Synthesis, Structure, and Catalytic Activity of Palladium(II) Complexes of New CNC Pincer-Type N-Heterocyclic Carbene Ligands

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New CNC pincer-type N-heterocyclic carbene ligands with a central diarylamido moiety are presented. Palladium(II) pincer complexes of type [Pd(L)Cl] (L = bis[2-(3-alkylimidazolin-2-yliden-1-yl)-4-methylphenyl]amido) **5a**–**c** (**5a**, alkyl = benzyl; **5b**, alkyl = *n*-butyl; **5c**, alkyl = 2,4,6-trimethylbenzyl) were obtained from the corresponding silver carbene complexes and [PdCl₂(MeCN)₂] without addition of external bases. The palladium pincer complex **5a** was characterized by X-ray diffraction. The molecular structure of **5a** shows a distorted square-planar coordination geometry for the palladium atom. Pincer complexes **5a**–**c** have been shown to be active catalysts for the Suzuki–Miyaura reactions.

Introduction

Since the initial report on PCP ligands by Shaw,[1] investigation on pincer-type ligands **A** (Chart 1) has been increasing in recent years, owing to their potential for supporting unusual chemical properties on transition-metal centers.[2] Remarkable examples such as PNP ligands based on a neutral pyridine have been found to support a number of exciting catalytic and stoichiometric transformations.[3] On the other hand, N-heterocyclic carbenes (NHCs) have been employed with considerable success in

Chart 1
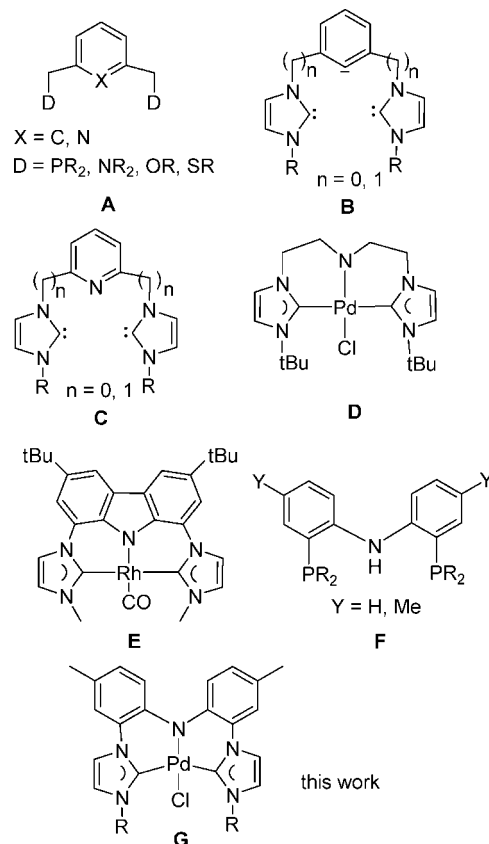
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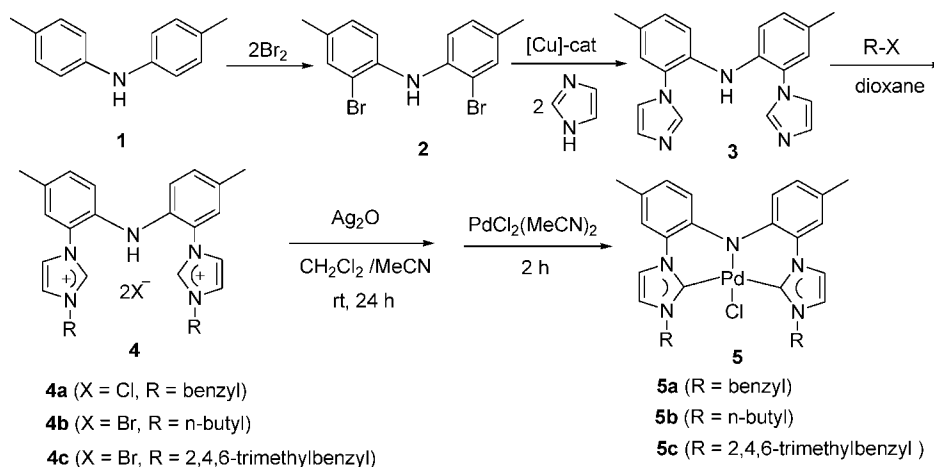(4) (a) Arduengo, A. J. *Acc. Chem. Res.* **1999**, *32*, 913. (b) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. (c) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290. (d) Nolan, S. P. *N-Heterocyclic Carbenes in Synthesis*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2006. (e) Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Angew. Chem., Int. Ed.* **2007**, *46*, 2768. (f) Hahn, F. E. *Angew. Chem., Int. Ed.* **2006**, *45*, 1348.
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coordination chemistry and various catalytic transformations.[4] Substitution of phosphine donors with NHCs has led to several kinds of NHC-containing pincer-type ligands, carbanionic **B**[5] and neutral **C**.[5a,6] Transition-metal complexes of pincer CNC ligands with an anionic amido backbone, **D** and **E**, were reported recently by Douthwaite et al.[7] and Kunz et al.,[8] respectively. The use of chelate and pincer coordination of these NHC ligands has opened a new dimension in the design and preparation of new stable catalysts.[9] A number of palladium complexes of

