Cis-chelated palladium(II) complexes of biphenyl-linked bis(imidazolin-2-ylidene): synthesis and catalytic activity in the Suzuki-Miyaura reaction

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Abstract

A new type of biaryl-linked bis(imidazolin-2-ylidene) ligand precursor and corresponding *cis*-chelated bis-N-heterocyclic carbene–Pd(II) complexes have been synthesized starting from 6,6′-dimethyl-2,2′-dinitro-1,1′-biphenyl. The catalytic activity of these NHC–Pd(II) complexes in the Suzuki–Miyaura reactions of aryl chlorides has also been investigated affording biaryls in good to excellent yields.

Keywords: Carbene ligand, N-heterocyclic carbene, palladium complexes, Suzuki cross-coupling, biaryl compounds

Introduction

With unique ligating properties and stability toward heat, air, oxygen and moisture compared to metal–phosphine complexes, catalysts that incorporate N-Heterocyclic carbenes (NHCs) as ligands have been applied to a broad range of organic transformations.[1] The reactivity and stability of NHC–metal complexes largely rely on the electronic and steric characteristics of the NHC ligands, which can be controlled by modifying the structures of NHC ligands. Among various NHC ligands, chelate bis-NHCs with a biaryl backbone not only yield more stable metal complexes, but also give interesting features that can provide fine-tuning of topological properties such as steric hindrance, bite angles and chirality.[1j] So far, two types of biaryl backbones in biaryl-linked bis-NHCs appeared in literature. The first one is 1,1′-binaphthyl. RajanBabu *et al.* reported the first chelated bis(imidazolin-2-ylidene) complexes of Pd(II) and Ni(II) with a binaphthyl backbone **A** (Figure 1) derived from 2,2′-bis(bromomethyl)-1,1′-binaphthyl.[2] Crabtree *et al.* synthesized a chiral proligand **B** (Figure 1) with a binaphthyl

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backbone from (*S*)-1,1′-binaphthyl-2,2′-diamine (BINAM) in two steps.[3] Shi *et al*. reported a series of bis(benzimidazolin-2-ylidene) complexes of transition metals **C** (Figure 1) derived from BINAM and their catalytic activities.[4] Another type of biaryl backbone that links the two NHCs is 1,1′-biphenyl. Shi *et al*. reported the Pd and Rh complexes of bis(benzimidazolin-2-ylidene) with a biphenyl backbone derived from H_8-BINAM **D** (Figure 1).[4c-e] They also reported the Rh, Ir and Pd complexes of bis(benzimidazolin-2-ylidene) with a biphenyl backbone derived from 1,1′-biphenyl-2,2′-diamine **E** (Figure 1).[5] These complexes showed high catalytic activities in the hydrosilylation of ketones and in the Heck reaction. Song recently synthesized Rh complexes of biphenyl-linked bis(benzimidazolin-2-ylidene) **E** (R = Me, Figure 1) from 6,6′-dimethyl-1,1′-biphenyl-2,2′-diamine.[6] It is noted that all of the chelated bis-NHC–metal complexes with a biphenyl backbone reported so far possess bis(benzimidazolin-2-ylidene) as carbene ligand, no metal complex of bis(imidazolin-2-ylidene) with a biphenyl backbone is reported, though imidazolin-2-ylidene as NHC ligand behaves differently from benzimidazolin-2-ylidene,[7] and is far more popular in the transition-metal catalysis. Since the imidazolin-2-ylidene rings in **A** (Figure 1) are linked to the binaphthyl backbone by two methylenes, and attempts to prepare chelated transition metal complexes of bis(imidazolin-2-ylidene) from proligand **B** failed,[3] transition metal complexes of bis(imidazolin-2-ylidene) in which the imidazolin-2-ylidene rings are directly attached on a biaryl backbone are unprecedented. In this paper, we report the synthesis and characterization of a new type of *cis*-chelated bis(imidazolin-2-ylidene)–Pd(II) complexes with a biphenyl backbone **F** (Figure 1). Their catalytic activities in the Suzuki–Miyaura coupling reactions of aryl chlorides are also described.

