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Palladium(II) Complexes of N-Heterocyclic Carbene Amidates Derived from Chalcogenated Acetamide-Functionalized 1*H*-Benzimidazolium Salts: Recyclable Catalyst for Regioselective Arylation of Imidazoles under Aerobic Conditions

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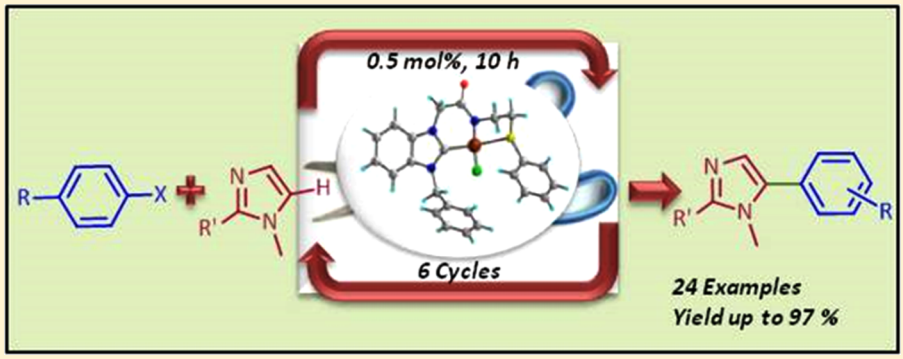
Supporting Information



ABSTRACT: The chalcogenated acetamide-functionalized 1*H*-benzimidazolium salt precursors $[1\text{-}(CH_2C(O)NH(CH_2)_2S/SePh)\text{-}3\text{-}R\text{-}C_7H_5N_2]^+ X^-$ (**L1**−**L4**; R = Me, CH_2Ph; X = Br, I) to C,N,S/Se ligands were synthesized by reaction of 1*H*-benzimidazole with 2-bromo-*N*-(2-phenylthio/seleno)ethyl)acetamide (**A1**/**A2**), followed by treatment with methyl/benzyl bromide/iodide. The reaction of **L1**−**L4** with Ag_2O followed by treatment with $[Pd(CH_3CN)_2Cl_2]$ resulted in complexes [Pd(C,N,E)Cl] (**C1**−**C4**), where the C,N^-,E pincer ligand was derived from **L1**−**L4**. **L1**−**L4** and **C1**−**C4** were characterized by elemental analyses, HR-MS, and ^1H, $^{13}C\{^1H\}$, and $^{77}Se\{^1H\}$ NMR spectroscopy. Single-crystal structures of **L2** and **C1**−**C3** established with X-ray diffraction reveal the geometry of palladium as being nearly square planar and alignment of NHC rings as being nearly perpendicular to the coordination plane of Pd. In **C1**−**C3** the Pd−C bond distances are in the range 1.974(5)−1.982(2) Å. The Pd−S bond lengths for **C1** and **C3** are 2.369(10) and 2.357(7) Å, respectively. In **C2**, the Pd−Se bond distance is 2.464(7) Å. **C1**−**C4** can be stored under ambient conditions for several months without decomposition, indicating their air and moisture insensitivity. Complexes **C1**−**C4** were all found to be efficient for regioselective C-5 arylation of imidazoles under aerobic conditions. The optimum catalyst loading for good conversion was found to be 0.5−1 mol %. A wide range of ArCl/Br can be used with the present catalysts. Complexes **C3** and **C4** appear to be more efficient than **C1** and **C2**. Similarly the complexes of selenium-containing ligands are more efficient as catalysts in comparison to their sulfur counterparts. **C1**−**C4** were found to be recyclable up to six times for regioselective arylation of imidazole with very little decrease in efficiency. The products of regioselective arylation of imidazole with few ArX were identified by X-ray diffraction on their single crystals.

INTRODUCTION

The atom-economical and environmentally friendly palladium-catalyzed direct arylation of heteroarenes with aryl halides is important in the context of pharmaceuticals, polymers, natural products, functional materials, and biological science.[1−4] In the case of imidazoles the C4 position is inactive for palladium-catalyzed direct arylation, whereas the C2 and C5 positions are reactive.[5] Nonpolar solvents in the presence of copper salt or strong base are reported suitable for C2 arylation and polar solvents (DMF or DMA) for C5 arylation in the presence of acetate or pivalate. The common catalytic system for arylation of imidazole is $Pd(OAc)_2$ associated with ligands such as PPh_3,[6] $AsPh_3$,[7] PCy_3,[8] P(*n*-Bu)Ad_2,[9] X-phos,[10] Xantphos,[11] and 1,10-phenanthroline.[12] N-heterocyclic carbenes (NHCs), due to their strong σ donation and tunable steric properties, are considered advantageous as ligands over phosphines.[13] Probably due to this σ donation their complexes are usually resistant to decomposition.[14] However, examples of palladium NHC complex catalyzed direct C−H arylation of imidazoles with aryl halides are few[15] and most of them suffer from two shortcomings: (i) limited scope of substrate (ArX or

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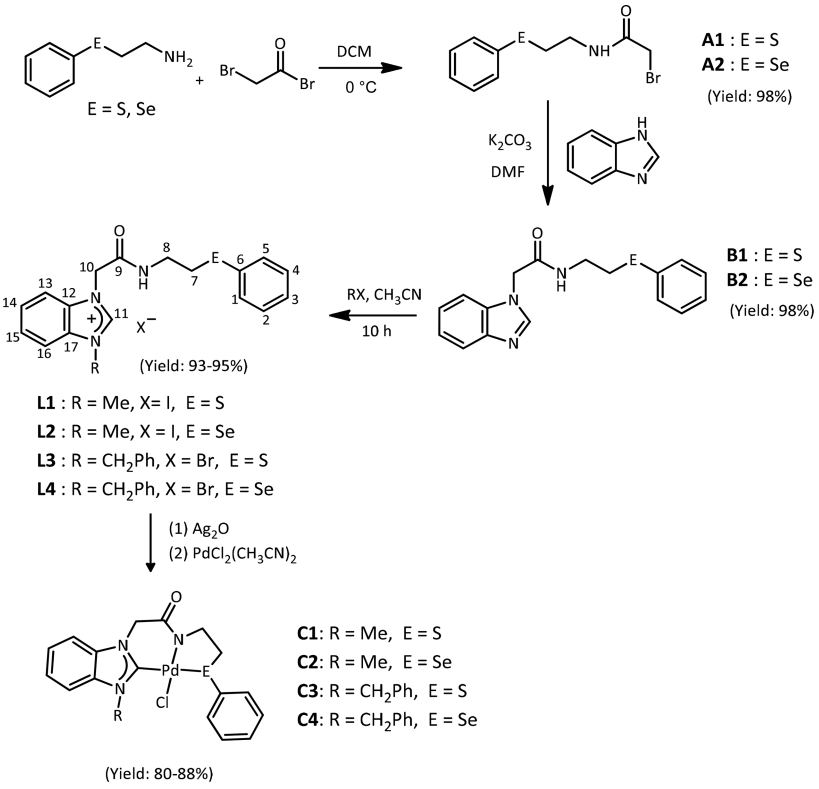
Scheme 1. Synthesis of L1−L4 and Their Pd(II) Complexes C1−C4



imidazole) and (ii) high loading (up to 5 mol % of Pd) of complex required for efficient catalysis. The arylation of C−H bond with palladium NHC complexes is challenging under aerobic conditions[16] because many times the real catalytic species with oxygen forms the peroxo derivative $LPd(O_2)$ rapidly, blocking the catalytic activity. Thus, an anhydrous and oxygen-free environment is needed for catalytic reactions.

NHCs functionalized with donor groups become chelating (sometimes pincer) type ligands. They have interesting properties[17a] and give metal complexes[17] of increased stability that are advantageous in catalysis. The combination of amidate and S/Se donor group can enhance the stability even in a nucleophilic solvent, as amidate N and S/Se would increase the electron density on palladium, shown to be advantageous in several catalytic reactions.[20,21b] Some N-heterocyclic carbene amidates have been reported in the past decade. Lee and co-workers[18] reported in 2007 palladium(II) and nickel(II) complexes of anionic amidate NHC ligands. Ghosh and co-workers synthesized nickel(II), palladium(II), gold(I), and silver(I) complexes of amido-functionalized NHCs.[19] Jung and co-workers have concluded that tridentate anionic amidate NHC ligands enhance the stability of Pd(II) complexes,[20] important in catalyst design. Some catalytic applications of palladium complexes of anionic amidate NHC ligands are known.[21] However, there has been only one report on direct C−H activation of imidazole with aryl bromides catalyzed by Pd complexes (2 mol %) of amidate NHC ligand.[15b]

Chalcogenated ligands have emerged as attractive alternatives to phosphines, as their transition-metal complexes are generally air and moisture insensitive.[22] The presence of a thioether group in an NHC ligand introduces hemilability suitable for catalysis. In 2013, our group reported the first selenium-containing NHC, and its Pd(II) complex[22a] was found promising for C−C coupling. In 2017, Singh and co-workers reported Hg(II) and Pd(II) complexes of a selenoether-bridged bis-carbene ligand[23] and explored them to catalyze Heck coupling. Thus, in continuation of our interest in selenium-containing NHCs and with the motivation of the better catalytic results with a selenium-containing NHC, it was thought worthwhile to design chalcogenated amidate NHC ligands. The advantages of both coordination with chalcogen (resulting efficient catalyst) and an amidate functionality (enhancing stability) appear to be tailored in such NHC ligands reported herein (Scheme 1). Their Pd complexes were explored as catalysts for the regioselective C−H arylation of imidazole under aerobic and mild reaction conditions and found to be reusable. To the best of our knowledge, such Pd complexes of selenated/sulfated NHC amidate ligands as catalysts for regioselective C−H arylation of imidazole are reported for the first time. Of course there has been a report on applications of Pd(II) complexes of C,N,O type donors as a catalyst for C−H arylation.[15b]

