ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

Sterically Encumbered Tetraarylimidazolium Carbene Pd-PEPPSI Complexes: Highly Efficient Direct Arylation of Imidazoles with Aryl Bromides under Aerobic Conditions

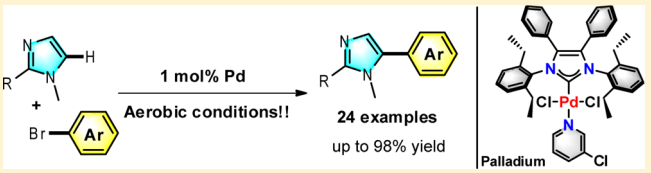
Xu-Xian He,[†] Yinwu Li,[‡] Bei-Bei Ma,[†] Zhuofeng Ke,*[,‡] and Feng-Shou Liu*[,†]

[†]School of Chemistry and Chemical Engineering, Guangdong Pharmaceutical University, Zhongshan, Guangdong 528458, People's Republic of China

[‡]MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, School of Materials Science and Engineering, Sun Yat-sen University, Guangzhou 510275, People's Republic of China

Supporting Information

ABSTRACT: A series of sterically encumbered tetraarylimidazolium carbene Pd-PEPPSI complexes were conveniently prepared and fully characterized. These sterically encumbered Pd-PEPPSI complexes act as active precatalysts for the direct arylation of imidazoles with aryl bromides under aerobic conditions. The catalytic performance of Pd-PEPPSI complexes in cross-coupling processes is investigated. Under the optimal protocols, the cross-coupling reactions regioselectively produced C5-arylation products in moderate to excellent yields, which could tolerate a wide range of functional aryl bromides.



INTRODUCTION

Over the past decade, the palladium-catalyzed direct arylation reactions of heteroarenes with aryl halides have become some of the most reliable approaches to assemble skeletons for pharmaceuticals and functional materials.[1,2] These reactions exploit the direct activation of the C−H bonds of heteroarenes, which are atom economical and environmentally friendly and avoid the need for prefunctionalization of organometallic derivatives in traditional palladium-catalyzed cross-couplings.[3] However, it is also quite challenging for the arylation of imidazoles, because a kinetically significant aryl C−H bond activation step is involved.[4] By far, $Pd(OAc)_2$ species associated with various phosphines or nitrogen-based ligands are the most common catalytic systems for direct arylation of imidazoles. Ligands such as PPh_3,[5] $AsPh_3$,[6] Pcy_3,[7] $P(2\text{-furyl})_3$,[8] P(*n*-Bu)Ad_2,[9] dppb,[10] X-phos,[11] and Xantphos[12] as well as 1,10-phenanthroline[13] have been commonly employed. In parallel, the recent development of N-heterocyclic carbenes (NHCs) as prospective ligands has been regarded as promising, since their strong σ donation and easily tunable steric properties have important advantages over their phosphine counterparts.[14] For instance, Lee and co-workers have shown that Pd(**L**)(PCy_3)-$(OAc)_2$ (**L** = 1,3-dibenzylimidazol-2-ylidene) successfully catalyzed direct C5-arylation reactions between imidazoles and aryl halides.[14c] Recently, Huynh found that the heterotetrakis(carbene) complexes $[PdX_2(^iPr_2\text{-bimy})]_2(\mu\text{-ditz})$ (X = Br, CH_3COO, CF_3COO; $^iPr_2$-bimy = 1,3-diisopropylbenzimidazolin-2-ylidene; μ-ditz = diNHC ligand 1,2,4-trimethyltriazolidine-3,5-diylidene) can catalyze the direct C−H arylation of imidazoles with aryl iodides and aryl bromides in moderate yields.[14d]

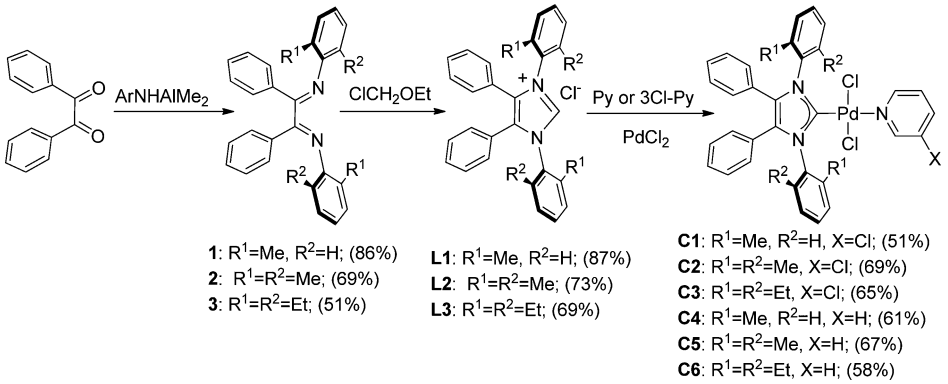
Despite the significant progress that has been achieved in traditional palladium-catalyzed cross-coupling reactions,[15] the application of NHC palladium complexes to the direct C−H arylation of imidazoles with aryl halides is relatively rare and some shortcomings still remain. In most cases, the substrate scope is generally limited, and a high palladium loading of 2.5−5 mol % is required in these catalytic processes. Moreover, even though NHC palladium precursors are generally stable to heat and moisture, their catalytic species are often sensitive to the presence of oxygen, forming the unreactive peroxo species $LPd(O_2)$ rapidly, which demands an anhydrous and oxygen-free environment during their catalytic reactions.[16] Consequently, it is challenging to achieve direct C−H bond arylation under aerobic conditions with the NHC palladium complexes.

The catalytic activities of NHC palladium complexes are directly related to the unique properties of the supporting NHCs: their σ-donor character and their steric environment. Both properties have strong effects on the oxidative addition and reductive elimination processes in palladium-catalyzed cross-coupling reactions. Therefore, the development of a new NHC catalytic system to overcome these difficulties is highly desired. To date, although the design of NHC palladium complexes is mainly based on tuning steric hindrance in *N*-phenyl rings, it is noteworthy that the introduction of bulky ligands into the skeleton of NHC palladium complexes has emerged as a powerful strategy.[17] For example, César and Lavigne found that the adjunction of one or two *N*,*N*-dimethyl groups into the backbone framework of IPr, which greatly

Received: May 13, 2016

DOI: 10.1021/acs.organomet.6b00391
Organometallics XXXX, XXX, XXX−XXX

Scheme 1. Synthesis of Tetraarylimidazolium Palladium Complexes



increased the electron-donating ability of the carbene ligand, result in highly efficient catalytic performance in the Buchwald–Hartwig amination reaction.[17d] However, the synthetic procedures for these complexes involve multiple steps with harsh reaction conditions. Moreover, it is notable that NHCs with diaryl backbones, namely tetraarylimidazolium carbenes, also show great electron-donor ability.[18] Inspired by the promisingly strong σ-donation ability of the tetraarylimidazolium carbenes, we envision that strong binding of these kinds of electron-rich and bulky carbene ligands will help in the validation of the Pd–$C_{carbene}$ bond and enhance the stability of palladium complexes. Therefore, an expected excellent reactivity throughout the course of direct arylation could be achieved under mild reaction conditions. Herein, we describe a series of generally applicable Pd-PEPPSI complexes with a "larger steric hindrance backbone" (Scheme 1) for efficient and direct C-5 arylation of imidazoles with aryl bromides.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Tetraarylimidazolium Carbene Ligands and the Pd-PEPPSI Complexes. The procedures for the synthesis of sterically encumbered tetraarylimidazolium carbene ligands and the corresponding Pd-PEPPSI complexes **C1–C6** are shown in Scheme 1. Previously, the key intermediates of α-diimine compounds were prepared by intermolecular cyanide-catalyzed aldimine coupling or simply acid-catalyzed condensation.[19] However, the preparation of α-diimines bearing steric bulk in the *N*-phenyl rings with a diphenyl backbone failed using traditional methods. To overcome this synthetic challenge, we undertook a strategy to condense anilines onto benzil via trimethylaluminum-promoted routes, and it afforded the desired products **1–3** in high yields.[20] The respective imidazolium salts **L1–L3** were subsequently obtained by the cyclization of the α-diimines with chloromethyl ethyl ether, giving moderate to high yields (69–87%). The formation of a NC*H*N bond in the imidazolium salts was confirmed by the characteristic signals in ^{1}H NMR spectra, in which the resonance of imidazolium C–H protons appeared at δ 10.06–11.61 ppm. We considered that unsymmetrical 2-methyl substitution on the *N*-phenyl moiety, of both the α-diimine (**1**) and imidazolium salt (**L1**), would exhibit isomers. However, there no splitting of peaks was observed in the NMR spectrum, which indicates the rapid rotation of the C_{Ar}–N bond in these cases in solution. Nevertheless, attempts to synthesize the imidazolium salt with a 2,6-diisopropyl group on the *N*-phenyl rings did not lead to the desired product, instead giving a black oil of complicated composition. To access this compound, a variety of methods, such as using $ZnCl_2$/paraformaldehyde and AgOTf/chloromethyl pivalate, were explored; however, this resulted in no benefit.[21]

With these imidazolium salts in hand, we then started metalation studies using the one-pot method developed by Organ and co-workers for the synthesis of Pd-PEPPSI complexes.[22a] Thus, using K_2CO_3 as base and pyridine or 3-chloropyridine as solvent, the treatment of ligand precursors **L1–L3** with $PdCl_2$ smoothly afforded **C1–C6** in moderate yields of 51–69%. To our delight, all of these Pd-PEPPSI complexes proved to be both air- and moisture-stable and could be stored on the shelf. They were readily soluble in dichloromethane and chloroform but insoluble in diethyl ether and hydrocarbon solvents. The structures of **C1–C6** were fully characterized by NMR, ESI-MS, and elemental analysis and further confirmed by X-ray single-crystal diffraction. In the ^{1}H NMR spectra of **C1–C6**, the resonances for the imidazolium C–H protons (NC*H*N) had disappeared, and the chemical shifts of other protons were similar to those of the corresponding precursors. The chemical shift of the α-hydrogen on pyridines appeared at δ 8.58–8.50 ppm, which was observed to be shifted upfield in comparison with their corresponding free pyridines (δ 8.62 ppm).[22b] In the ^{13}C NMR spectra, the signals of the Pd–$C_{carbene}$ in **C1–C6** appear at 153.7–150.1 ppm, which were similar to those of the reported Pd-PEPPSI complexes.[23] Moreover, unlike the behavior of α-diimine (**1**) and imidazolium salt (**L1**), **C1** and **C4** exhibited two isomers in solution, indicating that the molecules could adopt syn and anti configurations. Reasonably, the C_{Ar}–N bond rotation which would freely occur in the case of **1** and **L1** would be retarded when the coordinated palladium was used.

