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Chalcogenated NHC

Palladium Complexes of Thio/Seleno-Ether Containing *N*-Heterocyclic Carbenes: Efficient and Reusable Catalyst for Regioselective C-H Bond Arylation

Ramprasad Bhatt,[a] Nattamai Bhuvanesh,[b] Kamal Nayan Sharma,*, [c] Hemant Joshi,*, [d]

Abstract: The synthesis of the novel S,C_{NHC} type half-pincer ligand precursors (**L1** and **L2**) is described herein by using the atom economy reactions of 1-(2-(phenylthio)ethyl)-1*H*-imidazole with benzyl bromide and bromodiphenylmethane, respectively. The analogous reaction of 1-(2-(phenylselanyl)ethyl)-1*H*-imidazole with 2-bromoethyl phenyl sulfide has also resulted in a imidazolium bromide (**L3**) which is a precursor of novel S,C_{NHC},Se type pincer ligand. The route of silver-NHC transmetalation was employed to get the palladium complexes [Pd(**L1**/**L2**−HBr)Cl_2] (**C1** and **C2**) and [Pd(**L3**−HBr)Cl]BF_4 (**C3**). The imidazolium bromide (**L1**-**L3**) and palladium complexes (**C1**-**C3**) were characterized by using multinuclear NMR and HR-MS. The structure and bonding in the complexes **C1** and **C2** were validated by X-ray crystallography. Thermally, robust and moisture/air insensitive palladium complexes **C1**-**C3** have been explored in the catalysis of C-H bond arylation of imidazoles. The protocol operates under mild reaction conditions in open air with an excellent regioselective C-H bond arylation at C-5 position in imidazoles. All the complexes were found to be efficient (yield up to 97% in 12 h) in the catalysis, however, the activating pincer ligand framework containing Pd catalyst **C3**, was found to be utmost effective among the three catalysts. Only 0.5 mol% catalyst loading is required to achieve admirable yield of the desired cross-coupled products. A wide range of substrates was examined and developed protocol was applicable to all derivatives with high functional group tolerance and greater efficiency. More importantly, the catalyst **C3** has also been found recyclable up to five cycles with minor decrease in efficiency which is highly desirable feature for the development of economical and sustainable industrial reaction processes. The PPh_3 and Hg poisoning tests have established the complete homogeneous nature of the catalysis.

Keywords: *N*-heterocyclic carbenes, pincer ligand, reusable catalyst, regioselective C-H bond arylation, imidazole, chalcogenoether

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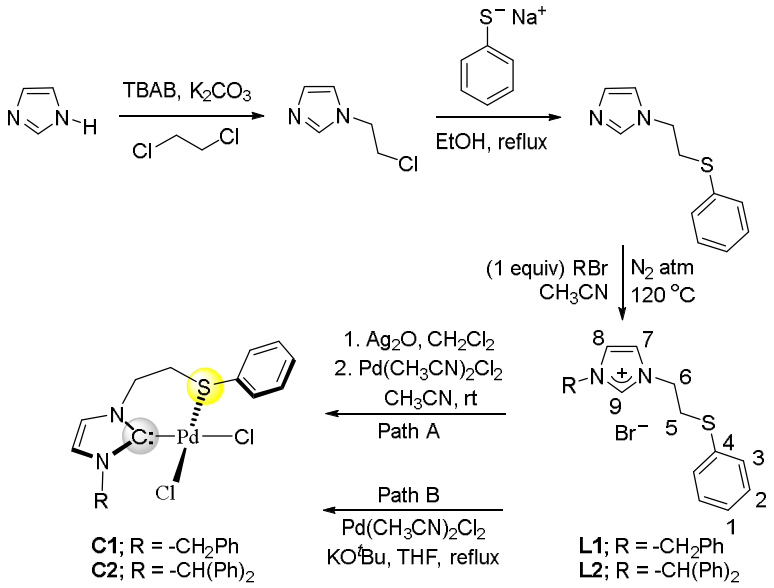
■ Introduction

