Nonchelate and Chelate Complexes of Palladium(II) with N-Heterocyclic Carbene Ligands of Amido Functionality

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The imidazolium ligand precursors $[L^1H^1H^2]Cl$ and $[L^2H^1{}_2H^2]Cl$ (H^1 = N*H*C═O, H^2 = NC*H*N) for the potentially bidentate and pincer-type amido-NHC ligands were synthesized in 66−78% yields. Selective deprotonation of H^2 in these salts with pyridine in the presence of palladium chloride resulted in the monodentate palladium(II) complexes $Pd(L^1H^1)(py)Cl_2$ and $Pd(L^2H^1{}_2)(py)Cl_2$. The use of K_2CO_3 in pyridine or DMF led to the double and triple deprotonations of the ligand precursors, giving the bis-bidentate and pincer-type palladium(II) complexes $PdL^1{}_2$ and $PdL^2(py)$, respectively. Intriguingly, in certain cases, both the cis and the trans isomers of $PdL^1{}_2$ were formed and isolated in pure forms. A theoretical study indicates that the trans-$PdL^1{}_2$ is thermodynamically more stable than the cis isomer (ca. 5.8 kcal mol^{-1}). All the new complexes are characterized by NMR (1D and 2D) and single-crystal X-ray diffraction studies. A systematic study of the new complexes in Suzuki coupling reactions revealed the following order of activities: $Pd(L^1H^1)(py)Cl_2 > PdL^2(py) > PdL^1{}_2$.

Introduction

Palladium complexes of N-heterocyclic carbene (NHC) ligands are attracting a considerable amount of interest because of their easy accessibility, high thermal stability, and remarkable catalytic activities in various C−C coupling reactions.[1] Much effort has also been devoted to the synthesis of palladium complexes with functionalized NHC ligands. For example, the combination of a nitrogen donor, such as pyridine, and an NHC moiety is of intense interest, and some palladium complexes with multidentate ligands display intriguing coordination chemistry and effective catalytic activities.[2−4] It is generally accepted that the chelate effect imparted on their metal complexes offers extra stability for the generation of robust metal complexes, which are highly desirable for catalytic applications, especially those requiring harsh reaction conditions. On the other hand, chelate ring opening is believed to be important during the catalytic cycle for incoming substrates. Hence, many transition metal complexes with functionalized NHC ligands for catalytic purposes reported by others[3−8] and us[9] were based on neutral donors (i.e., hemilabile functionalized NHC ligands).

Herein, we report on palladium(II) complexes with potential chelating ligands, L^1 and L^2, shown in Scheme 1. Our interest in L^1 and L^2 stems from the fact that palladium complexes with anionic functionalized NHC ligands are rare.[10] In fact, these anionic ligands are more common with electropositive metals[11,12] because the anionic donor can act as an anchor to inhibit the dissociation of the NHC moiety from the metal center.[12] In this work, our controlled deprotonation of the imidazolium precursors, $[L^1H^1H^2]Cl$ and $[L^2H^1{}_2H^2]Cl$ (H^1 = N*H*C═O, H^2 = NC*H*N), afforded various monodentate and mulitdentate NHC

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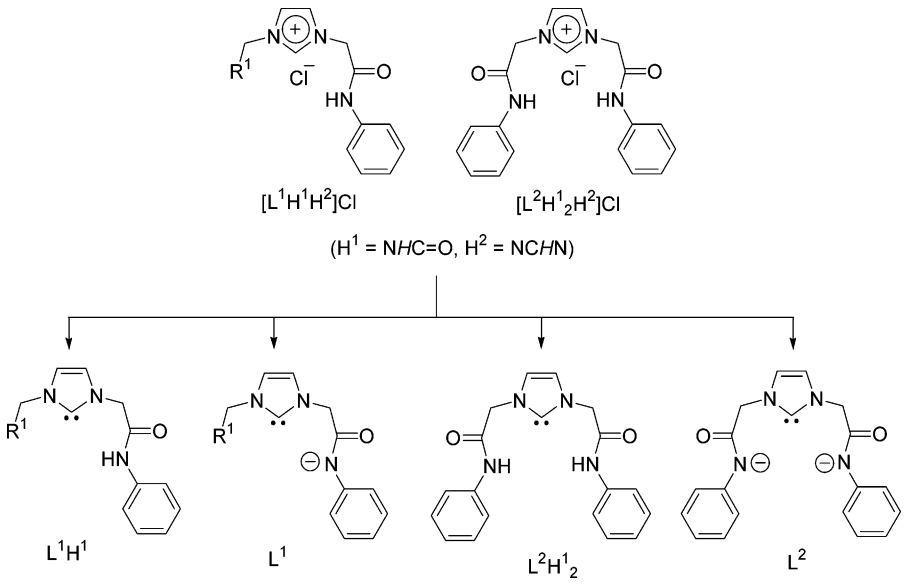
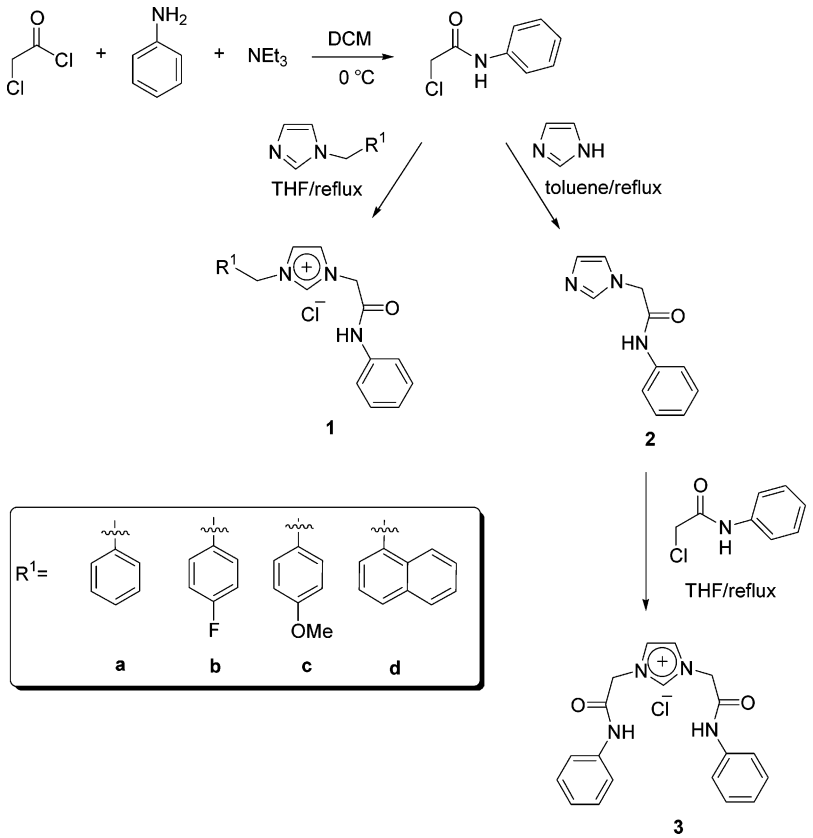
Scheme 1



Scheme 2



complexes of palladium, which are characterized by NMR (1D and 2D) and solid-state structural studies. A systematic study on these monodentate and mulitdentate complexes provides evidence that the stable chelate ring of palladium NHC complexes has a detrimental effect on catalytic activity.

Results and Discussion

Preparation of Imidazolium Derivatives. The preparation of the ligand precursors $[L^1H^1H^2]Cl$ (**1**) (H^1 = N*H*C=O, H^2 = NC*H*N) and $[L^2H^1{}_2H^2]Cl$ (**3**) is presented in Scheme 2. The common intermediate for **1** and **3** is 2-chloro-*N*-phenylacetamide. Simple quaternization reactions with imidazole derivatives afforded **1** in good yields. Precursor **3** was prepared via the imidazole derivative **2**. The ^{1}H NMR spectra of both **1** and **3** exhibit two sharp, downfield signals at 9.5 and 11.0 ppm, attributed to either the N*H* or the NC*H*N protons. Addition of D_2O, for example, to a solution of **1a** in DMSO-d_6 shows the collapse of the downfield signal at 11.25 ppm, revealing its N*H* proton identity. The more upfield signal is, therefore, assignable to the NC*H*N proton. The NMR data of **1** and **3** are comparable to those reported for several relevant imidazolium precursors.[13]

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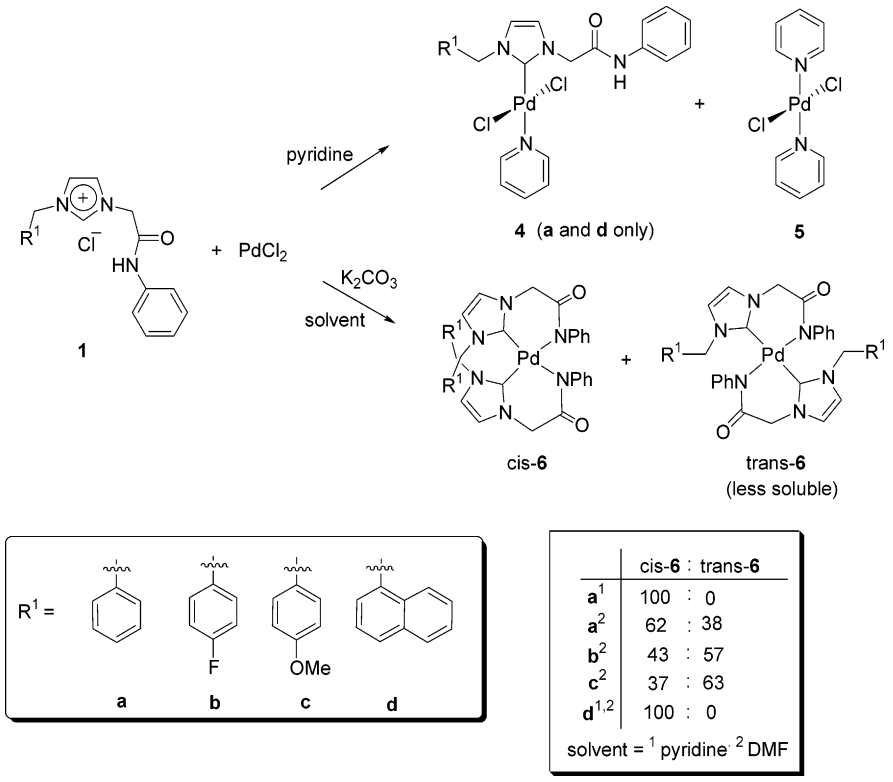
Scheme 3



