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Zwitterionic Palladium Complexes: Room-Temperature Suzuki–Miyaura Cross-Coupling of Sterically Hindered Substrates in an Aqueous Medium

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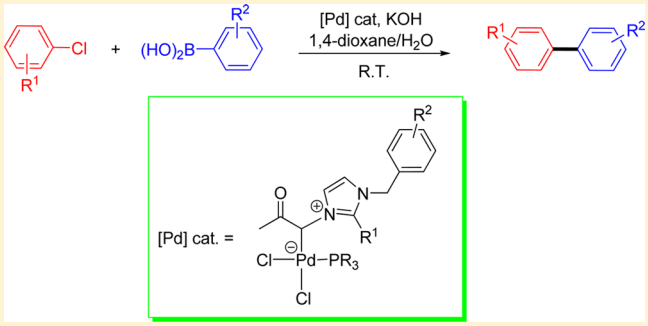
Supporting Information

ABSTRACT: A series of new imidazolium chlorides were straightforwardly prepared from the reactions between chloroacetone and imidazole derivatives. Deprotonation of the methylene proton next to the ketone group in these salts by pyridine led to the formation of a monodentate ligand that coordinated to palladium, readily forming zwitterionic anionic palladium pyridine complexes bearing a formal positive charge on the ligand ancillary. The pyridine ligand in the zwitterionic complexes can be facilely replaced by phosphine ligands. Seven of these new complexes were successfully characterized by X-ray crystallography. The zwitterionic phosphine complexes were highly efficient in catalyzing room-temperature Suzuki–Miyaura reactions between sterically hindered aryl chlorides and arylboronic acids in an aqueous medium.



INTRODUCTION

Zwitterionic metal complexes that exhibit formal charge separation within an overall neutral molecular framework are currently attracting interest.[1,2] Over the past few years, a wide scope of zwitterionic cationic metal complexes, in particular those of the platinum-group metals (PGM),[1] have been reported and some of them exhibited promising catalytic properties.[3−8] In contrast, zwitterionic complexes with reverse polarity, that is complexes with formal negative charges on the metal centers and positive charges on the ancillary ligands,[2] are less common and well-documented examples were mostly derived from phosphonium ylides or conjugated equivalents.[9,10]. Zwitterionic metalate derived from ammonium,[11−13] iminium,[14,15] and sulfonium[16] ancillaries are also known. Recently, we have reported a unique class of zwitterionic anionic palladium complexes derived from imidazole derivatives (Chart 1).[17,18] These complexes, including palladalactams and CC-type palladacycles, can be classified as "mesoionic" or "truly zwitterionic", since no nonzwitterionic connected Lewis structure can be drawn by resonance of the π electrons.[2] They were essentially formed by deprotonation of the methylene protons between the imidazole ring and the C═O group of the ligands. Since in those complexes the ligand also contained PhNC═O functionalities, the formation of chelate rings due to C−H or N−H activation occurred as well. To further our exploration on the chemical properties of this type of complexes, we hoped to understand if the amido functionality was mandatory or if it could be replaced by other functional groups, thus avoiding the formation of chelate rings. Herein we found that a simple ketone group could be employed and indeed monodentate zwitterionic anionic palladium complexes could be achieved readily. Since the metal centers of the new complexes may have significant negative charge, which is a crucial factor for activation of carbon−halide bonds in C−C coupling reactions, we envisioned the possibility of utilizing the new complexes in Suzuki−Miyaura cross-coupling of aryl chlorides. Although catalyst systems have been developed for the use of readily available and low cost aryl chlorides in the cross-coupling reactions,[19−22] the use of sterically hindered substrates at room temperature remains one of the challenges in this field.[23] To our delight, a new complex reported herein could be employed as a precatalyst to address this problem in an aqueous medium.

RESULTS AND DISCUSSION

Design and Synthesis of Ligand Precursors. Scheme 1 shows the target imidazolium salts **1a−f**, which are the ligand precursors for the preparation of zwitterionic palladium complexes. Since an unsubstituted imidazolium salt at the C2 position of the imidazole ring contains an acidic NC*H*N proton which can be deprotonated easily to form NHC complexes,[19,24−33] we chose to block the C2 position with methyl (**1a−c**) and aryl groups (**1d−f**). In addition, in order to understand the electronic effect of the ligands on the palladium centers which could be important to their subsequent catalytic

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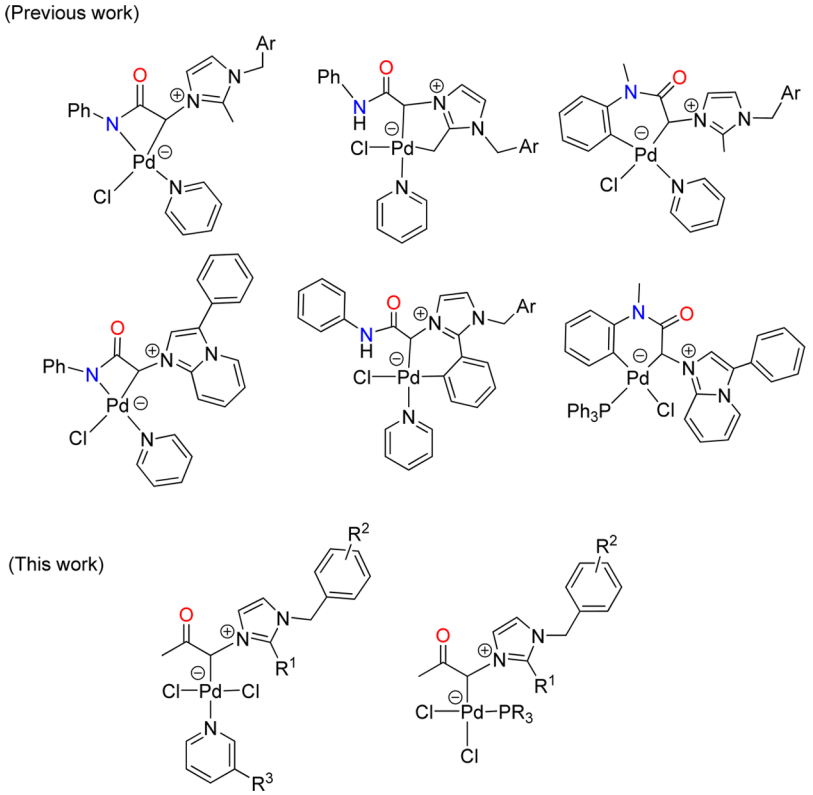
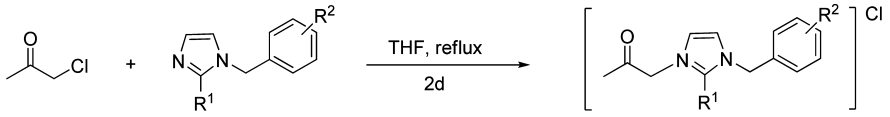
Chart 1. Zwitterionic Anionic Palladium Complexes Derived from Imidazole Derivatives



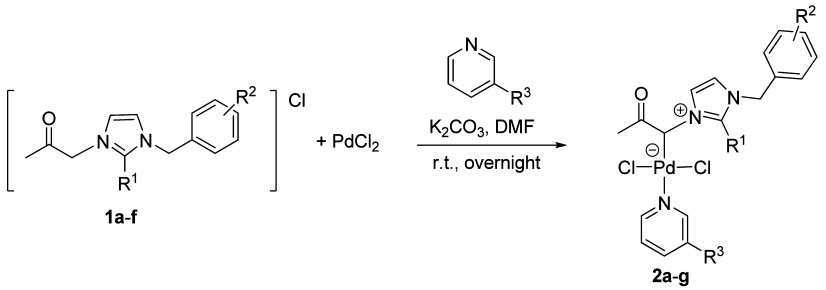
Scheme 1. Synthesis of Ligand Precursors 1a−f



1a-f

R_1= CH_3: R_2 = H (**1a**), 3-OCH_3 (**1b**), 4-F (**1c**);
R_1= Ph: R_2 = H (**1d**), 3-OCH_3(**1e**), 4-F (**1f**)

Scheme 2. Synthesis of Zwitterionic Palladium Complexes 2a−g



1a-f

2a-g

R^1= CH_3, R^3 = H: R^2 = H (**2a**), 3-OCH_3 (**2b**), 4-F (**2c**);
R^1= Ph, R^3 = H: R^2 = H (**2d**), 3-OCH_3 (**2e**), 4-F (**2f**);
R^1= Ph, R^3 = Cl: R^2 = 3-OCH_3 (**2g**)

performance, the two sets of ligand precursors consist of electron-neutral benzyl, electron-withdrawing 4-fluorobenzyl, and electron-donating 3-methoxybenzyl groups on the imidazolium rings. These salts were straightforwardly prepared by quaternization reactions between chloroacetone and the appropriate imidazole derivatives in THF. They precipitated out as white solids with 56−92% yields. Most of these salts are hygroscopic. In general, the methyl and methylene proton signals in **1a−c** resonate at slightly lower field than those in **1d−f**. For **1a−c**, the proton signals for the ketone methyl groups were observed at ca. 2.25 ppm, whereas those in **1d−f** appeared at ca. 2.14 ppm. The methyl protons on the imidazolium rings in **1a−c** were observed at ca. 2.51 ppm. For **1a−c**, the methylene group next to the ketone group resonates at ca. 5.84 ppm, whereas that attached to the aryl ring was observed at a higher field at ca. 5.37 ppm. For **1d−f**, these

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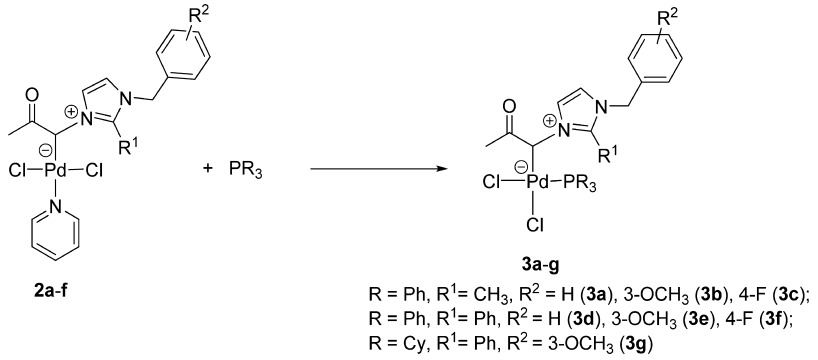
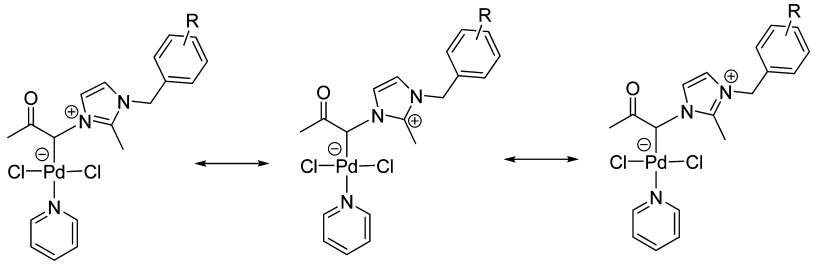
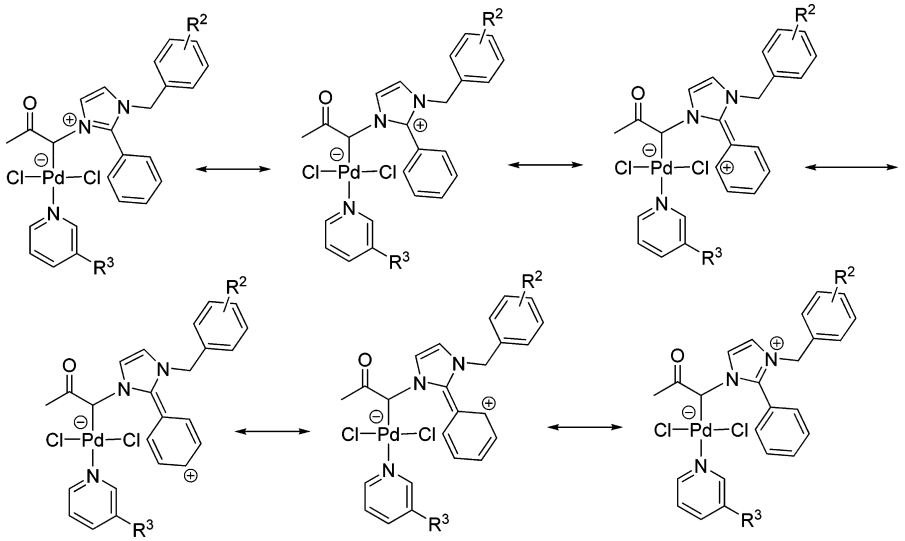
Scheme 3. Synthesis of Zwitterionic Palladium Complexes 3a−g