The direct C-H bond arylation of aromatic heterocycles is a prominent protocol for the industrial synthesis of polymers, functional materials, pharmaceuticals, and natural products.[1] The palladium catalyzed arylation at C-4 carbon in imidazole is less favored[2] as compared to the C-2 and C-5 positions.[2-3] The use of polar solvents and base (acetate or pivalate) selectively activates the C-5 position for arylation, whereas the C-2 position is most likely to be arylated in the presence of non-polar solvents in combination with a strong base such as potassium or sodium *tert*-butoxide and a copper salt. The most commonly used catalytic systems for arylation of imidazole typically involve palladium precursors with bulky, sterically hindered, and electron-rich phosphines such as XPhos,[4] PCy_3,[5] PPh_3,[6] Xantphos,[7] $AsPh_3$,[8] and 1,10-phenanthroline[9] as supporting ligand to make the metal center electron-rich which in turn glides the oxidative addition step. In contrast to the direct C-H activation, there are only few examples[1a, 10] reported for the palladium mediated C-H bond activation of imidazole and most of these suffer from drawbacks like: (i) high catalyst loading (>2 mol% Pd), (ii) long reaction times and high reaction temperature (~140 ºC), (iii) indiscrimination of C-2 and C-5 position, (iv) limited substrate scope, and (v) requirement of moisture free inert atmosphere. Direct arylation of imidazole under aerobic conditions is thought-provoking due to the formation of peroxo species [**L**Pd$(O)_2$], which prevents the oxidative addition of the substrates. The *N*-heterocyclic carbenes (NHCs) are considered advantageous due to the availability of two electrons, strong σ-donating and week π-accepting coordination behavior which provides their metal complexes a unique balance of stability versus reactivity, highly desirable for catalysis.[11] Due to the strong soft donor properties of organochalcogen ligands and their applicability under mild reaction conditions in open air, their metal complexes have also emerged as better alternative of phosphine based catalytic systems in the organic transformations.[12] The combinatory activating effect of NHC and chalcogen (S/Se) on the catalytic activity was also proven beneficial in improving the potential of palladium catalyst of chalcogen containing NHCs.[13] Therefore, due the unique features of these complexes discussed above, we herein plan

to explore the Pd(II) complexes of novel NHC based pincer (S,C_{NHC},Se) and half pincer (S,C_{NHC}) organochalcogen ligands for the catalysis of regioselective C-H bond activation in imidazoles. To the best of our knowledge, no metal complex of S,C_{NHC},Se pincer type has been reported yet. Moreover, the effect of pincer and half-pincer coordination of ligand on the catalytic activity of the palladium metal is also investigated for the regioselective C-5 arylation of imidazole. Owing to the novel combination of coordination sites and protective environment of the pincer ligand in the Pd(II)-S,C_{NHC},Se complex, it was found to be more efficient as compared to the half-pincer (S, C_{NHC}) ligated Pd(II) complexes for the catalysis of C-H arylation in imidazole working in open air along with mild reaction conditions.

■ Results and discussion

The functionalization of the 1*H*-imidazole with a thioether moiety to prepare (2-(phenylthio)ethyl)-1*H*-imidazole was achieved by employing an analogous procedure reported earlier for the synthesis of the benzimidazole derivative.[13c] 1-(2-(Phenylthio)ethyl)-1*H*-imidazole on atom economy reaction with benzyl bromide and bromodiphenylmethane in acetonitrile has resulted in thioether based NHC ligand precursors **L1**, and **L2** respectively. The palladium complexes of thioether-NHC (**C1** and **C2)** were then synthesized by using the route of silver carbene transmetalation[14] reaction in which the appropriate imidazolium bromide (**L1** or **L2**) was reacted with Ag_2O in CH_2Cl_2 in inert atmosphere followed by the reaction with CH_3CN solution of $Pd(CH_3CN)_2Cl_2$. The reaction proceeds through *in situ* generated silver-carbene complex transmetalation route. The direct route for the preparation of **C1** and **C2** using a strong base, potassium *tert*-butoxide, was also successfully employed; however, relatively lower yield of the desired complexes was obtained. The ^{1}H, ^{13}C{^{1}H} NMR, and mass spectra of newly synthesized ligands and complexes **L1**, **L2**, **C1,** and **C2** are provided in Figures s1-s12 in the Supporting Information (SI) and are found to be in agreement with their structures as proposed in Scheme 1.