RESULTS AND DISCUSSION

The preparations of amide-functionalized 1*H*-benzimidazolium salts **L1−L4** and palladium(II) complexes **C1−C4** derived from them are shown in Scheme 1. **A1**/**A2** (Scheme 1) was prepared by nucleophilic substitution reaction of 2-(phenylthio/seleno)ethanamine with bromoacetyl bromide at 0 °C. The treatment of **A1**/**A2** with 1*H*-benzimidazole in the presence of potassium carbonate in DMF gave **B1**/**B2**, which was subjected to methylation/benzylation to obtain the chalcogenated amide-functionalized 1*H*-benzimidazolium salts **L1−L4** in nearly quantitative yield (93−95%). **L1−L4** have good solubility in common organic solvents such as DMSO, DMF, $CHCl_3$, CH_2Cl_2, and CH_3CN and are insoluble in

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diethyl ether and hexane. They were authenticated with HR-MS and ^{1}H, $^{13}C\{^{1}H\}$, and $^{77}Se\{^{1}H\}$ NMR spectra. The ^{1}H NMR spectra show a characteristic singlet due to $-NCH_3$ for **L1** and **L2** and $-NCH_2Ph$ for **L3** and **L4** (see the Experimental Section and Figures S5−S8 in the Supporting Information). The signals of H_{11} observed in the ^{1}H NMR spectra of **L1**−**L4** are in agreement with the signal of a similar proton, reported earlier, in the spectrum of a related benzimidazolium salt[20,22a] and indicate its high acidity. The Ag_2O acting as a mild base predominantly replaces the carbenic proton[24] of azolium salt without deprotonation of other acidic protons. Thus, H_{11} is substituted by Ag, giving the Ag-NHC complex as a white solid on treating benzimidazolium salts **L1**−**L4** with Ag_2O in CH_2Cl_2 a under nitrogen atmosphere and in the absence of light (Scheme 1). On addition of the Ag-NHC complex to a suspension of $[Pd(CH_3CN)_2Cl_2]$ in CH_3CN at room temperature [Pd-(C,N$^-$,E)Cl] (**C1**−**C4**) resulted.

C1−**C4**, isolated as yellow solids, were found to be air and moisture insensitive and storable for several months as solids under ambient conditions. They are readily soluble in polar solvents such as CH_2Cl_2, CH_3CN, DMF, and DMSO and sparingly in nonpolar solvents such as *n*-hexane and diethyl ether. **C1**−**C4** were characterized with ^{1}H, $^{13}C\{^{1}H\}$, and $^{77}Se\{^{1}H\}$ NMR spectra and HR-MS. Their ^{1}H and $^{13}C\{^{1}H\}$ spectral data (see the Experimental Section and Figures S9−S12 and S34−S38 in the Supporting Information) are consistent with their molecular structures depicted in Scheme 1. The deshielding of signals in $^{77}Se\{^{1}H\}$ NMR spectra implies coordination of Se with palladium(II). The signal of carbene (around 165 ppm) in the $^{13}C\{^{1}H\}$ NMR spectra of **C1**−**C4** (Figures S34−S36 and S38 in the Supporting Information) supports palladation at the carbene carbon atom.[22a] In HR-MS of **L1**−**L4**, peaks appearing at *m*/*z* 326.1321, 374.0766, 402.1637, and 450.1076, respectively, are ascribed to benzimidazolium cations (Figures S43−S46 in the Supporting Information). In HR-MS of **C1**, the peak appearing at *m*/*z* 448.0306 may be ascribed to $[M - Cl + H_2O]^+$ (Figure S47 in the Supporting Information), and for **C2**−**C4**, peaks appearing at *m*/*z* 477.9641, 506.0520, and 553.9975 may be ascribed to their cationic fragments $[M - Cl]^+$ (Figures S48−S50 in the Supporting Information).

Crystal Structures. Single crystals of **C1**−**C3** suitable for X-ray diffraction were grown by slow evaporation of their concentrated solutions made in CH_2Cl_2/diethyl ether under ambient conditions. The single crystal of **L2** was obtained by layering its solution in CH_2Cl_2 with diethyl ether at ambient temperature. Figures 1−4 show the molecular structures of **L2** and complexes **C1**−**C3** along with their selected bond lengths and angles relevant to the geometry of the central atom. Their crystal data and structure refinement parameters are summarized in Tables S1−S4 in the Supporting Information. In complexes **C1**−**C3**, palladium has a distorted-square-planar geometry, as bond angles on Pd are close to 90 and 180°. The ligands are coordinated to palladium in a tridentate mode by amido nitrogen, chalcogen, and the carbene carbon, forming one five-membered and another six-membered chelate ring. The NHC ring is nearly perpendicular to the coordination plane of Pd. The Pd−N bond lengths in **C1**−**C3** are 2.008(3), 2.012(4), and 2.014(18), Å respectively, consistent with those of an amidate NHC Pd complex (1.992(3) Å).[25a] The Pd−N bond length reported for a neutral amine NHC Pd complex is 2.058(12) Å.[25b] In an anionic amide NHC Pd complex the

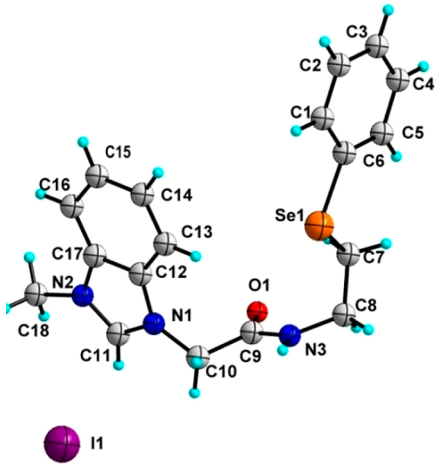

Figure 1. Molecular structure of **L2**. Selected bond distances (Å): Se(1)−C(6) 1.911(5); Se(1)−C(7) 1.954(5); O(1)−C(9) 1.224(5); N(3)−C(9) 1.333(5); N(3)−C(8) 1.463(6). Selected bond angles (deg): C(6)−Se(1)−C(7) 101.1(2); C(11)−N(1)−C(10) 125.7(4); C(9)−N(3)−C(8) 120.6(4); O(1)−C(9)−N(3) 125.0(4); O(1)−C(9)−C(10) 120.4(4); N(3)−C(9)−C(10) 114.6(4).

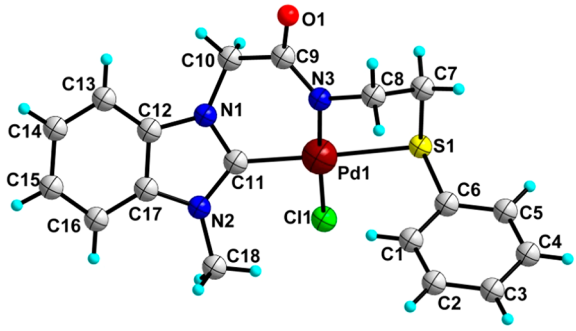

Figure 2. Molecular structure of **C1**. Selected bond distances (Å): Pd(1)−C(11) 1.978(3); Pd(1)−N(3) 2.008(3); Pd(1)−Cl(1) 2.317(9); Pd(1)−S(1) 2.369(10). Selected bond angles (deg): N(3)−Pd(1)−C(11) 87.50(12); C(11)−Pd(1)−Cl(1) 95.75(9); N(3)−Pd(1)−S(1) 85.31(8); Cl(1)−Pd(1)−S(1) 91.61(3); N(3)−Pd(1)−Cl(1) 176.00(8); C(11)−Pd(1)−S(1) 171.82(9).

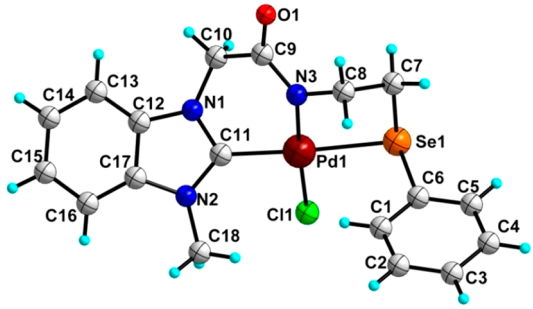

Figure 3. Molecular structure of **C2**. Selected bond distances (Å): Pd(1)−C(11) 1.974(5); Pd(1)−N(3) 2.012(4); Pd(1)−Cl(1) 2.312(14); Pd(1)−Se(1) 2.464(7). Selected bond angles (deg): N(3)−Pd(1)−C(11) 87.32(19); C(11)−Pd(1)−Cl(1) 96.00(15); N(3)−Pd(1)−Se(1) 85.61(12); Cl(1)−Pd(1)−Se(1) 91.17(4); N(3)−Pd(1)−Cl(1) 175.87(13); C(11)−Pd(1)−Se(1) 172.51(14).