Preparation of Monodentate Complexes of Palladium(II). A reaction of the ligand precursor **1a** or **1d** with $PdCl_2$ in pyridine produced a mixture of palladium(II) complex **4** and *trans*-dichlorobis(pyridine)palladium(II) (**5**) in ca. 1:1 ratio (Scheme 3). The synthetic method is similar to that for the structurally related NHC−$PdCl_2$−3-chloropyridine complexes reported in a very recent article.[14a] The difference is that in our case an extra potassium carbonate was not added in order to avoid further deprotonation of H^1 in **1** leading to the formation of a chelate complex (vide infra). Our initial attempt to purify the crude products resulted in crystals of *trans*-dichlorobis(pyridine)palladium(II) only.[15] Complexes **4a** and **4d** in pure forms (32 and 28% yields, respectively) can be obtained eventually by subjecting the respective crude mixtures to a column of silica gel and eluting with 1:1 ethyl acetate−hexane. These complexes are highly stable toward air and moisture, with good solubility in common organic solvents. Their ^{1}H NMR spectra in the downfield region show the absence of sharp signals due to NC*H*N protons at ca. 9.4 ppm, indicating the successful formation of carbene complexes. However, the broad N*H* signals at 9.04 ppm and signals due to pyridine are observed. All these NMR data indicate that **4a** and **4d** are monodentate NHC complexes, $Pd(L^1H^1)(py)Cl_2$, which were subsequently confirmed by solid-state structural studies (vide infra). The assignment of the carbene signal in the $^{13}C\{^1H\}$ NMR spectrum of **4a** is tricky. According to the DEPT experiment, only three, instead of the required four, quaternary carbon signals are observed at 134.6, 137.6, and 164.5 ppm. The downfield signal can be due to either *C*═O or the carbene carbon. To clarify the signal assignment, we carried out a 2D NMR study and HMBC correlations were found from the two methylene protons (5.49 and 5.85 ppm) to the signal at 151.1 ppm, indicating that this CH carbon signal (established by DEPT) is accidentally equivalent to the carbene resonance (Figure 1). The HMBC experiment also establishes that the more upfield signal at 5.49 ppm is due to the methylene protons between the amido group and NHC moiety. In contrast, the carbene singlet of **4d** is slightly more upfield at 150.9 ppm, without overlapping with the *C*H signal at 151.2 ppm. Notably, these carbene chemical shifts at ca. 151 ppm are very upfield compared with those in other NHC complexes of palladium(II) reported in the literature.[16]

Complex **7** was similarly prepared by reacting the ligand precursor, $[L^2H^1{}_2H^2]Cl$, in neat pyridine (Scheme 4). However, attempted purification of the crude product consisting of **7** and **5** by column chromatography was unsuccessful. Crystals of **7** and **5**, however, can be obtained from the mixture by vapor diffusion of ether into its DMF solution. The structure of **7**, $Pd(L^2H^1{}_2)(py)Cl_2$, was confirmed by subsequent structural study on a crystal picked manually.

Preparation of Bidentate and Pincer-Type Complexes of Palladium(II). Since complexation reactions in pyridine lead to the preferential deprotonation of the NC*H*N but not the N*H* protons, we sought to add an additional base, K_2CO_3, in the hope of mediating double deprotonation of $[L^1H^1H^2]Cl$ and triple deprotonation of $[L^2H^1{}_2H^2]Cl$ for the formation of bidentate and pincer-type palladium(II) complexes of L^1 and L^2, respectively. The effort indeed produced the neutral $PdL^1{}_2$ (**6**) and $PdL^2(py)$ (**8**), which were subsequently confirmed by structural studies (vide infra). Markedly, either the cis or trans isomers of **6** can be successfully isolated by conducting the reactions in different solvents. For example, using pyridine as solvent leads to pure *cis*-**6a**, whereas switching to DMF yielded a mixture of cis and trans isomers (see the cis/trans ratio in Scheme 2; the ratio is

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(16) For representative examples: see refs 2b, 4b,c, 6a.

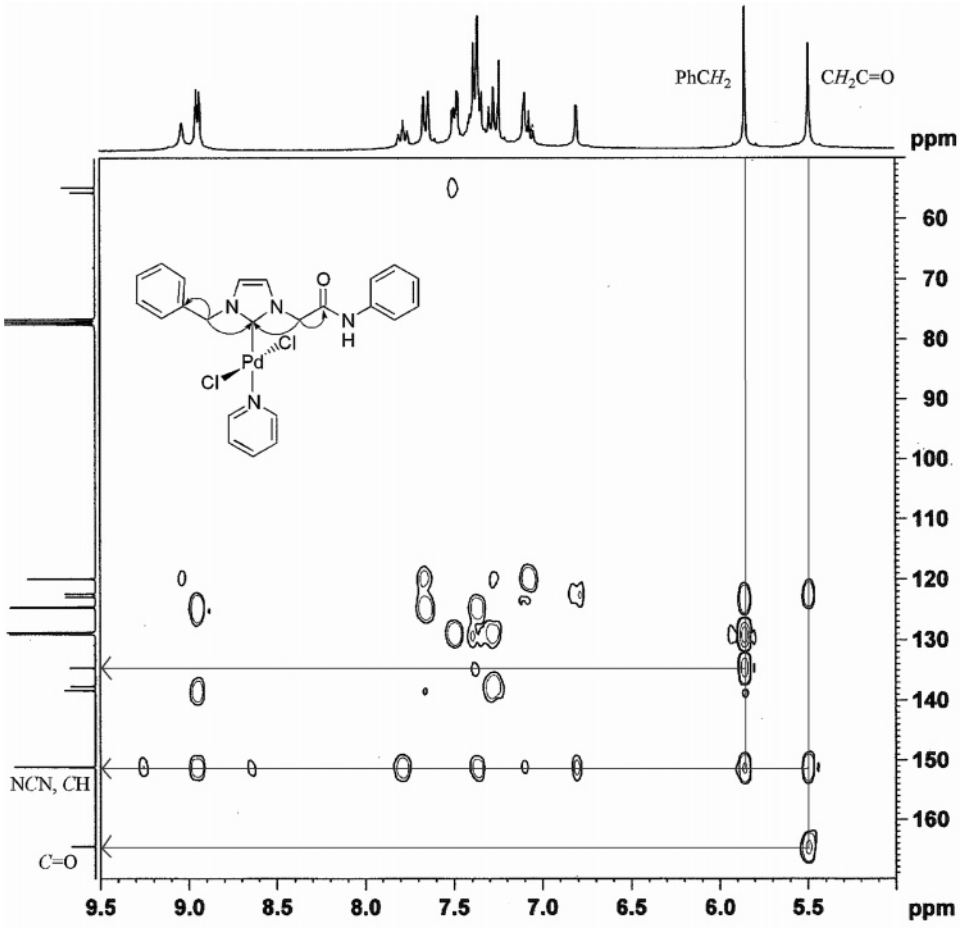
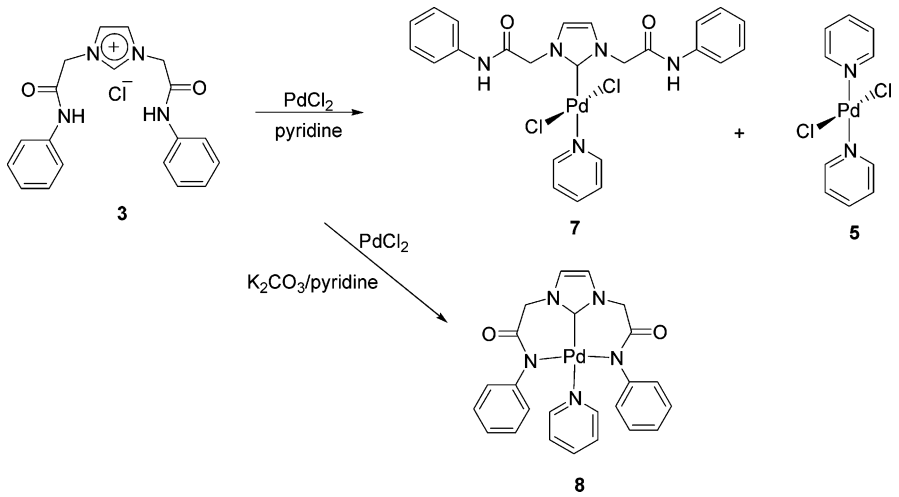


Figure 1. HMBC NMR spectrum and selected HMBC (H→C) of **4a**.

Scheme 4



calculated on the basis of the integration values from the ^{1}H NMR spectra of the reaction mixture). The pure trans product of **6** can be obtained in general by simple washing of the mixture with methanol. Like **4**, both cis and trans isomers of **6** are highly stable and can be stored in air indefinitely. Generally, the cis isomer displays a much better solubility than the trans product. For example, while *cis*-**6a** dissolves readily in halogenated solvents, *trans*-**6a** is only sparingly soluble. The ^{1}H NMR data fully support the formation of bis-bidentate complex **6**. Both cis and trans complexes are symmetry-related and display the diagnostic absence of the broad N*H* and the NC*H*N signals. In each complex, each proton on the two groups of methylene carbons becomes diastereotopic and therefore displays geminal splitting. Generally, except in *cis*-**6a**, the two diastereotopic signals due to the methylene spacer of the chelate rings show a larger difference in chemical shift than those of the dangling moiety (*cis*-**6a**: 0.43 vs 0.85 ppm; *trans*-**6a**: 0.86 vs 0.06 ppm; *trans*-**6b**: 0.62 vs 0.30 ppm; *trans*-**6c**: 0.66 vs 0.36 ppm; *cis*-**6d**: 0.43 vs 0.17 ppm). In the ^{13}C{^{1}H} NMR spectra of *cis*-**6**, there are two downfield quaternary carbon signals resonating closely at 165 and 166 ppm for the cis isomer and at 169 and 170 ppm for the trans isomer, making the assignments of the carbene and the carbonyl signals uncertain. For unambiguous signal assignments, we again carry out HMBC experiments,

which enable the assignments of the more upfield signals at 163.7 and 165.5 ppm for the carbene carbons in *cis*-**6a** and *cis*-**6d**, respectively (Figure 1S in the Supporting Information shows the HMBC spectrum of *cis*-**6a**). In contrast, the carbene signals are more downfield at 170.5, 170.4, and 170.3 ppm in *trans*-**6a**, *trans*-**6b**, and *trans*-**6c**, respectively. Hence, the general observation is that monodentate NHC complex **4** has the most upfield carbene resonance (∼151 ppm), followed by the cis isomer of the bis-bidentate NHC complex **6** (∼164 ppm) and then its trans isomer (∼170 ppm). It is worthy to note that **6** contains two ligands of L^1 per Pd, indicating that the bidentate ligand has a smaller steric bulk than many other bidentate NHC ligands that form 1:1 PdL complexes (L = bidentate NHC ligand) reported by us[17] and others.[18]

