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# Abnormal-NHC Palladium(II) Complexes: Rational Synthesis, Structural Elucidation, and Catalytic Activity

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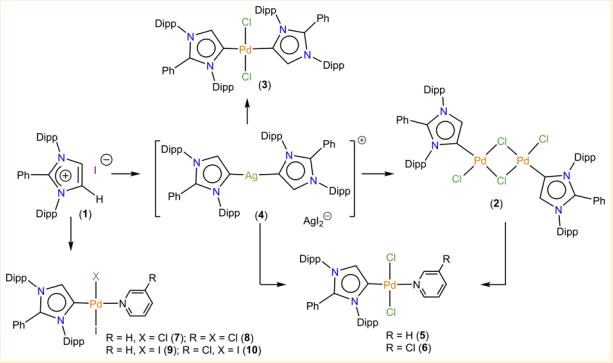
Supporting Information

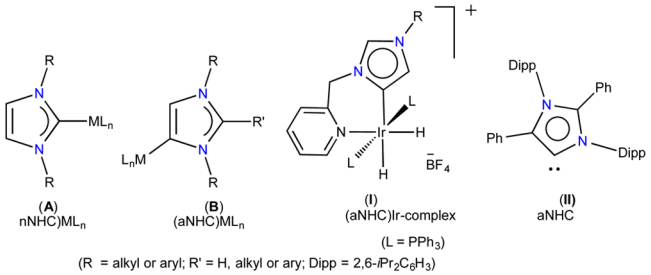
**ABSTRACT:** Reaction of a C2-arylated imidazolium iodide (IPrPh)I (**1**) (IPrPh = 1,3-bis(2,6-diisopropylphenyl)-2-phenyl-imidazolium) with $PdCl_2$ in the presence of $Ag_2O$ affords abnormal N-heterocyclic carbene (aNHC) palladium complexes $(aIPr^{Ph})PdCl_2$ (**2**) and $(aIPr^{Ph})_2PdCl_2$ (**3**) ($aIPr^{Ph}$ = 1,3-bis(2,6-diisopropylphenyl)-2-phenyl-imidazol-4-ylidene). Treatment of **2** with a pyridine gives Pd-PEPPSI-type complexes $(aIPr^{Ph})PdCl_2(L)$ (L = pyridine (py), **5**; L = 3-chloropyridine (3Cl-py), **6**). Compounds **5** and **6** are also accessible by a one-pot reaction of **1**, $PdCl_2$, and $Ag_2O$ in a pyridine solvent. While the use of a conventional base $K_2CO_3$ leads to the formation of mixed halide complexes $(aIPr^{Ph})Pd(Cl)I(L)$ (**7**, L = py; **8**, L = 3Cl-py), iodide derivatives $(aIPr^{Ph})PdI_2(L)$ (**9**, L = py; **10**, L = 3Cl-py) can be selectively prepared with addition of an excess of KI to the reaction mixture. Albeit in a low yield, a putative transmetalation agent $\{(aIPr^{Ph})_2Ag\}AgI_2$ (**4**) has been isolated and characterized. Compounds **2**−**10** are air stable crystalline solids and have been characterized by elemental analysis, mass spectrometry, and NMR spectroscopic studies. Molecular structures of **2**−**10** have been established by single crystal X-ray diffraction analyses. Catalytic activity of three representative compounds **2**, **5**, and **6** has been tested for the Suzuki-Miyaura cross-coupling reactions.




## INTRODUCTION

Ligands play an important role in the stability and activity of metal complexes.[1] N-heterocyclic carbenes (NHCs) are inarguably the most versatile two-electron carbon donor neutral ligands in transition metal catalysis and organometallic chemistry.[2] The development of highly advanced precatalysts for olefin metathesis, cross coupling reactions, and other transformations[2h,3] emphasizes the significance of NHCs. The strong $\sigma$-donor ability of NHCs has also been successfully exploited for stabilizing compounds featuring a low-valent main group element.[4] Easy-to-tune structural features coupled with a relatively robust nature of the $M-C_{(Carbene)}$ bond (Chart 1; A) further rationalize the multifarious success of NHCs beyond catalysis.[2a,5] While NHCs are fascinating entities in transition metal and main group chemistry, research continues toward the advancement of innovative carbon-donor ligands.[2,6] A relatively new type of NHC-complexes (B) in which the carbene coordinates to a metal at the C4 (or C5) position have been developed in the recent years.[7] Since normal NHCs (nNHCs) coordinate to metals at the C2 carbon atoms (A), C4, (or C5) carbenes (B) are therefore termed abnormal NHCs (aNHCs) (Chart 1). Experimental and theoretical data[5d,8] indicate that aNHCs are even stronger electron-donating species than nNHCs as well as CAACs (cyclic alkyl amino carbenes),[9] which promises exciting perspectives for their applications in catalysis and beyond.[10] As no canonical resonance form of aNHCs without the introduction of formal charges can be drawn, Bertrand described them as mesoionic carbenes (MICs).[11] Albeit as a result of serendipitous discovery, the first transition metal complex (I) (Chart 1) featuring an aNHC

**Chart 1. nNHC− (A) and aNHC− (B) metal complexes, first aNHC complex (I), and first stable free-aNHC (II)**

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was reported in 2001 by Crabtree.[12] In the past few years, several other aNHC-complexes have been described.[7d] However, the isolation of a stable noncoordinated aNHC remained a challenge until 2009 when Bertrand reported the first stable free-aNHC (II).[13]

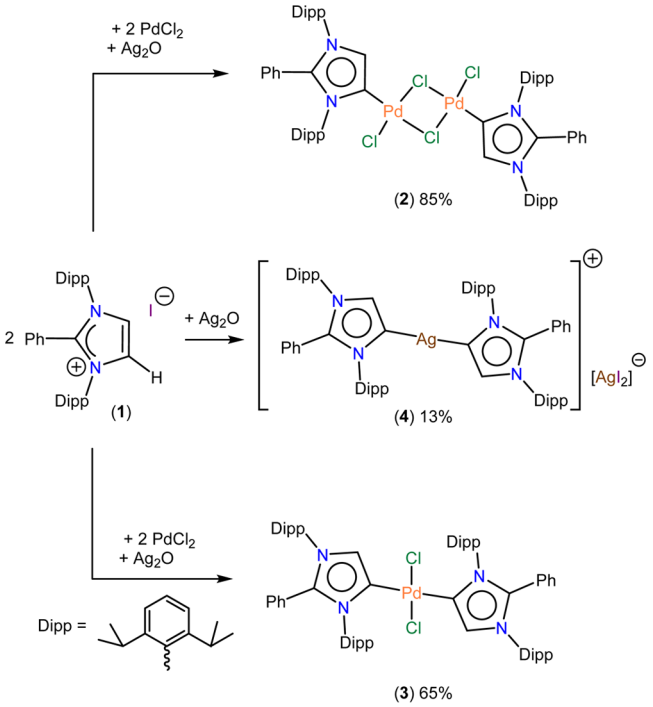
Despite being exceptionally electron rich ligands, applications of aNHCs in organometallic chemistry in comparison with nNHCs are rather limited.[2h,14] This is most likely due to the scarcity of their synthetic methods.[7d,10a,15] Therefore, developing new facile synthetic protocols to aNHC−metal complexes is highly important. Different synthetic strategies of aNHC−metal complexes have been developed during the past few years.[7a−d] The chelation assistance strategy has found to be quite useful but is so far limited to a few particular complexes.[16] The C2-protecting strategy, particularly with an aryl group, mostly delivers desired products and has even enabled access to a free stable aNHC (II).[7d,13] Thus, for preparing aNHC-complexes, C2-arylated imidazolium salts are an appropriate choice; nevertheless, the synthesis of these salts is rather demanding. In this context, direct arylation of NHCs is very appealing as a variety of NHCs can be readily prepared and some are also commercially available. Very recently, we reported the catalytic C2-arylation of an NHC using 0.5 mol % of $Pd_2(dba)_3$ (dba = dibenzylideneacetone).[17] This high-yield catalytic route enables access to a variety of C2-arylated imidazolium salts.[17] The palladium-NHC-metal−ligand partnership is considered a perfect union in organometallic catalysis that has particularly recognized enormous significance in many cross-coupling reactions.[2f] Therefore, we decided to check the suitability of our C2-arylated imidazolium salts in the synthesis of aNHC-palladium complexes and to explore their structure and catalytic activity.