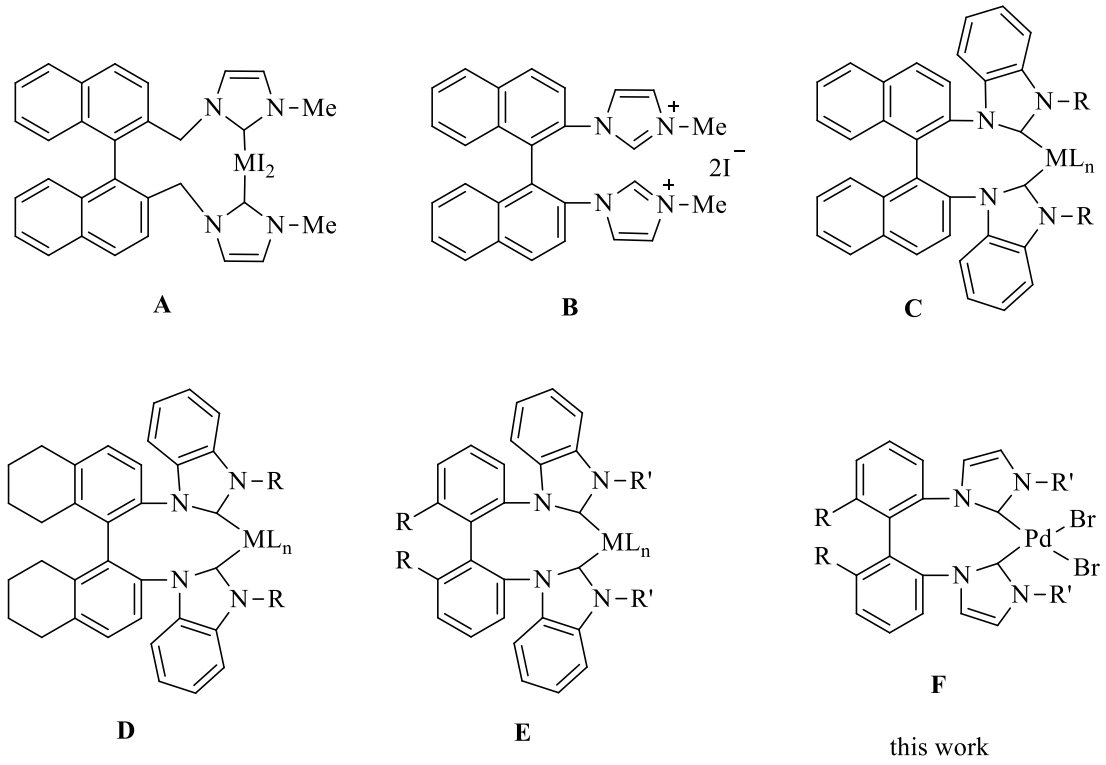


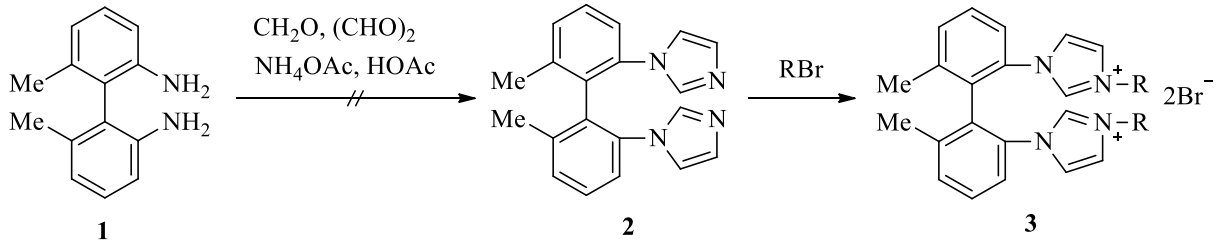
Figure 1. Types of NHC ligands and their metal complexes.

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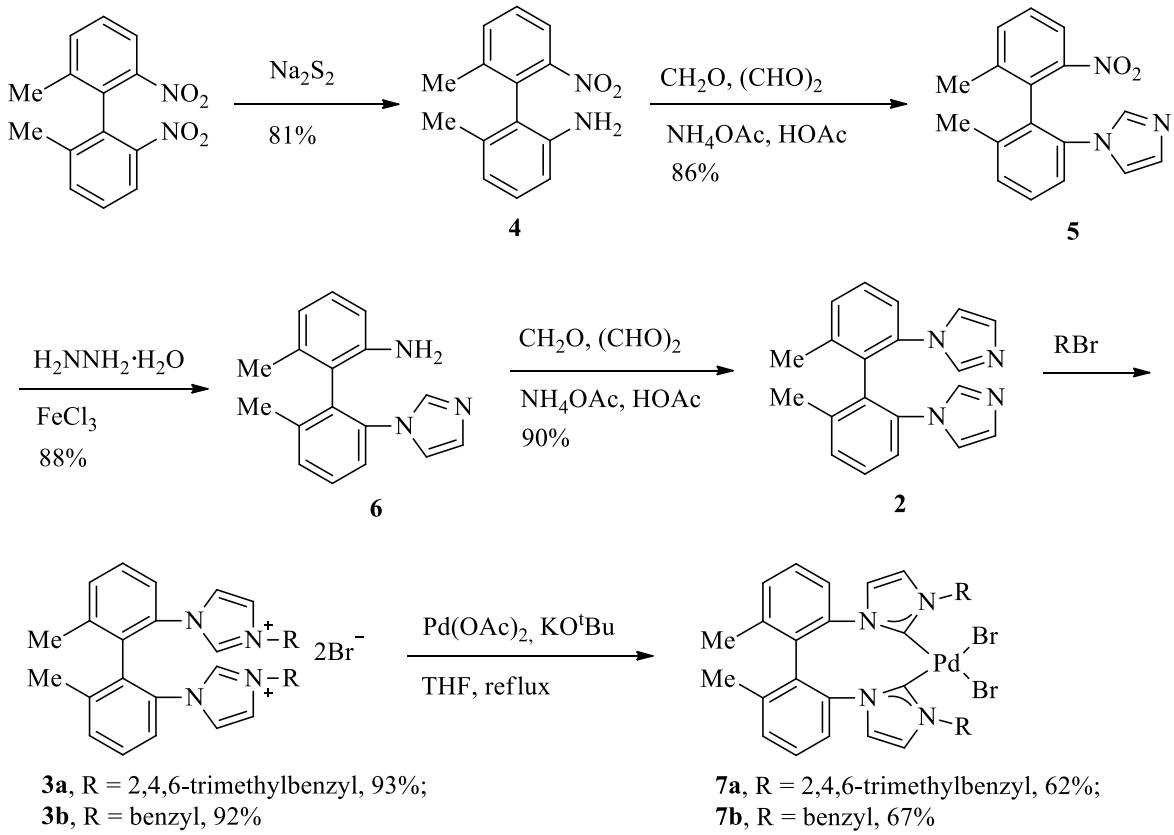
Results and Discussion