Scheme 1. Synthesis of the Diarylamido-Linked Bis-NHC Pincer Ligands and Their Pd(II) Complexes 5a–c

4a (X = Cl, R = benzyl)
4b (X = Br, R = n-butyl)
4c (X = Br, R = 2,4,6-trimethylbenzyl)

5a (R = benzyl)
5b (R = n-butyl)
5c (R = 2,4,6-trimethylbenzyl)

CNC pincer-type ligands have been found to be efficient catalysts for C–C bond formation reactions (Heck, Suzuki, Sonogashira).[5a,6,10] Other CNC pincer complexes of transition metals such as rhodium,[11] ruthenium,[12] cobalt,[13] chromium,[14] and iron[15] have also found applications in catalytic reactions (olefin methatesis, hydrogen transfer, hydrosilylation, hydroformylation, etc.).

Among various PNP pincer-type ligands, the recently emerging ligand **F** (Chart 1) with a diarylamido backbone has become attractive since it gives catalysts of unusual reactivity in activation of inert chemical bonds and catalytic formation of C–C bonds.[16] However, we were surprised that there has been no report on CNC pincer-type bis-NHC ligands based on a diarylamido backbone described to date. An anionic amido-CNC ligand may be viewed not only as a component of an organometallic chemist's "pincer toolbox" complementary to the CNC ligands but also as a chelate version of the *mer,trans*-(NHC)$_2$ motif.[9] Guided by the explorations of PNP ligand **F**, we envisioned that replacement of phosphine arms in ligand **F** with NHCs that have higher *trans* effect than N- or P-donors and are more tightly bound to the metal would produce new CNC pincer-type ligands that may display useful properties for catalytic applications, especially for those requiring harsh reaction conditions. Here, we report the synthesis of new pincer-type NHC–Pd complex **G**, which combines the electron-rich properties inherent to NHCs and the presence of a rigid diarylamido backbone as CNC ligand. The molecular structure of complex **5a** and the catalytic activity of **5a–c** in the Suzuki–Miyaura reactions are also described in this work.

Results and Discussion

Ligand and Metal Complex Synthesis. The synthetic routes to imidazolium salt precursors **4a–c** used to prepare the complexes are shown in Scheme 1. Bis(4-methylphenyl)amine **1** was prepared by the Buchwald–Hartwig protocol from the corresponding aniline and bromoarene.[17] Bromination of **1** was optimized to give **2** in good isolated yield.[18] Coupling of **2** with imidazole in a copper-catalyzed Ullmann reaction afforded bis(imidazolyl)-substituted diarylamine **3**, which was treated with R-X to give the corresponding bis(imidazolium) salts **4a–c**. ^{1}H and ^{13}C NMR spectroscopic data for **4a–c** obtained in CDCl$_3$ show spectra consistent with C_s symmetry, and in the ^{1}H NMR spectra, characteristic signals of the imidazolium salt NC(H)N protons are observed in the region between δ 9.95 and 10.52 ppm. These values fall in the range observed for related imidazolium salts.[6b,19] ^{1}H NMR resonances for the NH protons are observed at δ 7.84–8.56 ppm, which are similar to that for the reported (PNP)H ligand.[16b]

The choice of base for the synthesis of palladium complexes **5a–c** was found to be crucial. Attempts to prepare the palladium complexes by in situ deprotonation of **4a–c** with external strong bases including [n]BuLi, LDA, KO[t]Bu, and NaH followed by reaction with PdCl$_2$ or Pd(OAc)$_2$ were unsuccessful, leading only to the formation of intractable reaction mixtures. Transmetalation has proved to be a promising procedure to obtain NHC–metal complexes,[6c,20] which typically involves treatment