Herein, we report on a very facile rational synthetic route to a series of aNHC-palladium(II) complexes featuring a (aIPr$^{Ph}$)-$PdX_2$ (aIPr$^{Ph}$ = 1,3-bis(2,6-diisopropylphenyl)-2-phenyl-imidazol-4-ylidene; X = Cl or I) scaffold. All the complexes have been characterized by elemental analysis, NMR spectroscopy, and mass spectrometry. The molecular structures have been established by single crystal X-ray diffraction studies. Moreover, preliminary results of their catalytic activity for the Suzuki-Miyaura cross-coupling reactions are presented.

## RESULTS AND DISCUSSION

**Synthesis and Characterization.** Reaction of (IPrPh)I (**1**) (IPrPh = 1,3-bis(2,6-diisopropylphenyl)-2-phenyl-imidazolium) with $PdCl_2$ in the presence of $Ag_2O$ leads to the formation of palladium complexes (aIPr$^{Ph}$)$PdCl_2$ (**2**) and (aIPr$^{Ph}$)$_2PdCl_2$ (**3**) as pale yellow crystalline solids (Scheme 1). Albeit in a low yield, a putative transmetalation agent {(aIPr$^{Ph}$)$_2$Ag}$AgI_2$ (**4**) has been isolated and characterized (Scheme 1). Each of **2** and **3** exhibits corresponding peaks in the ESI-mass spectrum. Similarly, the ESI-mass spectrum of **4** shows a molecular ion peak for the cationic {(aIPr$^{Ph}$)$_2$Ag} part. $^1$H NMR spectra of compounds **2** and **3** exhibit four doublets for methyl protons of HC*Me*$_2$ groups, whereas methine protons (*H*CMe$_2$) appear as two multiplets, which is consistent with the asymmetrically substituted imidazol-backbone (C4/C5) positions. The signal due to the imidazolium backbone protons (for **1** at $\delta$ 8.38 ppm in $CDCl_3$) has completely disappeared and a new signal arises at 6.97 ppm for the remaining C5−H moiety. In addition, $C_6H_3$ protons show two sets of $^1$H NMR resonances. $^{13}$C NMR spectra of compounds **2** and **3** exhibit

**Scheme 1. Synthesis of aNHC Complexes 2−4**




corresponding signals for the aIPr$^{Ph}$ moiety in the expected regions.

Organ et al. incorporated pyridine (py) as a secondary ancillary (throwaway) ligand and coined the term "PEPPSI" (Pyridine-Enhanced-Precatalyst-Preparation-Stabilization-Induction) for (NHC)$PdCl_2$(py) type complexes.[18] Pd-PEPPSI complexes have been a considerable success and are therefore regarded as universal precatalysts for numerous cross-coupling reactions,[19] which further prompted interest in developing their more atom-economic synthetic methods.[20] Similarly, backbone functionalized[21] NHCs as well as NHCs with more specialized substituents at the imidazole nitrogen atoms[19b,e,22] have been developed to further improve the activity of Pd-PEPPSI complexes. However, Pd-PEPPSI complexes featuring a 1,3-imidazol-derived aNHC that have been structurally fully characterized are very scarce.[23] Addition of a small amount of pyridine to a dichloromethane solution of **2** cleanly yields Pd-PEPPSI type complex (aIPr$^{Ph}$)$PdCl_2$(L) (L = pyridine (py), **5**; L = 3-chloropyridine (3Cl-py), **6**) (Scheme 2). Compounds **5** and **6** can also be prepared in a one-pot reaction by using the silver-transmetalation strategy. Reaction of **1** and $PdCl_2$ in the presence of $Ag_2O$ leads to the clean formation of compounds **5** and **6** in a good yield. $K_2CO_3$ can also be used to deprotonate **1** in a pyridine solvent, however this leads to the formation of mixed halide compounds (aIPr$^{Ph}$)PdCl(I)(L) (L = py, **7**; L = 3Cl-py, **8**) (Scheme 2). Solution and solid-state analyses clearly support the consumption of **1** and formation of **7** and **8**. Nevertheless, complexes **7** and **8** exhibit somewhat complex NMR spectra due to diminished molecular symmetry and uncertain halide composition.[24] This can be avoided by the addition of an excess of KI to the reaction mixture, which exclusively affords iodo-derivatives (aIPr$^{Ph}$)$PdI_2$(L) (L = py, **9**; L = 3Cl-py, **10**) under similar experimental conditions. Compounds **5**−**10** are air stable yellow to pale-yellow solids. Except for **7** and **8**, **5**−**10** exhibit well-resolved $^1$H and $^{13}$C NMR resonances for the aIPr$^{Ph}$ and respective pyridine unit.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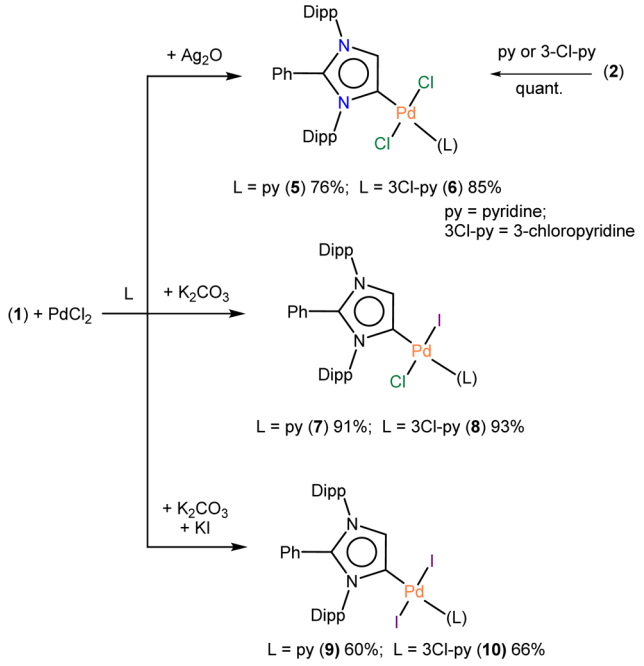
**Scheme 2. Synthesis of aNHC−Palladium Complexes 5−10**




$^{13}$C NMR spectra of **5**−**10** reveal corresponding signals for (aIPr$^{Ph}$) and pyridine ligands. Each of complexes **5**−**10** exhibits the corresponding peak for the [M−X] moiety (X = Cl or I) in the ESI mass spectrum.

**Molecular Structures.** Molecular structures of compounds **2**, **3** (Figure 1), **4** (Figure S3), **5**, **6** (Figure 2), **7** (Figure S6), **8** (Figure S7), **9**, and **10** (Figure 2) have been determined by single crystal X-ray diffraction studies. Compound **2** crystallizes as orange-yellow crystals upon storage of a solution (1:4 mixture of $CH_2Cl_2$ and $Et_2O$) at −30 °C for 1 week. Each of complexes **2**, **3**, and **5**−**10** features a 4-fold coordinated palladium atom with a distorted square planar geometry (Table 1). The Pd−C$_{(carbene)}$ bond length of 1.979 Å (average) of **2**, **3**, and **5**−**8** is in line with those of the NHC-Pd-PEPPSI complexes.[19e,25] The C−Pd−N bond angle of complexes **5**−**10** ranges from 173.20° to 175.02°. The Pd−N bond lengths (2.106−2.131 Å) in **5**−**10** are comparable with those of (NHC)$PdCl_2$(py) complexes, where steric hindrance imposed by the imidazole nitrogen substituents also plays a crucial role on the bond elongation. This may be attributed as an increased trans-effect of the aNHC ligand in **5**−**10**. The C−C$_{(carbene)}$−N (C5−C4−N3, Table 1) bond angle of the imidazole ring of complexes **5**−**10** is smaller by 3° when compared with that of the compound **1** (107.2°). This indicates increased s-character (carbene nature) of the C4 carbon atom that coordinates to the palladium. As expected, the N−C−N bond angle of the imidazole ring of **5**−**10** is comparable to that of the **1**.[17] The average Pd−Cl bond length of 2.30 Å of **5** and **6** is consistent with those of other four coordinated palladium complexes.[19e]