Single crystals of **C1**, **C2**, and **C4** suitable for X-ray diffraction studies were obtained by layering their dichloromethane solutions with hexane at ambient temperature (Figures 1–3). Because of the unsymmetrical substitution of the methyl in **C1** and **C4**, the solid molecules could adopt a syn or anti configuration. As can be seen in Figures 1 and 3, these two single crystals exhibited an anti configuration with the methyl fragments pointing toward each other above and below the NHC ring. The palladium atoms in these structures adopt a slightly distorted square planar coordination geometry with the NHC and pyridine ligands trans to each other. The *N*-phenyl rings were found to be approximately perpendicular to the NHC ring with dihedral angles of 71.10 (67.70), 81.83 (81.79), and 69.19° (67.87°), for complexes **C1**, **C2**, and **C4**, respectively. These data suggest that greater steric repulsion

DOI: 10.1021/acs.organomet.6b00391
Organometallics XXXX, XXX, XXX–XXX

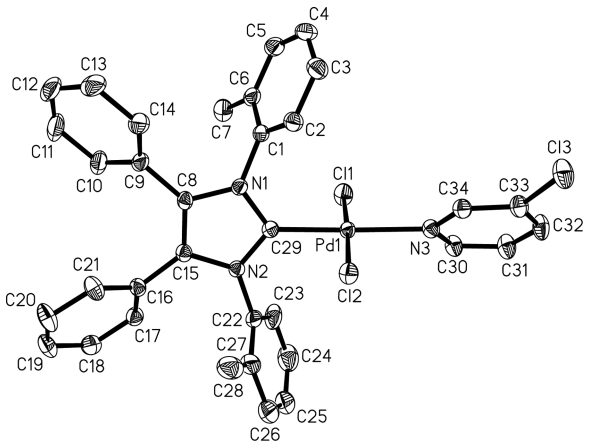


Figure 1. Molecular structure of **C1** depicted with 30% thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Pd(1)−C(29) 1.957(3), Pd(1)−N(3) 2.109(2), Pd(1)−Cl(1) 2.3083(9), Pd(1)−Cl(2) 2.3053(8); N(3)−Pd(1)−C(29) 177.69(11), N(3)−Pd(1)−Cl(1) 91.81(8), C(29)−Pd(1)−Cl(1) 89.29(9), N(3)−Pd(1)−Cl(2) 90.34(8), C(29)−Pd(1)−Cl(2) 88.63(9), Cl(1)−Pd(1)−Cl(2) 177.13(3).

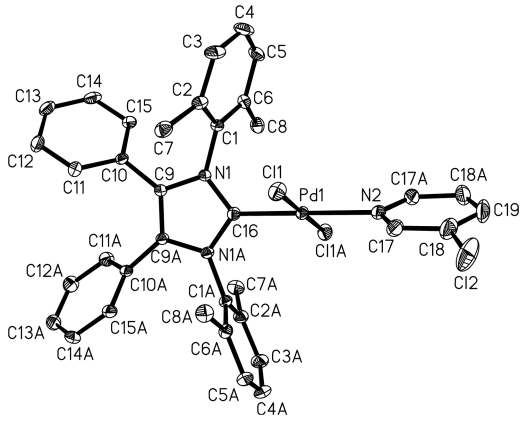


Figure 2. Molecular structure of **C2** depicted with 30% thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Pd(1)−C(16) 1.979(2), Pd(1)−N(2) 2.125(2), Pd(1)−Cl(1) 2.3086(5), Pd(1)−Cl(1A) 2.3086(5); N(2)−Pd(1)−C(16) 180.0, N(2)−Pd(1)−Cl(1) 89.735(11), C(16)−Pd(1)−Cl(1) 90.265(11), N(2)−Pd(1)−Cl(1A) 89.735(11), C(16)−Pd(1)−Cl(1A) 90.265(11), Cl(1)−Pd(1)−Cl(1A) 179.47(2).

of the bulky substituents on the *N*-phenyl ring would cause more shielding on the apical positions of the palladium center. Moreover, dihedral angles between the diphenyl framework and NHC ring were evaluated, which turned out to be 47.02 (43.74°), 49.33 (49.31) and 47.55° (46.13°) for complexes **C1**, **C2**, and **C4**, respectively. Obviously, the backbones of the diphenyl also exhibit a certain steric effect on retarding the rotation of the *N*-phenyl rings, which would provide further protection for the metal center. The Pd−N_{Py} and Pd−Cl bond lengths are quite similar to those for the reported Pd-PEPPSI complexes.[23] On the other hand, the Pd−$C_{carbene}$ bond length in **C2** (1.979(2) Å) is much longer than that of the [Pd(IMes)(3-ClPy)Cl_2] analogue (1.962(4) Å). This is presumably also due to the bulky steric hindrance brought about by the diphenyl framework. In order to further understand the spatial situation of the palladium center, the percent buried volumes (%V_{Bur}) of the investigated NHC ligands were obtained using the web application SambVca.[24]

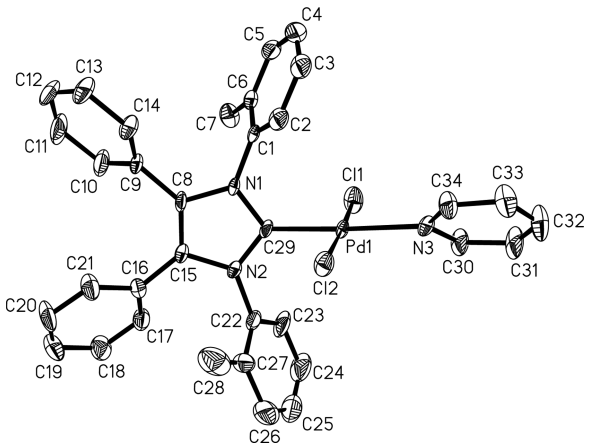


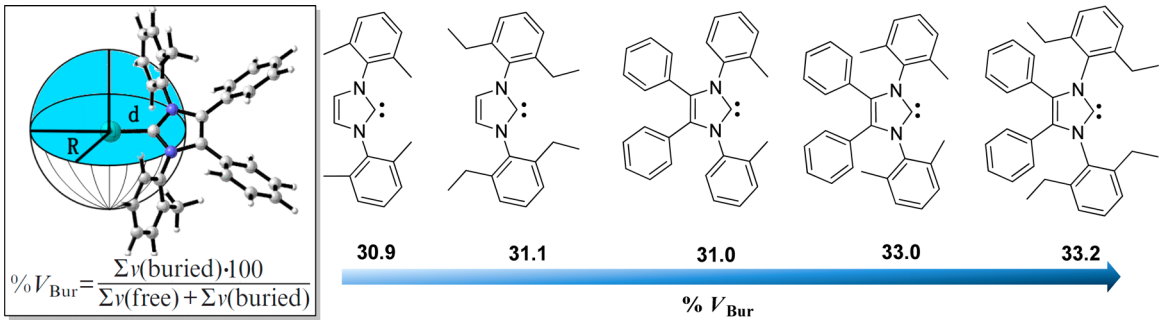
Figure 3. Molecular structure of **C4** depicted with 30% thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Pd(1)−C(29) 1.944(5), Pd(1)−N(3) 2.099(5), Pd(1)−Cl(1) 2.3044(16), Pd(1)−Cl(2) 2.3124(14),; N(3)−Pd(1)−C(29) 176.40(18), N(3)−Pd(1)−Cl(1) 92.32(13), C(29)−Pd(1)−Cl(1) 89.54(14), N(3)−Pd(1)−Cl(2) 91.14(13), C(29)−Pd(1)−Cl(2) 87.05(14), Cl(1)−Pd(1)−Cl(2) 176.45(5).

The Pd-PEPPSI complex structures were fully optimized with the BP86 functional[25] as implemented in the Gaussian09 program.[26] The triple-ζ SBK ECP basis set was used for palladium and the 6-31G* set was used for main-group atoms.[27] It was shown that the structural differences between optimized structures and solid-state structures are very small (Table S1 in the Supporting Information). As shown in Chart 1, the range of buried volumes lies between 30.9 and 33.2% for the NHC ligands in Pd-PEPPSI complexes. Unsurprisingly, with a buried volume of 31.0−33.2%, the tetraaryl NHC ligands were found to be more sterically encumbered than the IMe (%V_{Bur} = 30.9%) and IEt (%V_{Bur} = 31.1%) ligands.