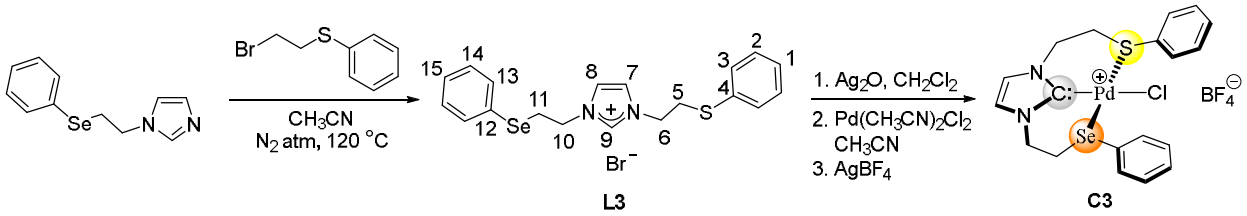


Scheme 1. Syntheses of palladium(II) complexes of thio-ether containing *N*-heterocyclic carbene based half-pincer ligand.

The most acidic H_9 proton attached to pre-carbene carbon (C_9) appeared as deshielded singlet at 10.21 and 9.60 ppm in the ^{1}H NMR of each imidazolium bromide salt **L1** and **L2**, respectively. This is consistent with imidazolium salts reported earlier (δ 9.5-12.0 ppm).[13b] The signal of this proton disappeared in the proton NMR of the complexes **C1** and **C2** which indicates the successful deprotonation of C_9 upon its coordination with Pd(II) during complexation. Furthermore, two signals in ^{1}H and ^{13}C{^{1}H} NMR of ligands (**L1** and **L2**) observed due to the presence of two adjacent –CH_2 groups, were found to be deshielded and appeared as four multiplets (or broad singlet) in the proton NMR spectrum of complexes (**C1** and **C2**), confirming diastereotopic nature of these protons arising due to the rigid six-membered chelate ring formed by the coordination of thioether NHC with Pd(II) in bidentate half-pincer (S^C_{NHC}) mode. Such phenomena was commonly observed in earlier reported six-membered chelate ring containing Pd(II) pincer complexes.[13b, 15] In the mass spectrum of imidazolium bromides (**L1** and **L2**), the intense peaks observed at (*m/z*) 295.1261 and 371.1566, respectively, correspond to imidazolium cations $[M - Br]^+$ of **L1** and **L2** salts. The mass spectrum of complex **C1** shows a peak at (*m/z*) 295.1260 which is related to $[(M + H) – PdCl_2]^+$ cationic species, while an intense peak observed at (*m/z*) 511.0207 in the mass spectrum of complex **C2** is

ascribed to $[M - Cl]^+$ cationic species. Both of these observations further strengthen the proposed structures of **C1** and **C2** given in Scheme 1.

In addition, the third new 3-(2-(phenylselanyl)ethyl)-1-(2-(phenylthio)ethyl)-1*H*-imidazolium bromide (**L3**) ligand, which is precursor to Se,C_{NHC},S type pincer ligand, was also prepared (yield ~88%) through an analogous atom economy reaction of selenoether of imidazole; 1-(2-(phenylselanyl)ethyl)-1*H*-imidazole[16] with 2-bromoethyl phenyl sulfide in acetonitrile at 120 °C under N_2 atm. The Pd(II) complex of this unique Se,C_{NHC},S type pincer ligand [Pd(**L3**-HBr)Cl]BF_4 (**C3**) was then prepared through the reaction of imidazolium bromide **L3** with $Pd(CH_3CN)_2Cl_2$ in presence of silver oxide followed by counter anion exchange with silver tetrafluoroborate. The ^1H, $^{13}C\{^1H\}$ NMR and HR-MS of **L3** and **C3** authenticating their molecular structures are provided in Scheme 2 and in Figures s13-s18 in the SI. A singlet at 9.65 ppm in the ^1H NMR spectra of **L1** is ascribed to highly deshielded H_9 proton of imidazolium salt **L3**, which on the complex (**C3**) formation, disappears owing to the removal of the acidic proton. Furthermore, the presence of four deshielded broad singlets in the ^1H NMR spectrum of **C3** confirmed the complex formation and the coordination of ligand to Pd in a tridentate Se,C_{NHC},S type pincer mode forming two six-membered chelate rings. Herein, the Pd(II) complex **C3** is the first example of metal complex of Se,C_{NHC},S type pincer ligand.



Scheme 2. Synthesis of palladium(II) complex of (Se,C_{NHC},S) type pincer.