Ligand and metal complex synthesis

Initially, we tried to synthesize the bis-NHC ligand precursor bis(imidazolium) salt **3** from commercially available 6,6′-dimethyl-1,1′-biphenyl-2,2′-diamine **1** (Scheme 1). However, attempted methods, including the procedure that described by Crabtree for the synthesis of structurally similar **B** (Figure 1) with a binaphthyl backbone from 1,1′-binaphthyl-2,2′-diamine,[3] were unsuccessful.



Scheme 1. Attempted unsuccessful synthetic route.



Scheme 2. Synthetic route to *cis*-chelated bis-NHC-Pd(II) complexes with a biphenyl backbone.

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We then turned our attention to the synthesis of the desired biphenyl-linked bis(imidazolin-2-ylidene)–palladium(II) complexes by a synthetic route outlined in Scheme 2. 2-Amino-2′-nitro-6,6′-dimethyl-1,1′-biphenyl **4** was prepared from the starting compound 2,2′-dimethyl-6,6′-dinitro-1,1′-biphenyl following the literature procedure.[8] Compound **5** was obtained in 86% yield by refluxing the mixture of **4**, glyoxal and formaldehyde. Catalytic reduction of **5** with hydrazine hydrate in the presence of $FeCl_3 \cdot 6H_2O$ and active carbon in methanol afforded **6** in 88% yield. With the same procedure as that described for **5**, the biphenyl-linked bisimidazole **2** was produced in 90% yield. The desired bisimidazolium salts **3a** and **3b** were obtained in yields more than 90% by alkylation of **2** with RX in dioxane at 85 ºC. ^{1}H and ^{13}C NMR spectroscopic data obtained for **3** show spectra consistent with a C_2 symmetric conformation, and in the ^{1}H NMR spectra, characteristic signals of the imidazolium salt NC(H)N protons are observed at 9.11 ppm for **3a** and δ 10.11 ppm for **3b**. These values fall in the range observed for related bisimidazolium salts.[9]

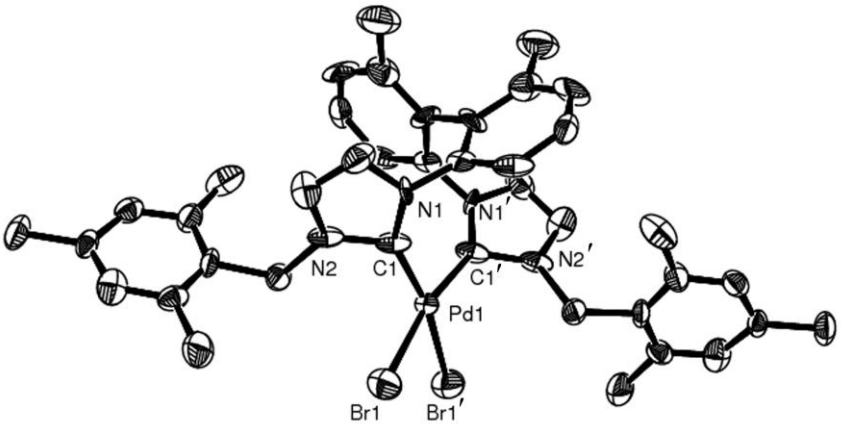


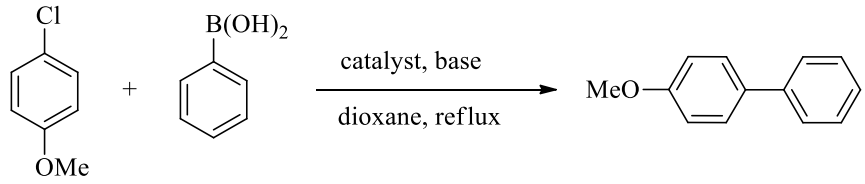
Figure 2. Molecular structure of complex **7a**. Hydrogen atoms and solvent have been omitted for clarity. Thermal ellipsoids are drawn at 30% probability level. Selected interatomic distances (Å) and angles (deg): Pd1–C1 = 1.830(19), Pd1–C1′ = 1.830(19), Pd1–Br1 = 2.499(2), Pd1-Br1′ = 2.499(2), C1–Pd1–Br1′ = 166.8(6), C1′–Pd1–Br1 = 166.8(6), C1–Pd1–C1′ = 93.1(8), Br1–Pd1–Br′ = 89.9(10).