Direct C−H Bond Arylation Catalyzed by Pd-PEPPSI Complexes. To verify the robust catalytic efficiency of the synthesized bulky Pd-PEPPSI complexes in hand, direct arylation reactions were carried out without the need for anhydrous conditions or an inert atmosphere. Initially, the reaction of 1-methyl-1*H*-imidazole (**7a**) with 1-bromo-4-chlorobenzene (**8a**) was examined as a model reaction in the presence of pivalic acid (PivOH) and K_2CO_3 in *N*,*N*-dimethylacetamide (DMAc) at 130 °C. In the preliminary studies, regioselective arylation on the C5 position was observed because the hydrogen on C5 is more reactive than that on the C4 position.[28] Moreover, in the course of this reaction, no cleavage of the carbon−chlorine bond of the product was detected. Then, a variety of palladium precatalysts were evaluated. As illustrated in entry 1 of Table 1, a yield of 49% was obtained when 5 mol % of $Pd(OAc)_2$ was applied, which is compatible with the results reported by Bellina.[29] However, the poor efficiency in the ligand-free catalytic system suggested that the catalytic species tend to be deactivated in the absence of ligand protection under aerobic conditions. In contrast, Pd-PEPPSI-IEt, with 2,6-diethyl substituents on each *N*-phenyl ring, was then evaluated. This resulted in a moderate efficiency of 52% yield when a palladium loading of 0.5 mol % was used (entry 2, Table 1). Moreover, the sterically bulky Pd-PEPPSI-IPr bearing 2,6-diisopropyl groups on the *N*-phenyl moiety afforded a very efficient yield of 93% (entry 3, Table 1). With the tetraarylimidazolium type of Pd-PEPPSI complexes in hand, we found that **C3**, bearing 2,6-diethyl substituents on *N*-

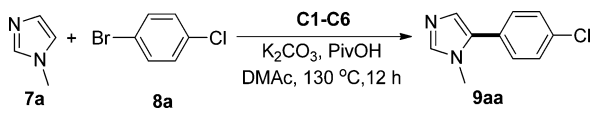
DOI: 10.1021/acs.organomet.6b00391
Organometallics XXXX, XXX, XXX−XXX

Chart 1. Comparison of the Buried Volume (%V_{Bur}) of NHC Ligands in Pd-PEPPSI Complexes[a]



[a]The buried volume of NHC ligands in the Pd-PEPPSI complexes were obtained via SambVca with DFT optimized [Pd(NHC)(3Cl-Py)Cl_2] structures. Parameters: sphere radius, 3.5; distance from the center of the sphere, 2.10; bond radii scaled by 1.17.

Table 1. Screening of the Precatalysts on Direct Arylation[a]



entry	cat.	Pd (mol %)	yield (%)[b]	selectivity (%)[d]
1	$Pd(OAc)_2$	5	49	99
2	Pd-PEPPSI-IEt	0.5	52	98
3	Pd-PEPPSI-IPr	0.5	93	98
4	**C1**	0.5	46	97
5	**C2**	0.5	59	96
6	**C3**	0.5	74	97
7	**C4**	0.5	43	98
8	**C5**	0.5	57	97
9	**C6**	0.5	64	96
10	**C1**	1	74	97
11	**C2**	1	83	97
12	**C3**	1	**88 (84)**[c]	98
13	**C4**	1	71	98
14	**C5**	1	66	97
15	**C6**	1	86	97

[a]Reaction conditions: 1-methyl-1*H*-imidazole (2 mmol), 1-bromo-4-chlorobenzene (1 mmol), palladium source (0.5−5 mol %), PivOH (0.3 mmol), K_2CO_3 (2 mmol), DMAc (3 mL), 130 °C, 12 h, in an aerobic atmosphere. [b]GC yield using (trifluoromethyl)benzene as an internal standard. [c]Isolated yields in parentheses. [d]Percent yield of the C5-arylated product (there is a trace amount of C4-arylated product).

phenyl ring, gave a satisfactory yield of 74% (entry 6, Table 1). Although **C3** exhibited lower productivity to some extent in comparison to commercial Pd-PEPPSI-IPr with a bulkier *N*-phenyl moiety, its catalytic efficiency was also promising. This study indicates that the shielding of the palladium center with bulky backbones could enhance the catalytic activity, proving the superiority of the tetraarylimidazolium Pd-PEPPSI complexes.

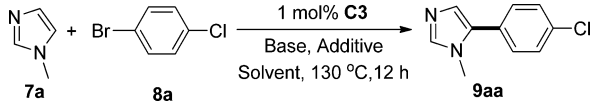
Moreover, the substituents on the *N*-phenyl ring on the NHC (**C1**−**C6**) were also found to play a key role in governing the efficiencies of catalysts. As can be seen in Table 1, the sterically demanding NHC ligands afforded higher conversion to the desired product. For example, **C1** (%V_{Bur} = 31.0%, Chart 1), with a 2-methyl substituent on the *N*-phenyl ring, showed moderate efficiency and provided a GC yield of 46% (entry 4, Table 1). In comparison, when the size of the substituent was increased through the use of 2,6-dimethyl and 2,6-diethyl substituents (**C2** and **C3**), higher yields of 59−74% were obtained (entries 5 and 6, Table 1). These observed results are in good agreement with the trends in the buried volumes of tetraaryl NHC ligands, implying that sterically bulky species would lead to fast reductive elimination, which suppresses undesired side reactions and catalyst decomposition in aerobic conditions. In addition to the dominant NHC ligands, the effect of ancillary ligands was also evaluated and it was found that 3-chloropyridine showed activities slightly higher than those of the pyridine analogues. Probably, the more electron-deficient ancillary ligands would favor their release from the Pd(0) during the reaction process, therefore liberating the catalytic species.[23] In order to promote the cross-coupling reaction further, a high palladium loading of 1 mol % was performed. To our delight, we found that **C3** was the optimal precatalyst, providing the desired coupling product in 88% yield (entry 12, Table 1).

This preliminary result encouraged us to optimize the reaction conditions with **C3** as precatalyst. As shown in Table 2, the bases were crucial to the efficiency of this reaction. Among a variety of bases screened, K_2CO_3 displayed the highest reactivity. K_3PO_4, KOAc, and Cs_2CO_3 were inferior, while NaO^{t}Bu shut down the reaction completely (entries 1−5, Table 2). The influence of the nature of the acid additives was subsequently examined. It is noteworthy that, in the absence of PivOH, the reaction delivered the product in poor to low yields (entries 6−14, Table 2). Obviously, the excellent performance of the acid additive of PivOH is consistent with a concerted metalation−deprotonation (CMD) pathway in the catalytic process.[30] Further screening of solvents revealed that DMAc was the best solvent for the present system. Other solvents, such as DMF, NMP, toluene, dioxane, and xylene, were less effective, and DMSO was ineffective. Thus, the optimal result was obtained by using 1 mol % of **C3**, K_2CO_3 as base, and PivOH as acid additive in DMAc at 130 °C for 12 h. Under these reaction conditions, minor side reactions, such as homocoupling of the aryl bromides and C-4 arylation of the imidazole, were observed during the course of this reaction.

With the optimized protocol in hand, we next set out to explore the substrate scope of the aryl bromides for the direct arylation of 1-methyl-1*H*-imidazole (Table 3). Gratifyingly, a wide range of functional groups on the aryl bromides, such as chloro, cyano, ester, nitro, aldehyde, acetyl, trifluoromethyl, and fluoro, were well tolerated, producing the corresponding products **9aa**−**ah**) in high to excellent yields (70−96%). It is noteworthy that the utilization of sterically hindered 1-naphthyl bromide afforded the desired coupling product **9aj** in excellent yield (94%). Moreover, we found that a heteroaryl bromide such as 4-bromoisoquinoline was compatible and a satisfactory

DOI: 10.1021/acs.organomet.6b00391
Organometallics XXXX, XXX, XXX−XXX

Table 2. Optimization of Conditions in Direct Palladium-Catalyzed Cross-Coupling Reactions[a]



entry	solvent	base	additives	yield (%)[b]	selectivity (%)[c]
1	DMAc	K_2CO_3	PivOH	88	98
2	DMAc	K_3PO_4	PivOH	74	98
3	DMAc	KOAc	PivOH	30	94
4	DMAc	Cs_2CO_3	PivOH	27	95
5	DMAc	NaOtBu	PivOH	NR	
6	DMAc	K_2CO_3		5	96
7	DMAc	K_3PO_4		19	91
8	DMAc	KOAc		NR	
9	DMAc	Cs_2CO_3		32	96
10	DMAc	NaOtBu		NR	
11	DMAc	K_2CO_3	HOAc	45	97
12	DMAc	K_2CO_3	PhCOOH	10	93
13	DMAc	K_2CO_3	CF_3COOH	NR	
14	DMAc	K_2CO_3	PivOH+TBAB	73	97
15	DMF	K_2CO_3	PivOH	63	97
16	NMP	K_2CO_3	PivOH	77	98
17	DMSO	K_2CO_3	PivOH	NR	
18	toluene	K_2CO_3	PivOH	17	97
19	dioxane	K_2CO_3	PivOH	23	97
20	xylene	K_2CO_3	PivOH	9	92

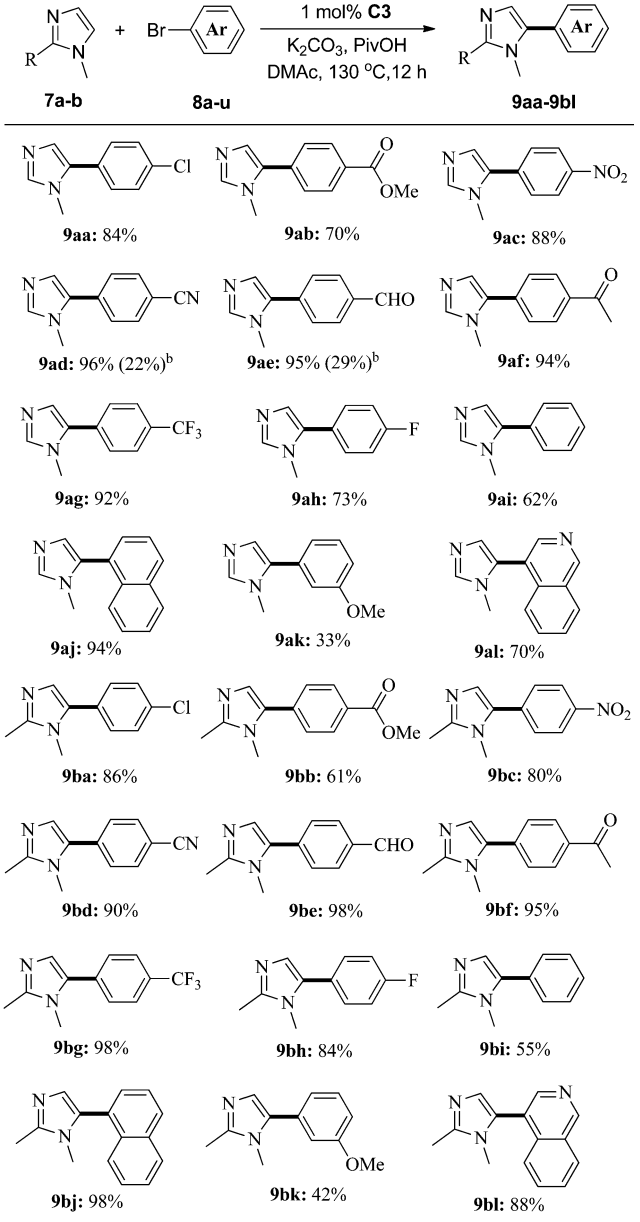
[a]Conditions: 1-methyl-1*H*-imidazole (2.0 mmol), 1-bromo-4-chlorobenzene (1.0 mmol), **C3** (1 mol %), additives (0.3 mmol), base (2 mmol), solvent (3 mL), 130 °C, 12 h, in an aerobic atmosphere. [b]GC yield using (trifluoromethyl)benzene as an internal standard. [c]Percent yield of the C5-arylated product (there is a trace amount of C4-arylated product).