Pincer-type complexes with, for example, a traditional [PCP] donor set displayed rich coordination chemistry and catalytic activities.[19] The pincer-type palladium(II) complex of L^2 featuring a NHC-based [NCN] donor set, $PdL^2(py)$ (**8**), was successfully prepared by employing similar condition for **6**, giving a pale yellow solid in 77% yield. Again, the absence of NC*H*N and N*H* proton signals indicates the successful coordination of L^2 on the palladium(II) ion. The ^{1}H NMR spectrum displays a singlet for the four methylene protons, in contrast to those in **6**. The carbene signal was observed at 152.7 ppm, which is significantly upfield than that in **6** but very similar to those in **4**. An upfield carbene resonance at ca. 150 ppm seems to be characteristic for a palladium(II) complex with a trans disposition of pyridine and carbene ligands.[2a,14]

Structural Characterizations. Crystals suitable for X-ray diffraction studies can be grown typically by either vapor diffusion or slow evaporation from a solution of the new compounds in highly polar solvents, such as methanol, DMF, chloroform, and DMSO. Most of the resultant structures (except **4a** and **4d**) show incorporation of these polar guest molecules, which are involved in hydrogen-bonding interactions with the amido moieties of the ligands. Figures 2−10 show the molecular structures with selected bond lengths and bond angles listed in the captions.

Complexes **4a**, **4d**, and **7** crystallize with their full molecules in their respective asymmetric units. A comparison of the three structures shows that the NHC ligand in **4d** exerts the largest trans influence on the pyridine, resulting in the shortest Pd−C bond of 1.958(3) Å (compared with 1.967(2) Å in **7** and 1.975(3) Å in **4a**) and the longest Pd−N bond of 2.133(4) Å (compared with 2.1167(19) Å in **7** and 2.073(2) Å in **4a**). An obvious difference between **4a** and **4d** is the almost coplanarity of the pyridine and the heterocyclic ring in **4a** (interplanar angle = 5.3(1)°), whereas the two rings in **4d** are closer to orthogonal, making an angle of 70.3(1)°. Notably, the new polymorph of **5** also arised from the different orientation of the pyridine rings.[15] In each of the structures, the NHC moiety is symmetrically coordinated to the palladium center with the two Pd−C−N angles almost equal (for example in **4a**, the two angles are 127.8(2)° and 127.2(2)°), contrasting those in the chelate complexes of **6**.

Complex *cis*-**6a** crystallizes in the monoclinic space group *C*2/*c* with one-half of the molecule in the asymmetric unit, and the palladium center is positioned at the special position of 2-fold symmetry. Complex *cis*-**6d** can be crystallized from DMF and methanol. The structure containing DMF (*cis*-**6d**) also crystallizes in space group *C*2/*c*, but with a full molecule appearing in general positions. On the other hand, the structure with methanol incorporation (*cis*-**6d′**) crystallizes in the hexagonal space group $R\bar{3}$. The geometric parameters of *cis*-**6d** and *cis*-**6d′** are similar (Figure 2S of the Supporting Information depicts the molecular structure of *cis*-**6d′**), but rather unexpectedly, the latter displays intriguing supramolecular feature (vide infra). A comparison of the structural data of chelate complexes with those of nonchelate complexes shows that in the bidentate mode the NHC moiety coordinates to the metal quite asymmetrically. As a typical example, the N−C−Pd bond angles in *cis*-**6a** are uneven, with ∠N2−C1−Pd1 = 119.69(12)° and ∠N1−C1−Pd1 = 135.37(12)°, a difference of ca. 16°. The Pd−C bonds in *cis*-**6a** (1.9662(15) Å) are similar to those in **4a** (1.975(3) Å).

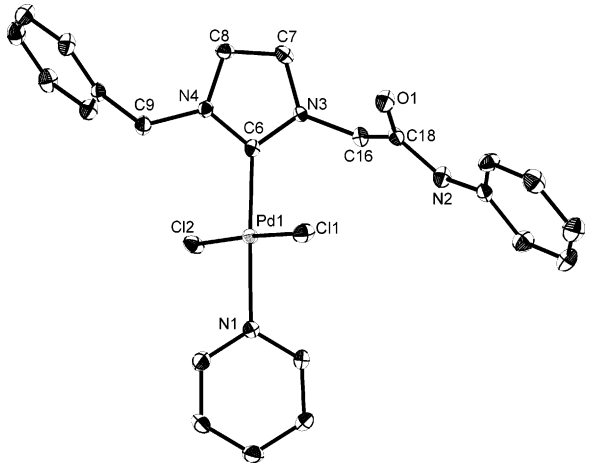


Figure 2. Thermal ellipsoid plot of **4a** at the 35% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): Pd1−C6, 1.975(3); Pd1−Cl1, 2.3080(9); Pd1−Cl2, 2.3028(9); Pd1−N1, 2.073(2). Selected bond angles (deg): C6−Pd1−Cl1, 92.28(9); C6−Pd1−Cl2, 90.91(9); N1−Pd1−Cl1, 88.14(7); N1−Pd1−Cl2, 88.82(7); C6−Pd1−N1, 177.28(15); Cl1−Pd1−Cl2, 175.65(4); N4−C6−Pd1, 127.8(2); N3−C6−Pd1, 127.2(2).

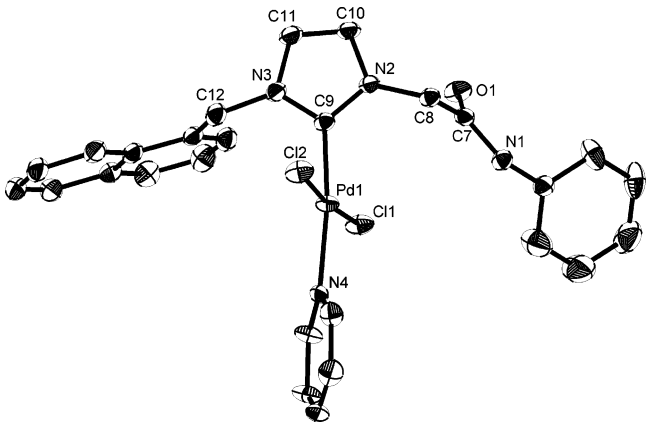


Figure 3. Thermal ellipsoid plot of **4d** at the 35% probability level. Hydrogen atoms are omitted for clarity (the phenyl group and the pyridine ligand are disordered; only one of the orientation with 0.40 site occupancy is shown for the phenyl group; the major orientation of the pyridine ligand with 0.60 site occupancy is shown). Selected bond distances (Å): Pd1−C9, 1.958(3); Pd1−Cl1, 2.2966(7); Pd1−Cl2, 2.3105(7); Pd1−N4, 2.133(4). Selected bond angles (deg): C9−Pd1−Cl1, 86.63(8); C9−Pd1−Cl2, 87.53(8); N4−Pd1−Cl1, 94.22(13); N4−Pd1−Cl2, 91.98(12); C9−Pd1−N4, 173.00(16); Cl1−Pd1−Cl2, 173.31(3); N2−C9−Pd1, 128.2(2); N3−C9−Pd1, 126.1(2).

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(18) For examples: see (a) Herrmann, W. A.; Schwarz, J. *Organometallics* **1999**, *18*, 4082. (b) Hermann, W. A.; Reisinger, C.-P.; Spiegler, M. *J. Organomet. Chem.* **1998**, *557*, 93.

(19) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759.

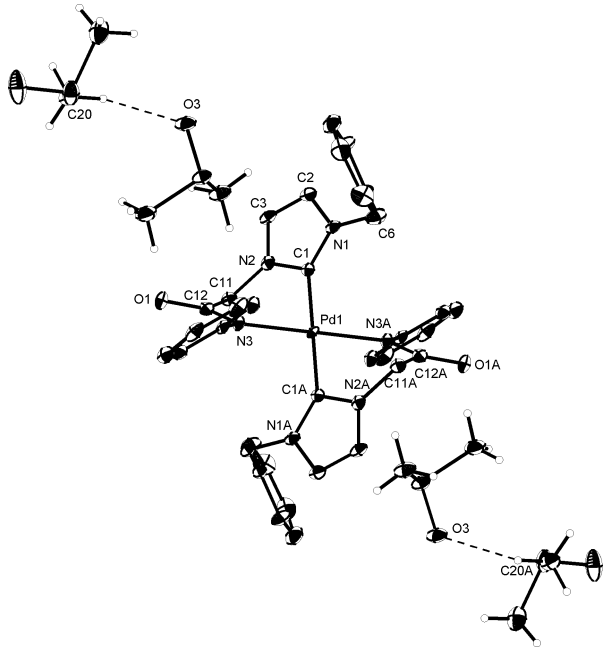


Figure 4. Thermal ellipsoid plot of *trans*-**6a**·4DMSO at the 35% probability level. Hydrogen atoms (except those on the guest DMSO molecules) are omitted for clarity. Selected bond distances (Å): Pd1−C1, 2.020(4); Pd1−N3, 2.051(4). Selected bond angles (deg): C1−Pd1−N3, 86.24(16); C1−Pd1−N3A, 93.76(16); C1−Pd1−C1A, 179.999(1); N3−Pd1−N3A, 180.0; N1−C1−Pd1, 136.9(3); N2−C1−Pd1, 118.3(3).

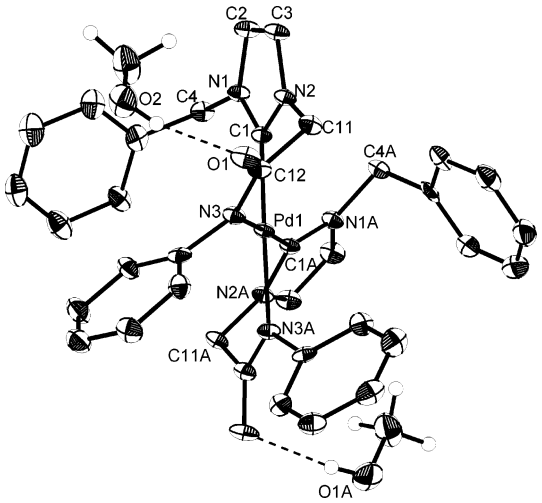


Figure 5. Thermal ellipsoid plot of *cis*-**6a**·2MeOH at the 35% probability level. Hydrogen atoms (except those on the guest methanol molecules) are omitted for clarity (the two phenyl groups are disordered; only the major orientations with 0.60 site occupancy are shown). Selected bond distances (Å): Pd1−C1, 1.9662(15); Pd1−N3, 2.0870(13). Selected bond angles (deg): C1−Pd1−N3, 85.77(6); C1−Pd1−C1A, 95.42(9); N3−Pd1−N3A, 93.07(8); C1−Pd1−N3A, 178.10(6); N1−C1−Pd1, 135.37(12); N2−C1−Pd1, 119.69(12).

