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Suzuki–Miyaura Cross-Coupling Reaction Catalyzed by PEPPSI-Type 1,4-Di(2,6-diisopropylphenyl)-1,2,3-triazol-5-ylidene (*tz*IPr) Palladium Complex

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Keywords: Homogeneous catalysis / Palladium / C–C coupling / Cross-coupling / Carbene ligands / Biaryls

A 1,4-di(2,6-diisopropylphenyl)-1,2,3-triazol-5-ylidene (*tz*IPr)-based PEPPSI-type palladium complex was developed as an excellent precatalyst for the Suzuki–Miyaura cross-coupling reaction. The complex showed high activity under mild conditions for the cross-coupling reactions between various types of aryl chlorides and aryl boronic acids regardless of the steric and electronic nature of the substrates.

Introduction

The transition-metal-catalyzed Suzuki–Miyaura cross-coupling reaction is one of the most widely used methods for forming carbon–carbon bonds.[1] A wide variety of organic compounds including polymers,[2] pharmaceuticals,[3] and natural products,[4] can be synthesized by applying this reaction. N-Heterocyclic carbenes (NHCs) have become popular ligands for the Pd-catalyzed Suzuki–Miyaura coupling reactions.[5] The NHCs are stronger neutral σ-donors and less oxidation-sensitive than tertiary phosphanes. Our group has recently reported that a more σ-donating C4 or C5 binding abnormal NHC, derived from C2-protected imidazolium salts, could be a better ligand than traditional NHC ligands in Pd-catalyzed Suzuki–Miyaura reactions.[6] To develop more versatile and active NHC ligands for C–C bond formation, we have investigated other types of NHC ligands. Among the various types of NHCs, those derived from substituted 1,2,3-trazolin-5-ylidene (*tz*NHC), first reported by Albrecht and co-workers, have recently been developed as promising ligands for homogeneous catalysis.[7] *tz*NHC precursors can be readily prepared by the [3+2] cycloaddition of an alkyne with an azide.[8]

To find a more active and versatile catalyst for the Suzuki–Miyaura reactions, we have been interested in developing better Pd catalysts using the *tz*NHC ligands. While preparing this manuscript, Fukuzawa and co-workers reported the synthetic, structural, and catalytic studies of *allyl* *tz*NHC Pd complexes.[9] In addition, Albrecht and co-workers recently reported *tz*NHC-based PEPPSI (PEPPSI = pyridine-enhanced precatalyst preparation, stabilization, and initiation, Figure 1) type Pd complexes,[12] in which appended groups of *tz*NHC are Me, *n*Bu, Ph, or Mes groups.[10] We have also investigated the possibility of using *tz*NHC for Pd-catalysis using more bulky 1,4-di(2,6-diisopropylphenyl)-1,2,3-triazol-5-ylidene (*tz*IPr), because it has been well-documented that ligands with increased steric bulk are more efficient in Pd-catalyzed Suzuki–Miyaura reactions.[11] Herein, we report our study on the synthesis and catalytic activity of a *tz*IPr-based PEPPSI-type Pd complex for Suzuki–Miyaura cross-coupling reactions.

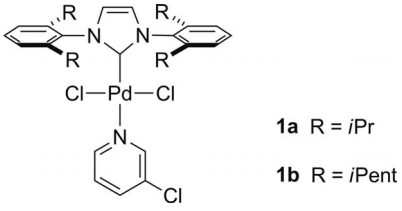

Figure 1. Structure of NHC-based PEPPSI-type Pd complexes developed by Organ.

Results and Discussion

The *tz*IPr-palladium complexes were conveniently synthesized by transmetallation from a silver carbene complex.[9a,10] A triazolium salt **2** was treated with silver oxide in dichloromethane at 35 °C for 16 h to generate the silver carbene complex **3** (Scheme 1). The crude silver carbene complex **3** was immediately used for the synthesis of palladium complex **4**. After treating **3** with $[PdCl_2(CH_3CN)_2]$,