In the presence of KO^{t}Bu, the obtained bisimidazolium salts **3a** and **3b** reacted with $Pd(OAc)_2$ in a refluxing THF solution producing the corresponding *cis*-chelated bis(imidazolin-2-ylidene)–palladium(II) complexes **7a** and **7b** as air- and moisture-stable yellow solids in 62% and 67% isolated yields, respectively. The first indication that the ligand is coordinated to palladium is the absence of the NC(H)N proton resonances in the ^{1}H NMR spectra of **7**. Notably, the signals for the carbene carbon atoms of **7a** and **7b** in the ^{13}C NMR spectra appear at 159.01 and 159.84 ppm, which are characteristic peaks for palladium–carbene complexes.[10] In addition, yellow single crystals of complex **7a** suitable for X-ray crystal structure analysis were grown

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from $CHCl_3$. On the basis of X-ray diffraction, the structure of complex **7a** is unambiguously determined, and one of the two enantiomers is depicted in Figure 1.[11] It is clearly shown that the bis-NHC ligand is coordinated to palladium in a *cis*-chelated fashion by the two carbene atoms, forming a nine-membered chelate ring. X-ray analysis of the crystal shows the geometry of the ligand around palladium to be distorted square planar with the C1–Pd–Br1' and C1′–Pd–Br1 angles of 166.8°. The C1–Pd–C1′ bond angle is determined to be 93.1°. The Br1–Pd–Br′ bond angle is 89.9°. The palladium–carbene distances (1.830 Å) are shorter than the Pd–$C_{carbene}$ bond distances (about 2.000 Å) found for complexes with two *cis*-positioned benzimidazolin-2-ylidene donor groups.[2,4e,i] The Pd–Br1 bond length is 2.499 Å. The two benzene rings in the biphenyl backbone form a dihedral angle of 85.7°. The dihedral angle of the NHC rings is 71.4°.

Table 1. Effect of base and solvent on the Suzuki–Miyaura cross-coupling of 1-chloro-4-methoxybenzene with phenylboronic acid.[a]



Entry	Catalyst	Base	Solvent	Yield (%)[b]
1	**7a**	K_2CO_3	dioxane	37
2	**7a**	K_3PO_4	dioxane	71
3	**7a**	NaOMe	dioxane	79
4	**7a**	KO^{t}Bu	dioxane	91
5 [c]	**7a**	KO^{t}Bu	dioxane	90
6	**7b**	KO^{t}Bu	dioxane	82
7	$Pd(OAc)_2$	KO^{t}Bu	dioxane	0
8	**7a**	KO^{t}Bu	THF	56
9	**7a**	KO^{t}Bu	DMF	58
10	**7a**	KO^{t}Bu	EtOH	< 5
11	**7a**	KO^{t}Bu	CH_3CN	32

[a]Reaction conditions: Pd catalyst (2 mol%), phenylboronic acid (1.25 mmol), 1-chloro-4-methoxybenzene (0.5 mmol), base (1.25 mmol), solvent (5.0 mL), 100 ^{o}C, 18 h under Ar.
[b]Isolated by silica gel column chromatography and based on 1-chloro-4-methoxybenzene.
[c]The catalyst was kept open to air for two days before it was used in the catalysis.

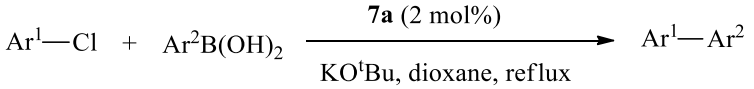
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Catalytic studies

The palladium-catalyzed Suzuki–Miyaura cross-coupling reaction has turned out to be one of the most powerful methods for the carbon–carbon bond formation in organic synthesis. Various palladium–NHC complex catalysts have been successfully employed in this reaction.[1,12] Herein, we turned our interest to investigate the catalytic activity of the biphenyl-linked *cis*-chelated bis-NHC–Pd(II) complexes **7a** and **7b** in the Suzuki–Miyaura cross-coupling reactions of aryl chlorides which are more attractive from the view of economic cost, but more challenging due to the less active nature of the carbon–chlorine bond. We chose to examine the coupling of 1-chloro-4-methoxybenzene with phenylboronic acid for the survey of the reaction parameters. As summarized in Table 1, the reaction conditions involving KO^{t}Bu and dioxane appear to be superior to the others (entry 4, Table 1). Complex **7a** appears to be more efficient than complex **7b** (entry 6, Table 1). It is noted that no product is observed when the reaction is performed in the absence of the ligand (entry 7, Table 1). Negligible decrease in catalytic activity is observed after the catalyst is kept open to air for two days (entry 5, Table 1), which further demonstrates the catalyst stability. In literature, most of reported complexes of chelated bis-NHC ligands which are often used to catalyze the Suzuki-Miyaura cross-coupling of aryl bromides or iodides,[4b, 4g, 12i] are inactive in catalyzing the coupling of aryl chlorides. The present chelated bis-NHC-Pd complex catalysts attain both stability and activity in the Suzuki-Miyaura reaction of aryl chlorides. It is also noted that, compared to some palladium complexes of monocarbene ligands,[1,12] the structures of bis-NHC ligands still need modification to further improve the catalytic activity.