Both *trans*-**6a** and *trans*-**6c** crystallize in space group $P\bar{1}$, whereas *trans*-**6b** crystallizes in $P2_1/c$. In each case, the palladium center is situated in a special position of *i* symmetry and the two trans NHC moieties are coplanar. The Pd−carbene bond distance in the trans isomer is generally longer than those in the cis isomer and in **4**. For example, the distance is 2.020(4) Å in *trans*-**6a**, longer than those of 1.9662(15) and 1.975(3) Å in *cis*-**6a** and **4a**, respectively. The Pd−N bond of 2.051(4) Å in *trans*-**6a** is, however, slightly shorter than that of 2.0870(13) Å in *cis*-**6a**. From the molecular structures of **6**, it can be seen that the methylene spacers between the N-heterocyclic ring and the phenyl(naphthyl) ring are essential for the successful formation of these 1:2 Pd:L^1 complexes. Complex **8** was solved in the space group $P2_1/c$ with a full molecule in its asymmetric unit. The pyridine makes an angle of 36.5(8)° with the heterocyclic ring. The Pd−C distance of 1.924(3) Å is the shortest among all the palladium complexes.

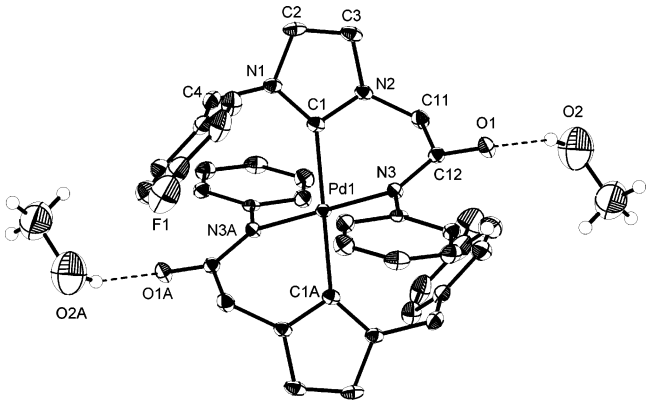


Figure 6. Thermal ellipsoid plot of *trans*-**6b**·2MeOH at the 35% probability level. Hydrogen atoms (except those on the guest methanol molecules) are omitted for clarity. Selected bond distances (Å): Pd1−C1, 2.016(3); Pd1−N3, 2.057(3). Selected bond angles (deg): C1−Pd1−N3, 85.16(12); C1−Pd1−N3A, 94.84(12); C1−Pd1−C1A, 180.0; N3−Pd1−N3A, 180.0; N1−C1−Pd1, 135.2(3); N2−C1−Pd1, 119.1(2).

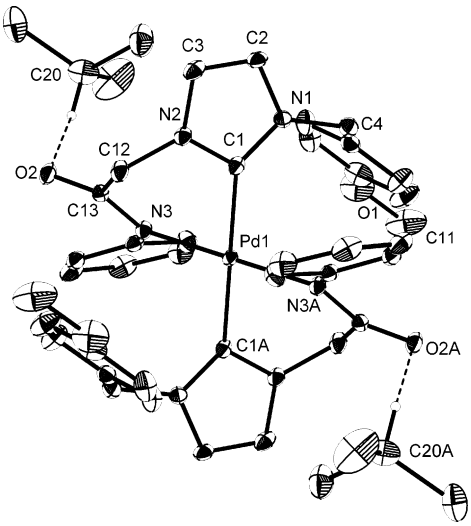


Figure 7. Thermal ellipsoid plot of *trans*-**6c**·2$CHCl_3$ at the 35% probability level. Hydrogen atoms (except those on the guest chloroform molecules) are omitted for clarity. Selected bond distances (Å): Pd1−C1, 2.013(3); Pd1−N3, 2.059(2). Selected bond angles (deg): C1−Pd1−N3, 86.10(10); C1−Pd1−N3A, 93.90(10); C1−Pd1−C1A, 180.0; N3−Pd1−N3A, 180.0; N1−C1−Pd1, 135.4(2); N2−C1−Pd1, 119.24(19).

Open-Channel Network. The supramolecular feature for the cis isomer of **6** is worthy of mentioning. While the packing of the trans isomer shows no special feature, the cis disposition of the amide carbonyl groups and the presence of guest methanol molecules allow the assembly of an open-channel coordination network via intermolecular hydrogen bonds of the type C−H···O. As depicted in Figure 11, the structure of *cis*-**6a**·2MeOH consists of open channels along the [001] direction. Unfortunately, the channels are self-penetrated by phenyl groups of the amido moieties. No such channel structure was observed

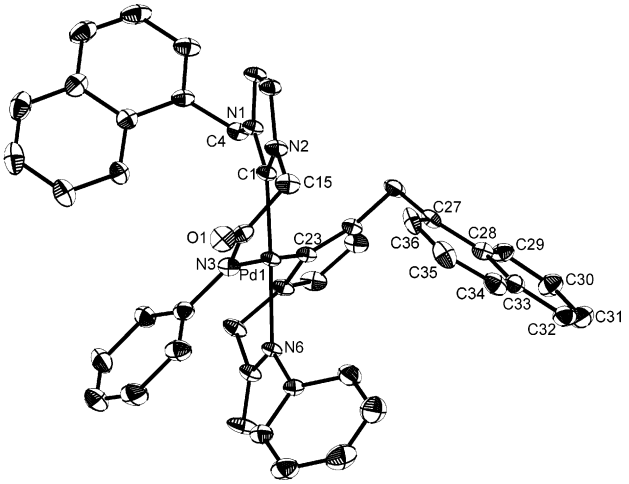


Figure 8. Thermal ellipsoid plot of *cis*-**6d**·0.5DMF at the 35% probability level (only the major orientation of the disordered naphthyl ring, C27−C36, is shown). Hydrogen atoms and the disordered DMF solvent are omitted for clarity. Selected bond distances (Å): Pd1−C1, 1.972(2); Pd1−C23, 1.972(2); Pd1−N3, 2.0851(19); Pd1−N6, 2.0818(17). Selected bond angles (deg): C1−Pd1−N3, 86.45(8); C1−Pd1−C23, 95.50(9); C23−Pd1−N6, 84.50(8); C1−Pd1−N6, 177.70(8); C23−Pd1−N3, 177.01(9); N3−Pd1−N6, 93.46(7); N1−C1−Pd1, 133.51(16); N2−C1−Pd1, 120.89(16).

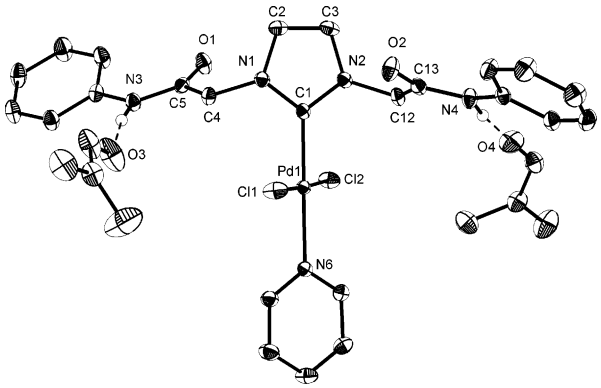


Figure 9. Thermal ellipsoid plot of **7**·2DMF at the 35% probability level. Hydrogen atoms (except those on the nitrogen atoms) are omitted for clarity. Selected bond distances (Å): Pd1−C1, 1.967(2); Pd1−Cl1, 2.2973(6); Pd1−Cl2, 2.2953(6); Pd1−N6, 2.1167(19). Selected bond angles (deg): C1−Pd1−Cl1, 88.85(7); C1−Pd1−Cl2, 88.37(7); N6−Pd1−Cl1, 92.15(5); N6−Pd1−Cl2, 90.64(6); C1−Pd1−N6, 178.96(9); Cl1−Pd1−Cl2, 176.98(3); N1−C1−Pd1, 127.85(19); N2−C1−Pd1, 126.55(19).

in the structure of *cis*-**6d**·DMF, bearing similar *N*-naphthylmethyl groups. The presence of a guest methanol seems to be crucial, and we were hoping that crystals of *cis*-**6d** obtained from methanol would display similar channel structure. Indeed, the structure of *cis*-**6d**·MeOH (*cis*-**6d′**) contains, in contrast to that in *cis*-**6a**·2MeOH, a honeycomb motif with hydrophobic channels parallel to the *c*-axis (see also Figure 11). The channels consist of phenyl and naphthyl rings of the ligands with the channel diameter of about 6.3 Å. The honeycomb motif derived from compounds containing amide functionality is known;[20] for example, an intriguing infinite rosette structure was derived from trimesic amide in methanol.[20a]

Relative Stability of Cis and Trans Isomers of 6. A DFT calculation was carried out to gain insight into the relative

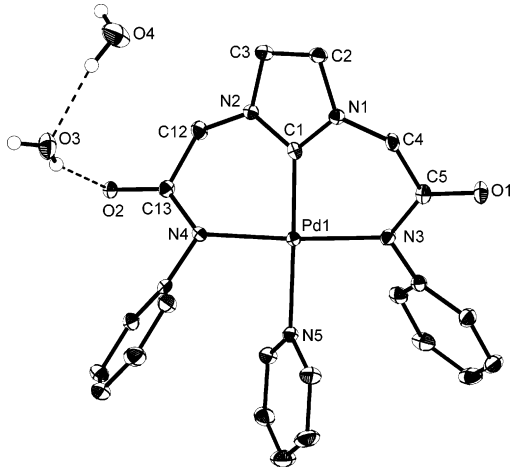


Figure 10. Thermal ellipsoid plot of **8**·2H_2O at the 35% probability level. Hydrogen atoms (except those on the guest water molecules) are omitted for clarity. Selected bond distances (Å): Selected bond distances: Pd1−C1, 1.924(3); Pd1−N3, 2.051(3); Pd1−N4, 2.053(3); Pd1−N5, 2.106(3). Selected bond angles: C1−Pd1−N3, 88.06(12); C1−Pd1−N4, 87.89(12); N3−Pd1−N5, 93.16(11); N4−Pd1−N5, 90.91(10); C1−Pd1−N5, 178.44(12); N3−Pd1−N4, 175.90(11); N1−C1−Pd1, 126.9(2); N2−C1−Pd1, 126.5(2).

stability of the cis and trans isomers of **6a**. The optimized geometrical parameters for *cis*-**6a** and *trans*-**6a** are in fine agreement with those from the structural data. For example, the computed Pd−carbene distances in *cis*-**6a** and *trans*-**6a** are 2.019 and 2.043 Å, respectively, which are comparable to those of 1.9662(15) and 2.020(4) Å from their structures. With the CPCM model, the energy of reaction for converting *cis*-**6a** to *trans*-**6a** is −5.8 kcal/mol, indicating that the latter isomer is thermodynamically more stable. A variable-temperature NMR study for *cis*-**6a** in DMF-d_7 was performed to see if *cis*-**6a** can be converted to the thermodynamic product. However, no reaction occurred even when the solution was heated to 95 °C, reflecting the kinetic stability of *cis*-**6a** below this temperature.