Pd−N bond length is reported as 2.006(4) Å,[25c] consistent with the length of the Pd−N bonds in complexes **C1**−**C3**. The geometry around N3 is approximately trigonal planar, as shown by the sums of bond angles at N3 of 357.9° (**C1**),

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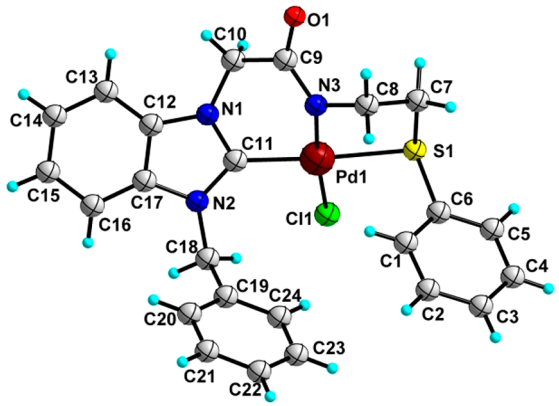


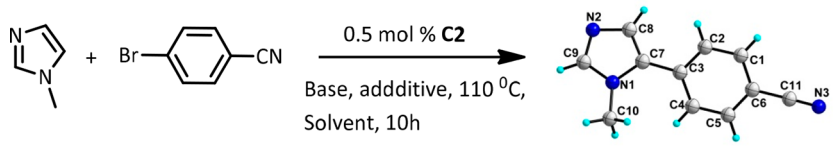
Figure 4. Molecular structure of **C3**. Selected bond distances (Å): Pd(1)−C(11) 1.982(2); Pd(1)−N(3) 2.014(18); Pd(1)−Cl(1) 2.311(6); Pd(1)−S(1) 2.357(7). Selected bond angles (deg): N(3)−Pd(1)−C(11) 87.53(8); C(11)−Pd(1)−Cl(1) 97.72(6); N(3)−Pd(1)−S(1) 85.90(6); Cl(1)−Pd(1)−S(1) 88.88(3); N(3)−Pd(1)−Cl(1) 173.61(6); C(11)−Pd(1)−S(1) 173.39(6).

358.18° (**C2**), and 354.6° (**C3**). The Pd−C bond distances 1.978(3), 1.974(5) and 1.982(2) Å in **C1**−**C3**, respectively, are similar to the values 1.978(4)−1.989(4) Å reported for [$PdCl_2$(S,C_{NHC})ligand] complexes.[26] The Pd−Se bond distance (2.464(7) Å) in **C2** is longer than the value of 2.3909(15) Å reported for Pd(II) complexes of selenium-containing N-heterocyclic carbenes.[22a] The Pd−S bond distances of **C1** and **C3** (2.369(10) and 2.357(7) Å, respectively) are consistent with the value 2.3079(3) Å reported for a Pd−S bond of a Pd(II) complex of a thioether-functionalized imidazolium salt.[25d] The Pd−Cl bond distances of **C1**−**C3**, 2.317(9), 2.312(14), and 2.311(6) Å, respectively, are consistent with the range 2.303(18)−2.330(10) Å reported for amidate NHC Pd complexes.[25a]

In the crystals of **C1**−**C3**, supramolecular structural patterns (Figures S101−S103 in the Supporting Information) develop due to secondary interactions (Table S5 in the Supporting Information for interatomic distances) arising most probably due to packing.

Catalytic Regioselective Arylation of C−H Bond of Imidazole. Complexes **C1**−**C4** were explored as catalysts for direct C−H bond arylation of imidazole with aryl halides, under ambient conditions. The conversions were monitored with ^{1}H NMR spectroscopy. The arylation of 1-methyl-1*H*-imidazole with 4-bromobenzonitrile was chosen as a model reaction. In the presence of pivalic acid, K_2CO_3, and 0.5 mol % of catalyst loading under aerobic conditions, good conversion (Table 1; entry 5) resulted. The yield of regioselective arylation at the C5 position was 97% with catalyst **C2**. The yield became poor when K_2CO_3 was replaced with other bases: viz., Cs_2CO_3, KOH, KO^{t}Bu, and KOAc (Table 1; entries 1−4). Probably K_2CO_3 and PivOH provide a suitable combination of acid and base to generate coordinatively unsaturated Pd species, as proposed in the tentative mechanism in Scheme S1 (section B in the Supporting Information). The influence of solvent on direct C−H bond arylation of imidazole was studied. Polar aprotic solvents such as DMSO, DMA, DMF, 1,4-dioxane, and *N*-methylpyrrolidone (NMP) were examined, as their interaction with Pd via oxygen can stabilize the Pd-containing intermediates as proposed in tentative mechanism

Table 1. Optimization of Reaction Conditions for Direct Arylation Reaction[a]



Molecular structure of **1g**

entry no.	base (2 mmol)	additive	catalyst (mol %)	solvent (3 mL)	yield[b] (%)	selectivity[b] (%)
1	KOAc	PivOH	0.5	DMA	57	92
2	Cs_2CO_3	PivOH	0.5	DMA	11	96
3	KOH	PivOH	0.5	DMA	18	94
4	KO^{t}Bu	PivOH	0.5	DMA	10	94
5	K_2CO_3	PivOH	0.5	DMA	97	98
6	K_2CO_3	PivOH	0.5	DMSO	nd	
7	K_2CO_3	PivOH	0.5	DMF	72	96
8	K_2CO_3	PivOH	0.5	Dioxane	11	94
9	K_2CO_3	PivOH	0.5	NMP	70	95
10	K_2CO_3	PivOH	0.5	Toluene	9	95
11	K_2CO_3	PivOH	2	DMA	>99	98
12	K_2CO_3	PivOH	1	DMA	>99	98
13	K_2CO_3	PivOH	0.1	DMA	80	98
14	K_2CO_3	PivOH	0.05	DMA	69	98
15	K_2CO_3	-	0.5	DMA	nd	
16	K_2CO_3	PhCOOH	0.5	DMA	nd	
17	Cs_2CO_3	PhCOOH	0.5	DMA	9	95
18[c]	K_2CO_3	PivOH	0.5	DMA	nd	

[a]Reaction conditions: 4-bromobenzonitrile, 1 mmol; 1-methyl-1*H*-imidazole, 2 mmol; complex **C2**, 0.05−2 mol %; additives, 0.3 mmol; bath temperature, 110 °C; reaction time, 10 h; under aerobic conditions. [b]Determined with ^{1}H NMR. [c]Control experiment without **C2**: time, 24 h.

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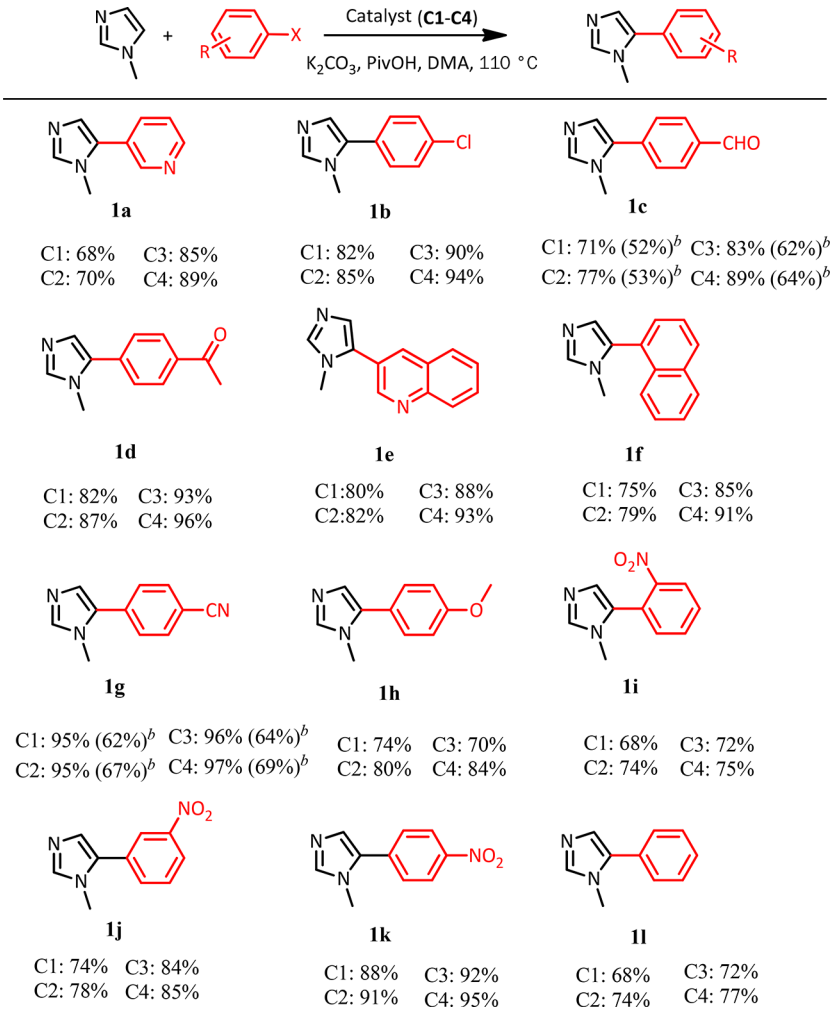
Table 2. Direct Arylation of 1-Methyl-1*H*-imidazole with Aryl Halides[a]



[a]Reaction conditions unless specified otherwise: aryl halide, 1 mmol; 1-methyl-1*H*-imidazole, 2 mmol; catalyst, 0.5 mol %; PivOH, 0.3 mmol; DMA, 3 mL; bath temperature, 110 °C; reaction time, 10 h under aerobic conditions; isolated yield. [b]Reaction conditions: aryl chloride, 1 mmol: catalyst, 1 mol %; reaction time, 20h.