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of the imidazolium salt with silver oxide to form the Ag−NHC complex, followed by transmetalation to a species such as [PdCl$_2$(MeCN)$_2$] to give the metal carbene complex.[7,21] We then turned to the synthesis of **5a−c** by transmetalation from the corresponding Ag−NHC derivatives. Although it was clearly observed that the reactions of imidazolium salts **4a−c** with silver oxide occurred when the dark reaction mixture turned pale, the corresponding pure Ag−NHC complex sample was not obtained. We found it best to add [PdCl$_2$(MeCN)$_2$] directly to the solution after filtering off the unreacted silver oxide and insoluble residues. The addition of [PdCl$_2$(MeCN)$_2$] immediately gave the desired product and a white suspension of silver chloride. The transmetalation reaction was followed by a ^{13}C NMR experiment in CDCl$_3$. The appearance of the signal at 180.5 ppm for the Ag−carbene carbon resonance after addition of silver oxide to the solution of **4a** in CDCl$_3$ clearly showed the in situ generation of the Ag−NHC complex. The appearance of the peak at 166.1 ppm for the Pd−carbene carbon resonance and the eventual disappearance of the signal at 180.5 ppm after addition of [PdCl$_2$(MeCN)$_2$] indicated the transmetalation of the Ag−NHC complex to [PdCl$_2$(MeCN)$_2$]. The products were isolated as an air- and moisture-stable yellow crystalline solid in moderate yields. The formation of **5a−c** is confirmed by the absence of the NH and the NC(H)N proton resonances in the ^{1}H NMR spectra, which demonstrate that the ligand is coordinated to palladium in a monoanionic bis-NHC form. Notably, the signals for the carbene carbon atoms of **5a−c** in the ^{13}C NMR spectra appear at 164.8−165.7 ppm, which are characteristic peaks for palladium carbene complexes.[5a,20c]

Interestingly, it is worth noting that the reaction of Ag−NHC complexes of **4a−c** with [PdCl$_2$(MeCN)$_2$] give amido−NHC complexes **5a−c**, where the signals of NH disappear. It has been noted that silver oxide is not sufficiently basic to deprotonate a secondary amine.[22] Therefore this implies that the reaction of Ag−NHC complexes of **4a−c** with [PdCl$_2$(MeCN)$_2$] proceeds with immediate loss of HCl and formation of amido−NHC complexes **5a−c**. That is unlike the reactivity known for the aliphatic amine (diethylamine) ligand in **D**; it is a Ag−NHC complex from amino−NHC [(NH{CH$_2$CH$_2$(C[NCHCHNBu^t])})$_2$]PdCl]Cl species that do not spontaneously lose HCl.[7] A strong base (such as NaH) is needed to deprotonate the NH subsequent to palladium(II) coordination, affording the amido−NHC complex [(N{CH$_2$CH$_2$(C-[NCHCH NBu^t])})$_2$)PdCl] (**D**). It is most likely that the product-adapted rigid ligand geometry and/or weaker diarylamine N−H bond are responsible for facile HCl loss.

Yellow single crystals of complex **5a** suitable for an X-ray diffraction study were grown from dichloromethane and diethyl ether. The molecular structure of complex **5a** is depicted in Figure 1. As expected, the monoanionic ligand is coordinated to palladium in a tridentate fashion by the amido nitrogen and the two carbene atoms, forming two six-membered chelate rings. The geometry about Pd is approximately square planar, with the C8−Pd−C8′ angle of 172.1(2)° being a consequence of the chelate constraint. N1, Pd1, and Cl1 lie on a crystallographic axis of symmetry. The two aromatic rings in **5a** are distinctly
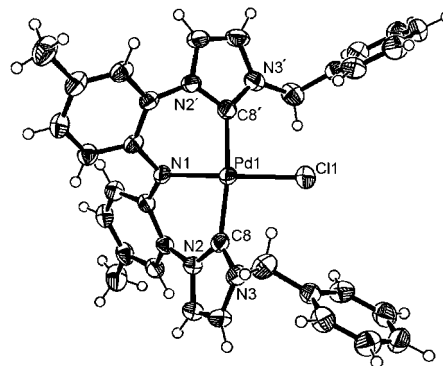
Figure 1. Molecular structure of complex **5a**, showing 30% probability displacement ellipsoids. Selected interatomic distances (Å) and angles (deg): Pd1−N1 = 2.006(4), Pd1−C8 = 2.002(3), Pd1−C8′ = 2.002(4), Pd1−Cl1 = 2.3187(16), N1−Pd1−Cl1 =180.0, C8−Pd−C8′ = 172.1(2).