Catalytic Studies. The palladium(II) complexes were tested in Suzuki coupling reactions of aryl bromides with phenylboronic acid (Table 3). The data clearly show that the monodentate NHC complex **4** is most reactive (entries 1−6). The tridentate complex **8** gave intermediate activities (entries 11−13), whereas **6** is the least efficient (entries 7−10). In general, the activities of **4**, **6**, and **8** are inferior to other palladium(II) catalysts based on functionalized NHC ligands with neutral donors, such as phosphine-NHC ligands[6] and pyridine-NHC ligands.[4] In these catalysts with neutral NHC ligands, generation of vacant coordination sites via decoordination from the neutral donor atoms is believed to be important (i.e., the ligands are hemilabile). However, the anionic donor in an anionic functionalized NHC ligand, such as L^1 and L^2, provides an anchor effect on the metal ion, such that availability of vacant sites becomes impossible and the stable chelate rings of the complex are most probably leading to the poor catalytic activities observed, especially in the bis-bidentate complex **6**. Interestingly, for an electropositive metal ion with an anionic functionalized NHC ligand, dissociation of the NHC moiety becomes favorable (i.e., hard−soft mismatch), which has been observed, for example, in a uranium(IV) alkoxy-NHC complex.[21] However, it is unlikely that such NHC dissociation can occur in palladium(II) complexes **6** and **8**. Recently, structurally relevant complexes of the type NHC−$PdCl_2$−3-chloropyridine have been shown

(20) (a) Palmans, A. R. A.; Vekemans, J. A. J. M. Kooijman, H.; Spek, A. L.; Meijer, E. W. *Chem. Commun.* **1997**, 2247. (b) Muthu, S.; Yip, J. H. K.; Vittal, J. J. *J. Chem. Soc., Dalton Trans.* **2002**, 4561.

(21) Arnold, P. L.; Blake, A. J.; Wilson, C. *Chem.−Eur. J.* **2005**, *11*, 6095.

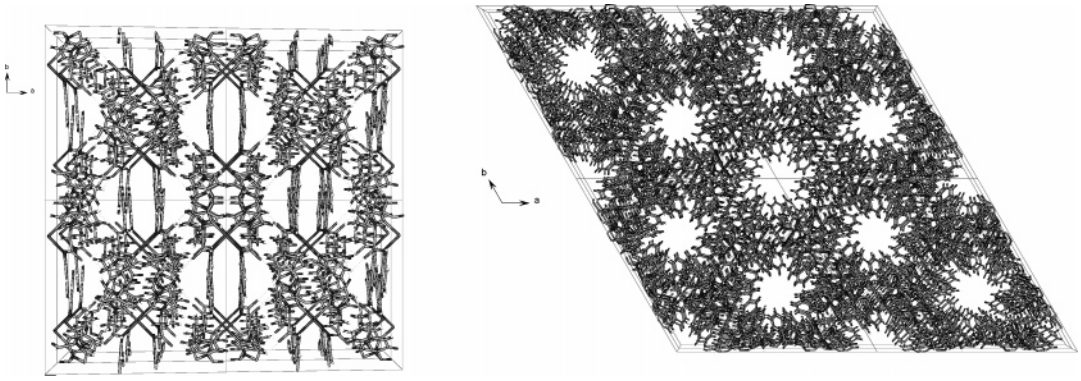


Figure 11. Left: open channels in *cis*-**6a**·2MeOH. Right: hydrophobic channels in *cis*-**6d**·MeOH.

Table 1. Crystallographic Data of 4−6

	4a	**4d**	*trans*-**6a**·4(C_2H_6OS)	*cis*-**6a**·2(CH_3OH)	*trans*-**6b**·2(CH_3OH)
empirical formula	$C_{23}H_{22}Cl_2N_4OPd$	$C_{27}H_{24}Cl_2N_4OPd$	$C_{36}H_{32}N_6O_2Pd$ ·4(C_2H_6OS)	$C_{36}H_{32}N_6O_2Pd$ ·2(CH_3OH)	$C_{36}H_{30}F_2N_6O_2Pd$ ·2(CH_3OH)
fw	547.77	597.80	999.59	751.16	787.14
cryst syst	orthorhombic	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_12_12_1$	$P2_1/c$	$P\bar{1}$	$C2/c$	$P2_1/c$
a, Å	5.1199(8)	16.5525(11)	9.4419(19)	16.6080(4)	10.9128(3)
b, Å	13.818(2)	16.4142(11)	11.375(3)	15.6949(4)	17.8089(5)
c, Å	32.194(5)	9.2128(6)	12.702(3)	14.2159(4)	9.3293(3)
α, deg	90	90	65.688(4)	90	90
β, deg	90	97.8550(10)	87.358(5)	100.240(2)	110.505(2)
γ, deg	90	90	69.092(5)	90	90
V, Å^3	2277.5(6)	2479.6(3)	1153.2(5)	3646.51(16)	1698.23(9)
D_c, mg m^{-3}	1.597	1.601	1.439	1.368	1.539
T, K	150(2)	150(2)	150(2)	150(2)	150(2)
Z	4	4	1	4	2
no. of unique data	5854	6397	5255	4676	4367
no. of params refined	284	364	281	248	234
R_1[a] [$I > 2\sigma I$]	0.0355	0.0354	0.0680	0.0264	0.0444
wR_2[b] (all data)	0.0606	0.0939	0.1788	0.0729	0.1340

[a] $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $wR_2 = [\sum(|F_o|^2 - |F_c|^2)^2/\sum(F_o^2)]^{1/2}$.

Table 2. Crystallographic Data of 6−8

	trans-**6c**·2($CHCl_3$)	*cis*-**6d**·0.5(C_3H_7NO)	*cis*-6d·CH_3OH (*cis*-6d′)	**7**·2(C_3H_7NO)	**8**·2(H_2O)
empirical formula	$C_{38}H_{36}N_6O_4Pd$ ·2($CHCl_3$)	$C_{44}H_{36}N_6O_2Pd$ ·0.5(C_3H_7NO)	$C_{44}H_{36}N_6O_2Pd$ ·CH_3OH	$C_{24}H_{23}Cl_2N_5O_2Pd$ ·2(C_3H_7NO)	$C_{24}H_{21}N_5O_2Pd$ ·2(H_2O)
fw	985.86	823.77	819.23	736.97	553.89
cryst syst	triclinic	monoclinic	hexagonal	monoclinic	monoclinic
space group	$P\bar{1}$	$C2/c$	$R\bar{3}$	$P2_1/n$	$P2_1/c$
a, Å	9.4368(3)	28.8517(14)	31.688(9)	9.0303(2)	8.3775(9)
b, Å	10.2941(3)	17.3518(8)	31.688(9)	23.7591(7)	29.923(3)
c, Å	13.0276(4)	19.8506(17)	22.273(7)	15.2864(4)	9.4386(10)
α, deg	70.192(2)	90	90	90	90
β, deg	75.905(2)	130.4840(10)	90	94.880(2)	94.538(2)
γ, deg	63.1950(10)	90	120	90	90
V, Å^3	1056.51(6)	7558.5(8)	19369(10)	3267.84(15)	2358.6(4)
D_c, mg m^{-3}	1.550	1.442	1.264	1.498	1.560
T, K	150(2)	150(2)	150(2)	150(2)	150(2)
Z	1	8	18	4	4
no. of unique data	4702	9732	8460	8047	5274
no. of params refined	260	557	541	401	323
R_1[a] [$I > 2\sigma I$]	0.0412	0.0327	0.0705	0.0351	0.0387
wR_2[b] (all data)	0.0957	0.0986	0.2141	0.0845	0.0843

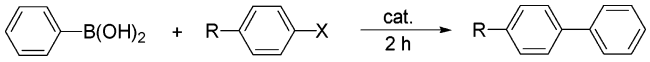
[a] $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $wR_2 = [\sum(|F_o|^2 - |F_c|^2)^2/\sum(F_o^2)]^{1/2}$.

to be highly effective in Suzuki and Negishi cross-coupling reactions.[14] The inferior catalytic activities of **4** compared with those of NHC−$PdCl_2$−3-chloropyridine can also be attributed to the formation of chelate complexes of the type **6**, under the basic catalytic condition.

Conclusions

In summary, we synthesized the imidazolium precursors $[L^1H^1H^2]Cl$ (**1**) and $[L^2H^1{}_2H^2]Cl$ (**3**) (H^1 = N*H*C═O, H^2 = NC*H*N) and successfully prepared the monodentate complexes $Pd(L^1H^1)(py)Cl_2$ (**4**) and $Pd(L^2H^1{}_2)(py)Cl_2$ (**7**), the bis-bidentate complex $PdL^1{}_2$ (**6**), and the pincer-type complex $PdL^2(py)$ (**8**) with appropriate ligand precursors under different basic conditions. Both the cis and trans isomers of **6** were formed in certain cases, and a DFT study indicates that the trans-$PdL^1{}_2$ (**6a**) is thermodynamically more stable than the cis isomer (ca. 5.8 kcal mol^{-1}). A systematic study of the new complexes in Suzuki coupling reactions afforded the following order of catalytic

Table 3. Suzuki Coupling with Aryl Bromides[a]



entry		X	R	yield (%)
1	**4a**	Br	COMe	100
2		Br	Me	73
3		Br	OMe	79
4	**4d**	Br	COMe	97
5		Br	Me	68
6		Br	OMe	56
7	*cis*-**6a**	Br	COMe	5
8	*trans*-**6a**	Br	COMe	4
9	*cis*-**6d**	Br	COMe	9
10	*trans*-**6b**	Br	COMe	3
11	**8**	Br	COMe	38
12		Br	Me	20
13		Br	OMe	17

[a] Reaction conditions: 1 mmol of aryl bromides, 1.5 mmol of $PhB(OH)_2$, 2.0 mmol of Cs_2CO_3 as base, 1 mol % of catalyst, 3 mL of 1,4-dioxane, 80 °C, GC yield.

activities: **4** > **8** > **6**. Our study reinforces the idea of incorporation of neutral donors, rather than anionic donors, in hemilabile functionalized NHC ligands for effective activities in palladium-catalyzed CC coupling reactions.