yield of 70% (**9al**) was obtained. However, introducing electron-donating substituents on the aryl bromide lowered the activity. For example, in the case of 3-bromoanisole, the reaction produced **9ak** in a much lower yield of 33%. Additionally, we investigated the direct arylation between other imidazoles and aryl bromides, such as 1,2-dimethyl-1*H*-imidazole (**7b**). As shown in Table 3, we were pleased to find that the cross-coupling products **9ba**–**bl** were obtained in good yields. A variety of aryl bromides bearing electron-withdrawing and electron-donating substituents, as well as heteroaryl bromides, were compatible. Moreover, more challenging aryl chlorides such as 4-chlorobenzonitrile and 4-chlorobenzaldehyde were used. However, this revealed that the efficiency decreased dramatically, affording the desired products **9ad**,**ae** in 22% and 29% yields, respectively.

CONCLUSION

In summary, a series of sterically encumbered tetraarylimidazolium carbene Pd-PEPPSI complexes have been conveniently synthesized and fully characterized. These complexes have been utilized for the direct arylation of imidazoles with aryl bromides, which demonstrated a powerful strategy in Pd-PEPPSI catalyst design on backbones. Remarkably, these protocols are atom economical and general for various coupling partners in moderate to excellent yields in aerobic conditions at a low palladium loading.

Table 3. Palladium-Catalyzed Direct Arylation of Imidazole with Aryl Bromides[a]



[a]Conditions: imidazoles (2.0 mmol), aryl bromide (1.0 mmol), **C3** (1 mol %), PivOH (0.3 mmol), K_2CO_3 (2 mmol), DMAc (3 mL), 130 °C, 12 h, in an aerobic atmosphere. Isolated yields are given . [b]Isolated yield in parentheses when aryl chloride was used as the substrate.

EXPERIMENTAL SECTION

Physical Measurements and Materials. 2-Aminotoluene, 2,6-dimethylaniline, and 2,6-diethylaniline were purchased from Aldrich Chemical and were distilled under reduced pressure before being used. Palladium chloride and trimethylaluminum (2 M, hexane) was purchased from Aldrich Chemical. Benzil, chloromethyl ethyl ether, pyridine, 3-chloropyridine, inorganic bases, and the solvents were purchased from Guangzhou Chemical Reagent Factory and were used as received. 1-Methyl-1*H*-imidazole, 1,2-dimethyl-1*H*-imidazole, and the aryl bromides were purchased from Darui Chemical Reagent Factory. The α-diimine compound [2,6-$(CH_3)_2C_6H_3$)N*=C(Ph)C-(Ph)=N(2,6-$(CH_3)_2$-C_6H_3)] (**2**) was prepared according to our previous report.[20] Pd-PEPPSI-IEt was synthesized according to literature methods.[23]

DOI: 10.1021/acs.organomet.6b00391
Organometallics XXXX, XXX, XXX−XXX

The NMR data of compounds were obtained on a Varian Mercury-Plus 400 MHz spectrometer at ambient temperature with the decoupled nucleus, using $CDCl_3$ as solvent, and referenced versus TMS as a standard. Elemental analyses were determined with a Vario EL Series Elemental Analyzer from Elementar. The X-ray diffraction data of single crystals were obtained with the $\omega-2\theta$ scan mode on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 173 K for **C1**, **C2**, and **C4**. The structure was solved using direct methods, and further refinement with full-matrix least squares on F^2 was obtained with the SHELXTL program package.[31] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms.

General Procedures for the Synthesis of α-Diimine Compounds. Aniline (24 mmol) was diluted in toluene under a nitrogen atmosphere, trimethylaluminum (12 mL, 2 M) was added through a syringe at ambient temperature, and then the reaction mixture was heated to 90 °C for 2 h. When the determined time was reached, the solution was cooled and the reaction mixture was carefully treated with benzil (2.10 g, 10 mmol). The reaction mixture was refluxed for another 6 h. After completion of the reaction, the reaction mixture was cooled to room temperature, hydrolyzed with 5% aqueous NaOH solution, and then stirred for another 1 h. After stirring was stopped for a moment, the mixture was layered, the aqueous layer was extracted three times with ethyl acetate, and then the organic layers were combined, dried over anhydrous magnesium sulfate, filtered, and concentrated under vacuum. The resulting crude oil was purified by column chromatography as bright yellow to yellow crystals.

*[(2-$CH_3C_6H_4$)N=C(Ph)C(Ph)=N(2-$CH_3C_6H_4$)] (**1**).* This compound was obtained as bright yellow crystals in 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 7.6 Hz, Ar-H, 4H), 7.47-7.39 (m, Ar-H, 6H), 6.93-6.87 (m, Ar-H, 4H), 6.77 (t, J = 7.2 Hz, Ar-H, 2H), 6.49 (d, J = 7.8 Hz, Ar-H, 2H), 1.28 (s, CH_3, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.5, 147.9, 138.3, 132.3, 130.9, 129.9, 128.7, 128.4, 125.5, 125.0, 116.7, 16.6.

*[(2,6-$(C_2H_5)_2C_6H_3$)N=C(Ph)C(Ph)=N(2,6-$(C_2H_5)_2C_6H_3$)] (**3**).* This compound was obtained as bright yellow crystals in 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.21 (s, Ar-H, 2H), 7.53 (s, Ar-H, 2H), 7.25 (t, Ar-H, 4H), 6.94 (d, Ar-H, 7H), 6.73 (s, Ar-H, 1H), 2.63-1.78 (m, CH_2, 8H), 1.07 (t, CH_3, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 165.3, 164.5, 146.7, 146.1, 138.1, 134.8, 131.8, 131.7, 131.0, 130.8, 129.6, 128.6, 127.8, 127.6, 125.8, 125.3, 124.9, 124.1, 24.7, 24.1, 13.6, 13.0.

General Procedures for the Synthesis of Tetraarylimidazolium Salts. α-Diimine compounds and chloromethyl ethyl ether were combined under a nitrogen atmosphere at room temperature, and then the reaction mixture was heated to 100 °C overnight. When the determined time was reached, the solution was cooled to room temperature, and the reaction mixture was treated with anhydrous Et_2O and stirred for 1 h, causing the formation of a great deal of precipitate. The solid was isolated by filtration and washed three times with anhydrous Et_2O. The resulting crude product was generally obtained in excellent purity, and no further purification was required.

*[(2-$CH_3C_6H_4$)NC(Ph)]$_2CH_2^+Cl^-$ (**L1**).* This compound was obtained as a yellowish powder (0.760 g, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.06 (s, C2-H, 1H), 7.98 (s, Ar-H, 2H), 7.39-7.18 (m, Ar-H, 15H), 6.60 (s, Ar-H, 1H), 2.19 (s, CH_3, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.0, 137.2, 133.9, 132.4, 131.0, 130.4, 129.9, 128.9 128.6, 124.8, 17.7. ESI-MS: m/z 401.0, [**L1** − Cl]$^+$ ($C_{29}H_{25}N_2^+$, calcd 401.52).

*[(2,6-$(CH_3)_2C_6H_3$)NC(Ph)]$_2CH_2^+Cl^-$ (**L2**).* This compound was obtained as a yellowish powder (0.684 g, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.44 (s, C2-H, 1H), 7.33 (m, Ar-H, 4H), 7.22 (s, Ar-H, 8H), 7.01 (m, Ar-H, 4H), 2.24 (s, CH_3, 12H) ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.1, 135.0, 131.9, 131.6, 131.0, 130.2, 129.6, 129.2, 128.9, 124.7, 18.3. ESI-MS: m/z 429.1, [**L2** − Cl]$^+$ ($C_{31}H_{29}N_2^+$, calcd 429.57).

*[(2,6-$(C_2H_5)_2C_6H_3$)NC(Ph)]$_2CH_2^+Cl^-$ (**L3**).* This compound was obtained as a yellowish powder (0.723 g, 69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.61 (s, C2-H, 1H), 7.48 (t, J = 7.7 Hz, Ar-H, 2H), 7.34- 7.29 (m, Ar-H, 4H), 7.24-7.19 (q, Ar-H, 6H), 7.01 (d, J = 8.0 Hz, Ar-H, 4H), 2.67-2.58 (m, CH_2, 4H), 2.43-2.36 (m, CH_2, 4H), 1.25 (t, J = 7.5 Hz, CH_3, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.1, 132.0, 131.3, 130.1, 130.0, 129.6, 128.7, 127.2, 126.7, 124.6, 24.1, 13.8. ESI-MS: m/z 485.3, [**L3** − Cl]$^+$ ($C_{35}H_{37}N_2^+$, calcd 485.68).