nonparallel, with an angle of ca. 61.58°. The twist in the chelate backbone presumably arises from repulsion between the two *ortho* hydrogens on the aromatic rings. ^{1}H NMR experiments showed that the benzylic CH$_2$ protons are still diastereotopic at 373 K in solution, indicating that they (two *ortho* hydrogens) also prevent ligand twisting in solution even at a high temperature. In addition, the NHC rings are not coplanar with the aryl backbone (two aromatic rings) and are all tilted by −29.94°. The palladium−carbene distances (Pd1−C8 = 2.002(3) Å and Pd1−C8′ = 2.002(4) Å) are very similar to the Pd−C$_{carbene}$ bond distances found for pincer complexes with two *trans*-positioned imidazolin-2-ylidene donor groups.[5a,6e] The Pd1−N1 bond distance of 2.006(4) Å is comparable with the distance observed in palladium(II) complexes of pyridine−NHC ligands,[6a,b,e] but is shorter than that in **D** (2.058(12) Å), while the Pd1−Cl1 distance of 2.3187(16) Å is similar to that found in **D**.[7]

Catalytic Studies. Although numerous palladium NHC catalysts have been employed in the Suzuki−Miyaura reactions,[4c−e,23] tridentate bis-NHC−palladium complexes that have been reported active in catalyzing this reaction are rare.[6b,24] It is reasonable to expect that the present complexes **5a−c** are potential efficient catalysts for the Suzuki−Miyaura reactions. The complexes **5a−c** are thermally stable and inert toward air and moisture in the solid state; these properties allowed for catalytic experiments under aerobic conditions. We chose to examine the coupling of 4-bromoanisole with phenylboronic acid for the survey of the reaction parameters. As summarized in Table 1, the reaction conditions involving Na$_2$CO$_3$ and dioxane appear to be superior to the others. It is important to note that no product formation is observed when the reaction is performed in the absence of **5a**.
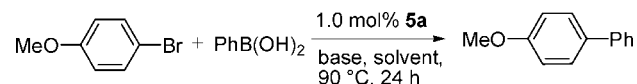
We attempted the cross-coupling reaction of various aryl bromides with arylboronic acids in dioxane at 90 °C in the presence of Na$_2$CO$_3$ as the base. The catalytic activity of complexes **5a−c** was tested under the same reaction conditions, as shown in Table 2. Complex **5a** appeared to be more efficient

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Table 1. Effect of Base and Solvent on the Suzuki−Miyaura Cross-Coupling of 4-Bromoanisole with Phenylboronic Acid[a]

$$\text{MeO} \!-\!\!\langle\!\!\langle \;\rangle\!\!\rangle\!-\!\text{Br} + \text{PhB(OH)}_2 \xrightarrow[\substack{\text{base, solvent,} \\ 90\,^{\circ}\text{C, 24 h}}]{1.0\;\text{mol\%}\;\mathbf{5a}} \text{MeO} \!-\!\!\langle\!\!\langle \;\rangle\!\!\rangle\!-\!\text{Ph}$$

entry	base	solvent	yield (%)[b]
1	Na₂CO₃	dioxane	89
2	K₂CO₃	dioxane	81
3	Cs₂CO₃	dioxane	Trace
4	KOᵗBu	dioxane	43
5	AcONa	dioxane	35
6	Na₂CO₃	THF	22
7	KOᵗBu	THF	16
8	Na₂CO₃	DMF	11
9	K₂CO₃	DMF	trace
10	Na₂CO₃	toluene	0
11	Na₂CO₃	ethanol	0

[a] Reaction conditions: 0.5 mmol of 4-bromoanisole, 0.75 mmol of phenylboronic acid, 1.0 mol % of **5a**, 1.0 mmol of base, 5.0 mL of solvent, 90 °C, under air. [b] Isolated by silica gel column chromatography and based on 4-bromoanisole.

Table 2. Catalytic Suzuki−Miyaura Cross-Coupling Reactions of Aryl Bromides with Arylboronic Acids[a]

$$\text{Ar}^1\text{-Br} + \text{Ar}^2\text{-B(OH)}_2 \xrightarrow[\text{Na}_2\text{CO}_3,\,90\,^{\circ}\text{C}]{\text{catalyst } \mathbf{5a\text{-}c}\;(1.0\,\text{mol\%})} \text{Ar}^1\text{-Ar}^2$$

entry	cat.	Ar¹	Ar²	t (h)	yield (%)[b]
1	**5a**	4-MeOPh−	Ph−	24	89
2	**5b**	4−MeOPh−	Ph−	24	85
3	**5c**	4-MeOPh−	Ph−	24	65
4	**5a**	3-NO₂Ph−	Ph−	20	90
5	**5b**	3-NO₂Ph−	Ph−	20	86
6	**5c**	3-NO₂Ph−	Ph−	20	77
7	**5a**	3-MeOPh−	Ph−	24	85
8	**5a**	4-MePh−	Ph−	24	88(4)[c]
9[d]	**5a**	4-BrPh−	Ph−	36	84
10	**5a**	4-CF₃Ph−	Ph−	20	88
11	**5a**	4-CNPh−	Ph−	20	91
12	**5a**	Ph−	4-MeOPh−	24	90
13	**5a**	4-MePh−	4-MeOPh−	24	87
14	**5a**	3-MeOPh−	4-MePh−	24	86
15	**5a**	3-NO₂Ph−	4-MePh−	20	91
16	**5a**	4-MeOPh−	3-NO₂Ph−	20	67