Experimental Section

General Procedures. All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. All solvents used were purified according to standard procedures.[22] Commercially available chemicals were purchased from Aldrich or Acros. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 300.13 and 75.48 MHz, respectively, on a Bruker AV-300 spectrometer. Chemical shifts for ^1H and ^{13}C spectra were recorded in ppm relative to the residual proton of $CDCl_3$ (^1H: 7.24 ppm; ^{13}C: 77.0 ppm) and DMSO-d_6 (^1H: 2.50 ppm; ^{13}C: 39.5 ppm). Elemental analyses and ES-MS mass spectra were performed on a Heraeus CHN-OS rapid elemental analyzer and a Finnigan/Thermo Quest MAT 95XL, respectively, at the Instruments Center of National Chung Hsing University, Taiwan. The syntheses of 1-benzyl-1*H*-imidazole, 1-(4-fluorobenzyl)-1*H*-imidazole, 1-(4-methoxybenzyl)-1*H*-imidazole, and 1-naphthalen-1-ylmethyl-1*H*-imidazole were according to the literature procedures.[17] 2-Chloroacetanilide and 2-imidazol-1-yl-*N*-phenylacetamide were prepared by following related literature procedures[23] (see Supporting Information for additional details).

Synthesis of 1a. A mixture of 1-benzyl-1*H*-imidazole (1.06 g, 6.70 mmol) and 2-chloroacetanilide (1.13 g, 6.70 mmol) in THF (30 mL) was heated at 70 °C for 2 days. After cooling, the white solid formed was filtered, washed with THF, and dried under vacuum. Yield: 1.70 g, 77%. Mp: 206−208 °C. Anal. Calcd for $C_{18}H_{18}N_3OCl$: C, 65.95; H, 5.53; N, 12.82. Found: C, 66.11; H, 5.49; N, 12.55. ^1H NMR (DMSO-d_6): δ 5.34 (s, 2H, CH_2C═O), 5.54 (s, 2H, PhCH_2), 7.07 (t, J_{HH} = 7.4 Hz, 1H, *p*-Ph-*H*), 7.32 (t, J_{HH} = 7.4 Hz, 2H, *m*-Ph-*H*), 7.40-7.44 (m, 5H, Ph-*H*), 7.66 (d, J_{HH} = 7.8 Hz, 2H, *o*-Ph-*H*), 7.84 (s, 1H, imi-*H*), 7.88 (s, 1H, imi-*H*), 9.46 (s, 1H, NC*H*N), 11.25 (s, 1H, N*H*). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 51.9 (*C*H_2), 52.3 (*C*H_2), 119.6 (*C*H), 122.3 (*C*H), 124.1 (*C*H), 124.8 (*C*H), 128.7 (*C*H), 129.1 (*C*H), 129.2 (*C*H), 129.4 (*C*H), 135.3 (CH$_2$*C*), 138.0 (*C*H), 138.9 (O═CN*C*), 164.1 (*C*═O).

Synthesis of 1b. The compound was synthesized following a procedure similar to that for **1a**. A mixture of 1-(4-fluorobenzyl)-1*H*-imidazole (6.02 g, 34.2 mmol) and 2-chloroacetanilide (5.79 g, 34.2 mmol) was used. Yield: 9.02 g, 76%. Mp: 185−190 °C. Anal. Calcd for $C_{18}H_{17}N_3FClO$: C, 62.52; H, 4.96; N, 12.15. Found: C, 62.30; H, 5.24; N, 12.15. ^1H NMR (DMSO-d_6): δ 5.30 (s, 2H, CH_2C═O), 5.51 (s, 2H, PhCH_2), 7.08 (t, J_{HH} = 7.2 Hz, 1H, *p*-Ph-*H*), 7.26-7.35 (m, 4H, Ar-*H* and *m*-Ph-*H*), 7.54 (t, J_{HH} = J_{HF} = 6.9 Hz, 2H, Ar-*H*), 7.64 (d, J_{HH} = 7.2 Hz, 2H, *o*-Ph-*H*), 7.82 (s, 1H, imi-*H*), 7.86 (s, 1H, imi-*H*), 9.38 (s, 1H, NC*H*N), 11.09 (s, 1H, N*H*). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 51.5 (*C*H_2), 51.9 (*C*H_2), 116.3 (d, J_{CF} = 21.6 Hz, *C*H), 119.6 (*C*H), 122.2 (*C*H), 124.1 (*C*H), 124.8 (*C*H), 129.2 (*C*H), 131.2 (*C*H), 131.6 (CH$_2$*C*), 138.0 (*C*H), 138.9 (O═CN*C*), 159.2 (d, J_{CF} = 102.3 Hz, *C*-F), 164.1 (*C*═O).

Synthesis of 1c. The compound was synthesized following a procedure similar to that for **1a**. A mixture of 1-(4-methoxybenzyl)-1*H*-imidazole (3.00 g, 15.90 mmol) and 2-chloroacetanilide (2.70 g, 15.90 mmol) was used. Yield: 3.75 g, 66%. Mp: 200−202 °C. Anal. Calcd for $C_{19}H_{20}N_3ClO_2$: C, 63.77; H, 5.63; N, 11.74. Found: C, 63.93; H, 5.48; N, 11.72. ^1H NMR (DMSO-d_6): δ 3.75 (s, 3H, OCH_3), 5.35 (s, 2H, CH_2C═O), 5.45 (s, 2H, PhCH_2), 6.98 (d, J_{HH} = 8.1 Hz, 2H, Ar-*H*), 7.07 (t, 1H, J_{HH} = 7.5 Hz, *p*-Ph-*H*), 7.31 (t, J_{HH} = 7.5 Hz, 2H, *m*-Ph-*H*), 7.45 (d, J_{HH} = 7.5 Hz, 2H, *o*-Ph-*H*), 7.67 (d, J_{HH} = 8.1 Hz, 2H, Ar-*H*), 7.83 (s, 1H, imi-*H*), 7.87 (s, 1H, imi-*H*), 9.45 (s, 1H, NC*H*N), 11.32 (s, 1H, N*H*). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 51.8 (*C*H_2), 55.6 (*C*H_2), 114.8 (*C*H), 119.6 (*C*H), 122.1 (*C*H), 124.7 (*C*H), 127.2 (CH$_2$*C*), 129.2 (*C*H), 130.6 (*C*H), 137.8 (*C*H), 139.0 (O═CN*C*), 156.0 (*C*-O), 164.2 (*C*═O).

Synthesis of 1d. The compound was synthesized following a procedure similar to that for **1a**. A mixture of 1-naphthalen-1-ylmethyl-1*H*-imidazole (4.60 g, 22.0 mmol) and 2-chloroacetanilide (3.70 g, 22.0 mmol) was used. Yield: 6.51 g, 78%. Mp: 218-220 °C. Anal. Calcd for $C_{22}H_{20}N_3ClO$: C, 69.93; H, 5.33; N, 11.12. Found: C, 69.29; H, 5.63; N, 10.94. ^1H NMR (DMSO-d_6): δ 5.31 (s, 2H, CH_2C═O), 6.05 (s, 2H, PhCH_2), 7.07 (t, J_{HH} = 7.5 Hz, 1H, *p*-Ph-*H*), 7.32 (t, J_{HH} = 7.5 Hz, 2H, *m*-Ph-*H*), 7.53-7.66 (m, 6H, Np-*H*), 7.85 (s, 1H, imi-*H*), 7.88 (s, 1H, imi-*H*), 8.03 (d, J_{HH} = 7.5 Hz, 2H, *o*-Ph-*H*), 8.19 (d, J_{HH} = 7.8 Hz, 1H, Np-*H*), 9.40 (s, 1H, NC*H*N), 11.17 (s, 1H, N*H*). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 50.3 (*C*H_2), 52.0 (*C*H_2), 119.6 (*C*H), 122.7 (*C*H), 123.5 (*C*H), 124.1 (*C*H), 124.7 (*C*H), 126.1 (*C*H), 126.8 (*C*H), 127.6 (*C*H), 127.9 (*C*H), 129.2 (*C*H), 130.0 (*C*H), 130.7 (quaternary *C*), 130.9 (quaternary *C*), 133.8 (CH$_2$*C*), 138.3 (*C*H), 139.0 (O═CN*C*), 164.2 (*C*═O).

Synthesis of 3. The compound was synthesized following a procedure similar to that for **1a**. A mixture of 2-imidazol-1-yl-*N*-phenylacetamide (0.57 g, 2.90 mmol) and 2-chloroacetanilide (0.49 g, 2.90 mmol) was used. Yield: 0.770 g, 73%. Mp: 188-190 °C. Anal. Calcd for $C_{19}H_{19}N_4O_2Cl$: C, 61.54; H, 5.16; N, 15.11. Found: C, 61.19; H, 5.24; N, 15.08. ^1H NMR (DMSO-d_6): δ 5.35 (s, 4H, CH_2C═O), 7.09 (t, J_{HH} = 7.5 Hz, 2H, *p*-Ph-*H*), 7.34 (t, J_{HH} = 7.5 Hz, 4H, *m*-Ph-*H*), 7.64 (d, J_{HH} = 7.5 Hz, 4H, *o*-Ph-*H*), 7.82 (s, 2H, imi-*H*), 9.25 (s, 1H, NC*H*N), 10.94 (s, 1H, N*H*). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 51.8 (*C*H_2), 119.7 (*C*H), 123.8 (*C*H), 124.2 (*C*H), 129.3 (*C*H), 138.9 (N*C*HN), 139.1 (O═CN*C*), 164.1 (*C*═O).