Scheme 4. Resonance Structures in 2a−c



Scheme 5. Resonance Structures in 2d−f



two sets of signals appeared at more upfield positions of ca. 5.46 and 5.25 ppm, respectively. The assignment of these signals was confirmed by the acquisition of an representative HMBC spectrum of **1a** (see the Supporting Information).

Synthesis of Zwitterionic Palladium Complexes. Since palladium NHC complexes with 3-chloropyridine as ligand, the so-called PEPPSI-type complexes, have been proven to be versatile in various cross-coupling reactions,[34−38] we targeted the preparation of new zwitterionic palladium complexes mimicking the PEPPSI skeleton. The new zwitterionic palladium complexes **2a−g** were successfully prepared by the complexation reactions among the ligand precursors, pyridine and 3-chloropyridine, and $PdCl_2$ using K_2CO_3 as base in DMF at ambient temperature (Scheme 2). The complexation conditions afforded the new complexes in decent to good yields (56−90%). Desirably, these new complexes have high stability in air and on dissolution. The ^1H and ^{13}C NMR spectra of all the complexes display characteristic signals for the pyridine ligands. For **2a−c**, the successful complexation was confirmed by the presence of methine protons at ca. 6.20 ppm, which were downfield from the original methylene signals at ca. 5.84 ppm in the ligand precursors. For **2d−f**, the methine signals appeared at ca. 5.89 ppm, which were also slightly downfield in comparison to the corresponding protons in the ligand precursors (ca. 5.46 ppm). We also prepared **2g**, in which the pyridine ligand in **2e** was replaced by 3-chloropyridine. The NMR data of this pair were very similar.

Since a phosphine ligand can enhance the electron density on the metal centers, allowing the activation of unreactive bonds via oxidative addition,[27,39] we also interested in replacing the pyridine ligands in **2a−f** with PPh_3 or PCy_3. The substitution reactions were successfully carried out by stirring a dichloro-

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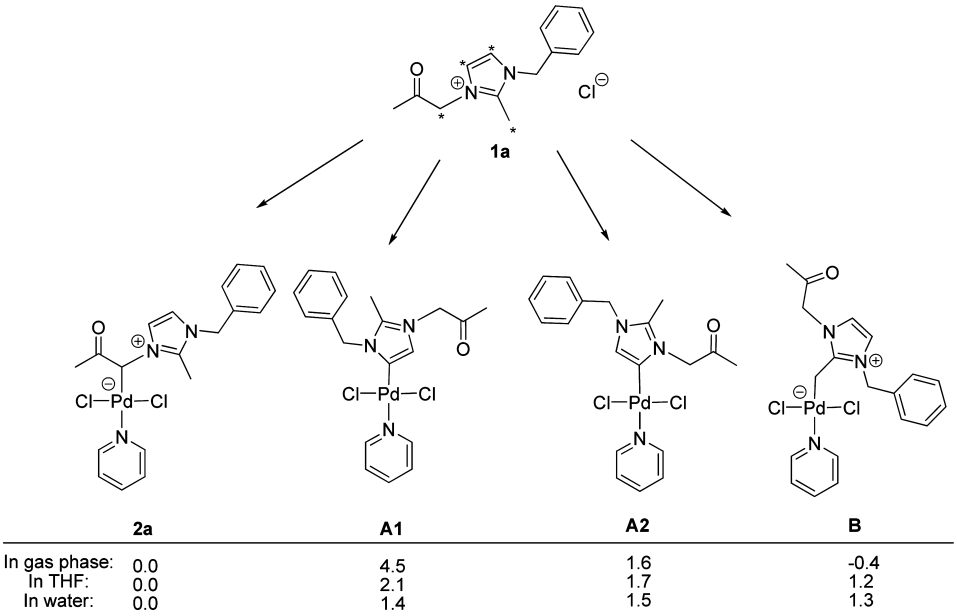
Scheme 6. Potential Palladium Complexes Formed from the Ligand Precursor 1a[a]



[a]Potential deprotonation sites are marked with asterisks. The relative free energies of complexes are listed (in units of kcal/mol).

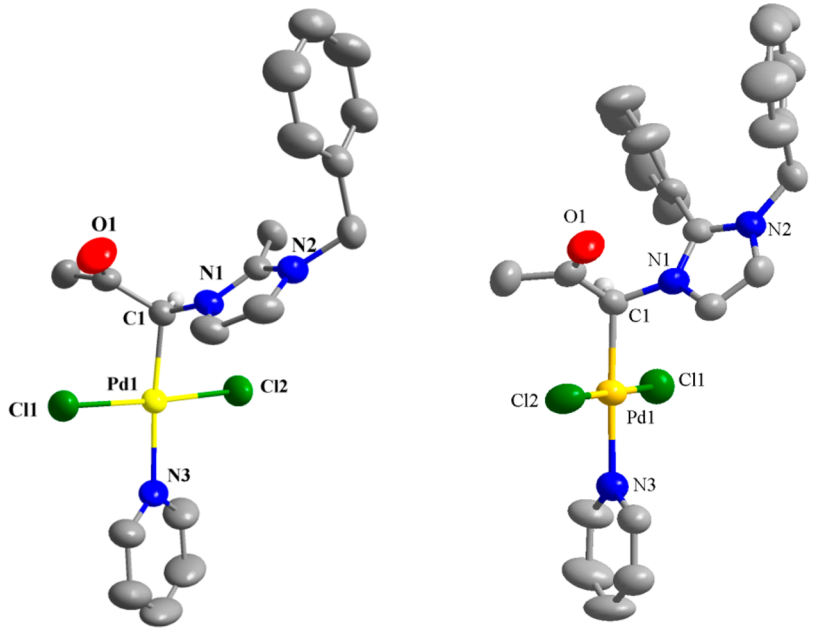


Figure 1. Molecular structures of **2a** (left) and **2d** (right) with 50% probability ellipsoids for non-H atoms. H atoms, except for that on C1, are omitted for clarity.

methane solution containing the respective compound and free phosphine at room temperature. The new complexes **3a–f** were also stable in air (Scheme 3). However, as indicated by ^{1}H NMR spectroscopy, decomposition commenced when solutions containing the compounds were exposed to air. For **3a–c**, the ^{31}P NMR signals were observed at ca. 32.3 ppm and those signals in **3d–c** were slightly more upfield at ca. 30.6 ppm. The NMR signals for the methine carbons appeared as singlets in **3a–f**, reflecting the cis geometry of these complexes. The methine proton signals in the phosphine complexes were observed at positions much more upfield, in contrast with those in the pyridine complexes **2a–f** (~4.15 ppm in **3a–c** vs ~6.20 ppm in **2a–c**; ~4.07 ppm in **3d–f** vs ~5.89 ppm in **2d–f**). The phosphine and the methine signals for the PCy_3 complex **3g** were observed at 39.3 and 4.48 ppm, respectively, which were downfield from those of the PPh_3 analogue **3e** at 30.6 and 4.06 ppm. The small $^{2}J_{CP}$ coupling constant of 25.6 Hz for the doublet signal of the coordinated methine carbon also implies a cis geometry of ligands in **3g**.

The fact that the NMR signals in palladium complexes derived from **1d–f** were generally upfield in comparison with those derived from **1a–c** is attributable to the greater delocalization of the positive charge in the latter set of complexes, resulting in less reduced electron density on the complexes (see Schemes 4 and 5).

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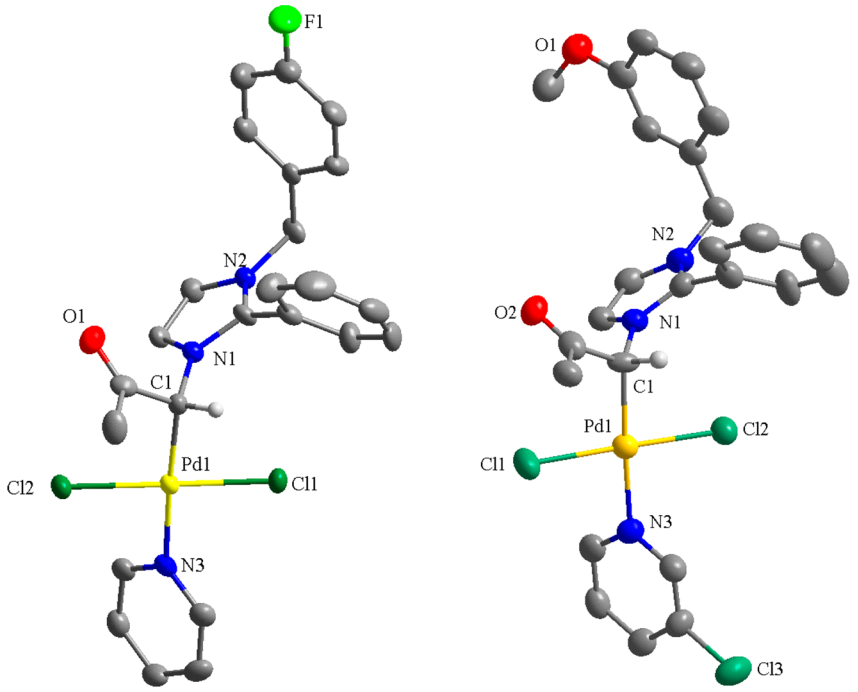

Figure 2. Molecular structures of **2f** (left) and **2g** (right) with 50% probability ellipsoids for non-H atoms. H atoms, except for that on C1, are omitted for clarity.