[a] Reaction conditions: 0.5 mmol of aryl bromide; 0.75 mmol of arylboronic acid; 1.0 mol % of catalyst; 1.0 mmol of Na₂CO₃; 5.0 mL of dioxane; 90 °C, under air. [b] Isolated by silica gel column chromatography and based on aryl bromides. [c] Self-coupling byproduct of phenylboronic acid in parentheses was detected by GC-MS. In this case the self-coupling byproduct could not be separated from the cross-coupling product by silica gel column chromatography. [d] 1.5 mmol of phenyl boronic acid, 2.0 mol % of catalyst; 2.0 mmol of Na₂CO₃. Product: 1,4-diphenylbenzene.

than **5b** and **5c**. They all proved to be thermally stable under air for the coupling of activated and deactivated aryl bromides with phenylboronic acid. No palladium black was observed in all attempts. The scope of the Suzuki−Miyaura reactions with respect to the aryl bromides and arylboronic acids component was investigated with **5a**. A variety of aryl bromides containing both electron-donating and electron-withdrawing substitutents tolerated well the reaction conditions, affording the corresponding biaryl products in good yields.

Conclusion

In summary, we have synthesized a new class of tridentate, monoanionic, meridionally coordinating pincer-type NHC ligand precursors and amido−NHC palladium(II) complexes. Complexes **5a−c** are stable toward moisture and air and tolerate high temperatures. They have been shown to be effective in

the Suzuki−Miyaura reactions of a variety of aryl bromides, even with less active aryl bromides. Most significantly, the present ligands are versatile since they can be further modified by changing the aromatic ring substituents or N-substituents in the imidazole moiety, thus tuning either the sterics and/or the electronics, which are very promising for the construction of highly active transition-metal catalysts. Further reactivity studies of complexes **5a−c** as well as the synthesis of other diarylamido NHC complexes are the subjects of our current research.

Experimental Section

General Procedures. Unless otherwise noted, all manipulations were performed under an argon atmosphere using standard Schlenk techniques. All solvents were dried according to standard procedures. Bis(4-methylphenyl)amine (**1**),[17] bis(2-bromo-4-methylphenyl)amine (**2**),[18] and [PdCl₂(MeCN)₂][25] were prepared according to literature procedures. All other reagents are commercially available and were used without further purification.

¹H (400 MHz, 600 MHz) and ¹³C (100 MHz, 150 MHz) NMR spectra were recorded using Bruker instruments. ¹H and ¹³C chemical shifts are reported in ppm and calibrated to TMS on the basis of the solvent as an internal standard (2.49 ppm, DMSO-d_6; 7.27 ppm, CDCl₃). 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. X-ray single-crystal diffraction data for **5a** were collected on an Enraf-Nonius CAD-4 diffractometer at 294(2) K with Mo Kα radiation (λ = 0.71073 Å) by ω/2θ 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.[26] 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 **5a**: formula C₃₄H₃₀N₅ClPd, M = 650.48, size 0.25 × 0.25 × 0.13 mm, monoclinic, space group C2/c, a = 16.337(4) Å, b = 9.571(3) Å, c = 18.747(9) Å, α = 90°, β = 100.79(3)°, γ = 90°, F(000) = 1328, V = 2879.6(18) Å³, T = 294(2) K, Z = 4, D(calcd) = 1.500 Mg/m³, μ = 0.770 mm⁻¹, range of h, k, l = −19/19, 0/11, −9/22, reflns collected 2864, unique reflns 2685, refinement method full-matrix least-squares on F^2, parameters 191, R1 = 0.0356 (observed data with $I > 2\sigma(I)$), wR2 = 0.0786, GOF = 1.038.

Bis[2-(imidazol-1-yl)-4-methylphenyl]amine (3). To a suspension of sodium hydride (60% mineral oil dispersion) (1.20 g, 30.0 mmol) in 30 mL of DMF was added imidazole (3.40 g, 50.0 mmol) with stirring at room temperature until hydrogen evolution ceased. Then, bis(2-bromo-4-methylphenyl)amine (1.76 g, 5.00 mmol) and copper powder (0.160 g, 2.50 mmol) were added to the reaction mixture, which was stirred at 140 °C for 48 h. The mixture was cooled to room temperature, diluted with dichloromethane and water, stirred for 1 h, and filtered. The organic layer was separated, washed with water and brine, and dried over anhydrous sodium sulfate. The solvent was removed in vacuo. Purification by column chromatography (silica gel), ethyl acetate/methanol = 10:1, followed by recrystallization from ethyl acetate gave the product as a white solid. Yield: 1.05 g (63.8%).