Synthesis of 4a. A mixture of **1a** (0.110 g, 0.350 mmol) and $PdCl_2$ (0.061 g, 0.350 mmol) in pyridine (15 mL) was heated at 100 °C overnight. After cooling, the solvent was removed completely under vacuum. The residue was extracted with dichloromethane (25 mL), and the solution was filtered through a plug of Celite. The solvent was completely removed under vacuum to give a crude product, which was then purified by subjecting it to a silica gel column and eluting with 1:1 ethyl acetate−hexane. The first band afforded pure **4a** as a pale yellow solid. Yield: 0.062 g, 32%. Mp: 210 °C. Anal. Calcd for $C_{23}H_{22}N_4OPdCl_2$: C, 50.43; H, 4.05; N, 10.23. Found: C, 50.04; H, 3.79; N, 10.54. ^1H NMR ($CDCl_3$): δ 5.49 (s, 2H, CH_2C═O), 5.85 (s, 2H, PhCH_2), 6.81 (d, J_{HH} = 2.1 Hz, 1H, imi-*H*), 7.05-7.10 (m, 2H, imi-*H* and Ph-*H*), 7.24 (t, J_{HH} = 8.1 Hz, 2H, Py-*H*), 7.32-7.41 (m, 5H, Ph-*H*), 7.48-7.50 (m, 2H, Ph-*H*), 7.65 (d, J_{HH} = 8.6 Hz, 2H, Ph-*H*), 7.78 (t, J_{HH}

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= 7.7 Hz, 1H, Py-*H*), 8.95 (m, 2H, *o*-Py-*H*), 9.04 (br s, 1H, N*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 54.8 (*C*H_2), 55.6 (*C*H_2), 119.9 (*C*H), 122.4 (*C*H), 122.9 (*C*H), 124.5 (*C*H), 124.6 (*C*H), 128.7 (*C*H), 128.9 (*C*H), 129.0 (*C*H), 134.6 (CH$_2$*C*), 137.6 (O═CN*C*), 138.3 (*C*H), 151.1 (overlapping *C*H and N*C*N), 164.5 (*C*═O). Crystals for structural determination were obtained by slow evaporation from a chloroform solution containing the compound.

Synthesis of 4d. The compound was prepared following a procedure similar to that for **4a**. A mixture of **1d** (0.140 g, 0.370 mmol) and $PdCl_2$ (0.065 g, 0.370 mmol) was used. The eluent used was ethyl acetate−hexane (4:6). Pure **4d** was obtained as a pale yellow solid. Yield: 0.061 g, 28%. Mp: 224 °C. Anal. Calcd for $C_{27}H_{24}N_4OPdCl_2$: C, 54.24; H, 4.05; N, 9.37. Found: C, 54.65; H, 4.49; N, 9.29. ^1H NMR ($CDCl_3$): δ 5.51 (s, 2H, CH_2C═O), 6.28 (s, 2H, PhCH_2), 6.57 (d, J_{HH} = 2.1 Hz, 1H, imi-*H*), 6.99 (d, J_{HH} = 2.1 Hz, 1H, imi-*H*), 7.07 (t, J_{HH} = 7.5 Hz, 1H, Ph-*H* or Np-*H*), 7.28 (t, J_{HH} = 7.5 Hz, 2H, Py-*H*), 7.36-7.41 (m, 2H, Ph-*H* or Np-*H*), 7.46-7.68 (m, 6H, Ph-*H* or Np-*H*), 7.80 (tt, J_{HH} = 7.5, 1.5 Hz, 1H, Py-*H*), 7.87-7.93 (m, 2H, Ph-*H* or Np-*H*), 8.21-8.24 (m, 1H, Ph-*H* or Np-*H*), 9.00 (m, 2H, *o*-Py-*H*), 9.04 (br s, 1H, N*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 53.2 (Ph*C*H$_2$), 55.9 (*C*H$_2$C═O), 119.9 (*C*H), 121.9 (*C*H), 122.7 (*C*H), 123.9 (*C*H), 124.6 (*C*H), 124.7 (*C*H), 125.3 (*C*H), 126.4 (*C*H), 127.4 (*C*H), 128.8 (*C*H), 129.1 (*C*H), 129.5 (quaternary *C*), 130.1 (*C*H), 131.5 (quaternary *C*), 133.9 (CH$_2$*C*), 137.7 (O═CN*C*), 138.4 (*C*H), 150.9 (N*C*N), 151.2 (*C*H), 164.6 (*C*═O). Crystals for structural determination were obtained by vapor diffusion of diethyl ether into a chloroform solution containing the compound.

Synthesis of *cis*-6a. A mixture of **1a** (0.110 g, 0.330 mmol), $PdCl_2$ (0.030 g, 0.170 mmol), and K_2CO_3 (0.090 g, 0.670 mmol) in pyridine (5 mL) was heated at 80 °C overnight. After cooling, the solvent was removed completely under vacuum. The residue was redissolved in dichloromethane (15 mL), and the organic layer was washed twice with water and dried with anhydrous $MgSO_4$. The volume of the solvent was reduced to ca. 3 mL under vacuum. Addition of diethyl ether gave a white solid, which was filtered, washed with diethyl ether, and dried under vacuum. Yield: 0.060 g, 53%. Mp: 280−282 °C. Anal. Calcd for $C_{36}H_{32}N_6O_2Pd$: C, 62.93; H, 4.69; N, 12.23. Found: C, 62.14; H, 4.44; N, 12.08. ^1H NMR (DMSO-d_6): δ 4.24 (d, $^2J_{HH}$ = 15.0 Hz, 2H, NCH_aH$_b$C═O), 4.37 (d, $^2J_{HH}$ = 15.0 Hz, 2H, NCH$_c$$H_d$Ph), 4.67 (d, $^2J_{HH}$ = 15.0 Hz, 2H, NCH$_a$$H_b$C═O), 5.22 (d, $^2J_{HH}$ = 15.0 Hz, 2H, NCH_cH$_d$-Ph), 6.53 (d, J_{HH} = 7.5 Hz, 4H, Ph-*H*), 6.63−6.76 (m, 6H, Ph-*H*), 7.08−7.10 (m, 4H, Ph-*H*), 7.42−7.44 (m, 6H, Ph-*H*), 7.59 (s, 2H, imi-*H*), 7.68 (s, 2H, imi-*H*). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 53.4 (Ph*C*H$_2$), 58.3 (*C*H$_2$C═O), 121.1 (*C*H), 122.8 (*C*H), 123.0 (*C*H), 126.0 (*C*H), 126.2 (*C*H), 127.6 (*C*H), 128.3 (*C*H), 129.3 (*C*H), 137.6 (CH$_2$*C*), 147.9 (O═CN*C*), 163.7 (N*C*N), 166.6 (*C*═O). Crystals were obtained by vapor diffusion of diethyl ether into a methanol solution containing the compound.

Synthesis of *trans*-6a. A mixture of **1a** (0.110 g, 0.330 mmol), $PdCl_2$ (0.0300 g, 0.170 mmol), and K_2CO_3 (0.090 g, 0.670 mmol) in DMF (10 mL) was heated at 65 °C overnight. After cooling, the solvent was removed completely under vacuum. The residue was redissolved in dichloromethane (15 mL), and the organic layer was washed twice with water and dried with anhydrous $MgSO_4$. After removal of the solvent under vacuum, the white solid remaining was a mixture of *cis*-**6a** and *trans*-**6a** (ratio = 62:38) according to ^1H NMR spectroscopy. Pure *trans*-**6a** can be obtained by washing the off-white solid with methanol. A white solid was obtained. Yield: 0.029 g, 25%. Mp: 301−304 °C. Anal. Calcd for $C_{36}H_{32}N_6O_2Pd$: C, 62.96; H, 4.70; N, 12.24. Found: C, 62.69; H, 4.59; N, 11.95. ^1H NMR (DMSO-d_6): δ 4.35 (d, $^2J_{HH}$ = 14.7 Hz, 2H, NCH_aH$_b$C═O), 4.87 (d, $^2J_{HH}$ = 4.5 Hz, 2H, NCH_cH$_d$Ph), 4.93 (d, $^2J_{HH}$ = 4.5 Hz, 2H, NCH$_c$$H_d$Ph), 5.21 (d, $^2J_{HH}$ = 14.7 Hz, 2H, NCH$_a$$H_b$C═O), 6.73 (t, J_{HH} = 7.1 Hz, 2H, Ph-*H*), 6.95 (t, J_{HH} = 7.1 Hz, 4H, Ph-*H*), 7.01 (d, J_{HH} = 1.8 Hz, 2H, imi-*H*), 7.30 (d, J_{HH} = 1.8 Hz, 2H, imi-*H*), 7.35-7.45 (m, 10H, Ph-*H*), 7.51 (d, J_{HH} = 7.8 Hz, 4H, Ph-*H*). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 52.1 (Ar*C*H$_2$), 58.0 (*C*H$_2$C═O), 121.4 (*C*H), 121.7 (*C*H), 122.2 (*C*H), 125.4 (*C*H), 127.0 (*C*H), 127.8 (*C*H), 128.2 (*C*H), 129.2 (*C*H), 138.6 (CH$_2$*C*), 150.9 (O═CN*C*), 169.3 (*C*═O), 170.5 (N*C*N). Crystals for structural determination were obtained by slow evaporation from a DMSO solution containing the compound.