General Procedures for the Synthesis of Pd-PEPPSI Compounds. A mixture of tetraarylimidazolium salt (1.1 mmol), palladium dichloride (0.177 g, 1 mmol), and K_2CO_3 (0.690 g, 10 mmol) in 3-chloropyridine or pyridine (4 mL) was stirred at 90 °C for 24 h. When the determined time was reached, the solution was cooled to room temperature and 20 mL of dichloromethane was added, and then the reaction mixture was placed on a short silica gel column and washed with substantial dichloromethane. Evaporation of the filtrate provided a yellow-brown solid. The solid was then washed and stirred with hexane (15 mL) for 1 h. The precipitate was isolated by filtration. The yellow solid was slowly treated with dichloromethane until it was dissolved completely, and then a large amount of Et_2O was added, causing the formation of a white precipitate. The suspension was filtered through a sintered funnel. Drying the solid in vacuo produced the desired palladium complexes as white powders.

*[(2-$(CH_3)C_6H_4$)NC(Ph)]$_2$CHPdCl$_2$(3-Cl-Py) (**C1**).* This compound was obtained as a white powder (0.352 g, 51%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.58 (m, Ar-H, 1H), 8.50-8.48 (m, Ar-H, 1H), 8.26 (m, Ar-H, 1H), 7.60 (m, Ar-H, 1H), 7.59 (m, Ar-H, 1H), 7.52 (m, Ar-H, 1H), 7.40-7.34 (m, Ar-H, 3H), 7.22-6.92 (m, Ar-H, 13H), 2.28 (s, CH_3, 2 H), 1.95 (s, CH_3, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 150.1, 149.1, 137.6, 136.7, 136.5, 136.3, 133.2, 132.2, 131.0, 130.9, 130.8, 130.2, 130.0, 129.6, 128.6, 128.5, 128.2, 128.1, 127.6, 127.4, 126.4, 126.2, 124.3, 18.5. Anal. Calcd for $C_{34}H_{28}Cl_3N_3Pd$: C, 59.06; H, 4.08; N, 6.08. Found: C, 59,09; H, 4.18; N, 5.98. ESI-MS: m/z 657.2, [**L1**PdCl(3-ClPy)]$^+$ ($C_{34}H_{28}Cl_2N_3Pd^+$, calcd 655.93); 401.0, [**L1** − Cl]$^+$ ($C_{29}H_{25}N_2^+$, calcd 401.52).

*[(2,6-$(CH_3)_2C_6H_3$)NC(Ph)]$_2$CHPdCl$_2$(3-Cl-Py) (**C2**).* This compound was obtained as a white powder (0.500 g, 69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.53-8.43 (m, Ar-H, 2H), 7.58-7.55 (m, Ar-H, 1H), 7.29-7.25 (m, Ar-H, 2H), 7.20-7.05 (m, Ar-H, 12H), 6.93-6.91 (m, Ar-H, 3H), 2.39 (s, CH_3, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 151.4, 150.4, 149.4, 137.4, 137.1, 136.0, 133.6, 131.9, 129.7, 129.4, 128.5, 128.3, 128.2, 127.6, 124.2, 19.9. Anal. Calcd for $C_{36}H_{32}Cl_3N_3Pd$: C, 60.10; H, 4.48; N, 5.84. Found: C, 60.26; H, 4.38; N, 5.71. ESI-MS: m/z 721.2, [**L2**PdCl$_2$(3-ClPy)]$^+$ ($C_{36}H_{32}Cl_3N_3Pd^+$, calcd 719.44); 610.0, [**L2**PdCl + K]$^+$ ($C_{31}H_{28}ClKN_2Pd^+$, calcd 609.54); 534.9, [**L2**Pd]$^+$ ($C_{31}H_{28}N_2Pd^+$, calcd 534.99); 429.1, [**L2** − Cl]$^+$ ($C_{31}H_{29}N_2^+$, calcd 429.57).

*[(2,6-$(C_2H_5)_2C_6H_3$)NC(Ph)]$_2$CHPdCl$_2$(3-Cl-Py) (**C3**).* This compound was obtained as a white powder (0.505 g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.50 (d, J = 2.3 Hz, Ar-H, 1H), 8.42 (m, Ar-H, 1H), 7.54 (m, Ar-H, 1H), 7.42 (t, J = 7.7 Hz, Ar-H, 2H), 7.25 (m, Ar-H, 4H), 7.19−7.12 (m, Ar-H, 2H), 7.10−7.02 (m, Ar-H, 5H), 6.94-6.76 (m, Ar-H, 4H), 3.17 (m, CH_2, 4H), 2.34 (m, CH_2, 4H), 1.15 (t, J = 7.5 Hz, CH_3, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 152.1, 150.3, 149.4, 141.8, 137.3, 135.0 , 133.7, 131.9, 129.9, 129.6, 128.4, 128.1, 127.7, 125.2, 124.2, 24.3, 13.1. Anal. Calcd for $C_{40}H_{40}Cl_3N_3Pd$: C, 61.95; H, 5.20; N, 5.42. Found: C, 62.07; H, 5.14; N, 5.28. ESI-MS: m/z 816.8, [**L3**PdCl$_2$(3-ClPy) + K]$^+$ ($C_{40}H_{40}Cl_3KN_3Pd^+$, calcd 814.64); 739.9, [**L3**PdCl(3-ClPy)]$^+$ ($C_{40}H_{40}Cl_2N_3Pd^+$, calcd 740.09); 700.1, [**L3**PdCl$_2$ + K]$^+$ ($C_{35}H_{36}Cl_2N_2PdK^+$, calcd 700.10); 665.1, [**L3**PdCl + K]$^+$ ($C_{35}H_{36}ClN_2PdK^+$, calcd 665.64); 591.2, [**L3**Pd]$^+$ ($C_{35}H_{36}N_2Pd^+$, calcd 591.09); 485.3, [**L3** − Cl]$^+$ ($C_{35}H_{37}N_2^+$, calcd 485.68).

*[(2-$(CH_3)C_6H_4$)NC(Ph)]$_2$CHPdCl$_2$(Py) (**C4**).* This compound was obtained as a white powder (0.340 g, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.50 (m, Ar-H, 2H), 8.28-8.26 (m, Ar-H, 1H), 7.92 (m, Ar-H, 1H), 7.59-7.34 (m, Ar-H, 5H), 7.21-6.93 (m, Ar-H, 14H), 2.29 (s, CH_3, 2H), 1.95 (s, CH_3, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 151.2, 151.1, 137.5, 136.7, 136.5, 136.3, 133.0, 131.1, 131.0, 130.9, 130.8, 130.2, 130.0, 129.5, 128.5, 128.4, 128.2, 128.1, 127.6, 126.3, 126.2, 18.7, 18.4. Anal. Calcd for $C_{34}H_{29}Cl_2N_3Pd$: C, 62.16; H, 4.45; N, 6.40. Found: C, 62.01; H, 4.48; N, 6.37. ESI-MS: m/z 586.6, [**L1**Pd(Py)]$^{2+}$ ($C_{34}H_{29}N_3Pd^+$, calcd 586.03); 401.0, [**L1** − Cl]$^+$ ($C_{29}H_{25}N_2^+$, calcd 401.52).

DOI: 10.1021/acs.organomet.6b00391
Organometallics XXXX, XXX, XXX−XXX

[(2,6-$(CH_3)_2C_6H_3$)NC(Ph)]$_2$CHPdCl$_2$(Py) (**C5**). This compound was obtained as a white powder (0.456 g, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.46 (m, Ar-H, 2H), 7.55 (m, Ar-H, 1H), 7.30-7.24 (m, Ar-H, 2H), 7.21-7.06 (m, Ar-H, 12H), 6.92 (m, Ar-H, 4H), 2.40 (s, CH_3, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 151.4, 137.3, 137.2, 137.0, 136.1, 133.5, 129.7, 129.3, 128.4, 128.3, 128.2, 127.7, 123.9, 19.9. Anal. Calcd for $C_{36}H_{33}Cl_2N_3Pd$: C, 63.12; H, 4.86; N, 6.13. Found: C, 63.27; H, 4.88; N, 6.02. ESI-MS: *m/z* 645.5, [**L2**PdCl$_2$+K]$^+$ ($C_{31}H_{28}Cl_2KN_2Pd^+$, calcd 644.99); 612.8, [**L2**Pd-(Py)]$^{2+}$($C_{36}H_{33}N_3Pd^{2+}$, calcd 612.09).

[(2,6-$(C_2H_5)_2C_6H_3$)NC(Ph)]$_2$CHPdCl$_2$(Py) (**C6**). This compound was obtained as a white powder (0.428 g, 58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.52-8.31 (m, Ar-H, 2H), 7.59-7.49 (m, Ar-H, 1H), 7.42 (t, *J* = 7.7 Hz, Ar-H, 2H), 7.24 (d, *J* = 7.7 Hz, Ar-H, 4H), 7.16 (t, *J* = 7.4 Hz, Ar-H, 2H), 7.08 (m, Ar-H, 6H), 6.89 (d, *J* = 7.5 Hz, Ar-H, 4H), 3.19 (m, CH_2, 4H), 2.35 (m, CH_2, 4H), 1.15 (t, *J* = 7.5 Hz, CH_3, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 153.7, 151.4, 141.9, 137.2, 135.1, 133.6, 129.9, 129.6, 128.3, 128.1, 127. 9, 125.1, 123.9, 24.3, 13.1. Anal. Calcd for $C_{40}H_{41}Cl_2N_3Pd$: C, 64.83; H, 5.58; N, 5.67. Found: C, 64.98; H, 5.61; N, 5.63. ESI-MS: *m/z* 706.7, [**L3**PdCl-(Py)]$^+$ ($C_{40}H_{41}ClN_3Pd^+$, calcd 705.65); 485.3, [**L3** − Cl]$^+$ ($C_{35}H_{37}N_2^+$, calcd 485.68).

