to give the corresponding dinuclear NHC–Pd complexes **3a**–**3d**. A single crystal for X-ray diffraction was obtained by recrystallization from CH_2Cl_2 and *n*-hexane.

*Complex **3a***

Yield 78 mg, 74% (Procedure 1); 97 mg, 92% (Procedure 2). Decomposition temperature > 247°C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 6.95 (s, 8H, *m*-ArH), 4.12 (q, J = 7.2 Hz, 2H, piperazine-NH), 3.92 (s, 8H, NCH_2CH_2N, imidazolidine), 2.52–2.47 (m, 4H, $HNCH_2CH_2NH$, piperazine), 2.44 (s, 24H, *o*-CH_3), 2.31 (s, 12H, *p*-CH_3), 2.28–2.25 (m, 4H, $HNCH_2CH_2NH$, piperazine). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 185.9 ($C_{carbene}$), 138.2 (*o*-C_{Ar}), 137.0 (N-C_{Ar}), 134.8 (*p*-C_{Ar}), 129.3 (*m*-C_{Ar}), 50.9 (NCH_2CH_2N, imidazolidine), 46.8 ($HNCH_2CH_2NH$, piperazine), 21.0 (*p*-CH_3), 19.0 (*o*-CH_3). FT-IR (KBr, cm^{-1}): 3179, 2916, 1606, 1493, 1453, 1380, 1308, 1270, 1085, 913, 885, 855. HR-

MS (ESI): calcd for $C_{46}H_{63}Cl_4N_6Pd_2$ $[M + H]^+$ 1055.1913; found 1055.1948. Anal. Calcd for $[PdCl_2Mes]_2(\mu$-piperazine) ($C_{46}H_{62}Cl_4N_6Pd_2$) (%): C, 52.43; H, 5.93; N, 7.98. Found (%): C, 52.62; H, 5.60; N, 8.12.

Complex ***3b***

Yield 95 mg, 78% (Procedure 1); 116 mg, 95% (Procedure 2). Decomposition temperature > 282°C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.38 (t, J = 7.6 Hz, 4H, *p*-ArH), 7.24 (d, J = 7.6 Hz, 8H, *m*-ArH), 3.97 (s, 8H, NCH_2CH_2N, imidazolidine), 3.39 (sept, J = 6.8 Hz, 8H, $CH(CH_3)_2$), 2.57–2.51 (m, 4H, $HNCH_2CH_2NH$, piperazine), 2.29–2.14 (m, 4H, $HNCH_2CH_2NH$, piperazine), 2.14 (br, 2H, piperazine-NH), 1.44 (d, J = 6.4 Hz, 24H, $CH(CH_3)_2$), 1.20 (d, J = 6.8 Hz, 24H, $CH(CH_3)_2$). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 187.9 ($C_{carbene}$), 147.5 (*o*-C_{Ar}), 135.2 (N-C_{Ar}), 129.3 (*p*-C_{Ar}), 124.2 (*m*-C_{Ar}), 53.6 (NCH_2CH_2N, imidazolidine), 46.9 ($HNCH_2CH_2NH$, piperazine), 28.6 ($CH(CH_3)_2$), 26.8 ($CH(CH_3)_2$), 24.0 ($CH(CH_3)_2$). FT-IR (KBr, cm^{-1}): 3179, 2956, 1589, 1455, 1383, 1363, 1327, 1271, 1056, 1010, 933, 885, 802. HR-MS (ESI): calcd for $C_{58}H_{87}Cl_4N_6Pd_2$ $[M + H]^+$ 1223.3791; found 1223.3817. Anal. Calcd for $[PdCl_2IPr]_2(\mu$-piperazine) ($C_{58}H_{86}Cl_4N_6Pd_2$) (%): C, 57.01; H, 7.09; N, 6.88. Found (%): C, 57.32; H, 7.372; N, 6.64.