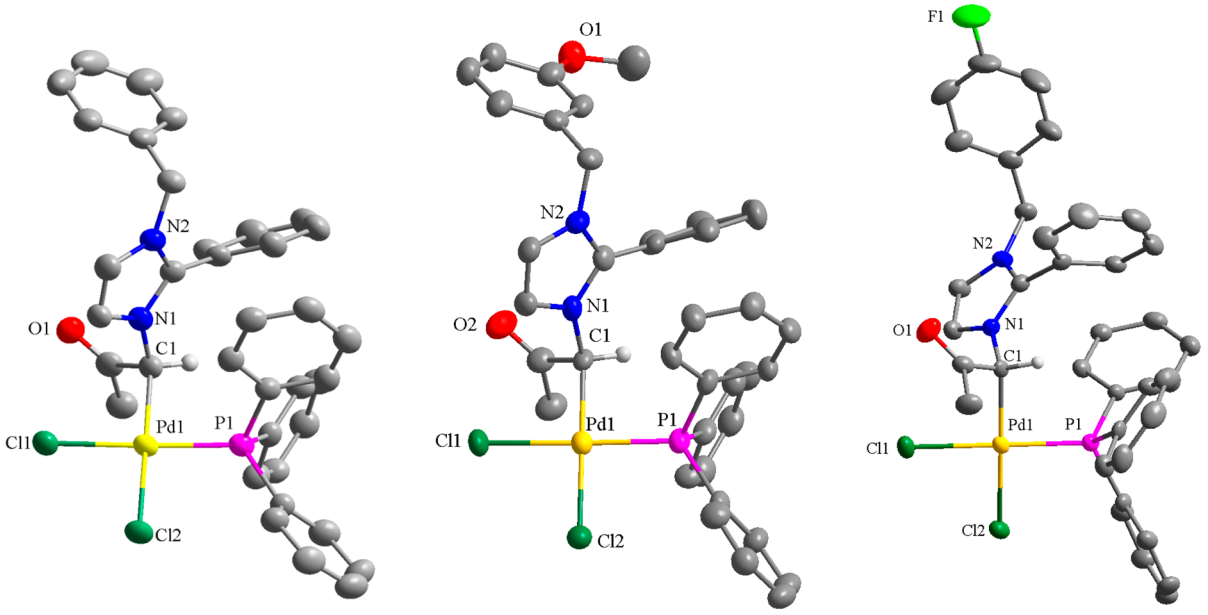

Figure 3. Molecular structures of **3d** (left), **3e** (middle), and **3f** (right) with 50% probability ellipsoids for non-H atoms. Hydrogen atoms, except for that on C1, are omitted for clarity.

It should be noted that there are other protons in the ligand precursor **1a** which could undergo deprotonation. Complexes **A1** and **A2** are abnormal NHC complexes formed from the deprotonation of the CH protons on the heterocyclic ring (Scheme 6). Relevant palladium abnormal carbene complexes have reported by others and us.[40−43] Complex **B** is a palladium complex formed by the deprotonation of the methyl group on the ligand precursor. Such kinds of complexes are also known in the literature.[44] Since the methylene proton in **1a** is the most acidic proton, it is obvious that **2a** should be formed easily. In fact, in the preparation of **2a**, the zwittterion and the side product *trans*-$PdCl_2(py)_2$ were formed exclusively even after prolonged heating at 80 °C overnight, indicating that **2a** is either kinetically stable or is indeed the thermodynamic product. To address this issue, a DFT calculation was performed to understand the relative stabilities of the different types of complexes. Our data shows that, in the gas phase, **B** is slightly lower in energy than **2a**, while in THF and in water **2a** is indeed the thermodynamically most stable species.

Molecular Structures. The pyridine complexes **2a,d,f,g** and the phosphine complexes **3d−f** have been established by X-ray diffraction studies (Figures 1−3). Selected bond distances and angles are given in Tables 1 and 2. The crystallographic studies confirmed the trans and cis geometries of the pyridine

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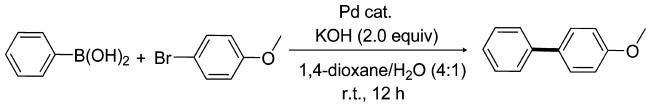
Table 1. Selected Bond Distances (Å) and Angles (deg) around Pd in 2

	2a	2d	2f	2g
Pd1−C1	2.051(3)	2.038(4)	2.040(5)	2.049(5)
Pd1−N3	2.165(3)	2.108(4)	2.114(4)	2.095(4)
Pd1−Cl1	2.3034(11)	2.3082(12)	2.3167(14)	2.3055(17)
Pd1−Cl2	2.3145(11)	2.2968(12)	2.3120(14)	2.3305(16)
C1−Pd1−Cl1	90.85(10)	87.74(12)	86.83(15)	93.94(17)
C1−Pd1−Cl2	86.08(10)	92.15(12)	92.44(15)	88.46(17)
N3−Pd−Cl1	91.65(9)	90.45(10)	90.24(12)	89.66(14)
N3−Pd−Cl2	91.45(9)	89.67(10)	90.49(12)	88.93(14)
C1−Pd−N3	174.47(13)	177.83(14)	176.48(17)	176.2(2)
Cl1−Pd−Cl2	176.90(4)	179.35(4)	179.22(5)	178.58(6)

Table 2. Selected Bond Distances (Å) and Angles (deg) around Pd in 3

	3d	3e	3f
Pd1−C1	2.094(6)	2.103(5)	2.097(5)
Pd1−P1	2.2370(16)	2.2359(16)	2.2515(13)
Pd1−Cl1	2.3531(16)	2.3687(15)	2.3869(13)
Pd1−Cl2	2.3480(14)	2.3476(17)	2.3530(13)
C1−Pd1−Cl1	89.60(16)	91.77(16)	89.86(13)
C1−Pd1−Cl2	178.14(17)	177.77(15)	179.00(13)
P1−Pd1−Cl1	176.51(5)	178.46(6)	179.45(5)
P1−Pd1−Cl2	93.02(6)	92.79(6)	90.95(5)
C1−Pd1−P1	87.51(16)	87.19(16)	89.90(13)
Cl2−Pd1−Cl1	89.94(5)	88.28(6)	89.29(5)

Table 3. Catalyst Screening for Room-Temperature Suzuki−Miyaura Coupling[a]



entry	cat.	yield (%)	entry	cat.	yield (%)
1	**2a**	13	8	**3a**	39
2	**2b**	5	9	**3b**	40
3	**2c**	6	10	**3c**	56
4	**2d**	6	11	**3d**	68
5	**2e**	16	12	**3e**	78
6	**2f**	5	13	**3f**	66
7	**2g**	11	14	**3g**	>99

[a]Reaction conditions: phenylboronic acid (0.6 mmol), bromoanisole (0.5 mmol), 1,4-dixoxane/H_2O (4/1, 2.0 mL), 2.5 mol % of Pd cat., GC yield.

and phosphine complexes, respectively. The palladium centers in all of the structures adopt a slightly distorted coordination geometry. The most important features are the shorter Pd−C distances in the pyridine complexes in comparison with those in the phosphine complexes. The Pd−C distance in the pyridine complexes varies in the range 2.03−2.06 Å, whereas that in the phosphine complex is in the range 2.09−2.11 Å. All of these Pd−C distances are long in comparison with the usual bond lengths in palladium complexes with normal and abnormal NHC ligands, which are typically below 2.0 Å.[40,45] Also notably, the Pd−N distance of 2.165(3) Å in **2a**, which contains a methyl group on the imidazole ring, is significantly longer than those in the other pyridine complexes featuring phenyl groups on the heterocyclic rings (2.09−2.12 Å), reflecting a greater trans influence exerted by the ligand derived from **1d−f**. The Pd−N distance of 2.095(4) Å in **2g**, featuring 3-chloropyridine as ligand, is comparable to those in palladium NHC complexes with the same pyridine ligand.[35,37,46,47]

Catalysis. Most of the Suzuki−Miyaura cross-coupling were conducted in organic solvents. Recently, efforts have been made to perform the reaction in green solvents under mild conditions.[48−52] Because of the zwitterionic nature of the new palladium complexes, we envisioned that the new zwitterionic palladium complexes may catalyze the cross-coupling in an aqueous medium. Initially, the coupling between 4-bromoanisole and phenylboronic acid was chosen as the benchmark reaction (Table 3). The reaction was carried out at room temperature in a 1,4-dioxane/water mixture (4/1) for 12 h, employing 2.5 mol % of palladium precatalyst. Pleasingly, the new complexes can deliver coupling activities and the phosphine complexes prevail over the pyridine complexes in catalyzing the reaction. Among the phosphine complexes screened, **3g** afforded the best yield of quantitative formation of 4-methyoxylbiphenyl (entry 14). The optimal ligand structure is derived from ligand precursor **1e**, bearing a phenyl group attached to the imidazolyl ring and an electron-releasing *N*-3-methoxybenzyl group.

Having the most active precatalyst **3g** in hand, the solvent and base were then optimized, employing the coupling between phenylboronic acid and 4-chloroacetophenone as the benchmark reaction (Table 4). Entries 1−3 show that the reaction did not proceed well when the reaction was conducted in toluene, 1,4-dioxane, or water. Toluene/water and THF/water solvent mixtures also did not work. Surprisingly, the reaction went smoothly, delivering a quantitative yield of product, when 1,4-dioxane/H_2O (4/1) was used as the solvent (entry 6). The use of KOH as base was preferred to NaOH, KO^{t}Bu, and K_3PO_4, producing the optimal yield (entry 6 vs entries 7−9). On application of the commonly used combinations of bases and solvents in the literature, Cs_2CO_3/1,4-dioxane[53,54] (entry 10) and K_3PO_4/toluene[55−57] (entry 11) produced inferior yields.

Then the substrate scope was investigated (Table 5). Complex **3g** allows a wide range of aryl chlorides and arylboronic acids with different electronic and steric properties to be employed as substrates. It was highly effective in catalyzing the coupling reaction with electron-poor substrates, such as 4-chloroacetophenone, 4-chlorobenzonitrile, and 4-chlorobenzaldehyde, affording yields of over 90% in 2−7 h (entries 1, 2, and 5). The electron-rich substrate 4-chloroanisole was also successfully utilized, affording an 80%

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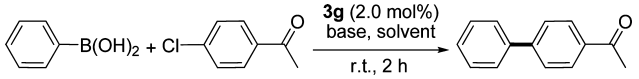
Table 4. Optimization of Reaction Conditions[a]



entry	base	solvent	yield (%)
1	KOH	toluene	6
2	KOH	1,4-dioxane	15
3	KOH	H_2O	11
4	KOH	toluene/H_2O (4/1)	5
5	KOH	THF/H_2O (4/1)	4
6	KOH	1,4-dioxane/H_2O (4/1)	>99
7	NaOH	1,4-dioxane/H_2O (4/1)	90
8	KO*t*-Bu	1,4-dioxane/H_2O (4/1)	17
9	K_3PO_4	1,4-dioxane/H_2O (4/1)	57
10	Cs_2CO_3	1,4-dioxane	12
11	K_3PO_4	toluene	21

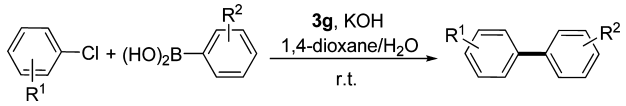
[a]Reaction conditions: phenylboronic acid (0.6 mmol), 4-chloroacetopheone (0.5 mmol), base (2.0 equiv), solvent (2.0 mL), **3g** (2.0 mol %), GC yield.