**Catalytic Study.** Catalytic activity of three representative palladium compounds **2**, **5**, and **6** was tested for the Suzuki-Miyaura cross-coupling reactions. All compounds were found to be active catalysts and afforded biaryls at room temperature. In a general procedure, a mixture of aryl halide (1 mmol) and phenylboronic acid (1.2 mmol) was treated with KOBu$^t$ (1.5 mmol) in the presence of a palladium precatalyst (**2**, **5**, or **6**). Analytic grade isopropanol was used as a solvent. In all cases (Table 2), 3 mol % of precatalyst was used. The progress of the

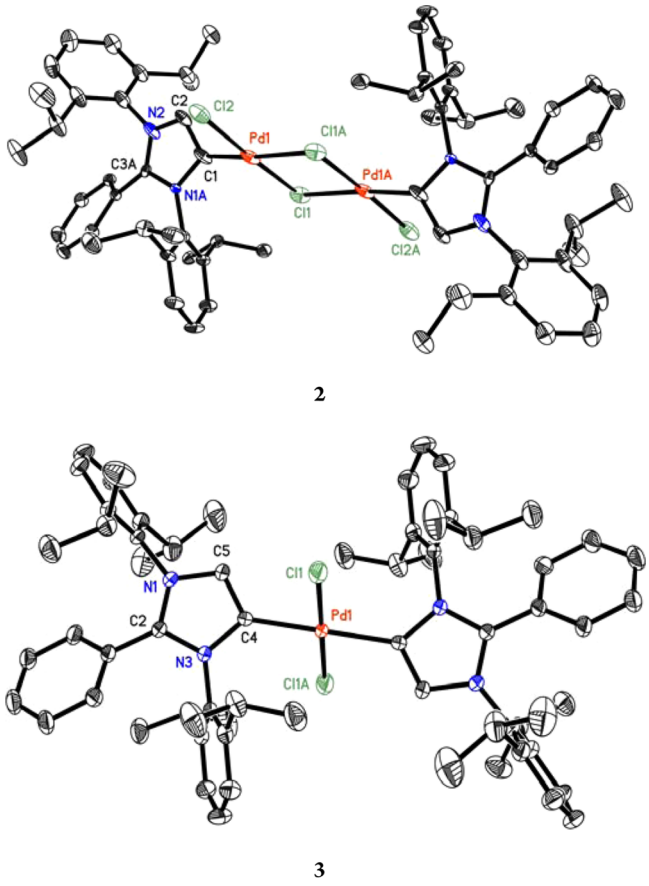



**Figure 1.** Solid-state molecular structures of compounds **2** and **3**. Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths and bond angles are given in Table 1.

reactions was monitored by GC/MS analysis (entries 1−13) or $^{19}$F NMR spectroscopy (entry 14). The results are listed in Table 2. In all cases the dimeric Pd-complex **2** was found to be more active than **5** and **6**, leading to good to excellent yields for coupling bromo- and iodoaryls (up to 100% conversion after 0.5 h in the case of *p*-iodonitrobenzene, entry 13). While moderate to good conversion of 4-chlorotoluene (55% after 24 h, entry 1) or 1-chloro-2-fluorobenzene (69% after 24 h, entry 14) was observed with **2**, only 12−31% conversion was achieved with **5** or **6** under similar experimental conditions. For coupling 4-bromotoluene with phenylboronic acid (entries 4−6), PEPPSI-complexes **5** and **6** were found to be somewhat slower than compound **2**. However, the 3-chloropyridine derivative (**6**) was found to be slightly more active catalyst than its pyridine analogue **5**.

## EXPERIMENTAL SECTION

**General.** All syntheses and manipulations, unless otherwise stated, were performed under an inert gas ($N_2$ or Ar) atmosphere using an MBraun glovebox or Schlenk techniques. Dichloromethane, $CD_2Cl_2$, $CDCl_3$ ($CaH_2$), 1,4-dioxane, THF, and toluene (Na/K-benzophenone) were dried by refluxing over an appropriate drying agent and stored under $N_2$. Other analytic grade solvents and reagents were used as received without further purification. $^1$H and $^{13}$C NMR spectra were recorded using a Bruker Avance III 500 or a Bruker Avance III 300 or a Bruker Avance DRX 500 spectrometer. Chemical shifts are given in $\delta$ ppm and are referenced to the solvent residual peak(s). $CDCl_3$: $^1$H, 7.26 and $^{13}$C, 77.16; $CD_2Cl_2$: $^1$H, 5.32 and $^{13}$C, 54.00; $C_6D_6$: 7.16 for



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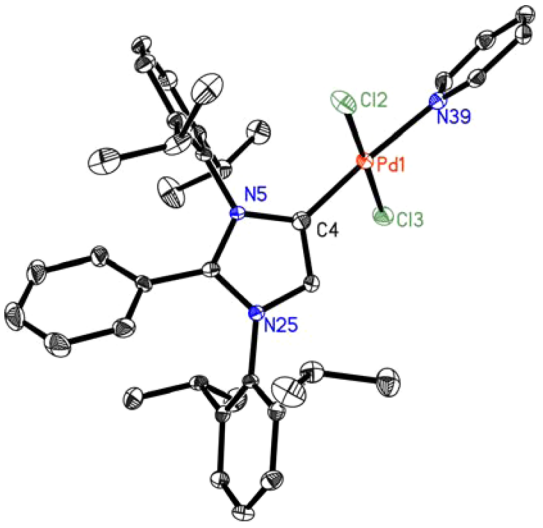


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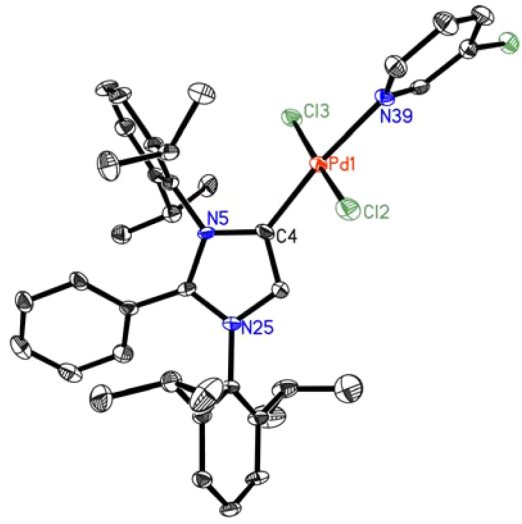


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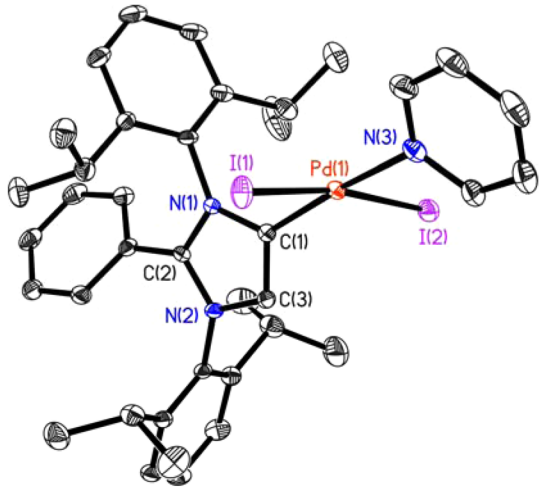


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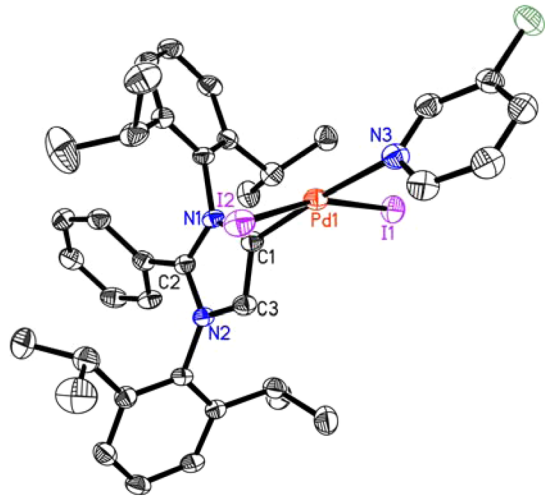


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**Figure 2.** Solid-state molecular structures of compounds **5**, **6**, **9**, and **10**. Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths and bond angles are given in Table 1.