Single crystal X-ray structures. The X-ray quality single crystals of complexes **C1** and **C2** were grown by its CH_3CN:Et_2O (4:1) solution under ambient conditions. The molecular structures of these complexes (**C1** and **C2**) were solved as outlined in crystallographic section (see SI, and Table s1) and are presented in Figures 1 and 2 along with key bond angles/distances provide in Table s2 of SI. However, the repeated attempts to get X-ray quality crystals of **C3**

were failed. In complex **C1**, a molecule of acetonitrile was found solvated (Figure 3). In both the complexes, **C1** and **C2**, the metal center Pd acquires a distorted square planar geometry with bond angles nearly 90° and 180°. The ligands (**L1** and **L2**) coordinate with Pd in a bidentate fashion through sulfur and carbene carbon forming a six-membered chelate ring in each case. Moreover, in both the Pd complexes, the imidazole ring is observed to be twisted at an angle of 47.7° and 43.9° with the coordination square plane of Pd center in **C1** and **C2**, respectively. Such kind of twisting in the imidazole ring and coordination plane of Pd also accounts that the overlapping of Pd d_{π} orbital with the p_z orbital of the NHC carbon is actually insignificant which in turn confirms very low π-accepting property of NHC ligands with metal center.[17] The palladium-sulfur bond lengths in complexes **C1** and **C2** are 2.290(2) and 2.2737(15) Å respectively, which is consistent with the earlier reported thioether-carbene–palladium complex.[13c] The palladium-carbon bond length values are 1.992(5) and 1.978(7) Å respectively, are in good corroboration with earlier reported values 1.973(3) for thioether consisting NHC Pd complex.[13c] Figures 3 and 4 show the unit cell representations of **C1** and **C2** and each complex contains four molecules. The unit cell of **C1** also has four CH_3CN molecules solvated within this.

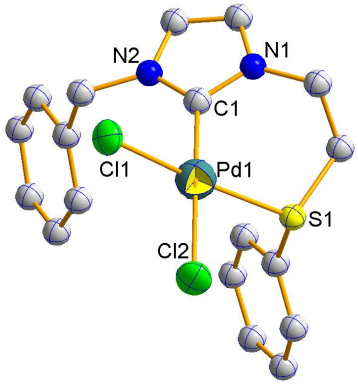


Figure 1: Crystal structure (50% probability) of **C1**.

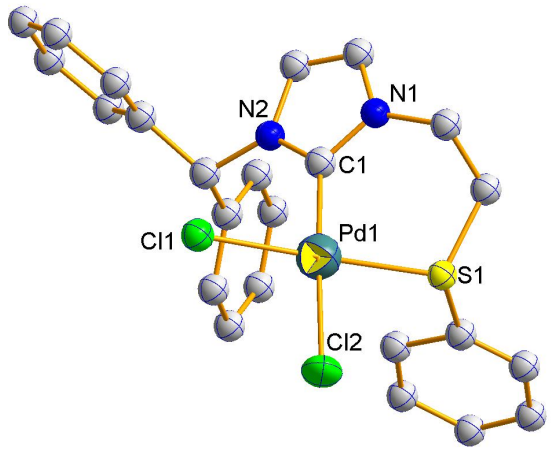


Figure 2: Crystal structure (50% probability) of **C2**.

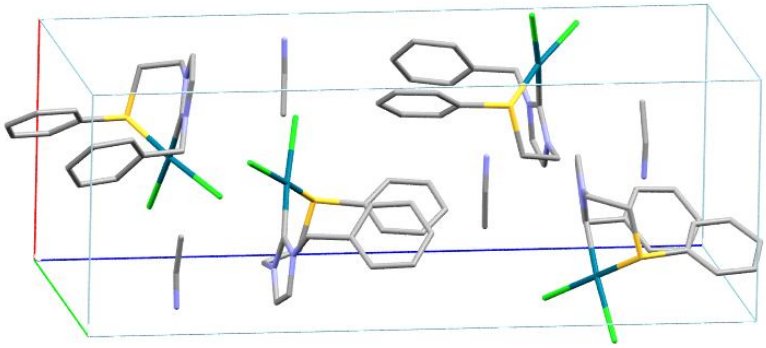


Figure 3. Unit cell diagrams of complex **C1**.