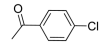
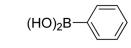
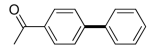
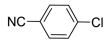
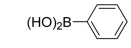
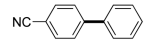
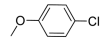
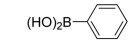
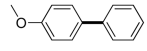
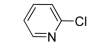
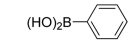
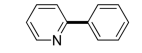
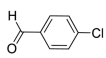
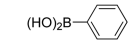
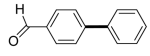
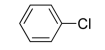
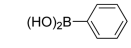
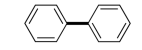
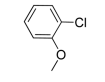
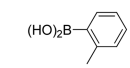
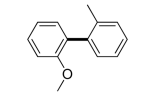
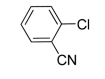
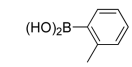
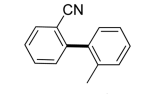
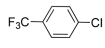
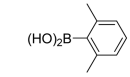
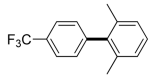
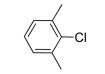
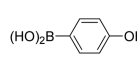
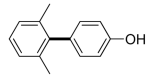
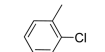
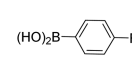
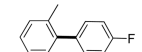
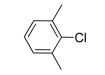
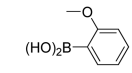
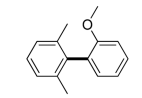
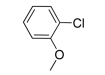
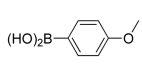
yield of product (entry 3). The coupling reaction between phenylboronic acid and chlorobenzene, however, gave a somewhat low 33% yield (entry 6). Arylboronic acids featuring different functional groups were tolerated (entries 7–20). The catalyst system allowed the use of both ortho-substituted aryl chlorides (entries 7, 8, 13, and 16–18) and arylboronic acids (entries 7, 8, 12, and 19) as coupling partners. Markedly, diortho-substituted compounds could also be successfully utilized (entries 9–12). For example, the di-ortho-substituted 2-chloro-*m*-xylene could react with the ortho-substituted 2-methoxylphenylboronic acid, affording a 69% yield of product (entry 12). Since the coupling reaction takes place in an aqueous medium, the use of unprotected 4-hydroxyphenylboronic acid was well tolerated, leading to the formation of coupled product with 2,6-dimethylchlorobenzene in a decent 65% yield (entry 10). The catalyst system is also applicable for coupling partners featuring heterocyclic aromatic (entries 4, 14, and 16) or anthracenyl rings (entries 14 and 15). Double arylation of the challenging substrate 1,4-dichlorobenzene also occurred readily, affording good yields of triaryl products (entries 19 and 20).

Finally the catalytic performance of **3g** was compared with that of the well-known $PdCl_2$(IPr)(3-chloropyridine)[37] (**4**) (Table 6). In Table 4, entry 3 (vide supra), we showed that a poor 11% yield of coupled product was produced using **3g** as catalyst in the coupling reaction between phenylboronic acid and 4-chloroacetophenone in water. In contrast, a good yield of 76% was formed when the bromo analogue was employed (entry 1). The yield was much superior to that obtained by **4** (entry 2). The activity of **3g** was slightly inferior to that of **4** in the coupling reaction between 4-chloroanisole and phenylboronic acid (entry 3 vs entry 4). In contrast, **3g** gave a better yield in the reaction with sterically hindered substrates (entry 5 vs entry 6).

Electrospray Mass Spectrometry (ES-MS). To understand the properties of the new complexes in solvent, ES-MS was performed, taking **2e** and **3g** as representative examples. ES-MS is based on a soft ionization technique which allows the smooth transfer of ions from solution to the gas phase with little fragmentation, and therefore it is ideal for the observation of short-lived molecular ions.[58] For the pyridine complex **2e**, the major metal-containing positive ion was observed at *m*/*z*

Table 5. Substrate Scope of Room-Temperature Suzuki–Miyaura Coupling Reactions[a]



Entry	ArCl	Ar(BOH)$_2$	Product	Time (h)	Yield (%)
1				2	>99[b]
2				7	94[b]
3				12	80[b]
4				12	88[b]
5				7	91
6				12	33
7				12	75
8				12	88
9				12	68
10				12	65
11				12	89
12				12	69
13				12	78
14				12	86
15				12	81
16				12	83
17				8	85
18				12	72
19				12	68[c]
20				12	66[c]

[a]Reaction conditions: phenyl- or arylboronic acid (0.6 mmol), aryl chloride (0.5 mmol), KOH (2.0 equiv), 1,4-dixoxane/H_2O (4/1, 2.0 mL), **3g** (2.0 mol %), isolated yield. [b]GC yield. [c]Reaction conditions: phenyl- or arylboronic acid (1.2 mmol), KOH (4.0 equiv), 1,4-dixoxane/H_2O (4/1, 3.0 mL).

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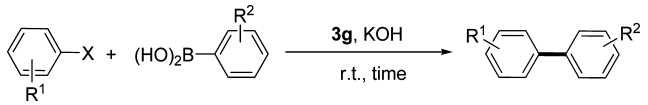
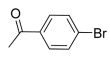
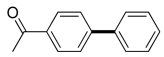
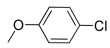
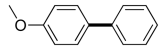
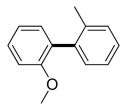
Table 6. Suzuki–Miyaura Coupling Reaction Catalyzed by 3g and 4[a]



Entry	Cat	Ar-X	R^2	Product	Solvent	Time	Yield (%)
1	**3g**		H		H_2O	2	76[b]
2	**4**						4[b]
3	**3g**		H		1,4-dioxane/H_2O (4:1)	12	80[b]
4	**4**						90[b]
5	**3g**		2-Me		1,4-dioxane/H_2O (4:1)	12	75[c]
6	**4**						60[c]

[a]Reaction conditions: phenyl- or arylboronic acid (0.6 mmol), aryl halide (0.5 mmol), KOH (2.0 equiv), 1,4-dixoxane/H_2O (4/1, (2.0 mL), **3g** or **4** (2.0 mol %). [b]GC yield. [c]Isolated yield.

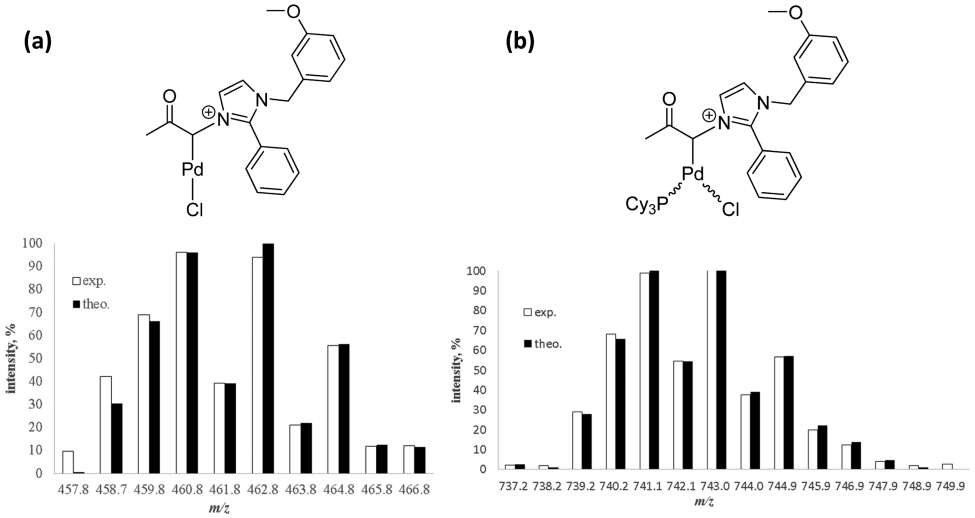


Figure 4. Major metal-containing positive ions observed in (a) **2e** and (b) **3g** by ES-MS.

462.8, corresponding to a two-coordinate $[PdLCl]^+$ species (Figure 4). The observed isotopic pattern matched well with that of theoretical calculations. In contrast, for the phosphine complex **3g**, where there may not be sufficient energy for PCy_3 to dissociate, a three-coordinate $[PdL(PCy_3)Cl]^+$ was detected at m/z 741.1 as the base peak. Thus, the ES-MS data were in accord with a proposition that, at room temperature, **3** could generate a $L(PR_3)Pd^0$ active species that was electron-rich for the activation of C–Cl bonds. In contrast, in the case of **2**, an electron-poor LPd^0 species was likely involved, leading to its poor coupling activities. It should be noted that the base peak observed in the spectra of **2e** was due to L^+. In contrast, the base peak in the spectrum of **3g** corresponds to the three-coordinate species. The high stability of this unsaturated species could also be attributed to the high effectiveness of **3g** in Suzuki–Miyaura cross-coupling among all the precatalysts tested.

X-ray Photoelectron Spectroscopy (XPS). We also probed the electron-donating properties of ligands in **3g** by XPS. The binding energies of Pd electrons in the core $3d_{3/2}$ and the $3d_{5/2}$ orbitals were found to be 341.8 and 336.4 eV, respectively. For comparison, the corresponding binding energies in a Pd(II) complex with a bidentate carbene with abnormal binding are much higher at ca. 348.0 and 342.6 eV.[59] We also reported a series of robust and electron-rich cis-Pd(II) complexes having phosphine and carbene ligands with higher binding energies of ca. 343 and 337 eV.[53] In fact, the binding energies in **3g** are close to those of 340.5 and 335.1 eV in Pd(0).[60] These exceptionally low binding energies indicate that the Pd(II) center in the **3g** is highly electron rich due to the electron-donating nature of the ligands.

■ CONCLUSIONS

We have successfully prepared a series of new imidazole derivatives which could be employed to prepare zwitterionic anionic palladium complexes. The zwitterion with PCy_3 was robust and highly electron rich, thus delivering efficient activities in room-temperature Suzuki–Miyaura cross-coupling conducted in a 1,4-dioxane/water mixture as solvent. Sterically hindered aryl chlorides and arylboronic acids were effectively utilized as substrates. Since the ligand precursors can be obtained readily by an nucleophilic substitution reaction between chloroacetone and imidazole derivatives, it can be expected that the replacement of the organic halide with appropriate hydrophilic compounds can yield water-soluble ligands. Currently, we are working along this direction to synthesize water-soluble zwitterionic palladium complexes and

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investigate their catalytic potentials on cross-coupling reactions in water.

EXPERIMENTAL SECTION

General Considerations. All manipulations were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were dried by standard procedures. Starting chemicals were purchased from commercial sources and used as received. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded at 300.13, 75.48, and 121.49 MHz, respectively. Elemental analyses were performed on a CHN-O elemental analyzer. ESI-MS was carried out on a sector field mass spectrometer. X-ray photoelectron spectroscopy was performed using Mg Kα radiation ($h\nu$ = 1253.6 eV).

Synthesis of 1a. A mixture of 1-benzyl-2-methyl-1*H*-imidazole (2.1 g, 12.2 mmol) and chloroacetone (0.97 mL, 12.2 mmol) in THF (30 mL) was placed in a Schlenk flask. The mixture was heated under reflux for 48 h. After the mixture was cooled, the white solid was collected on a frit, washed with THF, and dried under vacuum. Yield: 2.9 g (90%). ^{1}H NMR ($CDCl_3$): δ 2.24 (s, 3H, CH_3C=O), 2.49 (s, 3H, CH_3), 5.36 (s, 2H, CH_2), 5.85 (s, 2H, CH_2C=O), 7.10−7.25 (m, 5H, Ar *H*), 7.44 (d, 1H, *J* = 3.0 Hz, imi *H*), 7.81 (d, 1H, *J* = 3.0 Hz, imi *H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 10.5 (CH_3), 27.4 (CH_3C=O), 51.8 (CH_2), 57.6 (CH_2C=O), 121.1, 122.9, 127.4, 128.8, 129.1, 132.6 (quaternary *C*), 145.1 (NCN), 199.5 (*C*=O). HRMS (ESI): *m*/*z* calcd for $C_{14}H_{17}N_2O$ $[M - Cl]^+$ 229.1340, found 229.1333.