¹H NMR (400 MHz, CDCl₃): δ 7.51 (s, 2H, NC*H*N), 7.11−7.15 (m, 4H, imi-*H*), 7.04 (d, *J* = 8.4 Hz, 4H, Ar-*H*), 6.91 (s, 2H, Ar-*H*),

(25) Anderson, G. K.; Lin, M. *Inorg. Synth.* **1990**, *28*, 60.
(26) Scheldrick, G. M. *SHELXS-97 and SHELXL-97, Program for Solution and Refinement of Crystal Structures*; University of Göttingen: Germany, 1997.

4.90 (s, 1H, N*H*), 2.33 (s, 6H, ArC*H*$_3$). ^{13}C NMR (100 MHz, CDCl$_3$): δ 137.4, 135.6, 132.4, 130.2, 130.0, 130.0, 128.0, 127.8, 119.8 (Ar-*C*, imi-*C*), 20.5 (Ar*C*H$_3$). Mp: 141−142 °C. HRMS (MALDI): *m/z* calcd for C$_{20}$H$_{20}$N$_5$ ([M + H]$^+$) 330.1713, found 330.1729.

Bis[2-(3-benzylimidazolium)-4-methylphenyl]amine Dichloride (4a). A solution of **3** (0.329 g, 1.00 mmol) and benzyl chloride (0.378 g, 3.00 mmol) in 1,4-dioxane (20 mL) was heated under reflux for 4 days. Then the solvent was removed and the solid residue was washed with ether. The crude product was washed three times by dissolving in CH$_2$Cl$_2$ and precipitating with Et$_2$O, leaving a white solid. Yield: 0.524 g (90.0%).

^{1}H NMR (400 MHz, CDCl$_3$): δ 10.52 (s, 2H, NC*H*N), 8.56 (s, 1H, N*H*), 7.45−7.49 (m, 8H, imi-*H*, Ar-*H*), 7.30−7.32 (m, 6H, Ar-*H*), 7.01 (s, 4H, Ar-*H*), 7.00 (s, 2H, Ar-*H*), 5.66 (s, 4H, NC*H*$_2$), 2.22 (s, 6H, ArC*H*$_3$). ^{13}C NMR (100 MHz, CDCl$_3$): δ 137.8, 135.7, 133.3, 133.2, 132.2, 129.4, 129.2, 129.2, 127.1, 125.8, 123.3, 122.5, 122.2 (Ar-*C*, imi-*C*), 53.3 (N*C*H$_2$), 20.4 (Ar*C*H$_3$). Mp: 168−170 °C. MS (ESI): *m/z* 546.3 ([M − Cl]$^+$), 510.4 ([M − 2Cl − H]$^+$). HRMS (ESI): calcd for C$_{34}$H$_{32}$N$_5$ ([M − 2Cl − H]$^+$) 510.2652, found 510.2622.

Bis[2-(3-butylimidazolium)-4-methylphenyl]amine Dibromide (4b). A solution of **3** (0.329 g, 1.00 mmol) and 1-bromobutane (0.408 g, 3.00 mmol) in 1,4-dioxane (20 mL) was heated under reflux for 4 days. Then the solvent was removed and the solid residue was washed with ether. The crude product was washed three times by dissolving in CH$_2$Cl$_2$ and precipitating with Et$_2$O, leaving a white solid. Yield: 0.579 g (96.0%).

^{1}H NMR (400 MHz, CDCl$_3$): δ 9.95 (s, 2H, NC*H*N), 7.84 (s, 1H, N*H*), 7.64 (t, *J* = 1.8 Hz, 2H, imi-*H*), 7.53 (t, *J* = 1.8 Hz, 2H, imi-*H*), 7.09−7.16 (m, 6H, Ar-*H*), 4.44 (t, *J* = 7.4 Hz, 4H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 2.30 (s, 6H, ArC*H*$_3$), 1.85-1.93 (m, 4H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.34−1.40 (m, 4H, NCH$_2$CH$_2$C*H*$_2$CH$_3$), 0.96 (t, *J* = 7.4 Hz, 6H, NCH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C NMR (100 MHz, CDCl$_3$): δ 137.2, 136.0, 133.5, 132.4, 127.5, 126.0, 123.7, 123.0, 122.7 (Ar-*C*, imi-*C*), 50.1 (N*C*H$_2$CH$_2$CH$_2$CH$_3$), 31.8 (NCH$_2$*C*H$_2$CH$_2$CH$_3$), 20.4 (Ar*C*H$_3$), 19.6 (NCH$_2$CH$_2$*C*H$_2$CH$_3$), 13.6 (NCH$_2$CH$_2$CH$_2$*C*H$_3$). Mp: 126-128 °C. MS (ESI): *m/z* 522.2 ([M − Br]$^+$), 442.3 ([M − 2Br − H]$^+$). HRMS (ESI): calcd for C$_{28}$H$_{36}$N$_5$ ([M − 2Br − H]$^+$) 442.2965, found 442.2961.