General Procedure for Direct Arylation Promoted by Palladium Complexes. Unless otherwise noted, the direct C−H activation arylation reactions were carried out under aerobic conditions. The reaction temperatures are reported as the temperature of the heating vessel unless otherwise stated. All solvents were used as received, and no further purification was needed. A parallel reactor containing a stirring bar was charged with Pd-PEPPSI complexes (0.01 mmol), 1-methyl-1*H*-imidazole or 1,2-dimethyl-1*H*-imidazole (2.0 mmol), aryl bromide (1.0 mmol), base (2 mmol), acid additive (0.3 mmol), and 3 mL of solvent. The reaction was carried out at 130 °C for 12 h. After completion of the reaction, the reaction mixture was cooled to ambient temperature and 20 mL of water was added. The mixture was diluted with dichloromethane (5 mL), followed by extraction three times (3 × 5 mL) with dichloromethane. The organic layer was dried with anhydrous magnesium sulfate, filtered, and evaporated under reduced pressure. The crude cross-coupling products were purified by silica gel column chromatography using petroleum ether/dichloromethane (20/1) as eluent. The isolated cross-coupling products were characterized by ^{1}H NMR and ^{13}C NMR, and the spectra can be found in the Supporting Information.

5-(4-Chlorophenyl)-1-methyl-1H-imidazole (**9aa**).[8a] ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.52 (s, Ar-H, 1H), 7.41 (d, *J* = 8.6 Hz, Ar-H, 2H), 7.32 (d, *J* = 8.6 Hz, Ar-H, 2H), 7.10 (s, Ar-H, 1H), 3.65 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm)139.4, 133.9, 132.3, 129.6, 129.0, 128.5, 128.3, 32.5.

Methyl 4-(1-Methyl-1H-imidazol-5-yl)benzoate (**9ab**).[5b] ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.08 (d, *J* = 6.8 Hz, Ar-H, 2H), 7.56 (s, Ar-H, 1H), 7.46 (d, *J* = 6.9 Hz, Ar-H, 2H), 7.19 (s, Ar-H, 1H), 3.92 (s, CH_3, 3H), 3.70 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm)166.6 140.0, 134.2, 132.5, 130.0, 129.2, 129.1, 127.8, 52.2, 32.8.

1-Methyl-5-(4-nitrophenyl)-1H-imidazole (**9ac**).[32] ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.27 (d, *J* = 8.8 Hz, Ar-H, 2H), 7.56 (d, *J* = 8.8 Hz, Ar-H, 3H), 7.24 (s, Ar-H, 1H), 3.74 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 146.7, 140.8, 136.1, 131.5, 130.5, 128.7, 124.3, 33.3.

4-(1-Methyl-1H-imidazol-5-yl)benzonitrile (**9ad**).[14c] ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.72 (d, *J* = 9.4 Hz, Ar-H, 2H), 7.57 (s, Ar-H, 1H), 7.52 (d, *J* = 8.1 Hz, Ar-H, 2H), 7.21 (s, Ar-H, 1H), 3.72 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 140.6, 134.4 132.6, 129.8, 128.3, 126.2, 118.5, 111.3, 32.9.

4-(1-Methyl-1H-imidazol-5-yl)benzaldehyde (**9ae**).[14d] ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 10.02 (s, Ar-H, 1H), 7.92 (d, *J* = 10.0 Hz, Ar-H, 2H), 7.56 (d, *J* = 8.3 Hz, Ar-H, 3H), 7.22 (s, Ar-H, 1H), 3.73 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 191.8, 140.4, 135.8, 135.3, 132.3, 130.2, 129.8, 128.2, 33.1.

1-(4-(1-Methyl-1H-imidazol-5-yl)phenyl)ethanone (**9af**).[14d] ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.02 (d, *J* = 7.2 Hz, Ar-H, 2H), 7.56 (s, Ar-H, 1H), 7.51 (d, *J* = 8.5 Hz, Ar-H, 2H), 7.21 (s, Ar-H, 1H), 3.73 (s, CH_3, 3H), 2.63 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 197.4, 140.1, 136.1, 134.4, 132.4, 129.4, 128.8, 127.9, 32.9 26.6.

1-Methyl-5-(4-(trifluoromethyl)phenyl)-1H-imidazole (**9ag**).[13b] ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.67 (d, *J* = 8.1 Hz, Ar-H, 2H), 7.56−7.46 (m, Ar-H, 3H), 7.15 (s, Ar-H, 1H), 3.68 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 139.8, 133.3, 132.0, 129.9 (q, *J* = 32.0 Hz), 129.0, 128.3, 125.7 (q, *J* = 4.0 Hz), 125.3 (q, *J* = 270 Hz), 32.61 (s).

5-(4-Fluorophenyl)-1-methyl-1H-imidazole (**9ah**).[29] ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.52 (s, Ar-H, 1H), 7.41−7.33 (m, Ar-H, 2H), 7.15 (t, *J* = 8.7 Hz, Ar-H, 2H), 7.08 (s, Ar-H, 1H), 3.65 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 163.8 (d, *J* = 255.0 Hz), 139.0, 132.4, 130.3 (d, *J* = 8.0 Hz), 128.1, 125.9 (d, *J* = 4.0 Hz), 115.8 (d, *J* = 26.0 Hz), 32.5.

1-Methyl-5-phenyl-1H-imidazole (**9ai**).[14d] ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.52 (s, Ar-H, 1H), 7.47−7.34 (m, Ar-H, 5H), 7.11 (s, Ar-H, 1H), 3.66 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 138.9, 133.4, 129.7, 128.7, 128.4, 127.9, 127.4, 32.5.

1-Methyl-5-(naphthalen-1-yl)-1H-imidazole (**9aj**).[33] ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.97−7.89 (m, Ar-H, 2H), 7.65 (d, *J* = 8.1 Hz, Ar-H, 2H), 7.57−7.42 (m, Ar-H, 4H), 7.16 (s, Ar-H, 1H), 3.42 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 138.5, 133.7, 132.9, 131.1, 129.4, 129.2, 129.0, 128.4, 127.2, 126.7, 126.2, 125.5, 125.2, 32.0.

5-(3-Methoxyphenyl)-1-methyl-1H-imidazole (**9ak**).[34] ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.49 (s, Ar-H, 1H), 7.33 (t, *J* = 8.8 Hz, Ar-H, 1H), 7.09 (s, Ar-H, 1H), 6.99−6.87 (m, Ar-H, 3H), 3.82 (s, OCH_3, 3H), 3.66 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 159.6, 138.9, 130.9, 129.7, 127.8, 120.7, 114.2, 113.2, 55.2, 32.5.

5-(1-Methyl-1H-imidazol-5-yl)isoquinoline (**9al**).[34] ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.29 (s, Ar-H, 1H), 8.47 (s, Ar-H, 1H), 8.05 (d, *J* = 8.0 Hz, Ar-H, 1H), 7.74−7.62 (m, Ar-H, 4H), 7.20 (d, *J* = 0.9 Hz, Ar-H, 1H), 3.46 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 153.3, 144.4, 139.2, 135.3, 131.3, 130.4, 128.0, 127.7, 124.4, 121.0, 32.1.

5-(4-Chlorophenyl)-1,2-dimethyl-1H-imidazole (**9ba**).[14c] ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.38 (d, *J* = 8.7 Hz, Ar-H, 2H), 7.27 (d, *J* = 6.3 Hz, Ar-H, 2H), 6.94 (s, Ar-H, 1H), 3.50 (s, CH_3, 3H), 2.43 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 146.3, 133.6, 132.3, 129.7, 129.0, 128.9, 126.2, 31.3, 13.7.

Methyl 4-(1,2-Dimethyl-1H-imidazol-5-yl)benzoate (**9bb**).[34] ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.17−8.02 (m, Ar-H, 2H), 7.50−7.38 (m, Ar-H, 2H), 7.04 (s, Ar-H, 1H), 3.93 (s, CH_3, 3H), 3.56 (s, CH_3, 3H), 2.45 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 166.7, 147.1, 135.0, 132.6, 130.0, 128.9, 127.9, 127.1, 52.2, 31.6, 13.7.

1,2-Dimethyl-5-(4-nitrophenyl)-1H-imidazole (**9bc**).[32] ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.29 (d, *J* = 7.9 Hz, Ar-H, 2H), 7.53 (d, *J* = 8.5 Hz, Ar-H, 2H), 7.13 (s, Ar-H, 1H), 3.61 (s, CH_3, 3H), 2.48 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 148.0, 146.6, 136.5, 131.5, 128.4, 124.2, 124.1, 31.6, 14.0.

4-(1,2-Dimethyl-1H-imidazol-5-yl)benzonitrile (**9bd**).[14c] ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.71 (d, *J* = 8.6 Hz, Ar-H, 2H), 7.47 (d, *J* = 8.6 Hz, Ar-H, 2H), 7.07 (s, Ar-H, 1H), 3.58 (s, CH_3, 3H), 2.47 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 147.8, 135.1, 132.5, 131.9, 128.3, 127.9, 118.7, 110.9, 31.8, 13.6.

4-(1,2-Dimethyl-1H-imidazol-5-yl)benzaldehyde (**9be**).[14c] ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 10.01 (s, C*H*O, 1H), 7.97−7.86 (m, Ar-H, 2H), 7.58−7.47 (m, Ar-H, 2H), 7.07 (d, *J* = 2.4 Hz, Ar-H, 1H), 3.58 (s, CH_3, 3H), 2.45 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 191.5, 147.5, 136.4, 135.0, 132.4, 130.1, 128.2, 127.6, 31.7, 13.7.

1-(4-(1,2-Dimethyl-1H-imidazol-5-yl)phenyl)ethanone (**9bf**).[14c] ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.98 (d, *J* = 8.6 Hz, Ar-H, 2H), 7.43 (d, *J* = 8.5 Hz, Ar-H, 2H), 7.02 (s, Ar-H, 1H), 3.55 (s, CH_3, 3H), 2.59 (s, CH_3, 3H), 2.43 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 197.5, 147.2, 135.8, 135.2, 132.6, 128.8, 128.0, 127.2, 31.7, 26.6, 13.7.