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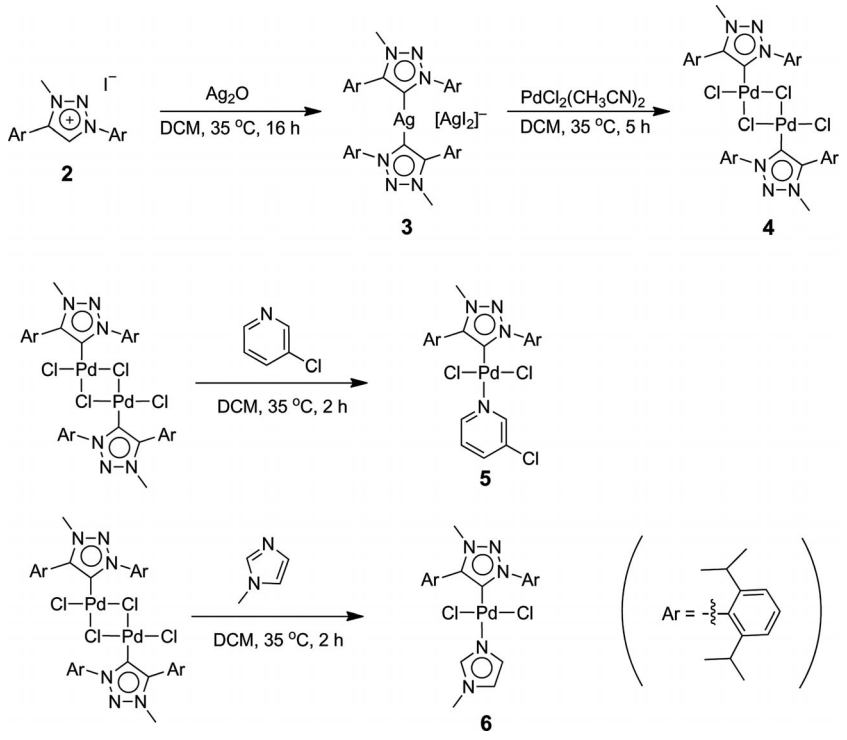


Scheme 1. Syntheses of *tz*NHC-Pd complexes.

dimeric Pd complex **4** was isolated as a yellow solid in 50% yield. Complexes **5** and **6** were synthesized by treating **4** with 3-chloropyridine and 1-methylimidazole, respectively. The structures of **4** and **5** were confirmed by X-ray crystallographic analysis as well as by NMR spectroscopy (Figure 2).[13] Unfortunately, no suitable crystals of complex **6** for X-ray crystallographic analysis were obtained; this complex was therefore characterized by NMR and mass analyses.

The Pd–C(NHC center) bond lengths in *tz*IPr Pd complexes **4** and **5** are 1.961 and 1.965 Å, respectively (Table 1).[14] These Pd–C(NHC center) bond lengths are in the same range as those of the reported *tz*NHC-Pd complexes.[9a,10] The bond lengths are also similar to those of traditional NHC-based Pd PEPPSI complexes. For example, in the case of *trans*-dichloro[1,3-bis(2,6-diisopropylphenyl)imidazolylidinium](3-chloropyridine) (**1a**), the length of Pd–C is 1.969(3) Å.[12d] It has been reported that