in Scheme S1 (section B in the Supporting Information). The use of DMA resulted in an excellent yield (Table 1; entry 5), as it gives optimum stability and is more reducing in nature than the other solvents explored. No coupled product was obtained in DMSO (Table 1; entry 6). In the case of DMF and NMP, 70−72% yield was obtained (Table 1; entries 7 and 9). In 1,4-dioxane, the yield was poor (Table 1; entry 8). The use of a nonpolar solvent gives poor conversion (Table 1; entry 10). The amount of catalyst was optimized. A loading of 0.5 mol % gave the maximum conversion (Table 1; entry 5). When the catalyst loading was lowered to 0.1 and 0.05 mol %, the yield dropped to 80% and 69%, respectively (Table 1; entries 13 and 14). The additive pivalic acid (PivOH) was found to be essential, as in its absence no product was obtained (Table 1; entry 15). Its role is to generate coordinatively unsaturated Pd as its proton neutralizes the anionic nitrogen of the amidate fragment, which helps in cleavage of the Pd−N bond, and that of a proton shuttle during aryl C−H bond cleavage.[27] A 0.3 mmol amount of pivalic acid was used, consistent with a concerted metalation−deprotonation (CMD) pathway of catalytic arylation of the C−H bond of imidazole.[27,31] The yield was negligible when PivOH was replaced with benzoic acid (Table 1; entry 16). Using other bases such as Cs_2CO_3 also resulted in poor yields in the presence of the additive benzoic acid (Table 1; entry 17). Benzoic acid being stronger than pivalic acid stabilizes the intermediate and does not allow further catalysis (see tentative mechanism in Scheme S1, section B in the Supporting Information). In the absence of catalyst, no product was obtained even after 24 h (Table 1, entry 18).

The conditions 1 mmol of 1-methyl-1*H*-imidazole, 0.5 mol % of Pd as a catalyst (complex **C2**), 2 mmol of K_2CO_3 as a base, 0.3 mmol of PivOH as an additive, 3 mL DMA as a solvent, and 110 °C as a reaction temperature under aerobic conditions gave the maximum yield in a reaction time of 10 h. However, in the course of the present catalytic reaction, C-4 arylation of the imidazole and homocoupling of the aryl bromides were observed to a very small extent.

With the optimized reaction conditions, the catalytic activity of all complexes **C1−C4** was explored for direct arylation of 1-methyl-1*H*-imidazole with aryl halides (Table 2). It was found that aryl halides with a wide range of functional groups such as chloro, aldehyde, acetyl, cyano, and nitro gave good to excellent yields (71−97%) (Table 2, **1b−d,g,i−k**). Heteroaryl bromides, viz. 3-bromopyridine (Table 2, **1a**), 3-bromoquinoline (Table 2, **1e**) also resulted in 70−93% yield when **C1−C4**

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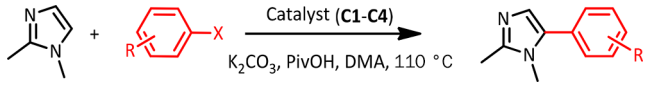
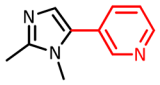
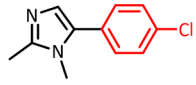
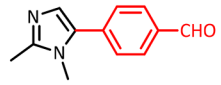
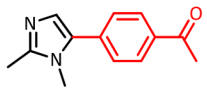
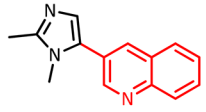
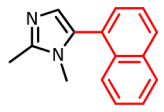
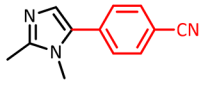
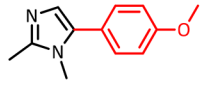
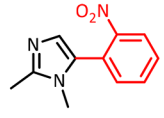
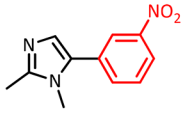
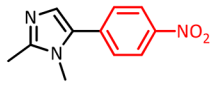
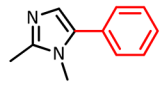
Table 3. Direct Arylation of 1,2-Dimethyl-1*H*-imidazole with Aryl Halides[a]



 **2a**	 **2b**	 **2c**
C1: 72% C3: 85% C2: 75% C4: 89%	C1: 85% C3: 91% C2: 91% C4: 96%	C1: 71% (62%)[b] C3: 83% (69%)[b] C2: 77% (69%)[b] C4: 89% (71%)[b]
 **2d**	 **2e**	 **2f**
C1: 81% C3: 91% C2: 88% C4: 97%	C1: 79% C3: 89% C2: 85% C4: 92%	C1: 70% C3: 83% C2: 70% C4: 89%
 **2g**	 **2h**	 **2i**
C1: 97% (65%)[b] C3: 94% (66%)[b] C2: 97% (66%)[b] C4: 97% (72 %)[b]	C1: 75% C3: 75% C2: 76% C4: 84%	C1: 68% C3: 79% C2: 76% C4: 85%
 **2j**	 **2k**	 **2l**
C1: 80% C3: 89% C2: 82% C4: 90%	C1: 89% C3: 92% C2: 92% C4: 96%	C1: 71% C3: 71% C2: 76% C4: 80%

[a]Reaction conditions unless specified otherwise: aryl halide, 1 mmol; 1,2-dimethyl-1*H*-imidazole, 2 mmol; catalyst, 0.5 mol %; PivOH, 0.3 mmol; DMA, 3 mL; bath temperature, 110 °C; reaction time, 10 h; under aerobic conditions; isolated yield. [b]Reaction conditions: aryl chloride, 1 mmol; catalyst, 1 mol %; reaction time, 20 h.

were used as catalysts. With sterically hindered 1-naphthyl bromide an excellent yield of 91% of the coupled product was obtained with **C4** (Table 2, **1f**). The 1-naphthyl group optimizes the stability of CMD transition state for catalysis. Substrates with electron-donating substituents afforded the desired coupled products in moderate yields of 70−84% (Table 2, **1h**). Such an effect is due to an increase in the stability of Ar−X bond. Moreover, the position of substituent relative to halogen (ortho, meta, and para) (Table 2, **1i**−**k**) on the aromatic ring also affected the efficiency of the catalyst. An ortho-substituted derivative gave low yields of 68−75% (Table 2, **1i**), followed by meta (74−85% yield) (Table 2, **1j**). The maximum yield was obtained in case of para-substituted derivatives (88−95% yield) (Table 2, **1k**). An ortho subsituent has the highest steric influence and a para substituent the least. The yield with 1-bromobenzene was 68−77% (Table 2, **1l**). The reaction was feasible with ArCl (Table 2, **1c**) and gave the desired product albeit in low yield (52−64%) with 1 mol % catalyst loading and in a reaction time of 24 h. This is due to high ArCl bond energy. **1b**,**f**,**g**,**l** are important intermediates of bioactive compounds and functional materials.[28] Another substituted imidazole, 1,2-dimethyl-1*H*-imidazole, was investigated for direct arylation with aryl and heteroaryl halides (Table 3) having various substituents (sterically hindering, electron donating, and withdrawing). The C5-monoarylated imidazole was obtained as the predominant product (yield up to 97%) in the process catalyzed with **C1**−**C4**. The regioselectivity of C5-arylated products is supported by the single-crystal structures of **1f**,**g** and **2k** established by X-ray diffraction (Figures 5−7 for molecular structures and Tables

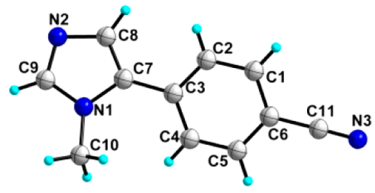


Figure 5. Molecular structure of **1g**.

S6 and S7 in the Supporting Information for details of crystal data and refinement). With ArCl the reaction was carried out for a longer time (20 h) to obtain a respectable yield. However, the yield was better than that of 1-methyl-1*H*-imidazole.

The catalytic performance of **C3** and **C4** is better in comparison to **C1** and **C2**. The efficiency of a catalyst having Se (**C2** and **C4**) was somewhat higher than that of their sulfur analogues (**C1** and **C3**), as reported earlier.[22b] Among

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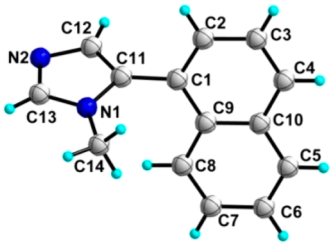

Figure 6. Molecular structure of **1f**.

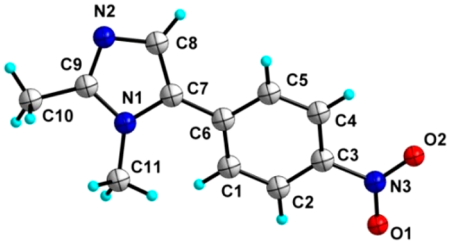

Figure 7. Molecular structure of **2k**.

complexes **C1−C4**, the more efficient performance of **C3** and **C4** having a benzyl group suggests that an increase in bulkiness at N2 of the benzimidazole moiety would stabilize the L′Pd^0 species on exposure to air and thus facilitate the reductive elimination process in the transformation. The arylation of 1-methyl-5-nitroimidazole, in which the C-5 position of the 1-methylimidazole was blocked with a nitro group, the expected C-4-arylated product resulted in <5% yield. With 1,4,5-trimethyl-1*H*-imidazole, in which both the C-4 and C-5 positions were blocked by methyl groups, the product having arylation at the C-2 position was not detected.