1,2-Dimethyl-5-(4-(trifluoromethyl)phenyl)-1H-imidazole (**9bg**).[34] ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.67 (d, *J* = 8.2 Hz,

DOI: 10.1021/acs.organomet.6b00391
Organometallics XXXX, XXX, XXX−XXX

Ar-H, 2H), 7.47 (d, J = 8.1 Hz, Ar-H, 2H), 7.02 (s, Ar-H, 1H), 3.55 (s, CH_3, 3H), 2.46 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 147.0, 134.1, 132.2, 129.9 (q, J = 33.0 Hz), 128.4, 128.1 (q, J = 271.0 Hz), 127.1, 125.7 (q, J = 4.0 Hz), 31.5, 13.7.

*5-(4-Fluorophenyl)-1,2-dimethyl-1H-imidazole (**9bh**).*[34] ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.30 (dd, J = 8.8 Hz, Ar-H, 2H), 7.10 (t, J = 8.7 Hz, Ar-H, 2H), 6.90 (s, Ar-H, 1H), 3.48 (s, CH_3, 3H), 2.43 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 163.6 (d, J = 246.0 Hz), 145.9, 132.5, 130.5 (d, J = 8.0 Hz), 126.6 (d, J = 3.0 Hz), 125.8, 115.8 (d, J = 22.0 Hz), 31.2, 13.6.

*1,2-Dimethyl-5-phenyl-1H-imidazole (**9bi**).*[14c] ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.47−7.39 (m, Ar-H, 2H), 7.38−7.31 (m, Ar-H, 3H), 6.94 (s, Ar-H, 1H), 3.52 (s, CH_3, 3H), 2.44 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 145.9, 133.5, 130.5, 128.6, 128.5, 127.6 125.8, 31.3, 13.7.

*1,2-Dimethyl-5-(naphthalen-1-yl)-1H-imidazole (**9bj**).*[10a] ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.91−7.88 (m, Ar-H, 2H), 7.66 (d, J = 8.1, Ar-H, 1H), 7.54−7.38 (m, Ar-H, 4H), 7.00 (s, Ar-H, 1H), 3.25 (s, CH_3, 3H), 2.50 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 145.4, 133.5, 132.8, 131.0, 129.0, 128.9, 128.3, 127.8, 126.8, 126.6, 126.0, 125.5, 125.2, 30.9, 13.5.

*5-(3-Methoxyphenyl)-1,2-dimethyl-1H-imidazole (**9bk**).*[14c] ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.33 (t, J = 8.1 Hz, Ar-H, 1H), 6.95 (s, Ar-H, 1H), 6.90 (m, Ar-H, 3H), 3.82 (s, CH_3, 3H), 3.52 (s, CH_3, 3H), 2.44 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 159.7, 145.9, 133.4, 131.6, 129.7, 125.5, 120.9, 114.4, 113.0, 55.3, 31.3, 13.5.

*4-(1,2-Dimethyl-1H-imidazol-5-yl)isoquinoline (**9bl**).*[10a] ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.25 (s, Ar-H, 1H), 8.43 (s, Ar-H, 1H), 8.08−7.92 (m, Ar-H, 1H), 7.78−7.55 (m, Ar-H, 3H), 7.04 (s, Ar-H, 1H), 3.30 (s, CH_3, 3H), 2.48 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 153.0, 146.3, 144.5, 135.3, 131.0, 128.2, 127.9, 127.5, 124.4, 121.9, 31.1, 13.6.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00391.

Details of NMR spectra of all α-diimines, N-heterocarbene salts, palladium complexes, and cross-coupling products (PDF)

Crystallographic data (CIF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail for Z.K.: kezhf3@mail.sysu.edu.cn.

*E-mail for F.-S.L.: fengshou2004@126.com.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Foundation for Distinguished Young Talents in Higher Education of Guangdong (no. Yq2013101), the NSFC (Grants 21203256 and 21473261), the Guangdong Natural Science Funds for Distinguished Young Scholar (no. 2015A030306027), and the Project of innovation for enhancing Guangdong Pharmaceutical University, provincial experimental teaching demonstration center of chemistry & chemical engineering. Computing facilities were supported in part by the Guangdong Province Key Laboratory of Computational Science, the Joint Funds of NSFC-Guangdong for Supercomputing Applications, and the National Supercomputing Center in Guangzhou. We also acknowledge Dr. Hui Huang's helpful discussion.

■ REFERENCES

(1) (a) Romero, N. A.; Margrey, K. A.; Tay, N. E.; Nicewicz, D. A. *Science* **2015**, *349*, 1326−1330. (b) Akita, Y.; Itagaki, Y.; Takizawa, S.; Ohta, A. *Chem. Pharm. Bull.* **1989**, *37*, 1477−1480. (c) Ohta, A.; Akita, Y.; Ohkuwa, T.; Chiba, M.; Fukunaga, R.; Miyafuji, A.; Nakata, T.; Tani, N.; Aoyagi, Y. *Heterocycles* **1990**, *31*, 1951−1958. (d) Aoyagi, Y.; Inoue, A.; Koizumi, I.; Hashimoto, R.; Tokunaga, K.; Gohma, K.; Komatsu, J.; Sekine, K.; Miyafuji, A.; Kunoh, J.; Honma, R.; Akita, Y.; Ohta, A. *Heterocycles* **1992**, *33*, 257−272.

(2) (a) Campeau, L. C.; Stuart, R.; Fagnou, K. *Aldrichim. Acta* **2007**, *40*, 35−41. (b) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174−238. (c) Satoh, T.; Miura, M. *Chem. Lett.* **2007**, *36*, 200−205. (d) Seregin, I.-V.; Gevorgyan, V. *Chem. Soc. Rev.* **2007**, *36*, 1173−1193. (e) Fairlamb, I. J. S. *Chem. Soc. Rev.* **2007**, *36*, 1036−1045. (f) Mori, A.; Sugie, A. *Bull. Chem. Soc. Jpn.* **2008**, *81*, 548−561. (g) Ackermann, L.; Vicente, R.; Kapdi, A. R. *Angew. Chem., Int. Ed.* **2009**, *48*, 9792−9826. (h) Bellina, F.; Rossi, R. *Tetrahedron* **2009**, *65*, 10269−10310. (i) Daugulis, O. *Top. Curr. Chem.* **2009**, *292*, 57−84. (j) Zhao, D.; You, J.; Hu, C. *Chem. - Eur. J.* **2011**, *17*, 5466−5492. (k) Verrier, C.; Lassalas, P.; Théveau, L.; Quéguiner, G.; Trécourt, F.; Marsais, F.; Hoarau, C. *Beilstein J. Org. Chem.* **2011**, *7*, 1584−1601. (l) Su, Y.-X.; Sun, L.-P. *Mini-Rev. Org. Chem.* **2012**, *9*, 87−117. (m) Mercier, L. G.; Leclerc, M. *Acc. Chem. Res.* **2013**, *46*, 1597−1605. (n) Rossi, R.; Bellina, F.; Lessi, M.; Manzinia, C. *Adv. Synth. Catal.* **2014**, *356*, 17−117. (o) Yuan, K.; Soulé, J.-F.; Doucet, H. *ACS Catal.* **2015**, *5*, 978−991. (p) El Kazzouli, S.; Koubachi, J.; Guillaumet, G. *RSC Adv.* **2015**, *5*, 15292−15327.

(3) (a) Hassan, J.; Sévignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359−1470. (b) De Meijere, A.; Diederich, F. *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; Wiley-VCH: Weinheim, Germany, 2004. (c) Corbet, J.-P.; Mignani, G. *Chem. Rev.* **2006**, *106*, 2651−2710. (d) Fairlamb, I. J. S. *Chem. Soc. Rev.* **2007**, *36*, 1036−1045.

(4) (a) Gorelsky, S. I. *Coord. Chem. Rev.* **2013**, *257*, 153−164. (b) Bellina, F.; Cauteruccio, S.; Rossi, R. *Curr. Org. Chem.* **2008**, *12*, 774−790. (c) De Ornellas, S.; Storr, T. E.; Williams, T. J.; Baumann, C. G.; Fairlamb, I. J. S. *Curr. Org. Synth.* **2011**, *8*, 79−101. (d) Shigenobu, M.; Takenaka, K.; Sasai, H. *Angew. Chem., Int. Ed.* **2015**, *54*, 9572−9576.

(5) (a) Pivsa-Art, S.; Satoh, T.; Kawamura, Y.; Miura, M.; Nomura, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 467−473. (b) Kondo, Y.; Komine, T.; Sakamoto, T. *Org. Lett.* **2000**, *2*, 3111−3113. (c) Li, W.; Nelson, D. P.; Jensen, M. S.; Hoerrner, R. S.; Javadi, G. J.; Cai, D.; Larsen, R. D. *Org. Lett.* **2003**, *5*, 4835−4837. (d) Koubachi, J.; El Kazzouli, S.; Berteina-Raboin, S.; Mouaddib, A.; Guillaumet, G. *Synlett* **2006**, *2006*, 3237−3242. (e) Koubachi, J.; El Kazzouli, S.; Berteina-Raboin, S.; Mouaddib, A.; Guillaumet, G. *J. Org. Chem.* **2007**, *72*, 7650−7655. (f) Iaroshenko, V. O.; Gevorgyan, A.; Mkrtchyan, S.; Arakelyan, K.; Grigoryan, T.; Yedoyan, J.; Villinger, A.; Langer, P. *J. Org. Chem.* **2015**, *80*, 2103−2119.

(6) Bellina, F.; Cauteruccio, S.; Mannina, L.; Rossi, R.; Viel, S. *J. Org. Chem.* **2005**, *70*, 3997−4005.

(7) (a) Liegault, B. T.; Lapointe, D.; Caron, L.; Vlassova, A.; Fagnou, K. *J. Org. Chem.* **2009**, *74*, 1826−1834. (b) Liegault, B. T.; Petrov, I.; Gorelsky, S. I.; Fagnou, K. *J. Org. Chem.* **2010**, *75*, 1047−1060.