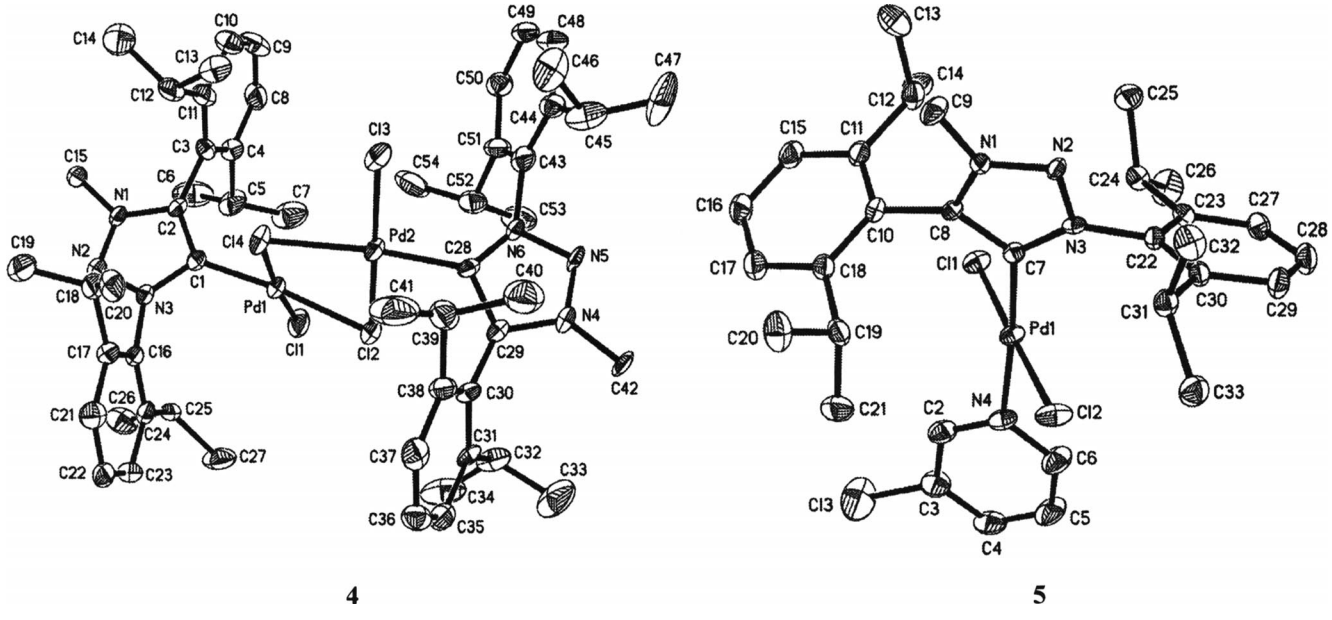


Figure 2. Crystal structure of **4** and **5** with thermal ellipsoids drawn at the 30% probability level.

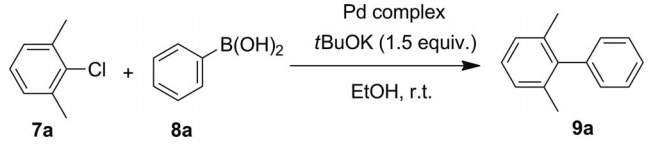
M–$C_{carbene}$ bond lengths are not so sensitive to small changes in bond order.[6] The Pd–N_{py} bond length of 2.089(2) Å of **5** was shorter than that of **1a** (2.137(2) Å).[12d] In the case of [(η^3-allyl)(*tz*IPr)Pd] and [(η^3-allyl)(IPr)Pd] complexes, the Pd–C(3) bond lengths [2.201(3) and 2.210(6) Å, respectively] are similar, leading Fukuzawa and co-workers to suggest similar *trans* influence of *tz*IPr and IPr ligands in [(η^3-allyl)(NHC)Pd] complexes.[9a] In our case, the significantly shorter Pd–N bond length of **5** may indicate less *trans* influence of *tz*IPr than IPr. The triazole torsional angles are 4–8°, indicating that the triazole rings are planar and in an aromatic system.

Table 1. Selected bond lengths [Å] and angles [°] of **4** and **5**.

	4		**5**
Pd(1)–C(1)	1.961(10)	Pd(1)–C(7)	1.965(2)
Pd(1)–Cl(2)	2.3002(7)	Pd(1)–Cl(1)	2.3002(7)
Pd(1)–Cl(4)	2.321(3)	Pd(1)–Cl(2)	2.2964(7)
C(1)–Pd(1)–Cl(1)	90.4(3)	C(7)–Pd(1)–Cl(1)	91.43(7)
C(1)–Pd(1)–Cl(4)	92.4(3)	C(7)–Pd(1)–Cl(2)	88.71(7)
Cl(1)–Pd(1)–Cl(4)	173.96(11)	Cl(2)–Pd(1)–Cl(1)	178.77(3)
N(3)–C(1)–C(2)	104.0(9)	N(3)–C(7)–C(8)	103.2(3)
N(1)–N(2)–N(3)	103.6(7)	N(1)–N(2)–N(3)	102.2(4)
N(2)–N(3)–C(7)	114.3(8)	N(2)–N(3)–C(1)	114.4(4)

Catalytic activities for the Suzuki–Miyaura reactions were screened with complexes **4**–**6** (Table 2), and 1-chloro-2,6-dimethylbenzene and boronic acid were selected as a model reaction. The reaction conditions were optimized and *t*BuOK and EtOH were identified as the best base and solvent, respectively (Table 3). Complexes **4** and **5** showed excellent activities in the cross-coupling reaction at room temperature. Complex **6** with 1-methylimidazole as a ligand showed slightly reduced activity, presumably due to slower dissociation of the imidazole ligand than pyridine.[15]