A comparison of the catalytic efficiency of **C1−C4** for arylation of imidazole with those of other Pd(II) complexes reported earlier for the same purpose has been made. Palladium phosphine functionalized NHC complexes (2.5 mol %, 140 °C, 18 h, N_2 atmosphere)[15a] and the dipalladium triazolidinediylidene complex *trans*-$[PdBr_2(CH_3CN)]_2(\mu$-ditz) (ditz = 1,2,4-trimethyltriazolidine-3,5-diylidene (2.5 mol %, 140 °C, 18 h, N_2 atmosphere)[15c] are less efficient than **C1−C4**. Liu and co-workers have reported tetraarylimidazolium carbene Pd PEPPSI complexes to be efficient as catalysts for arylation of imidazole at 1 mol % loading,[1a] which is higher than those of **C1−C4**. Recently Liu and co-workers synthesized a series of bulky bis(imino)acenaphthene (BIAN)-supported Pd PEPPSI complexes and applied them to direct arylation of azoles,[29a] but they were found to show low efficiency for chloro derivatives and nonrecyclability. An NHC Pd(II) Im complex is claimed to be efficient for C−H arylation with aryl chlorides, but the catalyst loading for good yields is 2−4 mol % and the reaction requires an inert atmosphere.[29b] Palladium(II) acetate complexes with phosphine and carbene ligands, $Pd(L)(PR_3)(OAc)_2$ (R = Ph/Cy; L = 1,3-dibenzylimidazol-2-ylidene), developed by Lee and co-workers are effective for direct C5-arylation of imidazoles with aryl chlorides when the catalyst loading is 2.5 mol %.[15d] The catalyst loading of **C1−C4** is lower than most of these Pd complexes reported for regioselective arylation of imidazole. However, there has been a very recent report on direct C−H functionalization of heterocyclic compounds with aryl bromides in which Pd(II) complexes of anionic amidate NHC ligands are catalysts. The optimum loading, reaction temperature, and time are 2 mol %, 140 °C, and 18 h, respectively.[15b] Thus, complexes **C1−C4** for regioselective arylation of imidazole are very promising under aerobic conditions, as the optimum loading is low and the reaction time is short.

The recyclability of complexes **C1−C4** for arylation of 1-methyl-1*H*-imidazole and 1,2-dimethyl-1*H*-imidazole was studied. A fresh lot of 1-methyl-1*H*-imidazole/1,2-dimethyl-1*H*-imidazole, 4-bromobezonitrile, pivalic acid, and base was added to the reaction vessel after completion of a cycle of the arylation reaction (see the Experimental Section). The complex catalyst showed good catalytic activity until the sixth cycle with some decrease in efficiency. The results of recycling experiments with complex **C1**, with respective yields after each run, are depicted in Figure 8. With the other three complexes the results of recyclability tests were found to be similar.

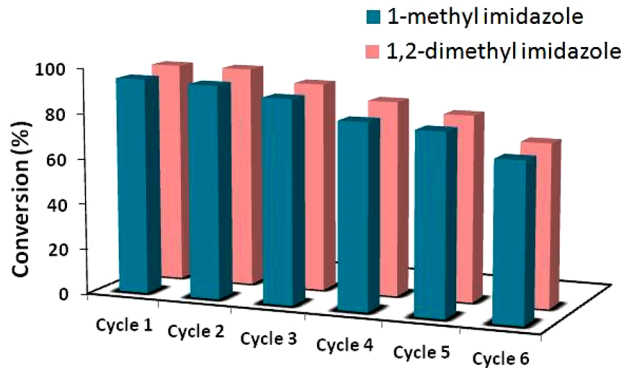

Figure 8. Catalytic life of **C1** tested under optimum conditions.

Nature of Catalysis. To ascertain the nature of catalytic reactions (homogeneous or heterogeneous), mercury and PPh_3 poisoning tests[30] were carried out. The presence of an excess of mercury (Pd/Hg (1/400), 5 mol % of PPh_3) in arylation of imidazole catalyzed by **C1−C4** under optimum reaction conditions showed a negligible inhibitive effect on the conversion (Table S8 in the Supporting Information). Thus, the present catalysis appears to be homogeneous in nature.

CONCLUSION

A simple method for the synthesis of [Pd(C,N$^-$,S/Se)Cl] (**C1−C4**), the first Pd(II) complexes of tridentate chalcogenated amide functionalized NHCs derived from *N*-alkyl-*N*′-(2-(phenylthio/selanyl)ethylacetamide)benzimidazolium salts (**L** = **L1−L4**) via a transmetalation reaction with silver, is reported. The carbene precursors **L1−L4** were synthesized by an easy route, and the Pd(II) complexes **C1−C4** were authenticated with HR-MS and multinuclei NMR. Single-crystal structures of **L2** and **C1−C3** were established with X-ray diffraction. The geometry of Pd in **C1−C3** is nearly square planar. The ligands behave as S/Se,N$^-$,C_{NHC} donors. The air- and moisture-stable complexes **C1−C4** effectively catalyze direct regioselective C−H functionalization reactions between imidazoles and aryl halides under aerobic conditions. With a low Pd loading the yield is good to excellent. In the substrates both electron-rich and -poor substituents are well tolerated: i.e., the yield is good to high. The catalyst remains active even in the sixth reaction cycle, for the regioselective arylation of imidazole.

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EXPERIMENTAL SECTION

Materials and Instrumentation. Palladium chloride, silver oxide, bromoacetyl bromide, diphenyl diselenide, 2-chloropropylamine hydrochloride, and sodium borohydride were procured from Sigma-Aldrich (USA). Thiophenol, benzimidazole, methyl iodide, base, pivalic acid, 1-methyl-1*H*-imidazole, 1,2-dimethyl-1*H*-imidazole, and various aryl halides were procured from local sources. 2-(Phenylthio)ethylamine[22d]/2-(phenylseleno)ethylamine[32] and $[Pd(CH_3CN)_2Cl_2]$[22a] were prepared by following the procedure reported earlier. Commercial nitrogen gas was used after passing it successively through traps containing solutions of alkaline anthraquinone, sodium dithionite, alkaline pyrogallol, concentrated H_2SO_4, and KOH pellets. Yields reported are of isolated coupled products which have purity ≥95% (established by ^{1}H NMR). The ^{1}H, ^{13}C{^{1}H}, and ^{77}Se{^{1}H} NMR spectra were recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300.13, 75.47, and 57.24 MHz, respectively, with chemical shifts reported in ppm relative to internal standards. Carbon-13 DEPT NMR experiments were used routinely to determine the number of hydrogen atoms linked to a carbon atom. Thin-layer chromatography (TLC) was performed using silica gel plates 60 F_{254} visualized with short-wavelength UV light (254 nm). Silica gel (100−200 mesh) was used for column chromatography. All reactions were carried out in glassware dried in an oven. Melting points were determined in an electrically heated apparatus by taking the sample in a glass capillary sealed at one end. High-resolution mass spectral (HR-MS) measurements were performed with an Bruker Micro TOF-Q II instrument, based on electron spray ionization (10 eV, 180 °C source temperature, and sodium formate as calibrant), taking the sample in CH_3CN. Single-crystal X-ray diffraction studies were carried out on a Bruker SMART APEX CCD diffractometer and Bruker D8 Quest CMOS diffractometer using a Mo Kα (λ = 0.71073 Å) sealed tube. The data frames were collected at T = 298 K using the program APEX3 and processed using the SAINT routine in APEX3. The structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL-2014/7 program. All hydrogen atoms were included in idealized positions, and a riding model was used for the refinement. Images were created using the program Diamond.

Synthesis of 2-Bromo-*N*-(2-(phenylthio/seleno)ethyl)-acetamide (A1/A2). Bromoacetyl bromide (1.211 g, 6.0 mmol) was added dropwise (with a dropping funnel) at 0 °C to a solution of 2-(phenylthio)ethylamine (0.919 g, 6.0 mmol)/2-(phenylseleno)-ethylamine (1.200 g, 6.0 mmol) in CH_2Cl_2 (30 mL) placed in a 50 mL round-bottom flask equipped with a magnetic stirrer. After the reaction mixture was stirred for 3 h at 0 °C, water (20 mL) was added. The aqueous layer was separated and extracted with CH_2Cl_2 (30 mL). The organic layer was washed with brine and dried over anhydrous Na_2SO_4, and its solvent was evaporated off under reduced pressure on a rotary evaporator, resulting in a white solid of **A1**/**A2** which was used further without any purification.

A1: white solid, yield 1.612 g (98%). ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm) 3.03 (t, 2H, J = 6.6 Hz, H_7), 3.27 (t, 2H, J = 6.6 Hz, H_8), 3.85 (s, 2H, H_{10}), 7.19−7.22 (m, 1H), 7.29−7.38 (m, 4H), 8.54 (s, 1H, N−H). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm) 29.4 (C_7), 31.2 (C_8), 39.2 (C_{10}), 125.8, 128.1, 129.1, 135.5 (C6), 166.1 (C9). HR-MS: $[M + Na]^+$ m/z 295.9721; calcd value for $C_{10}H_{12}BrNNaOS$ 295.9715 (ppm error δ: 2.0).