Synthesis of 1b. The compound was prepared by a procedure similar to that for **1a**. A mixture of 1-(3-methoxybenzyl)-2-methyl-1*H*-imidazole (2.5 g, 12.2 mmol) and chloroacetone (0.97 mL, 12.2 mmol) was used. Yield: 2.9 g (81%). ^{1}H NMR ($CDCl_3$): δ 2.28 (s, 3H, CH_3C=O), 2.52 (s, 3H, CH_3), 3.66 (s, 3H, OCH_3), 5.34 (s, 2H, CH_2), 5.88 (s, 2H, CH_2C=O), 6.67−6.76 (m, 3H, Ar *H*), 7.17 (t, 1H, *J* = 9.0 Hz, Ar *H*), 7.44 (d, 1H, *J* = 3.0 Hz, imi *H*), 7.83 (d, 1H, *J* = 3.0 Hz, imi *H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 10.5 (CH_3), 27.4 (CH_3C=O), 51.7 (CH_2), 55.2 (OCH_3), 57.7 (CH_2C=O), 112.9, 114.2, 119.3, 121.1, 122.9, 130.3, 134.1 (quaternary *C*), 145.3 (NCN), 160.0 (quaternary *C*), 199.5 (*C*=O). HRMS (ESI): *m*/*z* calcd for $C_{15}H_{19}N_2O_2$ $[M - Cl]^+$ 259.1446, found 259.1439.

Synthesis of 1c. The compound was prepared by a procedure similar to that for **1a**. A mixture of 1-(4-fluorobenzyl)-2-methyl-1*H*-imidazole (3.8 g, 20.2 mmol) and chloroacetone (1.6 mL, 20.2 mmol) was used. Yield: 5.2 g (92%). ^{1}H NMR ($CDCl_3$): δ 2.24 (s, 3H, CH_3C=O), 2.51 (s, 3H, CH_3), 5.40 (s, 2H, CH_2), 5.80 (s, 2H, CH_2C=O), 6.91 (t, 2H, *J* = 9.0 Hz, Ar *H*), 7.17−7.21 (m, 2H, Ar *H*), 7.53 (d, 1H, *J* = 3.0 Hz, imi *H*), 7.78 (d, 1H, *J* = 3.0 Hz, imi *H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 10.5 (CH_3), 27.4 (CH_3C=O), 51.0 (CH_2), 57.6 (CH_2C=O), 116.1 (d, *J* = 21.9 Hz, Ar *C*), 121.1, 122.9, 128.6 (quaternary *C*), 129.7 (d, *J* = 8.3 Hz, Ar *C*), 145.1 (NCN), 162.6 (d, *J* = 249.8 Hz, *C*F), 199.4 (*C*=O). HRMS (ESI): *m*/*z* calcd for $C_{14}H_{16}FN_2O$ $[M - Cl]^+$ 247.1246, found 247.1237.

Synthesis of 1d. The compound was prepared by a procedure similar to that for **1a**. A mixture of 1-benzyl-2-phenyl-1*H*-imidazole (1.6 g, 6.8 mmol) and chloroacetone (0.54 mL, 6.8 mmol) was used. Yield: 1.9 g (86%). Mp: 198.5−199.1 °C. ^{1}H NMR ($CDCl_3$): δ 2.14 (s, 3H, CH_3), 5.26 (s, 2H, CH_2), 5.49 (s, 2H, CH_2C=O), 6.97−7.00 (m, 2H, Ar *H*), 7.17−7.22 (m, 3H, Ar *H*), 7.29−7.32 (m, 2H, Ar *H*), 7.46 (t, 2H, *J* = 6.0 Hz, Ar *H*), 7.57 (t, 1H, *J* = 6.0 Hz, Ar *H*), 7.85 (d, 1H, *J* = 3.0 Hz, imi *H*), 8.31 (d, 1H, *J* = 3.0 Hz, imi *H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 27.2 (CH_3), 52.3 (CH_2), 57.5 (C=OCH_2), 120.3, 122.0, 124.3, 127.6, 128.8 (quaternary *C*), 129.0, 129.7, 129.9, 132.8, 133.1 (quaternary *C*), 145.1 (NCN), 199.4 (*C*=O). HRMS (ESI): *m*/*z* calcd for $C_{19}H_{19}N_2O$ $[M - Cl]^+$ 291.1497, found 291.1490.

Synthesis of 1e. The compound was prepared by a procedure similar to that for **1a**. A mixture of 1-(3-methoxybenzyl)-2-phenyl-1*H*-imidazole (3.3 g, 12.4 mmol) and chloroacetone (0.99 mL, 12.4 mmol) was used. Yield: 3.6 g (82%). ^{1}H NMR ($CDCl_3$): δ 2.11 (s, 3H, CH_3C=O), 3.61 (s, 3H, OCH_3), 5.20 (s, 2H, CH_2), 5.46 (s, 2H, CH_2C=O), 6.50−6.52 (m, 2H, Ar *H*), 6.70 (d, 1H, *J* = 9.0 Hz, Ar *H*), 7.07 (t, 1H, *J* = 9.0 Hz, Ar *H*), 7.30 (d, 2H, *J* = 9.0 Hz, Ar *H*), 7.45 (t, 2H, *J* = 9.0 Hz, Ar *H*), 7.55 (t, 1H, *J* = 6.0 Hz, Ar *H*), 7.86 (d, 1H, *J* = 3.0 Hz, imi *H*), 8.27 (d, 1H, *J* = 3.0 Hz, imi *H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 27.2 (CH_3C=O), 52.1 (CH_2), 55.1 (OCH_3), 57.5 (CH_2C=O), 113.0, 114.3, 119.5, 120.3, 122.1, 124.2, 129.6, 129.9, 130.0, 132.7 (quaternary *C*), 134.5 (quaternary *C*), 145.0 (NCN), 159.7 (quaternary *C*), 199.3 (*C*=O). HRMS (ESI): *m*/*z* calcd for $C_{20}H_{21}N_2O_2$ $[M-Cl]^+$ 321.1602, found 321.1595.

Synthesis of 1f. The compound was prepared by a procedure similar to that for **1a**. A mixture of 1-(4-fluorobenzyl)-2-phenyl-1*H*-imidazole (2.9 g, 11.6 mmol) and chloroacetone (0.92 mL, 11.6 mmol) was used. Yield: 2.3 g (56%). Mp: 126.3−126.9 °C. ^{1}H NMR ($CDCl_3$): δ 2.17 (s, 3H, CH_3), 5.29 (s, 2H, CH_2), 5.44 (s, 2H, CH_2C=O), 6.91 (t, 2H, *J* = 9.0 Hz, Ar *H*), 7.04−7.09 (m, 2H, Ar *H*), 7.38−7.40 (m, 2H, Ar *H*), 7.51 (t, 2H, *J* = 6.0 Hz, Ar *H*), 7.61 (t, 1H, *J* = 6.0 Hz, Ar *H*), 7.98 (d, 1H, *J* = 3.0 Hz, imi *H*), 8.24 (d, 1H, *J* = 3.0 Hz, imi *H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 27.3 (CH_3), 51.6 (CH_2), 57.6 (CH_2C=O), 116.0 (d, *J* = 21.8 Hz, Ar *C*), 120.5, 122.2, 124.3, 129.2 (quaternary *C*), 129.7, 129.9 (d, *J* = 9.0 Hz, Ar *C*), 130.1, 132.8 (quaternary *C*), 145.0 (NCN), 162.7 (d, *J* = 249.0 Hz, *C*F), 199.6 (*C*=O). HRMS (ESI): *m*/*z* calcd for $C_{19}H_{18}FN_2O$ $[M-Cl]^+$ 309.1403, found 309.1395.

Synthesis of 2a. In a 20 mL Schlenk flask, $PdCl_2$ (0.052 g, 0.29 mmol), **1a** (0.078 g, 0.29 mmol), pyridine (23.8 μL, 0.29 mmol), and K_2CO_3 (0.16 g, 1.2 mmol) were dissolved in dry DMF (10 mL) under a nitrogen atmosphere. The solution was stirred at room temperature for 12 h. The residue was washed with water and extracted twice with DCM. The extract was dried over anhydrous $MgSO_4$ and evaporated to dryness under vacuum to give a solid. Diethyl ether was added, and the yellowish solid that formed was collected on a frit and dried under vacuum. Yield: 0.082 g (56%). Mp: 160.8−161.3 °C. Anal. Calcd for $C_{19}H_{21}Cl_2N_3OPd$: C, 47.07; H, 4.36; N, 8.66. Found: C, 47.15; H, 4.60; N, 8.26. 1H NMR ($CDCl_3$): δ 2.50 (s, 3H, CH_3C=O), 2.66 (s, 3H, CH_3), 5.10 (s, 2H, CH_2), 6.20 (s, 1H, Pd−*CH*), 6.87 (d, 1H, *J* = 3.0 Hz, imi *H*), 7.15−7.18 (m, 2H, Ar *H*), 7.21−7.26 (m, 2H, Py *H*), 7.40−7.42 (m, 3H, Ar *H*), 7.65 (t, 1H, *J* = 9.0 Hz, Py *H*), 8.20 (d, 1H, *J* = 3.0 Hz, imi *H*), 8.88 (d, 2H, *J* = 3.0 Hz, Py *H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 10.9 (CH_3), 28.7 (CH_3C=O), 40.9 (Pd-*C*H), 51.7 (CH_2), 118.2, 124.0 (Py *C*), 126.2, 127.4, 129.3, 129.5, 132.0 (quaternary *C*), 137.2 (Py *C*), 140.7 (NCN), 151.5 (Py *C*), 204.8 (*C*=O).

Synthesis of 2b. The compound was prepared by a procedure similar to that for **2a**. A mixture of $PdCl_2$ (0.060 g, 0.34 mmol), **1b** (0.10 g, 0.34 mmol), pyridine (27.6 μL, 0.34 mmol), and K_2CO_3 (0.19 g, 1.4 mmol) was used. Yield: 0.11 g (63%). Mp: 175.6−176.3 °C. Anal. Calcd for $C_{20}H_{23}Cl_2N_3O_2Pd$: C, 46.6; H, 4.50; N, 8.16. Found: C, 46.38; H, 4.25; N, 7.75. ^{1}H NMR ($CDCl_3$): δ 2.50 (s, 3H, CH_3C=O), 2.66 (s, 3H, CH_3), 3.79 (s, 3H, OCH_3), 5.06 (s, 2H, CH_2), 6.19 (s, 1H, Pd−*CH*), 6.67−6.73 (m, 2H, Ar *H*), 6.87−6.92 (m, 2H, Ar *H*, imi *H*), 7.21−7.26 (m, 2H, Py *H*), 7.32 (t, 1H, *J* = 9.0 Hz, Ar *H*), 7.65 (t, 1H, *J* = 9.0 Hz, Py *H*), 8.19 (d, 1H, *J* = 3.0 Hz, imi *H*), 8.87 (d, 2H, *J* = 6.0 Hz, Py *H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 10.0 (CH_3), 28.8 (CH_3C=O), 41.1 (Pd-CH), 51.8 (CH_2), 55.4 (OCH_3), 113.3, 114.5, 118.3, 119.5, 124.2 (Py *C*), 126.3, 130.8, 133.5 (quaternary *C*), 137.4 (Py *C*), 140.9 (NCN), 151.6 (Py *C*), 160.4 (quaternary *C*), 204.9 (*C*=O).