Table 2. Activity of NHC-Pd complexes for the Suzuki–Miyaura reaction.[a]



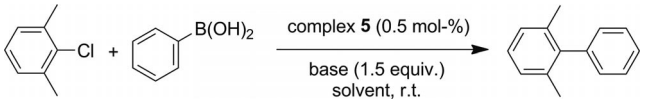
7a **8a** **9a**

Entry	Pd complex	Catalyst loading [mol-%]	Time [h][b]	Yield [%][c]
1	**5**	1.0	2	91
2	**5**	0.5	2	89
3	**5**	0.1	5	80
4	**4**	0.5	2	88
5	**6**	0.5	5	70

[a] Reaction conditions: 1-chloro-2,6-dimethylbenzene (1.0 mmol), boronic acid (1.1 equiv.), ethanol (1.0 mL/mmol halide). [b] Reaction progress was monitored by TLC analysis. [c] Isolated yield.

The scope of the Suzuki–Miyaura reactions catalyzed by **5** was evaluated (Table 4). Complex **5** exhibited good to excellent activities with various substrates at ambient temperature. *Ortho*-substituted biaryls are important structural motifs, and they are found in many biologically active compounds and organic materials.[16] Complex **5** performed well

Table 3. Screening for biaryl synthesis using complex **5**.[a]

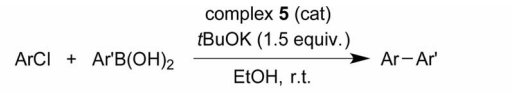


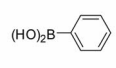
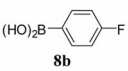
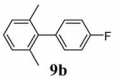
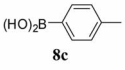
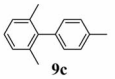
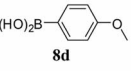
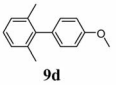
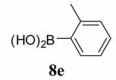
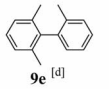
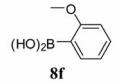
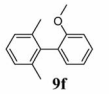
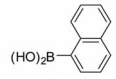
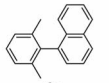
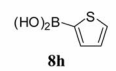
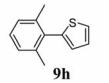
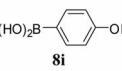
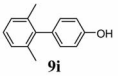
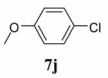
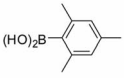
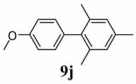
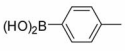
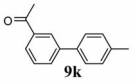
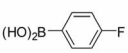
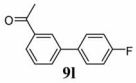
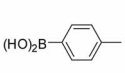
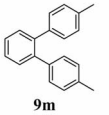
Entry	Base	Solvent	Yield [%][b]
1	*t*BuOK	EtOH	95
2	K_2CO_3	EtOH	24
3	Cs_2CO_3	EtOH	16
4	K_3PO_4	EtOH	87
5	NaOMe	EtOH	51
6	CsF	EtOH	43
7	*t*BuOK	1,4-dioxane	trace
8	*t*BuOK	toluene	trace
9	*t*BuOK	*t*BuOH	trace

[a] Reaction conditions: ArCl (0.5 mmol), boronic acid (1.1 equiv.), solvent (1.0 mL/mmol halide). [b] GC yield using dodecane as internal standard.