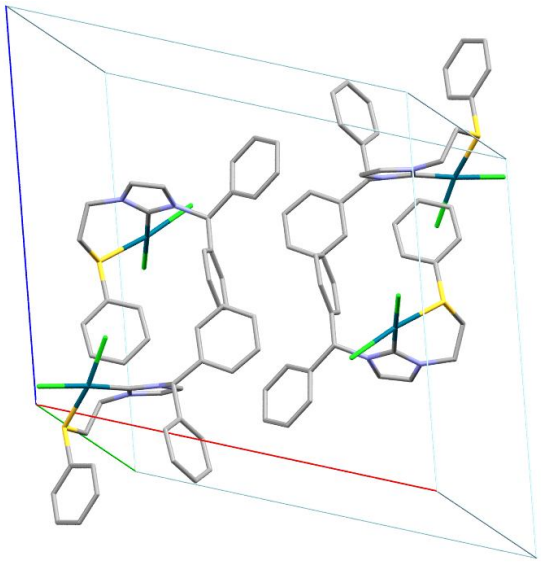
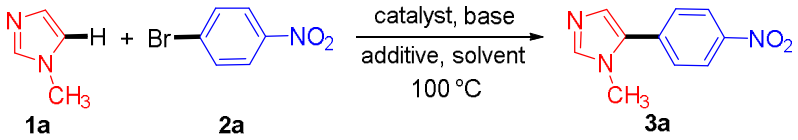


Figure 4. Unit cell diagrams of complex **C2**.

Regioselective C-H bond arylation of imidazoles. Considering the air/moisture sensitivity of the reported sterically hindered electron rich phosphine based metal catalytic

systems, the palladium complexes of phosphine-free ligands may be served as better alternatives for the catalysis of direct regioselective arylation. The present palladium complexes of chalcogenated *N*-heterocyclic carbene (**C1**-**C3**) were explored for their catalytic activity towards direct C-5 bond arylation in imidazoles. The reaction of *N*-methyl imidazole and 1-bromo-4-nitrobenzene was chosen as a model reaction for standardizations (Table 1). A reaction was first carried out using 1.0 mol% of **C1**, Cs_2CO_3 in *N*,*N*-dimethylacetamide (DMA) solvent without using any additive as shown in Table 1. However, in absence of additive, first entry resulted in no conversion of the desired product **3a**. Later, when benzoic acid was used as additive in next reaction under similar reaction conditions as entry 1, only traces of arylated product **3a** was observed (Table 1, entry 2). The reaction under similar conditions but in the presence of pivalic acid (PivOH) as an additive afforded **3a** in 38% yield and with better selectivity (96%) of arylation at the C-5 position over the C-2 position (Table 1, entry 3). The presence of PivOH is essential during the reaction as it participates in the proton shuttle event during the C-H bond cleavage. Greater steric bulk and higher pK_a of PivOH (5.03) as compared to benzoic acid (4.20) assists in driving the reaction to completion. Next, we screened different bases under similar reaction conditions as in entry 3. Reaction in presence of K_2CO_3 went smoothly with high yield of **3a** (86%) and excellent selectivity (>99%) of C-5 product (Table 1, entry 4). The yields of **3a** were lowered when bases like *t*-BuOK, *t*-BuONa, KOH, and KOAc were used instead of K_2CO_3 (Table 1, entries 5-8). Screening of different solvents for C-H bond arylation was studied next using a wide variety of polar and some non-polar solvents (DMA, DMF, DMSO, 1,4-dioxane, NMP, toluene, and THF). The desired coupled product **3a** was not formed in DMSO (Table 1, entry 10) while solvents like DMF and NMP gave moderate to high yields (76% and 68%) of **3a** (Table 1, entries 9 and 12). Solvents like 1,4-Dioxane, toluene, and THF resulted in poor yields (7-14%) of cross-coupled product (Table 1, entries 11, 13, and 14). Among all the screened solvents, DMA gave excellent yield as well as selectivity of the desired product (Table 1, entry 4), and hence was used in rest of the catalytic investigations.