Synthesis of 2c. The compound was prepared by a procedure similar to that for **2a**. A mixture of $PdCl_2$ (0.038 g, 0.21 mmol), **1c** (0.090 g, 0.32 mmol), pyridine (17.2 μL, 0.34 mmol), and K_2CO_3 (0.12 g, 0.84 mmol) was used. Yield: 0.054 g (51%). Mp: 145.4−146.7 °C. Anal. Calcd for $C_{19}H_{20}Cl_2FN_3OPd$: C, 45.39; H, 4.01; N, 8.35. Found: C, 45.04; H, 4.30; N, 8.04. ^{1}H NMR ($CDCl_3$): δ 2.50 (s, 3H, CH_3C=O), 2.67 (s, 3H, CH_3), 5.08 (s, 2H, CH_2), 6.19 (s, 1H, Pd−*CH*), 6.86 (d, 1H, *J* = 3.0 Hz, imi *H*), 6.99−7.26 (m, 6H, Ar *H*, Py *H*), 7.66 (t, 1H, *J* = 9.0 Hz, Py *H*), 8.19 (d, 1H, *J* = 3.0 Hz, imi *H*), 8.87 (d, 2H, *J* = 3.0 Hz, Py *H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 11.1 (CH_3), 28.8 (C=OCH_3), 41.2 (Pd-CH), 51.1 (CH_2), 116.8 (d, *J* = 21.8 Hz, Ar *C*), 118.1, 124.2 (Py *C*), 126.4, 128.0 (d, *J* = 3.7 Hz, Ar *C*), 129.6 (d, *J* = 9.0 Hz, Ar *C*), 137.4 (Py *C*), 140.8 (NCN), 151.6 (Py C), 163.1 (d, *J* = 250.5 Hz, *C*F), 205.0 (*C*=O).

Synthesis of 2d. The compound was prepared by a procedure similar to that for **2a**. A mixture of $PdCl_2$ (0.054 g, 0.31 mmol), **1d** (0.10 g, 0.31 mmol), pyridine (24.7 μL, 0.31 mmol), and K_2CO_3 (0.17

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g, 1.2 mmol) was used. Yield: 0.12 g (72%). Mp: 156.2−156.8 °C. Anal. Calcd for $C_{24}H_{23}Cl_2N_3O_2Pd$: C, 52.71; H, 4.23; N, 7.68. Found: C, 52.93; H, 4.59; N, 7.26. ^{1}H NMR ($CDCl_3$): δ 2.28 (s, 3H, CH_3), 4.96 (s, 2H, CH_2), 5.89 (s, 1H, Pd−CH), 7.03−7.07 (m, 4H, imi *H*, Ar *H*), 7.21−7.26 (m, 3H, Ar *H*, Py *H*), 7.35 (t, 4H, *J* = 3.0 Hz, Ar *H*), 7.60−7.67 (m, 3H, Ar *H*, Py *H*), 8.61 (d, 1H, *J* = 3.0 Hz, imi *H*), 8.89 (d, 2H, *J* = 3.0 Hz, Py *H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 28.3 (CH_3), 42.3 (Pd−CH), 52.0 (CH_2), 118.8, 121.5, 124.1 (Py *C*), 127.6, 128.0 (quaternary *C*), 129.2, 129.4, 132.4, 132.8 (quaternary *C*), 137.3 (Py *C*), 142.6 (NCN), 151.6 (Py *C*), 206.4 (*C*=O).

Synthesis of 2e. The compound was prepared by a procedure similar to that for **2a**. A mixture of $PdCl_2$ (0.050 g, 0.28 mmol), **1e** (0.10 g, 0.28 mmol), pyridine (22.7 μL, 0.28 mmol), and K_2CO_3 (0.16 g, 11.2 mmol) was used. Yield: 0.15 g (90%). Mp: 90.1−90.8 °C. Anal. Calcd for $C_{25}H_{25}Cl_2N_3O_2Pd$: C, 52.05; H, 4.36; N, 7.28. Found: C, 52.10; H, 4.77; N, 6.81. ^{1}H NMR ($CDCl_3$): δ 2.29 (s, 3H, CH_3C=O), 3.76 (s, 3H, OCH_3), 4.92 (s, 2H, CH_2), 5.89 (s, 1H, Pd−CH), 6.55 (t, 1H, *J* = 3.0 Hz, Ar *H*), 6.63 (d, 1H, *J* = 9.0 Hz, Ar *H*), 6.87 (dd, 1H, *J* = 9.0 Hz, 3.0 Hz, Ar *H*), 7.08 (d, 1H, *J* = 3.0 Hz, imi *H*), 7.21−7.29 (m, 5H, Ar *H*, Py *H*), 7.50−7.68 (m, 4H, Ar *H*, Py *H*), 8.62 (d, 1H, *J* = 3.0 Hz, imi *H*), 8.89 (d, 2H, *J* = 3.0 Hz, Py *H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 28.2 (C=OCH_3), 42.3 (Pd-CH), 51.9 (CH_2), 55.3 (OCH_3), 113.3, 114.4, 118.8, 119.6, 121.4, 124.1 (Py *C*), 127.9, 129.4, 130.5, 132.3 (quaternary *C*), 134.2 (quaternary *C*), 137.3 (Py *C*), 142.5 (NCN), 151.6 (Py *C*), 160.1 (quaternary *C*), 206.4 (*C*=O).

Synthesis of 2f. The compound was prepared by a procedure similar to that for **2a**. A mixture of $PdCl_2$ (0.050 mg, 0.29 mmol), **1f** (0.10 g, 0.29 mmol), pyridine (23.5 μL, 0.29 mmol), and K_2CO_3 (0.16 g, 11.6 mmol) was used. Yield: 0.14 g (87%). Mp: 150.8−151.4 °C. Anal. Calcd for $C_{24}H_{22}Cl_2FN_3OPd$: C, 51.03; H, 3.92; N, 7.44. Found: C, 50.60; H, 3.90; N, 7.20. ^{1}H NMR ($CDCl_3$): δ 2.29 (s, 3H, CH_3), 4.94 (s, 2H, CH_2), 5.88 (s, 1H, Pd−CH), 7.02−7.07 (m, 5H, Ar *H*, imi *H*), 7.21−7.26 (m, 4H, Ar *H*, Py *H*), 7.49−7.78 (m, 4H, Ar *H*, Py *H*), 8.63 (d, 1H, *J* = 3.0 Hz, imi *H*), 8.89 (d, 2H, *J* = 3.0 Hz, Py *H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 28.2 (CH_3), 42.3 (Pd-CH), 51.3 (CH_2), 116.4 (d, *J* = 21.8 Hz, Ar *C*), 118.6, 121.3, 124.1 (Py *C*), 124.9, 128.0, 128.6 (quaternary *C*), 129.6 (d, *J* = 8.3 Hz, Ar *C*), 132.4, 137.3 (Py *C*), 142.5 (NCN), 151.6 (Py *C*), 162.9 (d, *J* = 249.8 Hz, *C*F), 206.4 (*C*=O).

Synthesis of 2g. The compound was prepared by a procedure similar to that for **2a**. A mixture of $PdCl_2$ (0.056 g, 0.31 mmol), **1g** (0.11 g, 0.31 mmol), 3-chloropyridine (29.8 μL, 0.31 mmol), and K_2CO_3 (0.17 g, 12.4 mmol) was used. Yield: 0.13 g (69%). Mp: 133.3−134.1 °C. Anal. Calcd for $C_{25}H_{24}Cl_3N_3O_2Pd$: C, 49.12; H, 3.95; N, 6.87. Found: C, 49.28; H, 3.99; N, 6.66. ^{1}H NMR ($CDCl_3$): δ 2.29 (s, 3H, CH_3C=O), 3.76 (s, 3H, OCH_3), 4.92 (s, 2H, CH_2), 5.92 (s, 1H, Pd−CH), 6.55 (t, 1H, *J* = 3.0 Hz, Ar *H*), 6.63 (d, 1H, *J* = 9.0 Hz, Ar *H*), 6.88 (dd, 1H, *J* = 9.0 Hz, 3.0 Hz, Ar *H*), 7.08 (d, 1H, *J* = 3.0 Hz, imi *H*), 7.18−7.30 (m, 4H, Ar *H*, Py *H*), 7.61−7.67 (m, 4H, Ar *H*, Py *H*), 8.58 (d, 1H, *J* = 3.0 Hz, imi *H*), 8.84 (dd, 1H, *J* = 6.0 Hz, 3.0 Hz, Py *H*), 8.94 (d, 1H, *J* = 3.0 Hz, Py *H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 28.3 (CH_3C=O), 41.7 (Pd−CH), 52.0 (CH_2), 55.3 (OCH_3), 113.4, 114.5, 118.9, 119.7, 121.4, 124.6 (Py *C*), 128.0, 129.5, 130.6, 132.2 (quaternary *C*), 132.5 (Py *C*), 134.1 (quaternary *C*), 137.3 (Py *C*), 142.7 (NCN), 149.6 (Py *C*), 150.6 (Py *C*), 160.2 (quaternary *C*), 206.2 (*C*=O).

Synthesis of 3a. A mixture of **2a** (0.040 g, 0.083 mmol) and PPh_3 (0.022 g, 0.083 mmol) in dichloromethane (10 mL) was stirred in a 20 mL Schlenk flask at ambient temperature overnight. The solvent was removed completely under vacuum. The residue was washed thoroughly with THF to afford a yellowish solid. Yield: 0.040 g (73%). Mp: 136.2−136.5 °C. Anal. Calcd for $C_{32}H_{31}Cl_2N_2OPPd$: C, 57.54; H, 4.67; N, 4.19. Found: C, 57.26; H, 5.14; N, 4.25. ^{1}H NMR (DMSO-d_6): δ 1.39 (s, 3H, CH_3C=O), 2.17 (s, 3H, CH_3), 4.15 (d, 1H, *J* = 6.0 Hz, Pd-CH), 5.25−5.47 (m, 2H, CH_2), 7.24−7.66 (m, 21H, imi *H*, Ar *H*), 8.29 (s, 1H, imi *H*). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 8.8 (CH_3), 28.8 (CH_3C=O), 50.8 (CH_2), 53.7 (Pd-CH), 120.0, 126.8, 128.0, 128.2, 128.9 (d, *J* = 9.8 Hz, Ar *C*), 129.5, 130.4, 131.2 (d, *J* = 9.8 Hz, Ar *C*), 134.6 (d, *J* = 10.6 Hz, Ar *C*), 135.1 (quaternary *C*), 143.8 (NCN), 202.4 (*C*=O). ^{31}P{^{1}H} NMR (DMSO-d_6): δ 32.1.