We attempted the cross-coupling reactions of various aryl chlorides with arylboronic acids in dioxane at 100 ^{o}C in the presence of KO^{t}Bu. The scope of the Suzuki–Miyaura reactions with respect to the aryl chlorides and arylboronic acids component was investigated with **7a**. The results are shown in Table 2. A variety of aryl chlorides containing both electron-donating and electron-withdrawing substitutents tolerated well the reaction conditions, affording the corresponding biaryl products in good yields. The catalyst was less active for the Suzuki-Miyaura cross-coupling of heteroaryl chlorides (entries 13 and 14, Table 2).

Table 2. Catalytic Suzuki–Miyaura cross-coupling reactions of aryl chlorides with arylboronic acids.[a]



Entry	Ar^1	Ar^2	t (h)	Yield (%) [b]
1	4-MeOPh-	Ph-	18	91
2	3-MeOPh-	Ph-	18	90

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Table 2. Continued

Entry	Ar^1	Ar^2	t (h)	Yield (%) [b]
3	2-MeOPh-	Ph-	20	82
4	4-NO_2Ph-	Ph-	14	87
5	3-NO_2Ph-	Ph-	14	92
6	2-NO_2Ph-	Ph-	14	80
7	4-CNPh-	Ph-	16	85
8	Ph-	3-NO_2Ph	24	64
9	4-MeOPh-	4-MePh-	18	92
10	2-MeOPh-	4-MePh-	20	84
11	4-MePh-	3-NO_2Ph	24	61
12 [c]	4-MeOPh-	Ph-	18	90
13	3-pyridinyl	4-MeOPh-	22	71
14	2-pyridinyl	4-MeOPh-	24	30

[a]Reaction conditions: **7a** (2 mol%), arylboronic acid (1.25 mmol), aryl chloride (0.5 mmol), KO^{t}Bu (1.25 mmol), dioxane (5.0 mL), 100 ^{o}C under Ar.
[b]Isolated by silica gel column chromatography and based on aryl chlorides.
[c]$Pd(OAc)_2$ (2 mol%) and imidazolium salt **3a** (2 mol%) as catalyst.

Conclusions

In summary, we have synthesized a new type of biaryl-linked bis-NHC ligand precursors and the corresponding biaryl-linked *cis*-chelated bis-NHC–palladium(II) complexes. On the basis of X-ray diffraction, the structure of the complexes was determined. The complexes **7a** and **7b** are stable under moisture and air, and have been shown to be effective in the Suzuki–Miyaura reactions of a variety of aryl chlorides and arylboronic acids. The represent synthetic route here may also applied to the synthesis of other bis(imidazolin-2-ylidine) ligand precursors with a biaryl backbone. The present ligands could be further modified by changing the substituents on the benzene rings and/or the imidazole moieties, thus tuning either their steric or electronic characteristics for the construction of highly active transition metal–NHC catalysts.

Experimental Section

General. Unless otherwise noted, all manipulations were performed under an argon atmosphere using standard Schlenk techniques. All solvents were dried according to standard procedures. 2-Amino-2′-nitro-6,6′-dimethyl-1,1′-biphenyl was prepared according to literature procedures.[8] All other reagents are commercially available and were used without further purification. FT-IR

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measurements were recorded on a 17OSX Fourier transform infrared spectrometer. ^{1}H (400 MHz, 600 MHz) and ^{13}C (100 MHz, 150 MHz) NMR spectra were recorded using Bruker instruments. ^{1}H and ^{13}C chemical shifts are reported in ppm and calibrated to TMS on the basis of the solvent as an internal standard (7.27 ppm, $CDCl_3$). All NMR spectra were acquired at room temperature. Melting points were determined with an XRC-1 melting point apparatus and were uncorrected. GC–MS were recorded on an Agilent Technologies 6890-5973N. Mass spectra were obtained by using Bruker Daltonics Data Analysis 3.2. Elemental analyses were performed on a CARLO ERBA-1106 instrument.

X-Ray crystal structure determination and refinement.[11] X-ray single-crystal diffraction data for **7a** were collected on an Enraf-Nonius CAD-4 diffractometer at 294(2) K with Mo Kα radiation (λ = 0.71073 Å) by $\omega/2\theta$ scan mode. The structures were solved with direct methods using SHELXS-97 and refined by full-matrix least-squares refinement on F^2 with SHELXL-97. All atoms except hydrogen atoms were refined with anisotropic displacement parameters. In general, hydrogen atoms were fixed at calculated positions, and their positions were refined by a riding model.