Bis[2-(3-(2,4,6-trimethyl)benzylimidazolium)-4-methylphenyl]amine Dibromide (4c). A solution of **3** (0.329 g, 1.00 mmol) and 2,4,6-trimethylbenzyl bromide (0.533 g, 2.50 mmol) in 1,4-dioxane (20 mL) was heated under reflux for 6 h. Then the solvent was removed and the solid residue was washed with ether. The crude product was washed three times by dissolving in CH$_2$Cl$_2$ and precipitating with Et$_2$O, leaving a white solid. Yield: 0.702 g (92.9%).

^{1}H NMR (400 MHz, CDCl$_3$): δ 9.69 (s, 2H, NC*H*N), 8.08 (s, 1H, N*H*), 7.51 (s, 2H, imi-*H*), 7.31 (s, 2H, imi-*H*), 7.08−7.15 (m, 4H, Ar-*H*), 7.04 (s, 2H, Ar-*H*), 6.92 (s, 4H, Ar-*H*), 5.73 (s, 4H, NC*H*$_2$), 2.33 (s, 12H, ArC*H*$_3$), 2.30 (s, 6H, ArC*H*$_3$), 2.29 (s, 6H, ArC*H*$_3$). ^{13}C NMR (100 MHz, CDCl$_3$): δ 139.6, 138.4, 136.4, 135.2, 133.3, 132.3, 129.7, 127.2, 125.6, 125.4, 123.7, 122.0, 121.9 (Ar-*C*, imi-*C*), 48.3 (N*C*H$_2$), 21.1 (Ar*C*H$_3$), 20.3 (Ar*C*H$_3$), 20.0 (Ar*C*H$_3$). Mp: 166−168 °C. *m/z* 674.4 ([M − Br]$^+$), 594.5 ([M − 2Br − H]$^+$). HRMS (ESI): calcd for C$_{40}$H$_{44}$N$_5$ ([M − 2Br − H]$^+$) 594.3591, found 594.3583.

General Procedure for the Synthesis of [Bis(2-(3-alkylimidazolin-2-yliden-1-yl)-4-methylphenyl)amido]chloropalladium(II) (5a−c). A mixture of one of the bis(imidazolium) salts **4a−c** (0.100 mmol) and silver(I) oxide (27.6 mg, 0.120 mmol) in 5 mL of solvent (CH$_2$Cl$_2$/MeCN, v/v = 1:1) was stirred at room temperature for 24 h. The reaction mixture was filtered and washed with CH$_2$Cl$_2$ (5 mL × 2). The combined filtrate was reduced to 5 mL under vacuum. [PdCl$_2$(MeCN)$_2$] (25.8 mg, 0.100 mmol) in CH$_2$Cl$_2$ (3 mL) was added to the resulting solution and stirred at room temperature for 2 h. The reaction mixture was filtered and washed with CH$_2$Cl$_2$ (5 mL × 2). The combined solution was evaporated under reduced pressure to leave a raw product, which was purified by flash chromatography on silica gel (dichloromethane) to give a yellow solid.

[Bis(2-(3-benzylimidazolin-2-yliden-1-yl)-4-methylphenyl)amido]chloropalladium (5a). Yield: 61.3%. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 7.96 (d, *J* = 1.6 Hz, 2H, imi-*H*), 7.43 (s, 2H, Ar-*H*), 7.41 (d, 1.6 Hz, 2H, imi-*H*), 7.37 (s, 2H, Ar-*H*), 7.35 (d, *J* = 2.4 Hz, 2H, Ar-*H*), 7.22 (m, 6H, Ar-*H*), 6.80 (d, *J* = 8 Hz, 2H, Ar-*H*), 6.69 (d, *J* = 8 Hz, 2H, Ar-*H*), 5.95 (d, *J* = 14.8 Hz, 2H, NC*H*$_2$), 5.74 (d, *J* = 14.8 Hz, 2H, NC*H*$_2$), 2.28 (s, 6H, ArC*H*$_3$). ^{13}C NMR (100 MHz, DMSO-*d*$_6$): δ 164.8 (*C*$_{(carbene)}$), 141.3, 137.7, 131.3, 128.2, 127.8, 127.5, 127.4, 126.5, 123.9, 122.5, 121.5, 119.1 (Ar-*C*, imi-*C*), 51.9 (N*C*H$_2$), 20.1 (Ar*C*H$_3$). Mp: >280 °C. HRMS (MALDI): *m/z* calcd for C$_{34}$H$_{30}$N$_5$ClPd 649.1228, found 649.1246. Anal. Calcd for C$_{34}$H$_{30}$N$_5$ClPd: C, 62.78; H, 4.65; N, 10.77. Found: C, 62.50; H, 4.63; N, 10.68.