Synthesis of *trans*-6b. The compound was prepared following a similar procedure of *trans*-**6a**. A mixture of **1b** (0.200 g, 0.580 mmol), $PdCl_2$ (0.0540 g, 0.300 mmol), and K_2CO_3 (0.170 g, 1.21 mmol) was used. A minor modification is that the reaction had to be conducted at a lower temperature of 55 °C. Heating the mixture at 65 °C as stated for *trans*-**6a** resulted in decomposition products as evidenced by the formation Pd black. Following the same workup procedure for *trans*-**6a**, the crude product obtained was a mixture of cis and trans isomers in a ratio of 43:57. Pure *trans*-**6b** as a white solid can be obtained by washing the crude solid with methanol. Yield: 0.032 g, 15%. Mp: 283−285 °C. Anal. Calcd for $C_{36}H_{30}N_6O_2F_2Pd\cdot 2CH_3OH$: C, 57.98; H, 4.87; N, 10.68. Found: C, 57.36; H, 4.21; N, 10.45. ^1H NMR (DMSO-d_6): δ 4.38 (d, $^2J_{HH}$ = 14.6 Hz, 2H, NCH_aH$_b$C═O), 4.90 (d, $^2J_{HH}$ = 14.6 Hz, 2H, NCH_cH$_d$Ph), 5.00 (d, $^2J_{HH}$ = 14.6 Hz, 2H, NCH$_a$$H_b$C═O), 5.20 (d, $^2J_{HH}$ = 14.6 Hz, 2H, NCH$_c$$H_d$Ph), 6.74 (t, J_{HH} = 7.2 Hz, 2H, Ph-*H*), 6.95 (t, J_{HH} = 7.2 Hz, 4H, Ph-*H*), 7.10 (s, 2H, imi-*H*), 7.24-7.29 (m, 4H, Ph-*H*), 7.32 (s, 2H, imi-*H*), 7.37-7.42 (m, 4H, Ph-*H*), 7.50 (d, J_{HH} = 8.1 Hz, 4H, Ph-*H*). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 51.3 (Ar*C*H$_2$), 58.0 (*C*H$_2$C═O), 116.0 (d, J_{CF} = 21.6 Hz, *C*H), 121.6 (*C*H), 122.2 (*C*H), 125.4 (*C*H), 127.0 (*C*H), 130.0 (*C*H), 130.1 (*C*H), 134.8 (CH$_2$*C*), 150.8 (O═CN*C*), 163.8 (d, J_{CF} = 244.1 Hz, *C*-F), 169.3 (*C*═O), 170.4 (N*C*N). Crystals for structural determination were obtained by vapor diffusion of pentane into a methanol solution containing the compound.

Synthesis of *trans*-6c. The compound was prepared following a procedure similar to that for *trans*-**6a**. A mixture of **1c** (0.170 g, 0.470 mmol), $PdCl_2$ (0.0420 g, 0.230 mmol), and K_2CO_3 (0.130 g, 0.940 mmol) was used. A minor modification is the reaction temperature of 60 °C. Heating the mixture at 65 °C as stated for *trans*-**6a** resulted in decomposition products as evidenced by the formation Pd black. Following the same workup procedure for *trans*-**6a**, the crude product obtained was a mixture of cis and trans isomers in a ratio of 37:63. Pure *trans*-**6c** as a white solid can be obtained by washing the crude solid with methanol. Yield: 0.026 g, 16%. Mp: 320−323 °C. Anal. Calcd for $C_{38}H_{36}N_6O_4Pd$: C, 61.09; H, 4.86; N, 11.25. Found: C, 61.15; H, 4.90; N, 11.29. ^1H NMR (DMSO-d_6): δ 3.79 (s, 6H, CH_3), 4.38 (d, $^2J_{HH}$ = 14.4 Hz, 2H, NCH_aH$_b$C═O), 4.80 (d, $^2J_{HH}$ = 14.4 Hz, 2H, NCH_cH$_d$Ph), 5.04 (d, $^2J_{HH}$ = 14.4 Hz, 2H, NCH$_a$$H_b$C═O), 5.16 (d, $^2J_{HH}$ = 14.4 Hz, 2H, NCH$_c$$H_d$Ph), 6.73 (t, J_{HH} = 7.2 Hz, 2H, Ph-*H*), 6.92-6.99 (m, 10H, Ph-*H*), 7.06 (d, J_{HH} = 1.7 Hz, 2H, imi-*H*), 7.29 (d, J_{HH} = 1.7 Hz, 2H, imi-*H*), 7.33 (d, J_{HH} = 8.4 Hz, 4H, Ph-*H*), 7.52 (d, J_{HH} = 7.8 Hz, 4H, Ph-*H*). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 51.6 (Ar*C*H$_2$), 55.6 (*C*H$_3$), 58.1 (*C*H$_2$C═O), 114.5 (*C*H), 121.3 (*C*H), 121.4 (*C*H), 122.2 (*C*H), 125.5 (*C*H), 126.9 (*C*H), 129.4 (*C*H), 130.6 (CH$_2$*C*), 150.9 (O═CN*C*), 159.4 (*C*OMe), 169.3 (*C*═O), 170.3 (N*C*N). Crystals for structural determination were obtained by vapor diffusion of diethyl ether into a chloroform solution containing the compound.

Synthesis of *cis*-6d. The compound was prepared with a procedure similar to that for *cis*-**6a**. A mixture of **1a** (0.11 g, 0.290 mmol), $PdCl_2$ (0.0260 g, 0.140 mmol), and K_2CO_3 (0.0800 g, 0.580 mmol) was used. A white solid was obtained. Yield: 0.054 g, 47%. Mp: 278−280 °C. Anal. Calcd for $C_{44}H_{36}N_6O_2Pd\cdot 0.5H_2O$: C, 66.37; H, 4.68; N, 10.55. Found: C, 66.21; H, 4.60; N, 10.35. ^1H NMR ($CDCl_3$): δ 3.95 (d, $^2J_{HH}$ = 14.4 Hz, 2H, NCH_aH$_b$C═O), 4.38 (d, $^2J_{HH}$ = 14.4 Hz, 2H, NCH$_a$$H_b$C═O), 5.15 and 5.32 (AB doublets, $^2J_{HH}$ = 15.3 Hz, 4H, NCH_cH$_d$Ph), 6.73-6.89 (m, 14H, Ph-*H*, Np-*H*, imi-*H*), 7.08 (d, J_{HH} = 6.9 Hz, 2H, Np-*H*), 7.43-7.70

(m, 6H, Ph-*H* or Np-*H*), 7.68 (d, J_{HH} = 8.4 Hz, 2H, Np-*H*), 7.93 (t, J_{HH} = 6.6 Hz, 4H, Ph-*H* or Np-*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 51.5 (Ph*C*H_2), 58.5 (*C*H_2C═O), 121.0 (*C*H), 121.6 (*C*H), 122.1 (*C*H), 122.4 (*C*H), 125.4 (*C*H), 125.6 (*C*H), 125.8 (*C*H), 125.9 (*C*H), 126.6 (*C*H), 127.4 (*C*H), 129.3 (*C*H), 129.4 (*C*H), 130.1 (quaternary *C*), 130.7 (quaternary *C*), 133.7 (CH$_2$*C*), 146.6 (O═CN*C*), 165.5 (N*C*N), 166.5 (*C*═O). Crystals for structural determination were obtained by vapor diffusion of diethyl ether into a DMF or methanol solution containing the compound.

Synthesis of 7. The compound was prepared according to a procedure similar to that for **4a**. A mixture of **3** (0.32 g, 0.87mmol) and $PdCl_2$ (0.150 g, 0.870 mmol) was used. The ^1H NMR spectra showed a mixture of **7** and **5**, which was not separable following the procedure for **4a**. Crystals of **7** for structural determination were obtained by vapor diffusion of diethyl ether into a DMF solution of the mixture.

Synthesis of 8. A mixture of **3** (0.110 g, 0.310 mmol), $PdCl_2$ (0.055 g, 0.310 mmol), and K_2CO_3 (0.210 g, 1.50 mmol) in pyridine (5 mL) was heated at 80 °C overnight. After cooling, the solution was filtered through a plug of Celite. The solvent was removed completely under vacuum. The residue was redissolved in dichloromethane (ca. 3 mL). Upon addition of diethyl ether, pure **8** as a pale yellow solid was formed. Yield: 0.13 g, 77%. Mp: 344−346 °C. Anal. Calcd for $C_{24}H_{21}N_5O_2Pd$: C, 55.66; H, 4.09; N, 13.52. Found: C, 55.69; H, 4.08; N, 13.42. ^1H NMR ($CDCl_3$): δ 4.89 (s, 4H, C*H*$_2$), 6.60−6.83 (m, 12H, Ph-*H*, py-*H*), 7.00 (s, 2H, imi-*H*), 7.22 (t, J_{HH} = 7.8 Hz, 1H, py-*H*), 7.77 (d, J_{HH} = 4.8 Hz, 2H, py-*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 55.5 (*C*H$_2$), 120.8 (*C*H), 123.6 (*C*H), 127.0 (*C*H), 127.9 (*C*H), 136.4 (*C*H), 148.7 (O═CN*C*), 149.8 (*C*H), 152.7 (N*C*N), 167.2 (*C*═O). Crystals for structural determination were obtained by vapor diffusion of pentane into a pyridine solution containing the compound.

X-ray Data Collection. Typically, the crystals were removed from the vial with a small amount of mother liquor and immediately coated with silicon grease on a weighing paper. A suitable crystal was mounted on a glass fiber with silicone grease and placed in the cold stream of a Bruker APEX II with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 150(2) K. Crystallographic data are listed in Tables 1 and 2.

Solution and Structure Refinements. All structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares methods against F^2 with SHELXL-97.[24] Tables of neutral atom scattering factors, f' and f'', and absorption coefficients are from a standard source.[25] 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 (see Supporting Information for specific hydrogen atoms located from the difference maps). The structures for **4d**, *cis*-**6a**, *cis*-**6d**, and *cis*-**6d′** are disordered. The details for their disorder models were given in the Supporting Information. Structural discussion in the text is, generally, referred to the major orientation. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 625296 (**4a**), 625297 (**4d**), 625298 (**7**), 625299 (**8**), 625300 (*cis*-**6a**), 625301 (*cis*-**6d′**), 625302 (*cis*-**6d**), 625303 (*trans*-**6a**), 625304 (*trans*-**6b**), and 625305 (*trans*-**6c**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44-(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

Computational Details. We used the three-parameter hybrid of exact exchange and Becke's exchange energy functional,[26] plus Lee, Yang, and Parr's gradient-corrected correlation energy functional[27] (B3LYP). We used the 6-31G basis sets for H, C, N, and O. For Pd we used the LANL2DZ effective core potential plus basis functions.[28] The Gaussian03 suite of programs were used in our study.[29]

Suzuki Coupling Reactions. In a typical reaction, a mixture of aryl bromides (1.0 mmol), phenylboronic acid (1.5 mmol), Cs_2CO_3 (2.0 mmol), and palladium(II) precatalyst (1 mol %) in 3 mL of 1,4-dioxane was stirred at 80 °C for 2 h under nitrogen. The solution was allowed to cool to ambient temperature for GC analysis. GC yields were calculated using benzophenone (with 4-acetylbiphenyl and 4-phenyltoluene as products) or biphenyl (with 4-phenylanisole as product) as internal standards.

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Supporting Information Available: Full crystallographic data for all the structures are provided as a CIF file. Additional experimental details. A HMBC spectrum of *cis*-**6a**. A thermal ellipsoid plot of *cis*-**6d′**. This material is available free of charge via the Internet at http://pubs.acs.org.

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