A2: light yellow solid, yield 1.887 g (98%). ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm) 2.99 (t, 2H, J = 6 Hz, H_7), 3.33 (t, 2H, J = 6 Hz, H_8), 3.84 (s, 2H, H_{10}),7.24−7.33 (m, 3H), 7.48−7.52 (m, 2H), 8.55 (s, 1H, N−H). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm) 25.8 (C_7), 29.9 (C_8), 40.0 (C_{10}), 127.1, 129.7, 130.1 (C_6), 131.8, 166.5 (C_9). HR-MS: $[M + Na]^+$ m/z 343.9158; calcd value for $C_{10}H_{12}BrNNaOSe$ 343.9156 (ppm error δ: 0.4).

Synthesis of 2-(1*H*-Benzimidazol-1-yl)-*N*-(2-(phenylthio/seleno)ethyl)acetamide (B1/B2). In a 100 mL round-bottom flask, 2-bromo-*N*-(2-(phenylthio)ethyl)acetamide (0.882 g, 3.0 mmol)/2-bromo-*N*-(2-(phenylselenyl)ethyl)acetamide (**A1**/**A2**; 0.963 g, 3.0 mmol) was taken and stirred with DMF (4 mL) on a magnetic stirrer at room temperature. Subsequently benzimidazole (0.354 g, 3.0 mmol) and K_2CO_3 (0.442g, 3.2 mmol) were added and the reaction mixture was stirred at room temperature for 10 h. After completion of the reaction, the mixture was poured into water and extracted with ethyl acetate (3 × 25 mL). The organic layer was dried with anhydrous sodium sulfate. The solvent was evaporated off on a rotary evaporator, resulting in a white solid (**B1**/**B2**).

B1: white solid, yield 0.914 g (98%). ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm) 3.05 (t, 2H, J = 6 Hz, H_7), 3.30 (t, 2H, J = 6 Hz, H_8), 4.93 (s, 2H, H_{10}), 7.19−7.23 (m, 2H), 7.26−7.38 (m, 5H), 7.44 (d, 1H, J = 6.9 Hz), 7.66 (d, 1H, J = 6.9 Hz), 8.16 (s, 1H), 8.58 (s, 1H). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm) 31.4 (C_7), 38.4 (C_8), 46.7 (C_{10}), 110.2, 119.3, 121.5, 122.3, 125.8, 128.1, 129.1, 134.2, 135.5, 143.2, 144.8, 166.7 (C_9). HR-MS: $[M + H]^+$ m/z 312.1170; calcd value for $C_{17}H_{18}N_3OS$ 312.1165 (ppm error δ: 1.5).

B2: white solid, yield 1.053 g (98%). ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm) 3.03 (t, 2H, J = 9 Hz, H_7), 3.40 (t, 2H, J = 9 Hz, H_8), 4.92 (s, 2H, H_{10}), 7.21−7.32 (m, 5H), 7.43−7.52 (m, 3H), 7.67 (d, 1H, J = 6.6 Hz), 8.17 (s, 1H), 8.58 (s, 1H, N−H). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm) 25.7 (C_7), 39.3 (C_8), 46.8 (C_{10}), 110.3, 119.4, 121.6, 122.4, 126.7, 129.3, 129.6, 131.4, 134.3, 143.2, 144.9, 166.7 (C_9). ^{77}Se{^{1}H} NMR (DMSO-d_6, 25 °C, Me_2Se): δ (ppm) 268.74. HR-MS: $[M + H]^+$ m/z 360.0618; calcd value for $C_{17}H_{18}N_3OSe$ 360.0610 (ppm error δ: 2.3).

Synthesis of L1−L4. In a 50 mL round-bottom flask equipped with a magnetic stirrer were placed **B1** (0.934 g, 3.0 mmol)/**B2** (1.075 g, 3.0 mmol) with methyl iodide (0.426 g, 3.0 mmol)/benzyl bromide (0.513 g, 3.0 mmol) and acetonitrile (1 mL). The mixture was stirred at room temperature for 10 h under an N_2 atmosphere. The white solid obtained was filtered, washed with THF, and dried in vacuo to obtain **L1**−**L4**.

L1: white solid, yield 1.291 g (95%). Anal. Calcd for $C_{18}H_{20}IN_3OS$: C, 47.69; H, 4.45; N, 9.27. Found: C, 47.68; H, 4.45; N, 9.26. ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm) 3.09 (t, 2H, J = 6.9 Hz, H_7), 3.37 (t, 2H, J = 6.9 Hz, H_8), 4.15 (s, 3H, H_{18}), 5.32 (s, 2H, H_{10}), 7.19−7.22 (m, 1H), 7.30−7.39 (m, 4H), 7.69−7.72 (m, 2H), 7.91 (t, 1H, J = 2.4 Hz), 8.04 (t, 1H, J = 2.4 Hz), 8.79 (br, 1H), 9.73 (s, 1H). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm) 31.9 (C_7), 33.9 (C_8), 39.0 (C_{18}), 48.9 (C_{10}), 113.9, 114.1, 126.4, 127.0, 127.2, 128.7, 129.6, 131.9, 132.0, 135.8, 144.1, 165.2. HR-MS: $[M - I]^+$ m/z 326.1320; calcd value for $C_{18}H_{20}IN_3OS$ = 326.1321 (ppm error δ: 0.3).

L2: white solid, yield 1.410 g (94%). Anal. Calcd for $C_{18}H_{20}IN_3OSe$: C, 43.22; H, 4.03; N, 8.40. Found: C, 43.20; H, 4.02; N, 8.39. ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm) 3.05 (t, 2H, J = 6 Hz, H_7), 3.41 (t, 2H, J = 6 Hz, H_8), 4.15 (s, 3H, H_{18}), 5.30 (s, 2H, H_{10}), 7.26−7.33 (m, 3H), 7.50 (d, 2H, J = 7.2 Hz), 7.69−7.72 (m, 5H), 7.89−7.91 (m, 2H), 8.05 (d, 1H, J = 8.1 Hz), 8.79 (s, 1H), 9.71 (s, 1H). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm) 26.1 (C_7), 33.9 (C_8), 39.8 (C_{18}), 48.8 (C_{10}), 113.9, 114.1, 126.9, 127.2, 127.2, 129.8, 129.9, 131.8, 131.9, 132.0, 144.1, 165.1. ^{77}Se{^{1}H} NMR (DMSO-d_6, 25 °C, Me_2Se): δ (ppm) 269.26. HR-MS: $[M - I]^+$ m/z 374.0766; calcd value for $C_{18}H_{20}IN_3OSe$ 374.0767 (ppm error δ: 0.2).

L3: white solid, yield 1.374 g (95%). Anal. Calcd for $C_{24}H_{24}BrN_3OS$: C, 59.75; H, 5.01; N, 8.71. Found: C, 59.74; H, 5.01; N, 8.70. ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm) 3.09 (t, 2H, J = 6.0 Hz, H_7), 3.33−3.36 (br, 2H, H_8), 5.37 (s, 2H, H_{18}), 5.87 (s, 2H, H_{10}), 7.17−7.22 (m, 1H), 7.29−7.44 (m, 7H), 7.52 (d, 2H, J = 6.0 Hz), 7.64−7.69 (m, 2H), 7.94 (t, 1H, J = 6.0 Hz), 8.00 (t, 1H, J = 6.0 Hz), 8.95 (s, 1H), 9.99 (s, 1H). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm) 31.4 (C_7), 38.5 (C_8), 48.6 (C_{18}), 49.8 (C_{10}), 113.8, 113.9, 125.9, 126.7, 126.857, 128.2, 128.8, 129.0, 129.1, 130.5, 131.8, 133.9, 135.4, 143.6, 164.8. HR-MS: $[M - Br]^+$ (m/z) = 402.1637; calcd. value for $C_{24}H_{24}N_3OS$ = 402.1635 (ppm error δ: 0.7).

L4: White solid, Yield: 1.477 g (93%); Anal. Calcd for $C_{24}H_{24}BrN_3OSe$: C, 54.46; H, 4.57; N, 7.94. Found: C, 54.43; H, 4.56; N, 7.93. ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm) 3.05 (t, 2H, J = 6.0 Hz), 3.40 (t, 2H, J = 6.0 Hz), 5.35 (s, 2H),

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5.86 (s, 2H), 7.25−7.32 (m, 3H), 7.39−7.44 (m, 3H), 7.48−7.53 (m, 4H), 7.65 (t, 2H, J = 6.0 Hz), 7.92 (br, 1H), 8.00 (t, 1H, J = 6.0 Hz), 8.95 (s, 1H), 9.98 (s, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm) 25.6 (C_7), 40.1 (C_8), 48.6 (C_{18}), 49.9 (C_{10}), 113.8, 113.9, 126.7, 126.8, 127.3, 128.2, 128.8, 129.0, 129.3, 129.4, 130.5, 131.4, 131.7, 133.9, 143.5, 164.6. $^{77}Se\{^1H\}$ NMR (DMSO-d_6, 25 °C, Me_2Se): δ (ppm) 269.73. HR-MS: $[M - Br]^+$ m/z 450.1076; calcd value for $C_{24}H_{24}N_3OSe$ 450.1080 (ppm error δ: 5.9).