$^1$H, $^{13}$C, 128.06. ESI mass spectra were recorded with a Bruker Esquire 3000 spectrometer. Melting points were measured with an Electrothermal Melting Point apparatus. Elemental analyses were performed at the Institute for Inorganic Chemistry, Universität Bielefeld. $PdCl_2$, pyridine (py), 3-chloropydine (3Cl-py), KI, $K_2CO_3$, $Cs_2CO_3$, and $Ag_2O$ were used as received. (IPrPh)I (**1**) was prepared by employing the reported method.[17]

*Synthesis of [(aIPr$^{Ph}$)PdCl$_2$]$_2$ Compound (**2**).* To a Schlenk flask containing **1** (2.00 g, 3.44 mmol), $PdCl_2$ (0.61 g, 3.44 mmol), and $Ag_2O$ (0.39 g, 1.69 mmol) were added 30 mL of 1,4-dioxane and 20 mL of $CH_3CN$. The resulting reaction mixture was refluxed for 10 h with constant stirring. The volatiles were removed under reduced pressure and the residue was extracted with 20 mL dichloromethane. Drying under vacuum afforded an orange solid, which was washed with *n*-hexane. The residue was dissolved in 10 mL of dichloromethane, combined with 10 mL $Et_2O$, and stored at −30 °C for 20 h to obtained orange crystals of **2** (1.83 g, 85%). Elemental analysis for $C_{66}H_{80}N_4Cl_4Pd_2$ (1284): calcd. C, 61.74; H, 6.28; N, 4.36; found C 61.61, H 6.29, N 4.28. $^1$H NMR (300 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 0.68 (d, 6H, $J$ = 6.75 Hz, HC$Me_2$); 0.93 (d, 6H, $J$ = 6.86 Hz, HC$Me_2$); 1.22 (d, 6H, $J$ = 6.76 Hz, HC$Me_2$); 1.72 (d, 6H, $J$ = 6.60 Hz, HC$Me_2$); 2.44 (sept, 2H, $J$ = 6.75 Hz, HCMe$_2$); 2.78 (sept, 2H, $J$ = 6.65 Hz, HCMe$_2$); 6.80 (d, $J$ = 7.41 Hz, 2H, *o*-C$_6H_5$); 6.97 (s, 1H, NC*H*); 7.05 (t, $J$ = 7.00 Hz, 2H, *m*-C$_6H_5$); 7.21 (m, 3H, *p*-C$_6H_5$, *m*-C$_6H_3$), 7.29 (d, $J$ = 7.74 Hz, 2H, *m*-C$_6H_3$), 7.52 (m, 2H, *p*-C$_6H_3$), ppm. $^{13}$C{$^1$H} NMR (75 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 22.66, 24.20, 25.97, 26.50 (HC$Me_2$); 29.29, 29.41 (HCMe$_2$); 123.67, 125.13, 125.24, 125.48 ((NCCN, C$_6H_5$, C$_6H_3$); 126.81 (NCCN), 128.88, 130.09, 130.88, 131.24, 131.50, 132.32, 134.24, (C$_6H_5$, C$_6H_3$); 144.89 (NCN), 145.52, 146.13 (*ipso*-C$_6H_5$, C$_6H_3$) ppm.

*Synthesis of (aIPr$^{Ph}$)$_2$PdCl$_2$ Compound (**3**).* Compound **3** was prepared by employing a similar method as described for **2** using **1** (1.00 g, 1.69 mmol), $PdCl_2$ (0.15 g, 0.85 mmol), and $Ag_2O$ (0.20 g, 0.84 mmol) as an orange solid (0.60 g, 65%). Elemental analysis for $C_{66}H_{80}N_4Cl_2Pd$ (1106): calcd. C, 71.63; H, 7.29; N, 5.06; found C 71.74, H 7.32, N 4.89. MS (ESI, $m/z$ [M]): 1069.4 [M−Cl]$^+$. $^1$H NMR (300 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 0.68 (d, 6H, $J$ = 6.72 Hz, HC$Me_2$); 0.93 (d, 6H, $J$ = 6.85 Hz, HC$Me_2$); 1.22 (d, 6H, $J$ = 6.74 Hz, HC$Me_2$); 1.72 (d, 6H, $J$ = 6.57 Hz, HC$Me_2$); 2.44 (sept, 2H, $J$ = 6.82 Hz, HCMe$_2$); 2.78 (sept, 2H, $J$ = 6.65 Hz, HCMe$_2$); 6.80 (d, $J$ = 7.44 Hz, 2H, *o*-C$_6H_5$); 6.97 (s, 1H, NC*H*); 7.04 (t, $J$ = 7.55 Hz, 2H, *m*-



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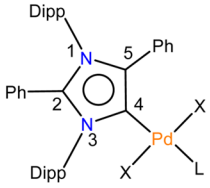
**Table 1. Selected Bond Lengths (Å) and Angles (deg) of Complexes 2, 3, and 5−10 (X = I/Cl)**




| Complex | C4–C5 | C4–Pd | Pd–N | Pd–X | C5–C4–N3 | N1–C2–N3 | C4–Pd–N | X–Pd–X |
|---|---|---|---|---|---|---|---|---|
| **2**[a] | 1.355(3) | 1.955(2) | - | 2.3059(8)<br>2.3199(8) | 99.1(3)/<br>110.1(3) | 103.9(6)/<br>110.2(5) | - | 177.48(2) |
| **3** | 1.358(3) | 2.030(2) | - | 2.3166(8) | 103.4(2) | 106.3(2) | - | 180.00(2) |
| **5** | 1.356(4) | 1.965(3) | 2.120(2) | 2.292(1)<br>2.330(1) | 104.5(2) | 106.8(2) | 174.59(11) | 178.68(3) |
| **6**[b] | 1.361(6)<br>1.357(6) | 1.984(4)<br>1.975(4) | 2.106(4)<br>2.116(4) | 2.304(2)<br>2.306(2)<br>2.308(2)<br>2.306(2) | 104.5(4)<br>105.2(4) | 106.4(4)<br>106.7(4) | 173.20(16)<br>173.49(16) | 179.60(5)<br>179.59(5) |
| **9** | 1.364(3) | 1.986(2) | 2.114(2) | 2.586(1)<br>2.627(1) | 104.17(18) | 106.52(17) | 173.74(8) | 169.48(1) |
| **10** | 1.367(4) | 1.981(3) | 2.131(3) | 2.601(1)<br>2.627(1) | 104.0(3) | 106.7(3) | 175.02(12) | 164.30(1) |

[a]The asymmetric unit contains one-half of the molecule; 52:48 population disordered structure (Figure S1). [b]Two molecules in the asymmetric unit (Figure S5).

$C_6H_5$); 7.20 (m, 3H, *p*-$C_6H_5$, *m*-$C_6H_3$); 7.29 (d, $J$ = 7.78 Hz, 2H, *m*-$C_6H_3$); 7.52 (m, 2H, *p*-$C_6H_3$), ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 22.67, 24.20, 25.97, 26.50 ($HCMe_2$), 29.30, 29.42 ($HCMe_2$), 123.71, 125.16, 125.26, 125.50 ((NCCN, $C_6H_5$, $C_6H_3$), 126.84 (NCCN), 128.89, 130.11, 130.90, 131.25, 131.52, 132.36, 134.28, ($C_6H_5$, $C_6H_3$), 144.91 (NCN), 145.56, 146.17 (*ipso*-$C_6H_5$, $C_6H_3$) ppm.

*Synthesis of [(alPr$^{Ph}$)$_2$Ag]AgI$_2$ Compound (**4**).* A 50 mL toluene suspension of **1** (1.00 g, 1.69 mmol) and $Ag_2O$ (0.39 g, 1.69 mmol) was refluxed for 8 h in the dark. Filtration afforded a solution, which was concentrated to 20 mL and stored at −30 °C. The crystalline solid was washed with cold toluene (2 × 20 mL) and dried under vacuum to yield **4** as a light brown solid (0.16 g, 13%). MS (ESI, $m/z$ [M]): 1035 $[M-AgI_2]^+$. $^1H$ NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ 0.83 (pseudo t, 12H, $HCMe_2$); 0.99 (d, 6H, $J$ = 6.91 Hz, $HCMe_2$); 1.41 (d, 6H, $J$ = 6.61 Hz, $HCMe_2$); 2.52 (sept, 2H, $J$ = 6.74 Hz, $HCMe_2$); 2.67 (sept, 2H, $J$ = 6.78 Hz, $HCMe_2$); 6.53 (m, 3H, $C_6H_5$); 6.88 (br, 1H, NC*H*); 6.85 (d, $J$ = 7.56 Hz, 2H, *m*-$C_6H_3$); 6.95 (d, 2H, *m*-$C_6H_3$); 7.03 (t, $J$ = 7.84 Hz, 1H, *p*-$C_6H_3$); 7.12 (t, $J$ = 7.84 Hz, 1H, *p*-$C_6H_3$); 7.16 (br, 2H, $C_6H_5$) ppm.