Crystal/refinement data for **7a**·4$CHCl_3$: formula $C_{44}H_{46}Br_2Cl_{12}N_4Pd$, M = 1322.47, size 0.46 × 0.42 × 0.40 mm, monoclinic, space group C 2/c, a = 23.163(4) Å, b = 11.430(3) Å, c = 21.000(3) Å, α = 90°, β = 91.57(3)°, γ = 90°, F(000) = 2632, V = 5558(2) $Å^3$, T = 294(2) K, Z = 4, D(calcd) = 1.580 mg/m^3, μ = 2.383 mm^{-1}, Max of h, k, l = 27, 13, 24, reflection collected 4920, independent reflections 4639 [R(int) = 0.0066]

2-(Imidazol-1-yl)-2′-nitro-6,6′-dimethyl-1,1′-biphenyl (5). 40% aqueous glyoxal (725 mg, 5.0 mmol) and 37% aqueous formaldehyde (405 mg, 5.0 mmol) was added to acetic acid (25 mL). The mixture was heated with stirring to 85 °C, and then **4** [8] (484 mg, 2 mmol) was added dropwise along with acetic acid (15 mL), water (5 mL), ammonium acetate (385 mg, 5.0 mmol) in 30 min. The mixture was stirred for 8 h at 85 °C and then cooled to room temperature. A saturated aqueous solution of $NaHCO_3$ was added and adjusted pH to 7–8. The mixture was extracted with dichloromethane (30 mL × 3). The organic layers were combined, dried over $MgSO_4$, and filtered. After solvent was evaporated, the residue was purified by flash chromatography on silica gel (CH_2Cl_2/MeOH, v/v = 30/1) to yield **5** as a pale yellow solid. Yield: 504 mg (86%). IR (KBr, cm^{-1}): 3134 (w), 3062 (w), 2921 (w), 1525 (vs), 1498 (s), 1366 (s), 1246 (m), 1103 (w), 1066 (s), 796 (m), 740 (m), 659 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.97 (s, 3H, $ArCH_3$), 2.02 (s, 3H, $ArCH_3$), 6.84 (s, 1H, imi-H), 6.91 (s, 1H, imi-H), 7.25 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H, Ar-H), 7.36–7.45 (m, 5H, Ar-H, imi-H). 7.79 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.7 (C), 138.9 (C), 137.7 (C), 137.3 (CH), 135.8 (C), 135.0 (CH), 132.4 (C), 130.9 (C), 130.6 (CH), 129.1 (CH), 129.0 (CH), 128.9 (CH), 124.1 (CH), 122.2 (CH), 120.3 (CH), 20.0 (CH_3), 19.8 (CH_3). Mp: 79–80 °C. MS (ESI): *m/z* 294.1 ($[M + H]^+$). Anal. Calcd for $C_{17}H_{15}N_3O_2$: C, 69.61; H, 5.15; N, 14.33. Found: C, 69.31; H, 5.10; N, 14.29.

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2-(Imidazol-1-yl)-2′-amino-6,6′-dimethyl-1,1′-biphenyl (6). Compound **5** (586 mg, 2.0 mmol), active carbon (590 mg) and $FeCl_3·6H_2O$ (10 mg, 0.05 mmol) were added to methanol (30 mL). The mixture was heated with stirring to reflux. Hydrazine hydrate (60 mmol, 3 mL) was added dropwise in 1 h. The mixture was refluxed for 17 h and then filtered. The filtrate was dried over $MgSO_4$. The solvent was evaporated, and the residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc, v/v = 9/1) to afford **6** as a white solid. Yield: 463 mg (88%). IR (KBr, cm^{-1}): 3313 (s), 3189 (m), 3113 (w), 3061 (w), 2921 (w), 1582 (s), 1464 (vs), 1311 (s), 1247 (s), 1072 (s), 908 (m), 832 (m), 785 (m), 748 (s), 662 (m). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.60 (s, 3H, $ArCH_3$), 2.00 (s, 3H, $ArCH_3$), 4.53 (s, 2H, $ArNH_2$), 6.37 (d, *J* = 7.2 Hz, 1H, Ar-H), 6.57 (d, *J* = 8.0 Hz, 1H, Ar-H), 6.79 (d, *J* = 0.8 Hz, 1H, imi-H), 6.89 (t, *J* = 7.8 Hz, 1H, Ar-H), 7.12 (t, *J* = 1.2 Hz, 1H, imi-H), 7.30–7.33 (m, 1H, Ar-H), 7.43–7.47 (m, 2H, Ar-H), 7.54 (s, 1H, imi-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9 (C), 139.5 (C), 137.3 (CH), 137.0 (C), 136.3 (C), 132.7 (C), 130.3 (CH), 128.9 (CH), 128.8 (CH), 128.7 (CH), 123.7 (CH), 121.8, 120.2 (CH), 120.1 (CH), 112.7 (CH), 19.7 (CH_3). Mp: 170–171 °C. MS (ESI): *m/z* 263.1 ($[M + H]^+$). Anal. Calcd. for $C_{17}H_{17}N_3$: C, 77.54; H, 6.51; N, 15.96. Found: C, 77.34; H, 6.32; N, 15.78.