Synthesis of 3b. The compound was prepared by a procedure similar to that for **3a**. A mixture of complex **2b** (0.18 g, 0.34 mmol) and PPh_3 (0.092 g, 0.34 mmol) was used. Yield: 0.17 g (71%). Mp: 179.1−181.2 °C. Anal. Calcd for $C_{33}H_{33}Cl_2N_2O_2PPd$: C, 56.79; H, 4.76; N, 4.01. Found: C, 56.90; H, 4.90; N, 3.90. ^{1}H NMR (DMSO-d_6): δ 1.39 (s, 3H, CH_3C=O), 2.17 (s, 3H, CH_3), 3.73 (s, 3H, OCH_3), 4.15 (d, 1H, *J* = 6.0 Hz, Pd−CH), 5.21 (m, 2H, CH_2), 6.77 (d, 1H, *J* = 6.0 Hz, Ar *H*), 6.96 (d, 1H, *J* = 9.0 Hz, Ar *H*), 7.31−7.66 (m, 18H, Ar *H*, imi *H*), 8.30 (s, 1H, imi *H*). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 8.7 (CH_3), 28.8 (CH_3C=O), 50.7 (CH_2), 53.7 (Pd−CH), 55.6 (OCH_3), 113.9, 114.1, 120.1, 126.8, 128.9 (d, *J* = 11.3 Hz, Ar *C*), 130.6 (d, *J* = 10.6 Hz, Ar *C*), 131.2, 134.6 (d, *J* = 10.6 Hz, Ar *C*), 134.9, 136.6 (quaternary *C*), 143.9 (NCN), 160.1 (quaternary *C*), 202.4 (*C*=O). ^{31}P{^{1}H} NMR (DMSO-d_6): δ 32.2.

Synthesis of 3c. The compound was prepared by a procedure similar to that for **3a**. A mixture of complex **2c** (0.12 g, 0.24 mmol) and PPh_3 (0.064 g, 0.24 mmol) was used. Yield: 0.077 g (48%). Mp: 171.9−172..6 °C. Anal. Calcd for $C_{32}H_{30}Cl_2FN_2OPPd$: C, 56.03; H, 4.40; N, 4.08. Found: C, 56.36; H, 4.66; N, 4.23. ^{1}H NMR ($CDCl_3$): δ 1.28 (s, 3H, CH_3C=O), 2.36 (s, 3H, CH_3), 4.25 (d, 1H, *J* = 6.0 Hz, Pd−CH), 4.96−5.26 (m, 2H, CH_2), 6.98 (t, 2H, *J* = 9.0 Hz, Ar *H*), 7.18−7.67 (m, 17H, Ar *H*), 7.98 (s, 1H, imi *H*), 8.51 (s, 1H, imi *H*). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 8.8 (CH_3), 28.8 (CH_3C=O), 50.1 (CH_2), 53.7 (Pd−CH), 116.4 (d, *J* = 21.8 Hz, Ar *C*), 119.8, 126.9, 128.9 (d, *J* = 9.8 Hz, Ar *C*), 130.5, 130.8 (d, *J* = 9.8 Hz, Ar *C*), 131.2 (d, *J* = 9.8 Hz, Ar *C*), 131.3, 134.6 (d, *J* = 11.3 Hz, Ar *C*), 143.8 (NCN), 162.5 (d, *J* = 245.2 Hz, *C*F), 202.4 (*C*=O). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 32.5.

Synthesis of 3d. The compound was prepared by a procedure similar to that for **3a**. A mixture of complex **2d** (0.12 g, 0.22 mmol) and PPh_3 (0.058 g, 0.22 mmol) was used. Yield: 0.15 g (90%). Mp: 180.5−181.1 °C. Anal. Calcd for $C_{37}H_{33}Cl_2N_2OPPd$: C, 60.87; H, 4.55; N, 3.83. Found: C, 60.48; H, 4.06; N, 3.59. ^{1}H NMR (DMSO-d_6): δ 1.52 (s, 3H, CH_3), 4.07 (d, 1H, Pd−CH), 5.05−5.20 (m, 2H, CH_2), 6.18 (s, 1H, Ar *H*), 6.96 (s, 2H, Ar *H*), 7.31−7.62 (m, 22H, Ar *H*), 8.03 (s, 1H, imi *H*), 8.72 (s, 1H, imi *H*). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 27.4 (CH_3), 51.7 (CH_2), 53.3 (Pd-CH), 121.5, 127.3, 127.8, 128.1, 128.9 (d, *J* = 9.8 Hz, Ar *C*), 129.3, 129.6 (d, *J* = 5.3 Hz, Ar *C*), 130.1, 130.8, 131.2, 131.8 (quaternary *C*), 132.6, 133.9 (d, *J* = 10.6 Hz, Ar *C*), 134.9 (quaternary *C*), 143.4 (NCN), 202.3 (*C*=O). ^{31}P{^{1}H} NMR (DMSO-d_6): δ 30.6.

Synthesis of 3e. The compound was prepared by a procedure similar to that for **3a**. A mixture of complex **2e** (0.15 g, 0.26 mmol) and PPh_3 (0.069 g, 0.26 mmol) was used. Yield: 0.17 g (85%). Mp: 191.4−192.1 °C dec. Anal. Calcd for $C_{38}H_{35}Cl_2N_2O_2PPd$: C, 60.05; H, 4.64; N, 3.68. Found: C, 59.99; H, 4.80; N, 3.24. 1H NMR (DMSO-d_6): δ 1.53 (s, 3H, CH_3), 3.68 (s, 3H, OCH_3), 4.07 (d, 1H, *J* = 9.0 Hz, Pd−CH), 5.07−5.09 (m, 2H, CH_2), 6.20 (s, 1H, Ar *H*), 6.49−6.54 (m, 2H, Ar *H*), 6.92 (d, 1H, *J* = 9.0 Hz, Ar *H*), 7.24−7.65 (m, 20H, Ar *H*), 8.04 (s, 1H, imi *H*), 8.72 (s, 1H, imi *H*). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 27.5 (CH_3), 51.6 (CH_2), 53.3 (Pd-CH), 55.5 (OCH_3), 113.7, 114.3, 120.0, 121.6, 127.3, 128.9 (d, *J* = 9.8 Hz, Ar *C*), 129.6 (d, *J* = 6.0 Hz, Ar *C*), 130.1, 130.5, 130.8, 131.2, 132.6, 133.9 (d, *J* = 10.5 Hz, Ar *C*), 134.9 (quaternary *C*), 136.3 (quaternary *C*), 143.4 (NCN), 159.8 (quaternary *C*), 202.3 (*C*=O). ^{31}P{^{1}H} NMR (DMSO-d_6): δ 30.6.

Synthesis of 3f. The compound was prepared by a procedure similar to that for **3a**. A mixture of complex **2f** (0.094 g, 0.16 mmol) and PPh_3 (0.043 g, 0.16 mmol) was used. Yield: 0.063 g (51%). Mp: 177.7−178.6 °C. Anal. Calcd for $C_{37}H_{32}Cl_2FN_2OPPd$: C, 59.41; H, 4.31; N, 3.74. Found: C, 59.40; H, 4.21; N, 3.80. ^{1}H NMR (DMSO-d_6): δ 1.51 (s, 3H, CH_3), 4.06 (d, 1H, *J* = 9.0 Hz, Pd−CH), 5.10 (s, 2H, CH_2), 6.18 (s, 1H, Ar *H*), 7.01−7.62 (m, 23H, Ar *H*), 8.02 (s, 1H, imi *H*), 8.72 (s, 1H, imi *H*). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 27.4 (CH_3), 51.0 (CH_2), 53.3 (Pd-CH), 116.2 (d, *J* = 21.8 Hz, Ar *C*), 121.5, 127.2 (quaternary *C*), 128.5 (d, *J* = 9.0 Hz, Ar *C*), 128.9 (d, *J* = 10.5 Hz, Ar *C*), 129.6 (d, *J* = 9.8 Hz, Ar *C*), 130.1, 130.6 (d, *J* = 7.5 Hz, Ar *C*), 131.2, 131.9 (d, *J* = 9.0 Hz, Ar *C*), 132.6, 133.9 (d, *J* = 10.5 Hz, Ar *C*), 134.9 (quaternary *C*), 143.3 (NCN), 162.4 (d, *J* = 245.2 Hz, *C*F), 202.3 (*C*=O). ^{31}P{^{1}H} NMR (DMSO-d_6): δ 30.7.

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Synthesis of 3g. The compound was prepared by a procedure similar to that for **3a**. A mixture of complex **2e** (0.17 g, 0.29 mmol) and PCy_3 (0.081 g, 0.29 mmol) was used. Yield: 0.19 g (84%). Mp: 151.2−151.9 °C dec. Anal. Calcd for $C_{38}H_{53}Cl_2N_2O_2PPd$: C, 58.65; H, 6.86; N, 3.60. Found: C, 58.80; H, 6.44; N, 3.33. ^{1}H NMR ($CDCl_3$): δ 1.10−1.28 (m, 9H, Cy *H*), 1.51−2.10 (m, 21H, Cy *H*), 2.41 (s, 3H, CH_3), 3.82 (s, 3H, OCH_3), 4.48 (d, 1H, J = 6.0 Hz, Pd-C*H*), 4.84 (d, 1H, J = 15.0 Hz, CH_aH_b), 5.58 (d, 1H, J = 15.0 Hz, CH_aH_b), 6.66 (d, 1H, J = 6.0 Hz, Ar *H*), 6.80 (s, 1H, Ar *H*), 6.88 (d, 1H, J = 6.0 Hz, Ar *H*), 7.24−7.28 (m, 2H, Ar *H*), 7.55−7.80 (m, 5H, Ar *H*, imi *H*), 9.08 (s, 1H, imi *H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 26.2 (d, J = 11.3 Hz, Cy CH_2), 26.5 (d, J = 18.1 Hz, Cy CH_2), 26.8 (d, J = 15.0 Hz, Cy CH_2), 27.0 (d, J = 8.3 Hz, Cy CH_2), 27.2, 27.7 (d, J = 11.3 Hz, Cy CH_2), 28.8, 29.7 (CH_3C═O), 31.9 (d, J = 18.8 Hz, Cy *C*), 33.9 (d, J = 24.9 Hz, Cy *C*), 51.4 (CH_2), 52.3 (d, J = 25.6 Hz, Pd−*C*H), 55.5 (OCH_3), 113.2, 114.3, 114.7, 118.9, 119.7, 121.0, 122.2, 129.0, 129.9, 130.3, 130.5 (quatenary *C*), 132.6 (quatenary *C*), 142.4 (N*C*N), 160.1 (quatenary *C*), 205.5 (*C*═O). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 39.3.

Room-Temperature Suzuki−Miyaura Cross-Coupling Reactions. In a typical reaction, a mixture of aryl halide (0.5 mmol), phenyl- or arylboronic acid (0.6 mmol), base (2.0 equiv), and palladium catalyst (2.0−2.5 mol %) in solvent (2.0 mL) was stirred at room temperature for an appropriate period of time (2−12 h) under nitrogen. GC yields were calculated by using benzophenone as an internal standard. In the standard workup, the solvent was removed completely under vacuum. A 1/1 ethyl acetate/water mixture (20 mL) was added. The organic layer was washed, separated, further washed with another 10 mL of ethyl acetate, and dried with anhydrous $MgSO_4$. The solvent was removed completely under high vacuum. Crude products were purified through flash column chromatography on 230−400 mesh silica gel using hexane or hexane/ethyl acetate as eluent in a suitable ratio according to the TLC experiments.