*Synthesis of (alPr$^{Ph}$)PdCl$_2$(py) Compound (**5**).* To a 5 mL DCM solution of **2** (0.20 g, 0.16 mmol) was added 0.2 mL of pyridine and the resulting reaction mixture was stirred at room temperature for 1 h. The volatiles were removed under vacuum and the residue was washed with *n*-hexane (2 × 10 mL). Drying under vacuum afforded compound **5** as a yellow solid (0.20 g, 90%). Mp.: 193 °C (dec.) MS (ESI, $m/z$ [M]): 684.3 $[M-Cl]^+$. Elemental analysis for $C_{38}H_{45}N_3Cl_2Pd$ (721): calcd. C 63.29, H 6.29, N 5.83; found C 62.41, H 6.29, N 5.71. $^1H$ NMR (500 MHz, $CDCl_3$, 25 °C): $\delta$ 0.74 (d, 6H, $J$ = 6.78 Hz, $HCMe_2$); 0.97 (d, 6H, $J$ = 6.85 Hz, $HCMe_2$); 1.30 (d, 6H, $J$ = 6.74 Hz, $HCMe_2$); 1.74 (d, 6H, $J$ = 6.58 Hz, $HCMe_2$); 2.59 (sept, 2H, $J$ = 6.80 Hz, $HCMe_2$); 3.08 (sept, 2H, $J$ = 6.69 Hz, $HCMe_2$); 6.85 (d, $J$ = 7.64 Hz, 2H, *o*-$C_6H_5$); 7.06 (t, $J$ = 7.91 Hz, 2H, *m*-$C_6H_5$); 7.16 (s, 1H, NC*H*); 7.19 (t, $J$ = 7.50 Hz, 1H, *p*-$C_6H_5$); 7.21 (m, 4H, *m*-$C_6H_3$, *p*-$C_6H_3$); 7.28 (d, $J$ = 8.52 Hz, 2H, *m*-$C_6H_3$); 7.47; 7.49 (dt, $J$ = 7.75, 13.04 Hz, 2H, *m*-$C_5NH_5$); 7.66 (tt, $J$ = 1.67, 7.64 Hz, 1H, *p*-$C_5NH_5$); 8.92; 8.93 (dd, $J$ = 1.62, 4.97 Hz, 2H, *o*-$C_5NH_5$) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C): $\delta$ 22.56, 23.94, 25.92, 26.10 ($HCMe_2$), 28.76, 28.87 ($HCMe_2$), 123.71, 124.08 124.72, 124.89 ($C_6H_5$, $C_6H_3$), 128.30 (NCPd), 128.35 (NCH), 129.55, 129.89 (*m*-$C_5NH_5$), 130.32, 130.35, 130.88, 132.30, 134.55 ($C_6H_5$, $C_6H_3$), 137.22 (*p*-$C_5NH_5$); 143.98; 145.21, 145.67 (*ipso*-$C_6H_5$, $C_6H_3$); 151.69 (*o*-$C_5NH_5$) ppm.

*Synthesis of (alPr$^{Ph}$)PdCl$_2$(3Cl-py) Compound (**6**).* To a 5 mL DCM solution of **2** (0.20 g, 0.16 mmol) was added 0.2 mL of 3-chloropyridine and the resulting reaction mixture was stirred at room temperature for 1 h. The volatiles were removed under vacuum and the residue was washed with *n*-hexane (2 × 10 mL). Drying under vacuum afforded compound **5** as a yellow solid (0.21 g, 89%). Mp.: 178 °C (dec.). MS (ESI, $m/z$ [M]): 720.2 $[M-Cl]^+$. Elemental analysis for $C_{38}H_{44}N_3Cl_3Pd$ (755): calcd. C 60.41, H 5.87, N 5.56; found C 60.68, H 6.05, N 5.45. $^1H$ NMR (500 MHz, $CDCl_3$, 25 °C): $\delta$ 0.75 (d, 6H, $J$ = 6.79 Hz, $HCMe_2$); 0.97 (d, 6H, $J$ = 6.88 Hz, $HCMe_2$); 1.30 (d, 6H, $J$ = 6.77 Hz, $HCMe_2$); 1.73 (d, 6H, $J$ = 6.58 Hz, $HCMe_2$); 2.58 (sept, 2H, $J$ = 6.84 Hz, $HCMe_2$); 3.06 (sept, 2H, $J$ = 6.67 Hz, $HCMe_2$); 6.85 (d, 2H, *o*-$C_6H_5$), 7.07 (t, 2H, *m*-$C_6H_5$), 7.15 (s, 1H, NC*H*), 7.20 (m, 2H, *p*-$C_6H_5$, 3Cl−$C_5H_4N$); 7.24 (d, 2H, *m*-$C_6H_3$), 7.29 (d, 2H, *m*-$C_6H_3$) 7.48 (m, 2H, *p*-$C_6H_3$); 7.67 (d, 1H, 3Cl−$C_5H_4N$); 8.88 (d, 1H, 3Cl−$C_5H_4N$); 8.99 (d, 1H, 3Cl−$C_5H_4N$) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C): $\delta$ 22.63, 23.93, 25.92, 26.10 ($HCMe_2$), 28.76, 28.96 ($HCMe_2$); 123.63, 124.50, 124.76, 124.94, 125.40 (*p*-$C_6H_5$, 3Cl-$C_5H_4N$), 128.26 (NCH), 128.39, 128.43 (*m*-$C_6H_5$), 129.56 (*o*-$C_6H_5$), 130.42, 130.45 (*p*-$C_6H_5$), 130.95, 132.15, 132.24 (*p*-$C_6H_3$), 134.47, 135.95, 137.33 (3Cl-$C_5H_4N$), 144.13, 14.91, 145.21, 145.66, 147.70, 149.06, 149.69, 150.76 (*ipso*-$C_6H_5$, *ipso*-$C_6H_3$, *ipso*-3Cl-$C_5NH_4$) ppm.

*Alternative One-Pot Synthesis of (alPr$^{Ph}$)PdCl$_2$(py) (**5**) and (alPr$^{Ph}$)PdCl$_2$(3Cl-py) (**6**).* To a pyridine suspension of **1** (1.82 g, 3.07 mmol) and $PdCl_2$ (0.55 g, 3.10 mmol) was added $Ag_2O$ (0.40 g, 1.72 mmol) in one portion and the resulting reaction mixture was stirred at 85 °C for 12 h. Removal of the volatiles under vacuum afforded a pale yellow residue, which was dissolved in 20 mL of DCM and filtered. The residue obtained after the removal of the volatiles under vacuum was washed with *n*-hexane and dried to obtain compound **5** as a yellow solid. Recrystallization (4 °C, 2 days) from a mixture of DCM and *n*-hexane (1:1) solution yielded yellow crystals of **5** (1.70 g, 76%).

Similarly, compound **6** was prepared as a yellow solid in 85% (2.0 g) yield by using **1** (1.83 g, 3.08 mmol), $PdCl_2$ (0.56 g, 3.23 mmol), and $Ag_2O$ (0.50 g, 2.15 mmol) in 10 mL of 3Cl-py.