to generate *ortho*-substituted biaryls under mild conditions. Cross-coupling products from *ortho*-disubstituted 1-chloro-2,6-dimethylbenzene (**7a**) and *para*-substituted phenylboronic acids were obtained in high yields (Table 4, entries 2–4). The 1-chloro-2,6-dimethylbenzene coupled with more sterically congested *ortho*-substituted phenylboronic acids to give the corresponding biaryls with good yields (Table 4, entries 5 and 6). Moreover, the reaction of **7a** with 1-naphthylboronic acid **8g** gave the coupling product **9g** in 73% yield (Table 4, entry 7). Functional group tolerance was also good. 2-Thienylboronic acid **8h** with **7a** gave the corresponding product **9h** in 85% yield (Table 4, entry 8). The cross-coupling reaction of **8i**, which possesses a hydroxyl group, proceeded smoothly to afford the desired product in 92% yield (Table 4, entry 9). Both electron-rich and electron-poor aryl chlorides worked effectively as cross-coupling partners, giving excellent yields of the corresponding product (Table 4, entries 10–12). Even with 1,2-dichlorobenzene, containing two C–Cl bonds, the doubly cross-coupled product **9m** was obtained with 55% yield (Table 4, entry 13). The challenging reaction of highly hindered substrates of **7a** and **8j** worked smoothly to give the coupling product **9n** in 82% yield with an increased reaction time of 24 h at an elevated temperature of 110 °C (Table 4, entry 14). Compared with the activity of IPr-based PEPPSI-type catalyst **1a**, with similar steric hindrance around the Pd center,[12d,12f] complex **5** exhibited better activity for the Suzuki–Miyaura reactions with aryl chlorides and for synthesis of sterically bulky biaryls. Organ and co-workers developed complex **1b**, which exhibits excellent activities for cross-coupling reactions, by increasing the steric bulk of the NHC ligand.[12f] Albrecht and co-workers showed that, in contrast to the homogeneous catalysis observed with the original PEPPSI systems, triazolylidene-based PEPPSI-type Pd complexes undergo a heterogenization process that generates palladium nanoparticles as the resting state of the catalyst.[10] Further catalyst development is in progress based on further increasing the steric bulk of the *tz*NHC ligands.

Table 4. Suzuki–Miyaura reactions catalyzed by complex **5**.[a]



Entry	ArCl	Ar'B(OH)$_2$	Ar–Ar'	Time[b]	Yield (%)[c]
1				2 h	90
2		 **8b**	 **9b**	2 h	85
3		 **8c**	 **9c**	2 h	82
4		 **8d**	 **9d**	2 h	92
5		 **8e**	 **9e** [d]	2 h	72
6		 **8f**	 **9f**	2 h	75
7		 **8g**	 **9g**	2 h	73
8		 **8h**	 **9h**	2 h	85
9		 **8i**	 **9i**	2 h	92
10	 **7j**	 **8j**	 **9j**	3 h	93
11[e]	 **7k**		 **9k**	15 h	91
12			 **9l**	19 h	99
13[f]	 **7m**		 **9m**	5 h	55
14[g]			**9n**	24 h	82

[a] Reaction conditions: ArCl (1.0 mmol), boronic acid (1.1 equiv.), complex **5** (0.5 mol-%), ethanol (1.0 mL/mmol ArCl). [b] Reaction time was determined by monitoring the reaction by TLC. [c] Isolated yield; average of at least two runs. [d] Yield was determined by ^{1}H NMR analysis due to contamination by a small amount of inseparable byproduct derived from homocoupling of boronic acids. [e] 1.5 equiv. of boronic acid used. [f] Reaction conditions: ArCl (0.5 mmol), boronic acid (3.0 equiv.), **5** (1.0 mol-%), *t*BuOK (2.0 equiv.). [g] Reaction conditions: ArCl (0.5 mmol), boronic acid (1.1 equiv.), 1,4-dioxane (1.0 mL/mmol ArCl), **5** (5 mol-%), 110 °C.

Conclusions

We have developed a *tz*NHC-based PEPPSI-type Pd complex as an excellent precatalyst for the Suzuki–Miyaura cross-coupling reaction. The complex showed high activity under mild conditions for the cross-coupling reactions between various types of aryl chlorides and aryl boronic acids regardless of the steric and electronic nature of the substrates.

Experimental Section

General Considerations: All reactions were carried out in oven-dried glassware under an inert atmosphere of dry argon or nitrogen. All reagents were purchased from Aldrich or Alfa Aesar and used as received. Analytical TLC was performed with Merck 60 F254 silica gel (0.25 mm thickness). Column chromatography was performed with Merck 60 silica gel (230–400 mesh). NMR spectra were recorded with a Bruker 300 MHz or a Bruker 400 MHz spectrometer. Tetramethylsilane was used as reference, the chemical shifts are reported in ppm, and the coupling constants in Hz. GC yields were obtained with an Agilent 7890A instrument equipped with an HP-5 column using dodecane as internal standard. Ligand **2** was synthesized as summarized in Scheme 2 and described below.

Scheme 2. Syntheses of 1,4-di(2,6-diisopropylphenyl)-1,2,3-triazolium iodide (**2**).