Table 1. Screening of reaction conditions for palladium catalyzed regioselective C-5 arylation of imidazole[a]



1a **2a** **3a**

Entry No.	Catalyst (mol%)	Base	Solvent (3 mL)	Additive	Yield[b] (%)	Selectivity[c]
1	**C1** (1.0)	Cs_2CO_3	DMA	—	nd	—
2	**C1** (1.0)	Cs_2CO_3	DMA	$PhCO_2H$	07	—
3	**C1** (1.0)	Cs_2CO_3	DMA	PivOH	38	96
4	**C1** (1.0)	K_2CO_3	DMA	PivOH	86	>99
5	**C1** (1.0)	*t*-BuOK	DMA	PivOH	23	92
6	**C1** (1.0)	*t*-BuONa	DMA	PivOH	21	92
7	**C1** (1.0)	KOAc	DMA	PivOH	32	94
8	**C1** (1.0)	KOH	DMA	PivOH	56	88
9	**C1** (1.0)	K_2CO_3	DMF	PivOH	76	>99
10	**C1** (1.0)	K_2CO_3	DMSO	PivOH	nd	—
11	**C1** (1.0)	K_2CO_3	1,4-dioxane	PivOH	13	94
12	**C1** (1.0)	K_2CO_3	NMP	PivOH	68	98
13	**C1** (1.0)	K_2CO_3	Toluene	PivOH	14	93
14	**C1** (1.0)	K_2CO_3	THF	PivOH	07	92
15	**C2** (1.0)	K_2CO_3	DMA	PivOH	89	>99
16	**C3** (1.0)	K_2CO_3	DMA	PivOH	97	>99
17	**C3** (2.0)	K_2CO_3	DMA	PivOH	98	>99
18	**C3** (0.5)	K_2CO_3	DMA	PivOH	95	>99
19	**C3** (0.1)	K_2CO_3	DMA	PivOH	67	>99
20[d]	**C3** (0.5)	K_2CO_3	DMA	PivOH	78	>99
21[e]	—	K_2CO_3	DMA	PivOH	nd	—
22[f]	**C3** (0.5)	K_2CO_3	DMA	PivOH	68	>99

[a]Reaction conditions: 1-bromo-4-nitrobenzene (1.0 mmol), *N*-methyl imidazole (2.0 mmol), additive (0.30 mmol), base (2.0 mmol), solvent (3 mL), temperature (100 °C), time (12 h), under open air conditions; [b]Isolated yield; [c]selectivity calculated by proton NMR; [d]reaction time (8 h); [e]Control experiment without catalyst; [f]temperature (70 °C).

The choice of catalyst (**C1-C3**) and catalyst loading were subsequently screened (Table 1, entries 15-19). A slight increase (3%) in the yield of **3a** was observed when the reaction in entry 4 was repeated with **C2** (1.0 mol%, Table 1, entry 15). The higher yield (97%) of **3a** was obtained using 1.0 mol% of **C3** under similar reaction conditions as entry 4 (Table 1, entry 16). On increasing the catalyst loading of **C3** to 2.0 mol%, there is no significant change in the yield of **3a** (Table 1, entry 17). Upon lowering the loading of catalyst **C3** to 0.5 mol%, **3a** was isolated

in 95% yield (Table 1, entry 18). On further decreasing the amount of **C3** to 0.1 mol%, yield of **3a** was significantly lowered (67%, Table 1, entry 19). When the reaction in entry 4 was stopped after eight hours, the yield was decreased (78%, Table 1, entry 20). The control experiments without the catalyst suggested no cross-coupled product (Table 1; entry 21). On decreasing the reaction temperature to 70 °C, yield of coupled product was decreased (Table 1; entry 22)