*Synthesis of (alPr$^{Ph}$)PdCl(I) (py) (**7**).* To a flask containing a mixture of **1** (1.00 g, 1.69 mmol), $PdCl_2$ (0.30 g, 1.69 mmol), and $K_2CO_3$ (1.5 g) was added 6 mL of pyridine. NMR analysis after 16 h stirring at 85 °C indicated the presence of 20% of the starting material **1**. The resulting mixture was further stirred at 85 °C for 8 h to obtain a yellow suspension. All the volatiles were removed under vacuum at 50 °C to yield a pale yellow residue. The residue was extracted with DCM (20 mL). Drying under vacuum afforded a yellow solid, which was washed



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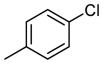
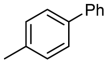
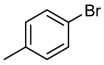
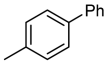
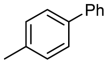
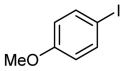
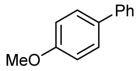
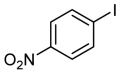
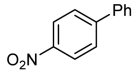
**Table 2. Catalytic Activity of Compounds 2, 5, and 6 in the Suzuki-Miyaura Cross-Coupling Reactions**

| Entry | Substrate (S) | Product (P) | Catalyst[a] | Conversion S → P, %[b] | | |
|---|---|---|---|---|---|---|
| | | | | 0.5 h | 2 h | 24 h |
| 1 |  |  | **2** | 11 | 35 | 55 |
| 2 | | | **5** | 6 | 6 | 12 |
| 3 | | | **6** | 4 | 10 | 31 |
| 4 |  |  | **2** | 81 | 100 | – |
| 5 | | | **5** | 9 | 20 | 59 |
| 6 | | | **6** | 22 | 52 | 83 |
| 7 |  |  | **2** | 87 | 94 | 100 |
| 8 | | | **5** | 75 | 85 | 96 |
| 9 | | | **6** | 83 | 83 | 100 |
| 10 |  |  | **2** | 42 | 77 | 95 |
| 11 |  |  | **2** | 74 | 75 | 79 |
| 12 |  |  | **2** | 82 | 87 | 95 |
| 13 |  |  | **2** | 100 | – | – |
| 14 |  |  | **2** | 16 | 38 | 69 |

[a]3 mol % loading. [b]Conversions were determined by GC/MS analysis (entries 1−13) and $^{19}$F NMR spectroscopy (entry 14).

with *n*-hexane (2 × 20 mL) and dried to obtain compound **7** (91%, 1.25 g) yield. Mp.: 186 °C (dec.). MS (ESI, *m*/*z* [M]): 776.2 [M−Cl]$^+$, 684.3 [M−I]$^+$. Elemental analysis for $C_{38}H_{45}N_3ClIPd$ (812): calcd. C 56.17, H 5.58, N 5.17; found C 56.17, H 6.04, N 5.21. $^1$H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta$ 0.70−0.72 (m, 6H, HC$Me_2$); 0.88−0.96 (m, 6H, HC$Me_2$); 1.26−1.30 (m, 6H, HC$Me_2$); 1.70−1.73 (m, 6H, HC$Me_2$); 2.51−2.59 (m, 2H, *H*CMe$_2$); 3.02−3.29 (m, 2H, *H*CMe$_2$); 6.82−6.85 (m, 2H, $C_6H_5$); 7.00−7.04 (m, 2H, $C_6H_5$); 7.11−7.28 (m, 8H, $C_6H_5$, $C_6H_3$, NC*H*); 7.42−7.50 (m, 2H, *m*-$C_5NH_5$); 7.58−7.65 (m, 1H, *p*-$C_5NH_5$); 8.85−8.96 (m, 2H, *o*-$C_5NH_5$) ppm. $^{13}$C{$^1$H} NMR (75 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 23.10, 23.14, 24.51, 26.41 (HC$Me_2$), 27.36, 29.58, 29.61, 29.69 (HCMe$_2$), 124.54, 124.82, 124.87, 124.90, 125.60, 125.64, 125.89, 129.10, 129.16, 130.38, 130.43, 130.94, 131.28, 131.73, 133.05, 138.13, 146.03, 146.68, 150.75, 152.33, 153.89, 154.63 (NCHCN, $C_6H_5$, $C_6H_3$, $C_5NH_5$) ppm.

*Synthesis of (alPr$^{Ph}$)PdCl(I)(3Cl-py) (**8**).* Compound **8** was prepared as a yellow solid by adopting a similar method as described for **7** using **1** (1.00 g, 1.69 mmol), $PdCl_2$ (0.30 g, 1.69 mmol) and $K_2CO_3$ (1.3 g) in 5 mL of 3-chloropyridine (3Cl-py). Yield found: 1.33 g, 93%. MS (ESI, *m*/*z* [M]): 810.2 [M−Cl]$^+$, 720.2 [M−I]$^+$. Elemental analysis for $C_{38}H_{44}Cl_2IN_3Pd$ (847): calcd. C 53.89, H 5.24, N 4.96; found C 53.60, H 5.44, N 4.78. $^1$H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta$ 0.65 (d, 6H, HC$Me_2$); 0.81−0.86 (m, 6H, HC$Me_2$); 1.18−1.23 (m, 6H, HC$Me_2$); 1.62−1.66 (m, 6H, HC$Me_2$); 2.48 (q, 2H, *H*CMe$_2$); 3.03−3.21 (m, 2H, *H*CMe$_2$); 6.74−6.77 (m, 2H, $C_6H_5$); 6.92−7.6.97 (m, 2H, $C_6H_5$); 7.05−7.10 (m, 2H, $C_6H_5$, NC*H*); 7.16−7.21 (m, 4H, $C_6H_3$), 7.29 (m, 1H, 3Cl−$C_5NH_4$); 7.35−7.44 (m, 2H, $C_6H_3$); 7.50−7.55 (m, 1H, 3Cl−$C_5NH_4$); 7.88 (d, 1H, 3Cl−$C_5NH_4$); 8.87−8.89 (m, 1H, 3Cl−$C_5NH_4$) ppm. $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$, 25 °C): $\delta$ 22.57, 23.95, 25.88, 26.74 (HC$Me_2$), 27.07, 28.82, 28.90 (HCMe$_2$), 123.56, 124.80, 125.14, 125.47, 129.56, 130.41, 130.95, 132.35, 133.32, 134.74, 137.17, 144.89, 145.63, 145.23, 145.68, 149.66, 150.73, 151.26, 152.16, 152.85 (NCHCN, $C_6H_5$, $C_6H_3$, 3Cl-$C_5NH_4$) ppm.

*Synthesis of (alPr$^{Ph}$)PdI$_2$(py) (**9**).* To a flask containing a mixture of **1** (0.67 g, 1.13 mmol), $PdCl_2$ (0.20 g, 1.13 mmol), KI (0.63 g, 3.80 mmol) and $K_2CO_3$ (1 g) was added 10 mL of pyridine. The resulting mixture was stirred at 85−90 °C for 16 h. After usual workup, compound **9** was isolated as yellow solid in 60% yield. Mp.: 185 °C (dec.). MS (ESI, *m*/*z* [M]): 904.0 [M]$^+$, 776.2 [M−I]$^+$. Elemental analysis for $C_{38}H_{45}N_3I_2Pd$ (904): calcd. C 50.46, H 5.02, N 4.65; found C 50.71, H 5.20, N 4.69. $^1$H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta$ 0.70 (d, $J$ = 6.75 Hz, 6H, HC$Me_2$); 0.87 (d, $J$ = 6.90 Hz, 6H, HC$Me_2$); 1.28 (d, $J$ = 6.78 Hz, 6H, HC$Me_2$); 1.71 (d, $J$ = 6.62 Hz, 6H, HC$Me_2$); 2.54 (sept, $J$ = 6.89 Hz, 2H, *H*CMe$_2$); 3.25 (sept, $J$ = 6.89 Hz, 2H, *H*CMe$_2$); 6.83−7.26 (m, 12H, NC*H*, $C_6H_5$, $C_6H_3$); 7.45 (m, 2H, *m*-$C_5NH_5$); 7.57 (tt, $J$ = 1.69, 7.68 Hz, 1H, *p*-$C_5NH_5$); 8.91 (dt, $J$ = 1.61, 5.02 Hz, 2H, *o*-$C_5NH_5$) ppm. $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$, 25 °C): $\delta$ 22.53, 24.05, 25.82, 26.99 (HC$Me_2$), 28.70, 28.78 (HCMe$_2$), 123.71, 124.02, 124.74, 124.94, 125.35, 128.23, 129.37, 130.29 ($C_6H_5$, $C_6H_3$ NCH), 130.36 (*m*-$C_5NH_5$),130.86, 132.03, 133.31 ($C_6H_5$, $C_6H_3$), 136.91 (*p*-$C_5NH_5$), 144.73, 145.15, 145.54, 153.81 (*o*-$C_5NH_5$) ppm.