1-Azido-2,6-diisopropylbenzene:[17] To a solution of 2,6-diisopropylaniline (1.773 g, 10.0 mmol) in 10% HCl (15 mL), a solution of $NaNO_2$ (0.690 g, 10.0 mmol) in water (3 mL) was added at 0–5 °C with vigorous stirring. The mixture was kept below 5 °C for 30 min, then a solution of NaN_3 (0.72 g, 11.0 mmol) in water (15 mL) was added dropwise while the temperature was maintained below 5 °C. After stirring for 3 h, the mixture was warmed to room temp. and poured into saturated aqueous $NaHCO_3$ (50 mL). After extraction with EtOAc (50 mL), the organic layer was washed with brine (50 mL), dried with Na_2SO_4, and concentrated in vacuo. The resi-

due was purified by flash silica gel column chromatography to give the product (1.015 g, 50%).

1-Iodo-2,6-diisopropylbenzene:[18] To a solution of 2,6-diisopropylaniline (1.773 g, 10.0 mmol) in acetone (15 mL), 10% HCl (15 mL) was added at room temperature. The resulting solution was cooled to 0 °C, and a solution of $NaNO_2$ (0.91 g, 13.0 mmol) in H_2O (3 mL) was added dropwise. The reaction mixture was stirred at 0 °C for 1 h, then a solution of KI (4.98 g, 30.0 mmol) in H_2O (10 mL) was added. After 6 h, the solution was extracted with Et_2O (3 × 50 mL) and the combined ether layers were washed with brine, dried, and concentrated. The residue was purified by flash silica gel column chromatography to afford 1-iodo-2,6-diisopropylbenzene (1.152 g, 40%).

1-Ethynyl-2,6-diisopropylbenzene:[19] Under an Ar atmosphere, a 50 mL Schlenk flask was charged with 1-iodo-2,6-diisopropylbenzene (576 mg, 2 mmol), HC≡CZnBr [3 mmol; prepared from HC≡CMgBr (0.5 M in THF, 3 mmol, 6 mL) and anhydrous $ZnBr_2$ (675 mg, 3 mmol) dissolved in THF (5 mL)], [$Pd(PPh_3)_4$] (115 mg, 0.1 mmol), and DMF (2 mL). The mixture was stirred for 18 h at 60 °C, then the reaction mixture was quenched with aqueous NaCl, extracted with Et_2O, dried with Na_2SO_4, and concentrated in vacuo. The product (141 mg, 38%) was separated by column chromatography using hexane as eluent.

1,4-Di(2,6-diisopropylphenyl)-1,2,3-triazole:[20] In a tube with a screw-cap, 1-azido-2,6-diisopropylbenzene (270 mg, 1.33 mmol), 1-iodo-2,6-diisopropylbenzene (225 mg, 1.21 mmol), and [(SIMes)-CuBr] (29 mg, 5 mol-%) were loaded. The reaction was heated at 70 °C. After 18 h, the liquid (starting material) became solid (target product), and was dissolved with EtOAc, and concentrated in vacuo. The product (336.9 mg, 71%) was separated by column chromatography (hexane/ethyl acetate, 15:1).

1,4-Di(2,6-diisopropylphenyl)-1,2,3-triazolium Iodide (2):[9a] Triazole **1** (140 mg, 0.36 mmol) was added to acetonitrile (1 mL) and methyl iodide (511 mg, 3.6 mmol) and the reaction mixture was heated at 60 °C for 24 h. Solvent was removed under vacuo and the solid residue was recrystallized (CH_2Cl_2/hexane); yield 169 mg (88%); yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.17 (d, J = 6.8 Hz, 6 H, ArCHCH$_3$CH_3), 1.27 (d, J = 6.8 Hz, 6 H, ArCHCH$_3$CH_3), 1.30 (d, J = 6.8 Hz, 6 H, ArCHCH$_3$CH_3), 1.33 (d, J = 6.8 Hz, 6 H, ArCHCH$_3$CH_3), 2.34–2.42 (m, 4 H, ArCHCH$_3$CH$_3$), 4.36 (s, 3 H, N-CH$_3$), 7.39 (d, J = 5.8 Hz, 2 H, ArH), 7.41 (d, J = 5.8 Hz, 2 H, ArH), 7.63–7.68 (m, 2 H, ArH), 9.29 (s, 1 H, H_{tz}) ppm. ^{13}C NMR (100 Hz, $CDCl_3$): δ = 23.2, 23.8, 24.4, 25.1, 29.2, 32.0 (ArCHCH$_3$CH$_3$ × 6), 40.2 (NCH$_3$), 117.1 (C_{Ar}), 124.3 (C_{Ar}), 124.9 (C_{Ar}), 130.6 (C_{tz}-H), 133.2 (C_{Ar}), 133.4 (C_{Ar}), 142.0 (C_{Ar}), 145.0 (C_{Ar}), 148.8 (C_{tz}-Ipr) ppm.