(8) (a) Bellina, F.; Cauteruccio, S.; Fiore, A. D.; Rossi, R. *Eur. J. Org. Chem.* **2008**, *2008*, 5436−5445. (b) Bellina, F.; Cauteruccio, S.; Di Fiore, A.; Marchetti, C.; Rossi, R. *Tetrahedron* **2008**, *64*, 6060−6072.

(9) (a) Chiong, H. A.; Daugulis, O. *Org. Lett.* **2007**, *9*, 1449−1451. (b) Joo, J. M.; Toure, B. B.; Sames, D. *J. Org. Chem.* **2010**, *75*, 4911−4920.

(10) (a) Bensaid, S.; Laidaoui, N.; El Abed, D.; Kacimi, S.; Doucet, H. *Tetrahedron Lett.* **2011**, *52*, 1383−1387. (b) Xu, X.; Zhao, L.; Li, Y.; Soulé, J.-F.; Doucet, H. *Adv. Synth. Catal.* **2015**, *357*, 2869−2882.

(11) Ackermann, L.; Althammer, A.; Fenner, S. *Angew. Chem., Int. Ed.* **2009**, *48*, 201−204.

(12) Ji, Y.; Plata, R. E.; Regens, C. S.; Hay, M.; Schmidt, M.; Razler, T.; Qiu, Y.; Geng, P.; Hsiao, Y.; Rosner, T.; Eastgate, M. D.; Blackmond, D. G. *J. Am. Chem. Soc.* **2015**, *137*, 13272−13281.

DOI: 10.1021/acs.organomet.6b00391
Organometallics XXXX, XXX, XXX−XXX

(13) (a) Shibahara, F.; Yamaguchi, E.; Murai, T. *Chem. Commun.* **2010**, *46*, 2471−2473. (b) Shibahara, F.; Yamaguchi, E.; Murai, T. *J. Org. Chem.* **2011**, *76*, 2680−2693. (c) Shibahara, F.; Yamauchi, T.; Yamaguchi, E.; Murai, T. *J. Org. Chem.* **2012**, *77*, 8815−8820. (d) Yamauchi, T.; Shibahara, F.; Murai, T. *J. Org. Chem.* **2014**, *79*, 7185−7192.
(14) (a) Touré, B. B.; Lane, B. S.; Sames, D. *Org. Lett.* **2006**, *8*, 1979−1982. (b) Joo, J. M.; Touré, B. B.; Sames, D. *J. Org. Chem.* **2010**, *75*, 4911−4920. (c) Kumar, P. V.; Lin, W.-S.; Shen, J.-S.; Nandi, D.; Lee, H. M. *Organometallics* **2011**, *30*, 5160−5169. (d) Guo, S.; Huynh, V. *Organometallics* **2014**, *33*, 2004−2011.
(15) (a) Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Angew. Chem., Int. Ed.* **2007**, *46*, 2768−2813. (b) Marion, N.; Nolan, S. P. *Acc. Chem. Res.* **2008**, *41*, 1440−1449. (c) Würtz, S.; Glorius, F. *Acc. Chem. Res.* **2008**, *41*, 1523−1533. (d) Díez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612−3676. (e) Fortman, G. C.; Nolan, S. P. *Chem. Soc. Rev.* **2011**, *40*, 5151−5169. (f) Valente, C.; Çalimsiz, S.; Hoi, K. H.; Mallik, D.; Sayah, M.; Organ, M. G. *Angew. Chem., Int. Ed.* **2012**, *51*, 3314−3332. (g) Hopkinson, M. N.; Richter, C.; Schedler, M.; Glorius, F. *Nature* **2014**, *510*, 485−486. (h) Leadbeater, N. E. *Chem. Commun.* **2014**, *50*, 1515−1518. (i) Izquierdo, F.; Manzini, S.; Nolan, S. P. *Chem. Commun.* **2014**, *50*, 14926−14937. (j) Valente, C.; Pompeo, M.; Sayah, M.; Organ, M. G. *Org. Process Res. Dev.* **2014**, *18*, 180−190. (k) Kaufhold, S.; Petermann, L.; Staehle, R.; Rau, S. *Coord. Chem. Rev.* **2015**, *304-305*, 73−87.
(16) Fantasia, S.; Nolan, S. P. *Chem. - Eur. J.* **2008**, *14*, 6987−6993.
(17) (a) Tu, T.; Fang, W.; Jiang, J. *Chem. Commun.* **2011**, *47*, 12358−12360. (b) Sayah, M.; Lough, A. J.; Organ, M. G. *Chem. - Eur. J.* **2013**, *19*, 2749−2756. (c) Pompeo, M.; Farmer, J. L.; Froese, R. D. J.; Organ, M. G. *Angew. Chem., Int. Ed.* **2014**, *53*, 3223−3226. (d) Zhang, Y.; César, V.; Storch, G.; Lugan, N.; Lavigne, G. *Angew. Chem., Int. Ed.* **2014**, *53*, 6482−6486. (e) Teci, M.; Brenner, E.; Matt, D.; Gourlaouen, C.; Toupet, L. *Dalton Trans.* **2015**, *44*, 9260−9268. (f) Valdés, H.; Poyatos, M.; Juaque, G.; Peris, E. *Chem. - Eur. J.* **2015**, *21*, 1578−1588.
(18) (a) Arduengo, A. J., III; Georlich, J. R.; Krafczyk, R.; Marshall, W. J. *Angew. Chem., Int. Ed.* **1998**, *37*, 1963−1965. (b) Powell, A. B.; Bielawski, C. W.; Cowley, A. H. *J. Am. Chem. Soc.* **2010**, *132*, 10184−10194. (c) Ogle, J. W.; Miller, S. A. *Chem. Commun.* **2009**, *45*, 5728−5730.
(19) (a) Powell, A. B.; Brown, J. R.; Vasudevan, K. V.; Cowley, A. H. *Dalton Trans.* **2009**, *38*, 2521−2527. (b) Ogle, J. W.; Zhang, J.; Reibenspies, J. H.; Abboud, K. A.; Miller, S. A. *Org. Lett.* **2008**, *10*, 3677−3680. (c) Helldörfer, M.; Backhaus, J.; Alt, H. G. *Inorg. Chim. Acta* **2003**, *351*, 34−42.
(20) Liu, F.-S.; Hu, H.-B.; Xu, Y.; Guo, L.-H.; Zai, S.-B.; Song, K.-M.; Gao, H.-Y.; Zhang, L.; Zhu, F.-M.; Wu, Q. *Macromolecules* **2009**, *42*, 7789−7796.
(21) (a) Dove, A. P.; Li, H.; Pratt, R.; Lohmeijer, B. G. G.; Culkin, D. A.; Waymouth, R. M.; Hedrick, J. L. *Chem. Commun.* **2006**, *40*, 2881−2883. (b) Teator, A. J.; Tian, Y.; Chen, M.; Lee, J. K.; Bielawski, C. W. *Angew. Chem., Int. Ed.* **2015**, *54*, 11559−11563. (c) Hahn, F. E.; Jahnke, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122−3172. (d) Benhamou, L.; Chardon, E.; Lavigne, G.; Bellemin-Laponnaz, S.; César, V. *Chem. Rev.* **2011**, *111*, 2705−2733.
(22) (a) O'Brien, C. J.; Kantchev, E. A. B.; Valente, C.; Hadei, N.; Chass, G. A.; Lough, A.; Hopkinson, A. C.; Organ, M. G. *Chem. - Eur. J.* **2006**, *12*, 4743−4748. (b) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176−2179.
(23) (a) Nasielski, J.; Hadei, N.; Achonduh, G.; Kantchev, E. A. B.; O'Brien, C. J.; Lough, A.; Organ, M. G. *Chem. - Eur. J.* **2010**, *16*, 10844−10853. (b) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176−2179.
(24) Poater, A.; Cosenza, B.; Correa, A.; Giudice, S.; Ragone, F.; Scarano, V.; Cavallo, L. *Eur. J. Inorg. Chem.* **2009**, *2009*, 1759−1766.
(25) (a) Perdew, J. P. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1986**, *33*, 8822−8824. (b) Perdew, J. P. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1986**, *34*, 7406−7406. (c) Becke, A. D. *Phys. Rev. A: At., Mol., Opt. Phys.* **1988**, *38*, 3098−3100.
(26) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 2009, Revision D.01*; Gaussian, Inc., Wallingford, CT, 2009.
(27) (a) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939−947. (b) Stevens, W. J.; Basch, H.; Krauss, M. *J. Chem. Phys.* **1984**, *81*, 6026−6033. (c) Stevens, W. J.; Krauss, M.; Basch, H.; Jasien, P. G. *Can. J. Chem.* **1992**, *70*, 612−630. (d) Cundari, T. R.; Stevens, W. J. *J. Chem. Phys.* **1993**, *98*, 5555−5565.
(28) Gorelsky, S. I. *Coord. Chem. Rev.* **2013**, *257*, 153−164.
(29) Perego, L. A.; Grimaud, L.; Bellina, F. *Adv. Synth. Catal.* **2016**, *358*, 597−609.
(30) Lafrance, M.; Fagnou, K. *J. Am. Chem. Soc.* **2006**, *128*, 16496−16497.
(31) (a) Sheldrick, G. M. *SHELXTL Version 5.1*; Bruker Analytical X-ray Instruments Inc., Madison, WI, 1998. (b) Sheldrick, G. M. *SHELXS-97, PC version*; University of Göttingen, Göttingen, Germany, 1997.
(32) Baghbanzadeh, M.; Pilger, C.; Kappe, C. *J. Org. Chem.* **2011**, *76*, 8138−8142.
(33) René, O.; Fagnou, K. *Adv. Synth. Catal.* **2010**, *352*, 2116−2120.
(34) Roger, J.; Doucet, H. *Tetrahedron* **2009**, *65*, 9772−9781.

DOI: 10.1021/acs.organomet.6b00391
Organometallics XXXX, XXX, XXX−XXX