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*Organometallics* XXXX, XXX, XXX−XXX

Table 3. Crystal Data and Collection Parameters of Compounds 2−4

| Compound | 2 | 3 | 4 |
|---|---|---|---|
| CCDC Number | 1487623 | 1494820 | 1498255 |
| Empirical formula | $C_{68}H_{84}Cl_8N_4Pd_2$ | $C_{94}H_{112}Cl_2N_4Pd$ | $C_{40}H_{48}AgIN_2$ |
| Formula weight [g/mol] | 1453.79 | 1475.17 | 791.57 |
| Temperature [K] | 100(2) | 100(2) | 100(2) |
| Wavelength [Å] | 0.71073 | 0.71073 | 0.71073 |
| Space group | $P\bar{1}$ | $P2_1/n$ | $P\bar{1}$ |
| Unit cell dimensions [Å] *a* | 10.282(2) | 16.581(2) | 15.240(2) |
| *b* | 11.538(2) | 12.031(2) | 16.277(2) |
| *c* | 15.223(3) | 20.983(3) | 17.354(3) |
| *α* [°] | 80.14(2) | 90 | 67.82(2) |
| *β* [°] | 78.85(2) | 99.25(2) | 72.16(2) |
| *γ* [°] | 83.87(3) | 90 | 89.60(3) |
| Volume [Å$^3$] | 1740.6(6) | 4131.4(11) | 3765.7(11) |
| Z | 1 | 2 | 4 |
| Absorption coefficient [mm$^{-1}$] | 0.865 | 0.336 | 1.383 |
| *F*(000) | 748 | 1568 | 1608 |
| Crystal size [mm$^3$] | 0.274 × 0.096 × 0.078 | 0.190 × 0.140 × 0.090 | 0.190 × 0.160 × 0.110 |
| Theta range for data collection [°] | 1.380 to 28.255 | 1.457 to 25.380 | 1.341 to 25.430 |
| Reflections collected/unique | 60420/8524 | 108043/7593 | 191628/13765 |
| $R_{int}$ | 0.0288 | 0.0707 | 0.0630 |
| Completeness | 100% | 100% | 100% |
| Max. and min transmission | 0.7457 and 0.7005 | 0.4288 and 0.3755 | 0.4287/0.3819 |
| Data/restraints/parameters | 8524/1084/582 | 7593/918/593 | 13769/729/877 |
| Goodness-of-fit on $F^2$ | 1.126 | 1.041 | 1.095 |
| Final *R* indices [I > 2*σ*(I)] | *R*1 = 0.0280 | *R*1 = 0.0436 | *R*1 = 0.0411 |
| | *wR*2 = 0.0591 | *wR*2 = 0.1093 | wR2 = 0.0853 |
| *R* indices (all data) | *R*1 = 0.0346 | *R*1 = 0.0557 | *R*1 = 0.0557 |
| | *wR*2 = 0.0624 | *wR*2 = 0.1184 | wR2 = 0.0912 |
| Largest diff. peak and hole (e.Å$^{-3}$) | 0.676 and −1.232 | 1.428 and −0.587 | 0.936 and −1.132 |

*Synthesis of (alPr$^{Ph}$)PdI$_2$(3Cl-py) (**10**).* Compound **10** was prepared by employing a similar method as described for **9** using **1** (0.33 g, 0.56 mmol), $PdCl_2$ (0.10 g, 0.56 mmol), KI (0.31 g, 1.87 mmol), and $K_2CO_3$ (1 g) in 5 mL of pyridine. Yield: 0.35 g, 66%. Mp.: 193 °C (dec.). MS (ESI, *m*/*z* [M]): 937.0 [M]$^+$, 812.1 [M−I]$^+$. Elemental analysis for $C_{38}H_{44}N_3ClI_2Pd$ (938): calcd. C 48.63, H 4.73, N 4.48; found C 48.90, H 4.81, N 4.60. $^1$H NMR (500 MHz, $CDCl_3$, 25 °C): *δ* 0.72 (d, 6H, *J* = 6.72 Hz, HC*Me*$_2$); 0.89 (d, 6H, *J* = 6.87 Hz, HC*Me*$_2$); 1.30 (d, 6H, *J* = 6.73 Hz, HC*Me*$_2$); 1.72 (d, 6H, *J* = 6.55 Hz, HC*Me*$_2$); 2.55 (sept, 2H, *J* = 6.78 Hz, *H*CMe$_2$); 3.24 (sept, 2H, *J* = 6.64 Hz, *H*CMe$_2$); 6.83−6.86 (m, 2H, *o*-$C_6H_5$); 7.02 (t, *J* = 7.95 Hz, 2H, *m*-$C_6H_5$); 7.13−7.17 (m, 2H, 3Cl−$C_5NH_4$); 7.22 (s, 1H, NC*H*); 7.27 (d, *J* = 8.09 Hz, 3H, *p*-$C_6H_5$, *m*-$C_6H_3$); 7.47 (dt, *J* = 7.75, 10.89 Hz, 2H, *p*-$C_6H_3$); 7.59 (dd, *J* = 1.30, 2.31, 8.22 Hz, 1H, 3Cl−$C_5NH_4$); 8.86 (dd, *J* = 1.36, 5.46 Hz, 1H, 3Cl−$C_5NH_4$); 8.95 (d, *J* = 2.29 Hz, 1H, 3Cl−$C_5NH_4$) ppm. $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$, 25 °C): *δ* 22.60, 24.13, 25.90, 27.08 (HC*Me*$_2$), 28.82, 28.88 (HCMe$_2$), 123.61, 123.76, 124.32 ($C_6H_5$), 124.84, 125.48 ($C_6H_3$), 128.33 ($C_6H_5$), 129.49 ($C_6H_5$), 130.41 (*p*-$C_6H_3$), 130.51 (3Cl-$C_5NH_4$), 130.97 (*p*-$C_6H_3$), 131.81 ($C_6H_5$), 132.07 ($C_6H_3$), 133.33 (NCH), 135.73 (NCPd), 137.11 (3Cl-$C_5NH_4$), 144.95 ($C_6H_5$), 145.26 (*ipso*-$C_6H_5$), 145.62 (*ipso*-$C_6H_3$); 151.88, 152.85 (3Cl-$C_5NH_4$) ppm.

**Catalytic Activity.** Phenyl boronic acid (Fluka Chemicals), KO$^t$Bu (Merck), 4-chlorotoluene (Merck), 4-bromotoluene (J. T. Baker Chemicals), 4-iodotoluene (Fluka Chemicals), 2-bromo-1,3-dimethylbenzene (Sigma-Aldrich), 1-bromonaphthalene (Sigma-Aldrich), 4-iodoanisole (Acros Organics), 1-iodo-4-nitrobenzene (Sigma-Aldrich), and 1-chloro-2-fluorobenzene (TCI Chemicals) were used without further purification. 2-Propanol (analytical grade, VWR Chemicals) was degassed by three freeze−pump−thaw cycles prior to use.

Phenyl boronic acid (1.2 mmol), KO$^t$Bu (1.5 mmol), and the precatalyst (**2**, **5**, or **6**) were added into a reaction vessel and evacuated for at least 45 min and then filled with $N_2$. 2-Propanol (6 mL) and 1.0 mmol of the aryl halide were added to the reaction vessel. The resulting brownish mixture was stirred at room temperature (22 °C). An aliquot (0.5 mL) of the reaction mixture was removed via a syringe after 0.5, 2, and 24 h intervals and quenched with 1 mL of water. Organic contents were extracted with dichloromethane (2 mL), dried over anhydrous $MgSO_4$, and GC-MS analyzed. The conversion was determined by GC analysis or NMR spectroscopy.