Complex 4: To a solution of **2** (749 mg, 1.41 mmol) in CH_2Cl_2 (20 mL), Ag_2O (326 mg, 1.41 mmol) was added. The mixture was stirred at 35 °C for 16 h in the dark, and filtered through Celite. [$Pd(CH_3CN)_2Cl_2$] (730 mg, 2.82 mmol) was added and, after stirring for 5 h at 35 °C, the product was separated by column chromatography (CH_2Cl_2); yield 410 mg (50%); yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.99 (d, J = 7.6 Hz, 6 H, ArCHCH$_3$CH_3), 1.02 (d, J = 6.8 Hz, 6 H, ArCHCH$_3$CH_3), 1.46 (d, J = 6.4 Hz, 6 H, ArCHCH$_3$CH_3), 1.27–1.30 (m, 6 H, ArCHCH$_3$CH_3), 2.57–2.62 (m, 2 H, ArCHCH$_3$CH$_3$), 2.63–2.71 (m, 2 H, ArCHCH$_3$CH$_3$), 3.73 (s, 3 H, N-CH$_3$), 7.31 (d, J = 8.0 Hz, 4 H, H_{Ar}), 7.57 (dd, J = 7.6, 15.2 Hz, 2 H, H_{Ar}) ppm. ^{13}C NMR (100 Hz, $CDCl_3$): δ = 22.8, 24.6, 25.0, 25.8, 29.0, 31.0 (ArCHCH$_3$CH$_3$ × 6), 37.3 (NCH$_3$), 122.4 (C_{Ar}), 124.0 (C_{Ar}), 131.1 (C_{tz}-Pd), 135.0 (C_{Ar}), 138.1 (C_{Ar}), 142.0 (C_{Ar}), 146.2 (C_{Ar}), 150.2 (C_{tz}-Ipr) ppm. HRMS: m/z calcd. for $C_{54}H_{74}N_6Cl_3Pd_2$ [M – Cl]$^+$ 1123.3110; found 1123.3115. $C_{54}H_{74}Cl_4N_6Pd_2$ (1161.83): calcd. C 55.82, H 6.42, N 7.23; found C 55.61, H 6.15, N 6.99.

Complex 5: Under an Ar atmosphere, a Schlenk flask was charged with 3-chloropyridine (41 mg, 0.36 mmol), **4** (209 mg, 0.18 mmol), and CH_2Cl_2 (1 mL). The reaction mixture was stirred for 3 h at 35 °C. After evaporation of all volatiles, the residue was washed with pentane and complex **5** was obtained. Yield: 247 mg (99%); yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.10 (d, J = 7.2 Hz, 6 H, ArCHCH$_3$CH_3), 1.13 (d, J = 6.8 Hz, 6 H, ArCHCH$_3$CH_3), 1.46 (d, J = 6.4 Hz, 12 H, ArCHCH$_3$CH_3), 2.96–3.07 (m, 4 H, ArCHCH$_3$CH$_3$), 3.84 (s, 3 H, N-CH$_3$), 7.08 (dd, J = 5.6, 8.0 Hz, 1 H, H_{Py}), 7.36 (d, J = 4.8 Hz, 2 H, H_{Ar}), 7.38 (d, J = 4.4 Hz, 2 H, H_{Ar}), 7.52–7.56 (m, 3 H, $H_{Ar/Py}$), 8.63 (dd, J = 1.2, 5.6 Hz, 1 H, H_{Py}), 8.71 (d, J = 2.0 Hz, 1 H, H_{Py}) ppm. ^{13}C NMR (100 Hz, $CDCl_3$): δ = d 22.8, 24.6, 25.0, 25.8, 29.1, 31.0 (ArCHCH$_3$CH$_3$ × 6), 37.4 (NCH$_3$), 123.1 (C_{Ar}), 123.9 (C_{Ar}), 124.0 (C_{Py}), 124.3 (C_{Ar}), 131.1 (C_{Ar}), 132.0 (C_{tz}-Pd), 135.6 (C_{Py}), 137.3 (C_{Py}), 142.6 (C_{Ar}), 146.3 (C_{Ar}), 149.5 (C_{tz}-Ipr), 150.3 (C_{Py}), 150.5 (C_{Py}) ppm. HRMS: m/z calcd. for $C_{32}H_{41}N_4Cl_2Pd$ [M – Cl]$^+$ 657.1743; found 657.1744. $C_{32}H_{41}Cl_3N_4Pd$ (694.46): calcd. C 55.34, H 5.95, N 8.07; found C 55.08, H 5.85, N 7.75.