Synthesis of Complexes C1−C4. **L1/L2/L3/L4** (0.272/0.300/0.289/0.317 g, 0.60 mmol) was dissolved in dry CH_2Cl_2 (30 mL). Under a nitrogen atmosphere solid Ag_2O (0.139 g, 0.60 mmol) was added. The reaction mixture was stirred at room temperature for 5 h with exclusion of light and then filtered with a Celite pad. The filtrate obtained was concentrated to 15 mL on a rotary evaporator. Thereafter, a suspension of $[Pd(CH_3CN)_2Cl_2]$ (0.156 g, 0.60 mmol) in CH_3CN at room temperature under a nitrogen atmosphere was added to the filtrate. The reaction mixture was further stirred for 6 h and filtered with a Celite pad. Thereafter, the filtrate was evaporated to dryness on a rotary evaporator to give a yellow solid. Dichloromethane was added slowly to the yellow solid until it dissolved completely. Thereafter diethyl ether (30 mL) was added, resulting in the formation of a yellow precipitate of **C1−C4** which was filtered and dried in vacuo.

C1: light yellow solid, yield 0.235 g (84%). Anal. Calcd for $C_{18}H_{18}ClN_3OPdS$: C, 46.36; H, 3.89; N, 9.01. Found: C, 46.32; H, 3.86; N, 9.08. Mp: 196 °C. ^1H NMR (300 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm) 2.87 (t, 2H, J = 6 Hz), 3.58 (br, 2H), 4.25 (s, 3H), 4.98 (s, 2H), 7.43−7.54 (m, 5H), 7.75−7.78 (m, 1H), 7.90−7.93 (m, 1H), 8.10−8.13 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm) 29.0, 34.8, 50.1, 51.9, 111.4, 111.7, 124.0, 124.3, 129.7, 130.3, 132.3, 132.6, 133.8, 164.8, 166.6. HR-MS: $[M - Cl + H_2O]^+$ m/z 448.0306; calcd value for $C_{18}H_{20}N_3O_2PdS$ = 448.0312 (ppm error δ: 1.3).

C2: yellow solid, yield 0.271 g (88%). Anal. Calcd for $C_{18}H_{18}ClN_3OPdSe$: C, 42.13; H, 3.54; N, 8.19. Found: C, 42.19; H, 3.51; N, 8.18. Mp: 210 °C. ^1H NMR (300 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm) 2.82 (br, 2H), 3.10 (br, 2H), 4.25 (s, 3H), 4.95 (s, 2H), 7.32−7.50 (m, 6H), 7.76 (br, 1H), 7.91 (br, 1H), 8.13 (br, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm) 34.1, 34.7, 51.2, 51.9, 111.3, 111.7, 123.9, 124.2, 126.8, 129.4, 129.9, 131.6, 133.2, 133.8, 164.9, 166.8. $^{77}Se\{^1H\}$ NMR (DMSO-d_6, 25 °C, Me_2Se): δ (ppm) 404.93. HR-MS: $[M - Cl]^+$ m/z 477.9641; calcd value for $C_{18}H_{18}N_3OPdSe$ 477.9656 (ppm error δ: 3.1).

C3: yellow solid, yield 0.283 g (87%). Anal. Calcd for $C_{24}H_{22}ClN_3OPdS$: C, 53.15; H, 4.09; N, 7.75. Found: C, 53.16; H, 4.09; N, 7.76. Mp: 200 °C. ^1H NMR (300 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm) 2.84 (t, 2H, J = 6 Hz), 3.56 (br, 2H), 5.03 (s, 2H), 6.21 (s, 2H), 7.30−7.47 (m, 10H), 7.70 (d, 1H, J = 7.5 Hz), 7.93 (d, 1H, J = 7.5 Hz), 8.00 (d, 2H, J = 7.5 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm) 40.2, 49.6, 51.7, 52.1, 111.7, 112.1, 124.0, 124.4, 127.3, 127.8, 128.0, 128.6, 129.1, 129.6, 130.1, 132.3, 133.0, 136.6, 165.5, 166.8. HR-MS: $[M - Cl]^+$ m/z 506.0520; calcd value for $C_{24}H_{22}N_3OPdS$ 506.0521 (ppm error δ: 3.9).

C4: yellow solid. yield 0.287 g (80%). Anal. Calcd for $C_{24}H_{22}ClN_3OPdSe$: C, 48.92; H, 3.76; N, 7.13. Found: C, 48.91; H, 3.75; N, 7.12. Mp: 220 °C. ^1H NMR (300 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm) 3.14 (br, 2H), 3.36 (br, 2H), 3.49 (br, 2H), 5.01 (s, 2H), 7.27−7.50 (m, 11H), 7.73 (d, 1H, J = 6.9 Hz), 7.94 (d, 1H, J = 8.4 Hz), 8.04 (d, 2H, J = 8.4 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm) 34.5, 50.0, 51.8, 52.6, 112.1, 112.6, 124.4, 124.8, 126.9, 127.9, 128.3, 129.1, 129.9, 130.2, 133.3, 133.4, 133.6, 137.0, 166.1, 167.5. $^{77}Se\{^1H\}$ NMR (DMSO-d_6, 25 °C, Me_2Se): δ (ppm) 409.20. HR-MS: $[M - Cl]^+$ m/z 553.9975; calcd value for $C_{24}H_{22}N_3OPdSe$ 553.9971 (ppm error δ: 0.8).

General Procedure for Arylation Reaction. An oven-dried flask (50 mL) was charged with 1-methyl-1*H*-imidazole (2.0 mmol) or 1,2-dimethyl-1*H*-imidazole (2.0 mmol), aryl halide (1.0 mmol), base (2.0 mmol), acid additive (0.30 mmol), catalyst (one of **C1−C4**), and 3 mL of solvent. The flask was placed in an oil bath at 110 °C under aerobic conditions, and the reaction mixture was stirred. The reaction monitored by TLC was carried out until maximum conversion to product occurred. After completion of the reaction, the mixture was cooled to room temperature and 30 mL of water was added. This mixture was extracted with dichloromethane (3 × 15 mL). The combined extract was washed with water and dried over anhydrous Na_2SO_4. The solvent of the extract was removed under reduced pressure with a rotary evaporator to obtain the product. The crude products were purified by column chromatography on silica gel using dichloromethane/methanol (20/1) as an eluent. The isolated cross-coupled products were authenticated with ^1H and $^{13}C\{^1H\}$ NMR spectra given in Figures S51−S98 in the Supporting Information. For X-ray crystallography suitable crystals of **1f,g** and **2k** were grown by diffusion of ether vapor into a dichloromethane solution of these compounds.

General Procedure for Reusability of Complex C1. In a 50 mL round-bottom flask, 4-bromobenzonitrile (1.0 mmol), 1-methyl-1*H*-imidazole/1,2-dimethyl-1*H*-imidazole (2.0 mmol), pivalic acid (0.30 mmol), K_2CO_3 (2.0 mmol), and catalyst **C1** (0.5 mol %) in DMA (3 mL) were heated on a bath (110 °C) for 10 h. Thereafter the mixture was cooled to room temperature. An aliquot (100 μL) was taken for analysis by ^1H NMR spectroscopy, and a new batch of 4-bromobenzonitrile (1.0 mmol) and 1-methyl-1*H*-imidazole/1,2-dimethyl-1*H*-imidazole (2.0 mmol) with other reagents was added. The reaction mixture was stirred at 110 °C for another 10 h. The aliquot analysis by ^1H NMR and fresh substrate addition with reagents was repeated six times.

Procedure for Hg/PPh_3 Poisoning Test. In a round-bottom flask, 4-bromobenzonitrile (1.0 mmol), 1-methyl-1*H*-imidazole (2.0 mmol), pivalic acid (0.30 mmol), and K_2CO_3 (2.0 mmol) were added to DMA (3 mL). An excess of Hg/PPh_3 (Hg/Pd 400/1)/(PPh_3/Pd 5/1) was added. Thereafter the complex catalyst (one of **C1−C4**: 0.5 mol %) was added and the reaction carried out for 10 h under optimum conditions. After standard workup of the reaction mixture, percent conversion was determined with ^1H NMR.

NMR Data of Arylated Products. *3-(1-Methyl-1H-imidazol-5-yl)pyridine (**1a**).*[29a] Pale yellow oil. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 3.70 (s, 3H), 7.17 (s, 1H), 7.37−7.45 (m, 1H), 7.58 (s, 1H), 7.71−7.74 (m, 1H), 8.60−8.68 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 32.5, 123.5, 123.6, 125.9, 129.0, 129.9, 135.5, 139.9, 149.2.

*5-(4-Chlorophenyl)-1-methyl-1H-imidazole (**1b**).*[1a] Pale yellow solid. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 3.65 (s, 3H), 7.08 (s, 1H), 7.31 (d, 2H, J = 8.4 Hz), 7.40 (d, 2H, J = 8.4 Hz), 7.51 (s, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 32.3, 128.0, 128.1, 128.7, 129.4, 132.0, 133.6, 139.1.

*4-(1-Methyl-1H-imidazol-5-yl)benzaldehyde (**1c**).*[1a] Off-white solid. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 3.76 (s, 3H), 7.25 (s, 1H), 7.59 (d, 3H, J = 8.1 Hz), 7.96 (d, 2H, J = 8.4 Hz), 10.05 (s, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 32.9, 128.2, 129.7, 130.1, 132.2, 135.2, 135.8, 140.4, 191.5.

*1-(4-(1-Methyl-1H-imidazol-5-yl)phenyl)ethanone (**1d**).*[1a] Light yellow solid. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 2.64 (s, 3H), 3.73 (s, 3H), 7.22 (s, 1H), 7.51 (d, 2H, J = 8.4 Hz), 7.57 (s, 1H), 8.02 (d, 2H, J = 8.1 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 26.6, 32.9, 128.0, 128.8, 129.3, 132.4, 134.4, 136.1, 140.2, 197.4.