**Single Crystal X-ray Analysis of Compounds 2, 5, 6, 7, and 8.** Suitable single crystals were selected from the mother liquor and covered with perfluorinated polyether oil on a microscope slide, which was cooled with a nitrogen gas flow using the X-Temp2 device.[26] The diffraction data of compounds **2**, **6**, **7**, and **8** were collected at 100 K on a Bruker D8 three circle diffractometer, equipped with a SMART APEX II CCD detector and an INCOATEC microfocus source (Mo $K_\alpha$ radiation) with INCOATEC Quazar mirror optics (Tables 3 and 4). The diffraction data of compound **5** were collected at 100 K on a Bruker D8 three-circle diffractometer, equipped with a SMART APEX II CCD detector and an INCOATEC microfocus source (Ag $K_\alpha$ radiation) with INCOATEC Quazar mirror optics. The data were integrated with SAINT.[27] For compound **6**, a multiscan absorption correction with TWINABS[28] was applied. For compounds **2**, **5**, **7**, and **8**, a multiscan absorption correction with SADABS[29] was applied. In addition, a 3*λ*-correction in SADABS[29] was applied to compounds **2**, **7**, and **8**. The structure solutions were performed with Bruker Intrinsic Phasing - SHELXT[30] and the structure refinement was performed with SHELXL,[31] using the graphical user interface SHELXLE.[32] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were assigned to ideal positions and refined using a riding model. Their $U_{iso}$ values were constrained to 1.5 $U_{eq}$ of their pivot atoms for terminal sp$^3$ carbon atoms and 1.2 times for all other carbon atoms.

**Single Crystal X-ray Analysis of Compounds 9 and 10.** Single crystals suitable for X-ray diffraction measurement were picked, suspended in a Paratone-N/paraffin oil mixture, mounted on a glass fiber and transferred onto the goniometer of the diffractometer. The



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Table 4. Crystal Data and Collection Parameters of Compounds 5−10

| Compound | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|
| CCDC Number | 1445486 | 1445487 | 1445484 | 1445485 | 1446056 | 1446057 |
| Empirical formula | $C_{38}H_{45}Cl_2N_3Pd$ | $C_{38}H_{44}Cl_3N_3Pd$ | $C_{38}H_{45}Cl_{1.06}I_{0.94}N_3Pd$ | $C_{38}H_{44}Cl_{1.74}I_{1.26}N_3Pd$ | $C_{38}H_{45}Cl_{0.15}I_{1.85}N_3Pd$ | $C_{38}H_{44}Cl_1I_2N_3Pd$ |
| Formula weight [g/mol] | 721.07 | 755.51 | 807.46 | 871.06 | 890.61 | 938.41 |
| Temperature [K] | 100(2) | 100(2) | 100(2) | 100(2) | 100.0 (1) | 100.0 (1) |
| Wavelength [Å] | 0.56086 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 1.54184 |
| Space group | $P2_1/n$ | $P\bar{1}$ | $P2_1/n$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| Unit cell dimensions [Å] $a$ | 9.437(2) | 9.537(2) | 9.151(3) | 9.2685(3) | 9.2753(3) | 9.630(2) |
| $b$ | 25.014(3) | 15.348(2) | 24.824(3) | 11.811(3) | 11.7625(4) | 11.7753(3) |
| $c$ | 15.126(2) | 24.812(3) | 15.418(2) | 18.420(6) | 18.2798(8) | 18.6313(5) |
| $\alpha$ [°] | 90 | 91.36(2) | 90 | 103.33(2) | 101.143(4) | 102.384(2) |
| $\beta$ [°] | 100.00(2) | 91.14(2) | 100.47(2) | 96.42(3) | 96.316(4) | 97.461(2) |
| $\gamma$ [°] | 90 | 99.93(3) | 90 | 103.24(2) | 102.930(3) | 103.547(2) |
| Volume [Å$^3$] | 3516.4(10) | 3610.2(10) | 3589.4(10) | 1857.0(10) | 1881.08(14) | 1897.19(9) |
| Z | 4 | 4 | 4 | 2 | 2 | 2 |
| Absorption coefficient [mm$^{-1}$] | 0.379 | 0.766 | 1.438 | 1.705 | 2.053 | 17.584 |
| $F$(000) | 1496 | 1560 | 1632 | 871 | 881.5 | 924 |
| Crystal size [mm$^3$] | 0.193 × 0.126 × 0.057 | 0.217 × 0.213 × 0.117 | 0.280 × 0.079 × 0.068 | 0.278 × 0.082 × 0.077 | 0.222 × 0.162 × 0.126 | 0.24 × 0.033 × 0.02 |
| Theta range for data collection [°] | 1.256 to 20.556 | 1.347 to 28.307 | 1.574 to 29.044 | 1.154 to 26.664 | 1.823 to 29.999 | 2.473 to 71.996 |
| Reflections collected/unique | 75942/7228 | −/17928 (2 twin domains) | 187613/9067 | 54131/7826 | 110480/10943 | 68190/7465 |
| $R_{int}$ | 0.0834 | − (merged) | 0.0323 | 0.0401 | 0.0359 | 0.0522 |
| Completeness | 100.0% | 100.0% | 100.0% | 100.0% | 99.8% | 100.0% |
| Max. and min transmission | 0.4254 and 0.3871 | 0.4311 and 0.34956 | 0.7458 and 0.6777 | 0.7454 and 0.6573 | 0.859 and 0.709 | 0.726 and 0.136 |
| Data/restraints/parameters | 7228/0/406 | 17928/0/828 | 9067/7/413 | 7826/6/422 | 10943/1/409 | 7465/0/414 |
| Goodness-of-fit on $F^2$ | 1.022 | 1.195 | 1.199 | 1.102 | 1.106 | 1.036 |
| Final $R$ indices [I > 2sigma(I)] | $R1$ = 0.0385, $wR2$ = 0.0839. | $R1$ = 0.0507 $wR2$ = 0.1319 | $R1$ = 0.0227 $wR2$ = 0.0508 | $R1$ = 0.0280, $wR2$ = 0.0614 | $R1$ = 0.0279 $wR2$ = 0.0706 | $R1$ = 0.0295 $wR2$ = 0.0776 |
| $R$ indices (all data) | $R1$ = 0.0596, $wR2$ = 0.0913 | $R1$ = 0.0543, $wR2$ = 0.1335 | $R1$ = 0.0247 $wR2$ = 0.0514 | $R1$ = 0.0343 $wR2$ = 0.0641 | $R1$ = 0.0307 $wR2$ = 0.0720 | $R1$ = 0.0327 $wR2$ = 0.0800 |
| Largest diff. peak and hole (e.Å$^{-3}$) | 1.783 and −0.793 | 2.051 and −1.110 | 0.568 and −0.506 | 0.765 and −0.549 | 2.945 and −0.868 | 1.387 and −0.607 |

crystals were kept at 100 K during data collection. The measurement of **9** was carried out with Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å) on a SuperNova, single source at offset, Eos diffractometer. The data collection of **10** was carried out with Cu K$\alpha$ radiation ($\lambda$ = 1.5418 Å) on a SuperNova, Dual, Cu at zero, Atlas diffractometer (Table 4). Using Olex2[33] the structures were solved by direct methods and refined by full-matrix least-squares cycles with SHELXL.[31] Hydrogen atoms were refined using a riding model with $U$(H) = 1.5 $U_{eq}$ for $CH_3$ groups and $U$(H) = 1.2 $U_{eq}$ for all others.

## CONCLUSION

In conclusion, high-yield rational synthesis routes to palladium(II) complexes **2**, **3**, and **5**−**10** featuring an 1,3-imidazole derived aNHC ligand have been described. All complexes have been fully characterized by NMR spectroscopy and mass spectrometry studies. Molecular structures of **2**−**10** have been determined by single crystal X-ray diffraction analyses. Preliminary investigations on the catalytic activity of three representative compounds **2**, **5**, and **6** for the Suzuki-Miyaura cross-coupling reactions are presented. Compounds **2** and **6** are highly active catalysts and afford biaryls in a good to excellent yield at room temperature.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00662.

NMR plots of compounds **2**−**10** and Structure reports for **2**−**10** (PDF)
Crystallographic data for **2** (CIF)
Crystallographic data for **3** (CIF)
Crystallographic data for **4** (CIF)
Crystallographic data for **5** (CIF)
Crystallographic data for **6** (CIF)
Crystallographic data for **7** (CIF)
Crystallographic data for **8** (CIF)
Crystallographic data for **9** (CIF)
Crystallographic data for **10** (CIF)

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### Notes

The authors declare no competing financial interest.



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