Complex ***3c***

Yield 86 mg, 80% (Procedure 1); 92 mg, 90% (Procedure 2). Decomposition temperature > 256°C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 6.94 (s, 8H, *m*-ArH), 3.92 (s, 8H, NCH_2CH_2N, imidazolidine), 2.62 (s, 12H, NCH_2CH_2N, DABCO), 2.46 (s, 24H, *o*-CH_3), 2.30 (s, 12H, *p*-CH_3). ^{13}C NMR (100 MHz, $CDCl^3$, δ, ppm): 182.6 ($C_{carbene}$), 138.1 (*o*-C_{Ar}), 137.0 (N-C_{Ar}), 134.8(*p*-C_{Ar}), 129.2(*m*-C_{Ar}), 50.9 (NCH_2CH_2N, imidazolidine), 48.5 (NCH_2CH_2N, DABCO), 21.0 (*p*-CH_3), 19.3 (*o*-CH_3). FT-IR (KBr, cm^{-1}): 3179, 2916, 1606, 1491, 1451, 1378, 1308, 1269, 1183, 1017, 929, 852, 808. HR-MS (ESI): calcd for $C_{48}H_{65}Cl_4N_6Pd_2$ $[M + H]^+$ 1081.2069; found 1081.2075. Anal. Calcd for $[PdCl_2IMes]_2(\mu$-DABCO) ($C_{48}H_{64}Cl_4N_6Pd_2$) (%): C, 53.40; H, 5.97; N, 7.78. Found (%): C, 53.61; H, 6.26; N, 7.88.

Complex ***3d***

Yield 102 mg, 82% (Procedure 1); 112 mg, 90% (Procedure 2). Decomposition temperature > 282°C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.38 (t, J = 7.6 Hz, 4H, *p*-ArH), 7.24 (d, J = 7.6 Hz, 8H, *m*-ArH), 3.99 (s, 8H, NCH_2CH_2N, imidazolidine), 3.44 (sept, J = 6.8 Hz, 8H, $CH(CH_3)_2$), 2.64 (s, 8H, NCH_2CH_2N, DABCO), 1.44 (d, J = 6.4 Hz, 24H, $CH(CH_3)_2$), 1.19 (d, J = 6.8 Hz, 24H, $CH(CH_3)_2$). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 184.7 ($C_{carbene}$), 147.6 (*o*-C_{Ar}), 135.2 (N-C_{Ar}), 129.3 (*p*-C_{Ar}), 124.1 (*m*-C_{Ar}), 53.6 (NCH_2CH_2N, imidazolidine), 48.8 (NCH_2CH_2N, DABCO), 28.6 ($CH(CH_3)_2$), 26.7 ($CH(CH_3)_2$), 24.0 ($CH(CH_3)_2$). FT-IR (KBr, cm^{-1}): 3158, 3064, 2964, 2868, 1588, 1479, 1382, 1359, 1323, 1298, 1268, 1178, 1103, 1053, 1013, 931, 806. HR-MS (ESI): calcd for $C_{60}H_{89}Cl_4N_6Pd_2$ $[M + H]^+$ 1249.3947; found 1249.3980. Anal. Calcd for $[PdCl_2SIPr]_2(\mu$-DABCO) ($C_{60}H_{88}Cl_4N_6Pd_2$) (%): C, 57.74; H, 7.11; N, 6.73. Found (%): C, 57.51; H, 7.42; N, 7.08.

General Procedure for Hiyama Coupling Reaction

A sealable reaction tube equipped with a magnetic stir bar was charged with aryl chloride (0.50 mmol), phenyltrialkyoxysilane (0.60 mmol), *n*-Bu_4NF (1.0 mmol), NHC–Pd complex (0.00125 mmol, 0.25 mmol%) and anhydrous toluene (2.0 ml). The mixture was stirred at 110°C for 8 h. After the reaction mixture was cooled to room temperature, the filtrate was concentrated with a rotary evaporator, and the residue was then subjected to purification via flash column chromatography with petroleum ether–EtOAc as an eluent to affoed the corresponding pure products.

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