X-ray Diffraction Studies. Samples were collected at 150(2) K on a X-ray diffractometer equipped with a CCD area detector and a graphite monochromator utilizing Mo Kα radiation (λ = 0.71073 Å). The unit cell parameters were obtained by least-squares refinement. Data collection and reduction were performed using the APEX2 and SAINT software.[61] Absorption corrections were performed using the SADABS program.[62] All of the structures were solved by direct methods and refined by full-matrix least-squares methods against F^2 with the SHELXTL software package.[63] All non-H atoms were refined anisotropically. All H atoms were fixed at calculated positions and refined with the use of a riding model. Crystallographic data are given in Tables S1 and S2 in the Supporting Information. CCDC files 988620 (**2a**), 988621 (**2d**), 988622 (**2f**), 988623 (**2g**), 988624 (**3d**), 988625 (**3e**), and 1002143 (**3f**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Studies. Enthalpies and free energies (at 298 K) of potential palladium complexes relative to those of **2a** were computed using the M06 density functional.[64] Solvent effects of THF and water were included using the PCM model.[65,66] The LANL2DZ effective core potential and basis function[67] was chosen for Pd, while the 6-31G(d) basis set was chosen for other atoms.

■ ASSOCIATED CONTENT

Supporting Information

Figures, tables, and CIF files giving full crystallographic data for all the structures determined in this paper NMR spectra for the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Stradiotto, M.; Hesp, K. D.; Lundgren, R. J. *Angew. Chem., Int. Ed.* **2010**, *49*, 494.
(2) Chauvin, R. *Eur. J. Inorg. Chem.* **2000**, *2000*, 577.
(3) Amer, I.; Alper, H. *J. Am. Chem. Soc.* **1990**, *112*, 3674.
(4) Thomas, J. C.; Peters, J. C. *J. Am. Chem. Soc.* **2001**, *123*, 5100.
(5) Lu, C. C.; Peters, J. C. *J. Am. Chem. Soc.* **2002**, *124*, 5272.
(6) Hesp, K. D.; McDonald, R.; Ferguson, M. J.; Stradiotto, M. *J. Am. Chem. Soc.* **2008**, *130*, 16394.
(7) Lundgren, R. J.; Rankin, M. A.; McDonald, R.; Schatte, G.; Stradiotto, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 4732.
(8) Cipot, J.; Vogels, C. M.; McDonald, R.; Westcott, S. A.; Stradiotto, M. *Organometallics* **2006**, *25*, 5965.
(9) Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 907.
(10) Belluco, U.; Michelin, R. A.; Mozzon, M.; Bertani, R.; Facchin, G.; Zanotto, L.; Pandolfo, L. *J. Organomet. Chem.* **1998**, *557*, 37.
(11) Brunet, J.-J.; Chauvin, R.; Chiffre, J.; Huguet, S.; Leglaye, P. *J. Organomet. Chem.* **1998**, *566*, 117.
(12) Gandelman, M.; Vigalok, A.; Shimon, L. J. W.; Milstein, D. *Organometallics* **1997**, *16*, 3981.
(13) Wehman-Ooyevaar, I. C. M.; Grove, D. M.; Kooijman, H.; Van der Sluis, P.; Spek, A. L.; Van Koten, G. *J. Am. Chem. Soc.* **1992**, *114*, 9916.
(14) Sleiman, H. F.; McElwee-White, L. *J. Am. Chem. Soc.* **1988**, *110*, 8700.
(15) Aumann, R.; Fröhlich, R.; Prigge, J.; Meyer, O. *Organometallics* **1999**, *18*, 1369.
(16) Dullaghan, C. A.; Carpenter, G. B.; Sweigart, D. A.; Choi, D. S.; Lee, S. S.; Chung, Y. K. *Organometallics* **1997**, *16*, 5688.
(17) Lee, J.-Y.; Huang, Y.-H.; Liu, S.-Y.; Cheng, S.-C.; Jhou, Y.-M.; Lii, J.-H.; Lee, H. M. *Chem. Commun.* **2012**, *48*, 5632.
(18) Chen, S.-J.; Lin, Y.-D.; Chiang, Y.-H.; Lee, H. M. *Eur. J. Inorg. Chem.* **2014**, *2014*, 1492.
(19) Bedford, R. B.; Cazin, C. S. J.; Holder, D. *Coord. Chem. Rev.* **2004**, *248*, 2283.
(20) Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **1998**, *37*, 3387.
(21) Liu, S.-Y.; Choi, M. J.; Fu, G. C. *Chem. Commun.* **2001**, 2408.
(22) Blug, M.; Guibert, C.; Le Goff, X.-F.; Mezailles, N.; Le Floch, P. *Chem. Commun.* **2008**, 203.
(23) Diebolt, O.; Braunstein, P.; Nolan, S. P.; Cazin, C. S. J. *Chem. Commun.* **2008**, 3190.
(24) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290.
(25) Hillier, A. C.; Grasa, G. A.; Viciu, M. S.; Lee, H. M.; Yang, C.; Nolan, S. P. *J. Organomet. Chem.* **2002**, *653*, 69.
(26) Herrmann, W. A.; Öfele, K.; von Preysing, D.; Schneider, S. K. *J. Organomet. Chem.* **2003**, *687*, 229.
(27) Christmann, U.; Vilar, R. *Angew. Chem., Int. Ed.* **2005**, *44*, 366.
(28) Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Angew. Chem., Int. Ed.* **2007**, *46*, 2768.
(29) Würtz, S.; Glorius, F. *Acc. Chem. Res.* **2008**, *41*, 1523.
(30) Marion, N.; Nolan, S. P. *Acc. Chem. Res.* **2008**, *41*, 1440.
(31) Organ, M. G.; Çalimsiz, S.; Sayah, M.; Hoi, K. H.; Lough, A. J. *Angew. Chem., Int. Ed.* **2009**, *48*, 2383.
(32) de Frémont, P.; Marion, N.; Nolan, S. P. *Coord. Chem. Rev.* **2009**, *253*, 862.
(33) Fliedel, C.; Braunstein, P. *Organometallics* **2010**, *29*, 5614.
(34) Valente, C.; Çalimsiz, S.; Hoi, K. H.; Mallik, D.; Sayah, M.; Organ, M. G. *Angew. Chem., Int. Ed.* **2012**, *51*, 3314.

(35) Organ, M. G.; Çalimsiz, S.; Sayah, M.; Hoi, K. H.; Lough, A. J. *Angew. Chem., Int. Ed.* **2009**, *48*, 2383.
(36) Pompeo, M.; Froese, R. D. J.; Hadei, N.; Organ, M. G. *Angew. Chem., Int. Ed.* **2012**, *51*, 11354.
(37) Nasielski, J.; Hadei, N.; Achonduh, G.; Kantchev, E. A. B.; O'Brien, C. J.; Lough, A.; Organ, M. G. *Chem. Eur. J.* **2010**, *16*, 10844.
(38) Ray, L.; Shaikh, M. M.; Ghosh, P. *Dalton Trans.* **2007**, *0*, 4546.
(39) Li, H.; Johansson Seechurn, C. C. C.; Colacot, T. J. *ACS Catal.* **2012**, *2*, 1147.
(40) Ke, C.-H.; Kuo, B.-C.; Nandi, D.; Lee, H. M. *Organometallics* **2013**, *32*, 4775.
(41) Gründemann, S.; Kovacevic, A.; Albrecht, M.; Faller, J. W.; Crabtree, R. H. *J. Am. Chem. Soc.* **2002**, *124*, 10473.
(42) Appelhans, L. N.; Zuccaccia, D.; Kovacevic, A.; Chianese, A. R.; Miecznikowski, J. R.; Macchioni, A.; Clot, E.; Eisenstein, O.; Crabtree, R. H. *J. Am. Chem. Soc.* **2005**, *127*, 16299.
(43) Grundemann, S.; Kovacevic, A.; Albrecht, M.; Faller Robert, J. W.; Crabtree, H. *Chem. Commun.* **2001**, *0*, 2274.
(44) Esposito, O.; Roberts, D. E.; Cloke, F. G. N.; Caddick, S.; Green, J. C.; Hazari, N.; Hitchcock, P. B. *Eur. J. Inorg. Chem.* **2009**, *2009*, 1844.
(45) Poulain, A.; Iglesias, M.; Albrecht, M. *Curr. Org. Chem.* **2011**, *15*, 3325.
(46) Baker, M. V.; Brown, D. H.; Simpson, P. V.; Skelton, B. W.; White, A. H. *Eur. J. Inorg. Chem.* **2009**, *2009*, 1977.
(47) Chen, M.-T.; Vicic, D. A.; Turner, M. L.; Navarro, O. *Organometallics* **2011**, *30*, 5052.
(48) Li, S.; Lin, Y.; Cao, J.; Zhang, S. *J. Org. Chem.* **2007**, *72*, 4067.
(49) Guo, M.; Zhang, Q. *Tetrahedron Lett.* **2009**, *50*, 1965.
(50) Verma, P. R.; Mandal, S.; Gupta, P.; Mukhopadhyay, B. *Tetrahedron Lett.* **2013**, *54*, 4914.
(51) Kinzel, T.; Zhang, Y.; Buchwald, S. L. *J. Am. Chem. Soc.* **2010**, *132*, 14073.
(52) Johansson Seechurn, C. C. C.; Parisel, S. b. L.; Colacot, T. J. *J. Org. Chem.* **2011**, *76*, 7918.
(53) Liao, C.-Y.; Chan, K.-T.; Tu, C.-Y.; Chang, Y.-W.; Hu, C.-H.; Lee, H. M. *Chem. Eur. J.* **2009**, *15*, 405.
(54) Bedford, R. B.; Cazin, C. S. J.; Coles, S. J.; Gelbrich, T.; Horton, P. N.; Hursthouse, M. B.; Light, M. E. *Organometallics* **2003**, *22*, 987.
(55) Lee, C.-C.; Ke, W.-C.; Chan, K.-T.; Lai, C.-L.; Hu, C.-H.; Lee, H. M. *Chem. Eur. J.* **2007**, *13*, 582.
(56) Bolliger, J. L.; Blacque, O.; Frech, C. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 6514.
(57) Wolfe, J. P.; Singer, R. A.; Yang, B. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 9550.
(58) Santos, L. S.; Knaack, L.; Metzger, J. O. *Int. J. Mass Spectrom.* **2005**, *246*, 84.
(59) Heckenroth, M.; Kluser, E.; Neels, A.; Albrecht, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 6293.
(60) Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomben, K. D. *Handbook of X-ray Photoelectron Spectroscopy*. Perkin-Elmer Corp.: Eden Prarie, MN, 1992.
(61) *APEX2 and SAINT*; Bruker AXS Inc., Madison, WI, USA, 2007.
(62) Sheldrick, G. M. *SADABS*; University of Göttingen, Göttingen, Germany, 1996.
(63) Sheldrick, G. *Acta Crystallogr., Sect. A* **2008**, *A64*, 112.
(64) Zhao, Y.; Truhlar, D. *Theor. Chem. Acc.* **2008**, *120*, 215.
(65) Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *106*, 5151.
(66) Cossi, M.; Scalmani, G.; Rega, N.; Barone, V. *J. Chem. Phys.* **2002**, *117*, 43.
(67) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.