Complex 6: Under an Ar atmosphere, a Schlenk flask was charged with 1-methylimidazole (7.1 mg, 0.086 mmol), **4** (50 mg, 0.043 mmol), and CH_2Cl_2 (0.5 mL). The reaction mixture was stirred for 3 h at 35 °C. The solvent was removed under vacuo, and the residue was purified by a flash chromatography on silica gel using CH_2Cl_2 as eluent. Yield: 34 mg (60%); yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.08 (d, J = 6.8 Hz, 6 H, ArCHCH$_3$CH_3), 1.11 (d, J = 6.8 Hz, 6 H, ArCHCH$_3$CH_3), 1.45 (d, J = 6.4 Hz, 12 H, ArCHCH$_3$CH_3), 3.00–3.07 (m, 4 H, ArCHCH$_3$CH$_3$), 3.46 (s, 3 H, N_{Im}-CH$_3$), 3.81 (s, 3 H, N-CH$_3$), 6.55 (dd, J = 2.0, 4.0 Hz, H_{Im}), 7.25 (dd, J = 1.8, 3.4 Hz, H_{Im}), 7.33 (d, J = 4.0 Hz, 2 H), 7.33 (d, J = 4.4 Hz, 2 H), 7.48–7.53 (m, 2 H), 7.76 (s, 1 H, H_{Im}) ppm. ^{13}C NMR (100 Hz, $CDCl_3$): δ = 22.9, 24.6, 25.0, 25.8, 29.0, 30.9 (ArCHCH$_3$CH$_3$ × 6), 34.0 (N_{Im}CH$_3$), 37.2 (NCH$_3$), 119.0 (C_{Ar}), 123.6 (C_{Ar}), 123.8 (C_{Ar}), 123.9 (C_{Ar}), 128.6 (C_{Ar}), 131.1 (C_{tz}-Pd), 136.2 (C_{Im}), 138.5 (C_{Im}), 142.1 (C_{Ar}), 145.2 (C_{Ar}), 146.4 (C_{Im}), 150.3 (C_{tz}-IPr) ppm. HRMS: m/z calcd. for $C_{31}H_{43}N_5ClPd$ [M – Cl]$^+$ 626.2242; found 626.2244. $C_{31}H_{43}Cl_2N_5Pd$ (663.02): calcd. C 56.16, H 6.54, N 10.56; found C 55.93, H 6.35, N 10.33.

Typical Procedure for 9a: A Schlenk flask was charged with 1-chloro-2,6-dimethylbenzene (70 mg, 0.5 mmol), boronic acid (67 mg, 0.55 mmol), *t*BuOK (84 mg, 0.75 mmol), complex **5** (17 mg, 0.025 mmol), and EtOH (0.5 mL) under Ar. The mixture was stirred at room temperature and, after the completion of the reaction (monitored by TLC), the reaction mixture was poured into saturated aqueous NaCl and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were washed with saturated aqueous NaCl (3 × 10 mL), dried with Na_2SO_4, filtered, and concentrated in vacuo. Purification was carried out by flash silica gel chromatography (hexane) to give product **9a** (162 mg, 89%) as a colorless liquid. Characterization data of all of the biaryl products have been previously reported, and the identities of **9a**–**n** were confirmed by ^{1}H NMR spectroscopic data comparison.

Supporting Information (see footnote on the first page of this article): Copies of the ^{1}H and ^{13}C NMR spectra of Pd complexes, and ^{1}H NMR spectra of biaryls **9**.

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[13] CCDC-889236 (for **4**) and -889237 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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