2,2′-Bis(imidazol-1-yl)-6,6′-dimethyl-1,1′-biphenyl (2). Compound **2** was similarly prepared as **5** from **4**. Yield: 565 mg (90%). IR (KBr, cm^{-1}): 3110 (m), 2924 (m), 1576 (m), 1494 (vs), 1313 (m), 1256 (s), 1109 (w), 1068 (s), 903 (w), 836 (m), 790 (m), 732 (s), 660 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.21 (s, 6H, $ArCH_3$), 6.39 (d, *J* = 1.2 Hz, 2H, imi-H), 6.87 (s, 2H, imi-H), 6.93 (s, 2H, imi-H), 7.05–7.07 (m, 2H, Ar-H), 7.36-7.38 (m, 4H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9 (C), 136.8 (CH), 135.6 (C), 131.5 (C), 130.2 (CH), 129.4 (CH), 128.7 (CH), 123.6 (CH), 119.8 (CH), 20.1 (CH_3). Mp: 129–131 °C. MS (ESI): *m/z* 314.2 ($[M + H]^+$). Anal. Calcd. for $C_{20}H_{18}N_4$: C, 76.41; H, 5.77; N, 17.82. Found: C, 76.33; H, 5.56; N, 17.65.

2,2′-Bis[3-(2,4,6-trimethylbenzyl)imidazolium-1-yl]-6,6′-dimethyl-1,1′-biphenyl dibromide (3a). Compound **2** (361 mg, 1.15 mmol), 1-(bromomethyl)-2,4,6-trimethylbenzene (1224 mg, 5.75 mmol) were dissolved in dioxane (5 mL). Under argon, the mixture was heated to 85 °C and stirred for 8 h. The resulting white solid **3a** was obtained after filtration and washing with diethyl ether. Yield: 791 mg (93%). IR (KBr, cm^{-1}): 3063 (s), 2922 (vs), 1606 (w), 1548 (s), 1481 (m), 1444 (m), 1215 (s), 1162 (m), 761 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.14 (s, 6H, $ArCH_3$, 2.28 (s, 6H, $ArCH_3$), 2.30 (s, 12H, $ArCH_3$), 5.68 (d, *J* = 14.8 Hz, 2H, $ArCH_2$), 5.97 (d, *J* = 14.8 Hz, 2H, $ArCH_2$), 6.88 (s, 4H, Ar-H), 7.10 (s, 2H, imi-H), 7.14 (s, 2H, imi-H), 7.51–7.54 (m, 4H, Ar-H), 7.58–7.62 (m, 2H, Ar-H), 10.11 (s, 2H, imi-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 139.5 (C), 139.2 (C), 138.5 (C), 135.9 (CH), 133.4 (CH), 133.2 (C), 130.9 (CH), 129.9 (CH), 129.8 (C), 126.8 (C), 125.4 (CH), 123.8 (CH), 123.4 (CH), 47.9 (CH_2), 21.1 (CH_3), 19.9 (CH_3), 19.7 (CH_3). Mp: > 250 °C. MS (ESI): *m/z* 290.2 ($[M - 2Br]^{2+}/2$). Anal. Calcd. for $C_{40}H_{44}Br_2N_4$: C, 64.87; H, 5.99; N, 7.56. Found: C, 64.54; H, 5.58; N, 7.75.

2,2′-Bis(3-benzylimidazolium-1-yl)-6,6′-dimethyl-1,1′-biphenyl dibromide (3b). 3b was prepared from **2** (361 mg, 1.15 mmol) in the same way as **3a** from **2** using bromomethylbenzene (983 mg, 5.75 mmol) as alkylating reagent in dioxane (5 mL). Yield: 693 mg (92%). IR (KBr, cm^{-1}): 3129 (w), 2959 (m), 2919 (m), 1613 (m), 1470 (s), 1374 (s), 1131 (m), 1030 (w), 856 (m),

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795 (m), 751 (s), 677 (m). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.07 (s, 6H, $ArCH_3$), 5.40 (s, 4H, $ArCH_2$), 7.20 (dd, *J* = 7.6 Hz, 1.6 Hz, 4H, Ar-H), 7.28 (t, *J* = 1.6 Hz, 2H, imi-H), 7.41-7.47 (m, 6H, Ar-H), 7.56-7.69 (m, 6H, Ar-H), 7.83 (t, *J* = 1.6 Hz, 2H, imi-H), 9.11 (t, *J* = 1.4 Hz, 2H, imi-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 139.2 (C), 136.1 (CH), 134.3 (CH), 133.0 (C), 132.8 (C), 130.5 (CH), 129.1 (CH), 128.9 (CH), 128.8 (CH), 128.4 (C), 124.6 (CH), 123.3 (CH), 123.0 (CH), 51.7 (CH_2), 19.74 (CH_3). Mp: > 250 °C. MS (ESI): *m/z* 248.1 ($[M - 2Br]^{2+}/2$). Anal. Calcd. for $C_{34}H_{32}Br_2N_4$: C, 62.21; H, 4.91; N, 8.53. Found: C, 62.34; H, 5.17; N, 8.65.