[Bis(2-(3-butylimidazolin-2-yliden-1-yl)-4-methylphenyl)amido]chloropalladium (5b). Yield: 63.2%. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 7.92 (d, *J* = 1.6 Hz, 2H, imi-*H*), 7.59 (d, *J* = 1.6 Hz, 2H, imi-*H*), 7.39 (s, 2H, Ar-*H*), 6.74 (d, *J* = 8 Hz, 2H, Ar-*H*), 6.66 (d, *J* = 8 Hz, 2H, Ar-*H*), 4.49−4.56 (m, 2H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 4.36-4.43 (m, 2H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 2.25 (s, 6H, ArC*H*$_3$), 1.73−1.82 (m, 4H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.20−1.29 (m, 4H, NCH$_2$CH$_2$C*H*$_2$CH$_3$), 0.83 (t, *J* = 7.4 Hz, 6H, NCH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C NMR (100 MHz, DMSO-*d*$_6$): δ 164.9 (*C*$_{(carbene)}$), 141.8, 131.8, 128.1, 126.8, 124.1, 123.0, 121.9, 118.9 (Ar-*C*, imi-*C*), 49.4 (N*C*H$_2$CH$_2$CH$_2$CH$_3$), 33.5 (NCH$_2$*C*H$_2$CH$_2$CH$_3$), 20.7 (Ar*C*H$_3$), 19.6 (NCH$_2$CH$_2$*C*H$_2$CH$_3$), 14.0 (NCH$_2$CH$_2$CH$_2$*C*H$_3$). Mp: 176-178 °C. HRMS (MALDI): *m/z* calcd for C$_{28}$H$_{34}$N$_5$ClPd 581.1618, found 581.1594. Anal. Calcd for C$_{28}$H$_{34}$N$_5$ClPd: C, 57.74; H, 5.88; N, 12.02. Found: C, 57.85; H, 5.96; N, 11.97.

[Bis{2-(3-(2,4,6-trimethylbenzyl)imidazolin-2-yliden-1-yl)-4-methylphenyl}amido]chloropalladium (5c). Yield: 64.1%. ^{1}H NMR (600 MHz, DMSO-*d*$_6$): δ 7.87 (d, *J* = 2.4 Hz, 2H, imi-*H*), 7.42 (d, *J* = 2.4 Hz, 2H, imi-*H*), 6.87 (s, 4H, Ar-*H*), 6.78 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 6.77 (s, 2H, Ar-*H*), 6.67 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 5.83 (d, *J* = 15 Hz, 2H, NC*H*$_2$), 5.73 (d, *J* = 15 Hz, 2H, NC*H*$_2$), 2.27 (s, 6H, ArC*H*$_3$), 2.23 (s, 12H, ArC*H*$_3$), 2.21 (s, 6H, ArC*H*$_3$). ^{13}C NMR (150 MHz, DMSO-*d*$_6$): δ 165.7 (*C*$_{(carbene)}$), 141.9, 138.2, 137.8, 131.8, 130.1, 129.7, 128.2, 126.9, 123.0, 122.1, 121.9, 119.2 (Ar-*C*, imi-*C*), 48.4 (N*C*H$_2$), 21.0 (Ar*C*H$_3$), 20.7 (Ar*C*H$_3$), 20.2 (Ar*C*H$_3$). Mp: >280 °C. HRMS (MALDI): *m/z* calcd for C$_{40}$H$_{42}$N$_5$ClPd 773.2162, found 773.2126. Anal. Calcd for C$_{40}$H$_{42}$N$_5$ClPd: C, 65.39; H, 5.76; N, 9.53. Found: C, 65.38; H, 6.00; N, 9.44.

Supporting Information Available: General procedure for the Suzuki−Miyaura reactions and analytical data for cross-coupling products. Copies of NMR spectra for **3**, **4a−c**, and **5a−c**, copies of ^{1}H NMR spectra of **5a** at elevated temperatures, and crystallographic information for **5a** in the form of CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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