*3-(1-Methyl-1H-imidazol-5-yl)quinoline (**1e**).*[33a] Light yellow oil. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 3.75 (s, 3H), 7.28 (s, 1H), 7.59−7.61 (m, 2H), 7.71−7.77 (m, 1H), 7.85 (d, 1H, J = 8.1 Hz), 8.12−8.15 (m, 2H), 8.97 (d, 1H, J = 2.1 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 32.5, 122.9, 127.1, 127.3, 127.6, 129.1, 129.2, 129.6, 129.9, 134.1, 139.8, 147.0, 149.8.

*1-Methyl-5-(naphthalen-1-yl)-1H-imidazole (**1f**).*[1a] Yellow oil. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 3.41 (s, 3H), 7.16 (s, 1H), 7.43−7.56 (m, 4H), 7.65 (d, 2H, J = 6.3 Hz), 7.92−7.94 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 31.9, 125.2, 125.4, 126.1, 126.7, 127.2, 128.3, 129.0, 129.2, 129.4, 131.1, 132.8, 133.6, 138.4.

*4-(1-Methyl-1H-imidazol-5-yl)benzonitrile (**1g**).*[33b] Off-white solid. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 3.71 (s,

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3H), 7.20 (s, 1H), 7.50 (d, 2H, J = 8.4 Hz), 7.56 (s, 1 H), 7.71 (d, 2H, J = 8.1 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 32.8, 111.2, 118.5, 128.2, 129.8, 131.6, 132.5, 134.3, 140.5.

*5-(4-Methoxyphenyl)-1-methyl-1H-imidazole (**1h**).*[33a] Light yellow solid. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 3.63 (s, 3H), 3.85 (s, 3H), 6.97 (d, 2H, J = 8.4 Hz,) 7.03 (s, 1H), 7.31 (d, 2H, J = 8.4 Hz), 7.50 (s, 1 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 32.3, 55.3, 114.2, 122.2, 127.5, 129.9, 133.2, 138.6, 159.4.

*1-Methyl-5-(2-nitrophenyl)-1H-imidazole (**1i**).* Yellow solid. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 3.47 (s, 3H), 7.03 (s, 1H), 7.44−7.47 (m, 1H), 7.59−7.70 (m, 3H), 8.06−8.09 (dd, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 31.9, 124.6, 127.7, 128.8, 130.1, 133.0, 133.8, 139.1, 149.6.

*1-Methyl-5-(3-nitrophenyl)-1H-imidazole (**1j**).* Yellow solid. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 3.65 (s, 3H), 7.24 (s, 1H), 7.59−7.66 (m, 2H), 7.75 (d, 1H, J = 7.5 Hz), 8.22−8.27 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 32.7, 122.5, 122.6, 129.5, 129.8, 131.0, 131.5, 134.0, 140.2, 148.5.

*1-Methyl-5-(4-nitrophenyl)-1H-imidazole (**1k**).*[1a] Yellow solid. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 3.78 (s, 3H), 7.23 (s, 1H), 7.59 (d, 3H, J = 8.7 Hz), 8.31 (d, 2H, J = 8.7 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 33.0, 124.2, 128.3, 130.3, 131.4, 136.3, 140.9, 146.9.

*1-Methyl-5-phenyl-1H-imidazole (**1l**).*[1a] Light yellow solid. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 3.67 (s, 3H), 7.11 (s, 1H), 7.33−7.47 (m, 5H), 7.52 (s, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 32.5, 127.9, 128.1, 128.5, 128.7, 129.8, 133.4, 139.1.

*3-(1,2-Dimethyl-1H-imidazol-5-yl)pyridine (**2a**).*[29a] Pale yellow oil. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 2.45 (s, 3H), 3.53 (s, 3H), 7.02 (s, 1H), 7.33−7.38 (m, 1H), 7.64−7.68 (m, 1H), 8.57−8.63 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 13.6, 31.3, 123.5, 126.6, 126.8, 130.0, 135.6, 146.9, 148.6, 149.0.

*5-(4-Chlorophenyl)-1,2-dimethyl-1H-imidazole (**2b**).*[1a] Off-white solid. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 2.45 (s, 3H), 3.51 (s, 3H), 6.95 (s, 1H), 7.28 (d, 2H, J = 8.67 Hz), 7.39 (d, 2H, J = 8.43 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 13.7, 31.3, 126.2, 128.9, 129.1, 129.7, 132.4, 133.6, 146.3.

*4-(1,2-Dimethyl-1H-imidazol-5-yl)benzaldehyde (**2c**).*[1a] Yellow solid. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 2.47 (s, 3H), 3.60 (s, 3H), 7.09 (s, 1H), 7.42−7.54 (m, 2H), 7.92−7.95 (m, 2H), 10.03 (s, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 13.8, 31.8, 127.7, 128.3, 130.2, 132.5, 135.1, 136.5, 147.6, 191.5.

*1-(4-(1,2-Dimethyl-1H-imidazol-5-yl)phenyl)ethanone (**2d**).*[1a] Light yellow solid. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 2.46 (s, 3H), 2.62 (s, 3H), 3.57 (s, 3H), 7.05 (s, 1H), 7.45 (d, 2H, J = 8.4 Hz), 8.02 (d, 2H, J = 8.4 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 13.7, 26.6, 31.7, 127.2, 128.0, 128.8, 132.6, 135.1, 135.8, 147.2, 197.5.

*3-(1,2-Dimethyl-1H-imidazol-5-yl)quinoline (**2e**).*[29a] Light yellow solid. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 2.43 (s, 3H), 3.55 (s, 3H), 7.08 (s, 1H), 7.53−7.55 (m, 1H), 7.65−7.68 (m, 1H), 7.79 (d, 1H, J = 8.1 Hz), 8.03−8.09 (m, 2H), 8.89 (d, 1H, J = 2.1 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 13.6, 31.3, 123.7, 127.1, 127.3, 127.5, 127.7, 129.2, 129.6, 130.1, 134.1, 146.9, 147.0, 150.2.

*1,2-Dimethyl-5-(naphthalen-1-yl)-1H-imidazole (**2f**).*[1a] Yellow oil. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 2.50 (s, 3H), 3.27 (s, 3H), 7.02 (s, 1H), 7.41−7.55 (m, 4H), 7.69 (d, 1H, J = 7.8 Hz), 7.91 (d, 1H, J = 8.1 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 13.5, 30.8, 125.1, 125.5, 125.9, 126.5, 127.0, 127.9, 128.2, 128.8, 128.9, 130.9, 132.7, 133.5, 145.3.

*4-(1,2-Dimethyl-1H-imidazol-5-yl)benzonitrile (**2g**).*[1a] Off-white solid. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 2.47 (s, 3H), 3.59 (s, 3H), 7.07 (s, 1H), 7.48 (d, 2H, J = 8.4 Hz), 7.72 (d, 2H, J = 8.4 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 13.7, 31.7, 110.9, 118.6, 127.7, 128.3, 131.8, 132.5, 135.1, 147.7.

*5-(4-Methoxyphenyl)-1,2-dimethyl-1H-imidazole (**2h**).*[33b] Pale yellow solid. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 2.44 (s, 3H), 3.48 (s, 3H), 3.84 (s, 3H), 6.89 (s, 1H), 6.96 (d, 2H, J = 8.4 Hz), 7.25−7.28 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ ppm: 12.8, 31.1, 55.3, 114.2, 122.0, 123.1, 130.2, 130.3, 145.3, 159.6.

*1,2-Dimethyl-5-(2-nitrophenyl)-1H-imidazole (**2i**).* Yellow solid. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 2.45 (s, 3H), 3.32 (s, 3H), 6.90 (s, 1H), 7.43 (d, 1H, J = 7.2 Hz), 7.56−7.70 (m, 2H), 8.04 (d, 2H, J = 7.8 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 13.4, 30.9, 124.5, 125.1, 126.5, 128.1, 129.8, 132.9, 133.7, 146.3, 149.4.

*1,2-Dimethyl-5-(3-nitrophenyl)-1H-imidazole (**2j**).* Yellow solid. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 2.48 (s, 3H), 3.60 (s, 3H), 7.08 (s, 1H), 7.62 (d, 1H, J = 7.8 Hz), 7.71 (d, 1H, J = 7.8 Hz), 8.19−8.23 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 13.7, 31.5, 122.2, 122.6, 127.4, 129.8, 131.2, 132.2, 134.0, 147.3, 148.4.

*1,2-Dimethyl-5-(4-nitrophenyl)-1H-imidazole (**2k**).*[33a] Yellow solid. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 2.49 (s, 3H), 3.62 (s, 3H), 7.13 (s, 1H), 7.53 (d, 2H, J = 8.7 Hz), 8.29 (d, 2H, J = 6.9 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 13.7, 31.8, 124.1, 128.1, 128.3, 131.5, 136.9, 146.6, 148.1.

*1,2-Dimethyl-5-phenyl-1H-imidazole (**2l**).*[1a] Yellow oil. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 2.44 (s, 3H), 3.52 (s, 3H), 6.95 (s, 1H), 7.34−7.37 (m, 3H), 7.39−7.45 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 13.7, 31.3, 125.8, 127.6, 128.6, 128.7, 130.6, 133.6, 145.9.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00246.

HR-MS and NMR spectra of ligands, complexes, and products of catalysis and X-ray data tables (PDF)

Accession Codes

CCDC 1837276−1837282 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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