2,2′-Bis(3-(2,4,6-trimethylbenzyl)imidazolin-2-yliden-1-yl)-6,6′-dimethyl-1,1′-biphenyl dibromopalladium(II) (7a). A mixture of **3a** (74 mg, 0.1 mmol), $Pd(OAc)_2$ (22 mg, 0.1 mmol) and KO^{t}Bu (17 mg, 0.15 mmol) in dioxane (10 mL) was refluxed for 8 h. The solvent was removed under reduced pressure and the residue was separated by silica gel chromatography (CH_2Cl_2/MeOH, v/v = 10/1) to give bis-NHC–Pd(II) complex **7a** as a yellow solid. Yield: 52 mg (62%). IR (KBr, cm^{-1}): 3035 (s), 1543 (s), 1459 (s), 1218 (s), 1102 (s), 796 (m), 716 (vs), 647 (m). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.92 (s, 6H, $ArCH_3$), 2.09 (s, 12H, $ArCH_3$), 2.28 (s, 6H, $ArCH_3$), 5.17 (d, *J* = 14.4 Hz, 2H, $ArCH_2$), 6.08 (d, *J* = 16.2 Hz, 2H, $ArCH_2$), 6.38–6.46 (m, 4H, imi-H), 6.85 (s, 4H, Ar-H), 7.20 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.37 (t, *J* = 7.5 Hz, 2H, Ar-H), 7.51–7.62 (m, 2H, Ar-H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 159.0 (C), 139.3 (C), 139.0 (C), 138.6 (C), 137.5 (C), 134.5 (C), 131.1 (CH), 129.7 (CH), 129.2 (CH), 127.8 (C), 124.3 (CH), 122.2 (CH), 120.2 (CH), 52.2 (CH_2), 21.0 (CH_3), 20.6 (CH_3), 19.7 (CH_3). Mp: > 250 °C. MS (ESI): *m/z* 844.1 (M^+). Anal. Calcd. for $C_{40}H_{44}Br_2N_4Pd$: C, 56.72; H, 5.24; N, 6.61. Found: C, 56.51; H, 5.28; N, 6.73.

2,2′-Bis(3-benzylimidazolin-2-yliden-1-yl)-6,6′-dimethyl-1,1′-biphenyldibromopalladium (7b). Complex **7b** was similarly obtained like **7a** as a yellow solid. Yield: 51 mg (67%). IR (KBr, cm^{-1}): 3087 (m), 2921 (m), 1568 (w), 1461 (vs), 1238 (vs), 1129 (m), 748 (s), 715 (vs). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.91 (s, 6H, $ArCH_3$), 5.44 (d, *J* = 15.0 Hz, 2H, $ArCH_2$), 6.02 (d, *J* = 15.0 Hz, 2H, $ArCH_2$), 6.49 (s, 2H, imi-H), 6.55(s, 2H, imi-H), 7.09–7.17 (m, 6H, Ar-H), 7.27 (t, *J* = 7.8 Hz, 2H, Ar-H), 7.33–7.35 (m, 6H, Ar-H), 7.42 (d, *J* = 7.8 Hz, 2H, Ar-H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 159.8 (C), 139.0 (CH), 137.4 (C), 135.3 (C), 134.5 (C), 130.9 (C), 129.7 (CH), 129.3 (CH), 128.7 (CH), 128.3 (CH), 124.1 (CH), 123.3 (CH), 121.7 (CH), 58.0 (CH_2), 19.7 (CH_3). Mp: > 250 °C. MS (ESI): *m/z* 762.0 (M^+). Anal. Calcd. for $C_{34}H_{32}Br_2N_4Pd$: C, 53.53; H, 4.23; N, 7.34. Found: C, 53.64; H, 4.12; N, 7.71.

General procedure for the Suzuki–Miyaura cross-coupling reaction

The flask containing aryl chloride (0.500 mmol), arylboronic acid (1.250 mmol), KO^{t}Bu (1.25mmol), bis-NHC–Pd(II) catalyst (0.01 mmol, 2 mol%) and 1,4-dioxane (5 mL) was maintained in an oil bath at 100 °C under Ar until the starting material was consumed as determined by TLC. The reaction mixture was extracted with Et_2O (10 mL × 3). The combined ether extracts were dried over $MgSO_4$. After evaporation of the solvent, the resulting crude product was purified by silica gel column chromatography. All of the cross-coupling products were identified by comparing their NMR spectra with those reported in literature.

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Supplementary Materials

Copies of NMR spectra for **2**, **3**, **5, 6** and **7**. CCDC-765782 contains the supplementary crystallographic data for **7a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.CCDC.cam.ac.uk/data_request/cif.

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