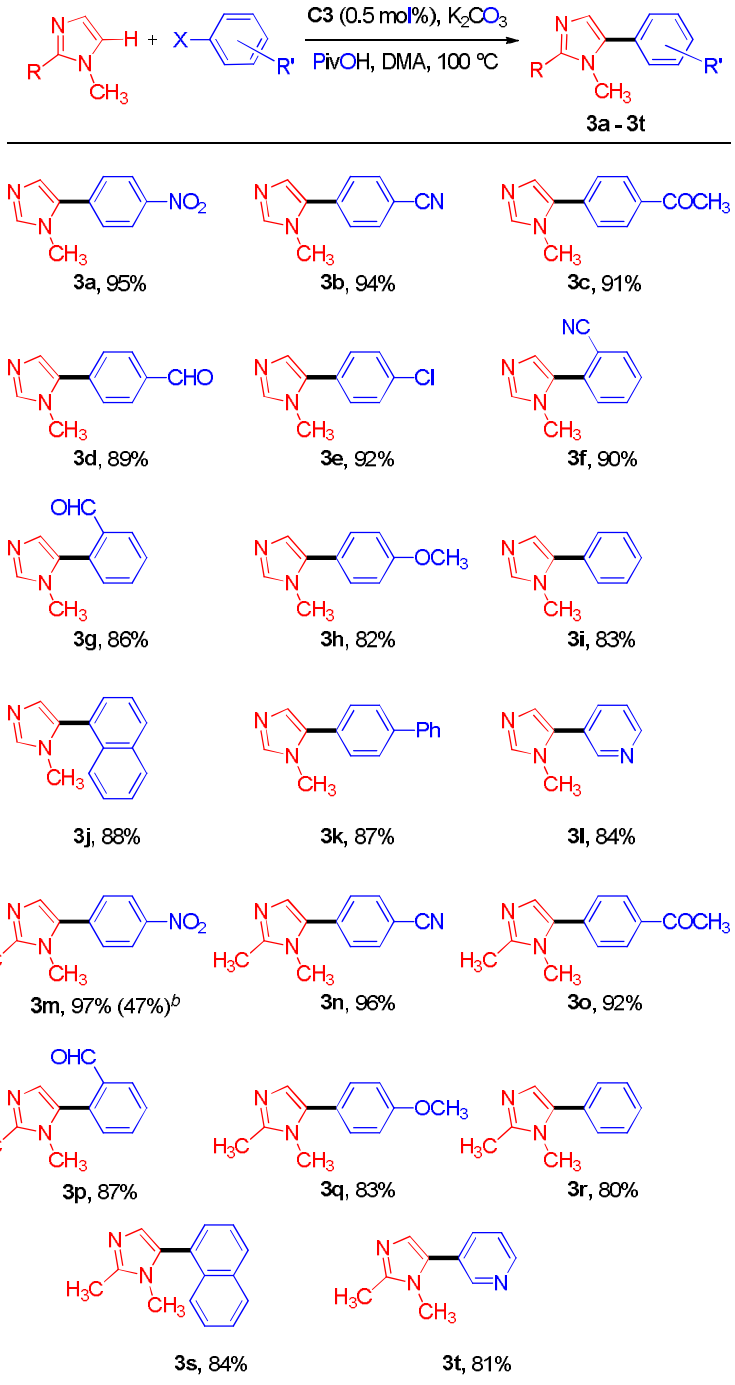
Among all screened conditions, 1.0 mmol of aryl bromide, 2.0 mmol of *N*-methyl imidazole, 2.0 mmol of K_2CO_3, 0.3 mmol of PivOH as an additive, 1.0 mol% of catalyst **C3** in 3 mL of DMA at 100 ºC under aerobic conditions provided the maximum yields of cross-coupled product **3a** in 12 h of shorter reaction time. A catalyst loading of 0.5 mol% of **C3** was used in further studies as it gave a good balance between low catalyst loading and high yield. We were intrigued that no C-2, C-4 arylated, or even homo-coupled products were observed during any of the reactions.

With the optimized reaction conditions in hand, we could now explore the substrate scope with different aryl bromides using catalyst **C3** (Table 2). It was observed that aryl bromides with a wide selection of functional groups, *e.g.* nitro, cyano, acetyl, chloro, aldehyde, and methoxy groups reacted smoothly to give admirable yields (82-97%) of cross-coupled products (Table 2, entry **3a**-**3h** and **3m**-**3q**). In addition, using the heteroaryl derivative (3-bromopyridine) with 1-methyl-1*H*-imidazole and 1,2-dimethyl-1*H*-imidazole resulted in the desired products in excellent yield (81-84%) (Table 2, entry **3l** and **3t**).

Introducing electron-donating groups on aryl bromide did not significantly impact the yields (82-83%) (Table 3, entries **3h** and **3q**). Even the position (*ortho vs. para*) of functional groups on aryl bromide did not affect the efficacy of the catalyst **C3**. The *ortho* substituted cyano and aldehyde groups resulted in excellent yields (86-90%, Table 2, entries **3f**, **3g**, and **3p**). Sterically bulky derivatives such as 1-bromonapthalene and 4-bromo-1,1'-biphenyl resulted in excellent yields of cross-coupled products (84-88%, Table 2, entries **3j**, **3k**, and **3s**). Some of these derivatives **3b**, **3e**, **3j**, and **3k** are important intermediates in making bioactive compounds[1],[18] and by using the present protocol these can be easily synthesized in one pot

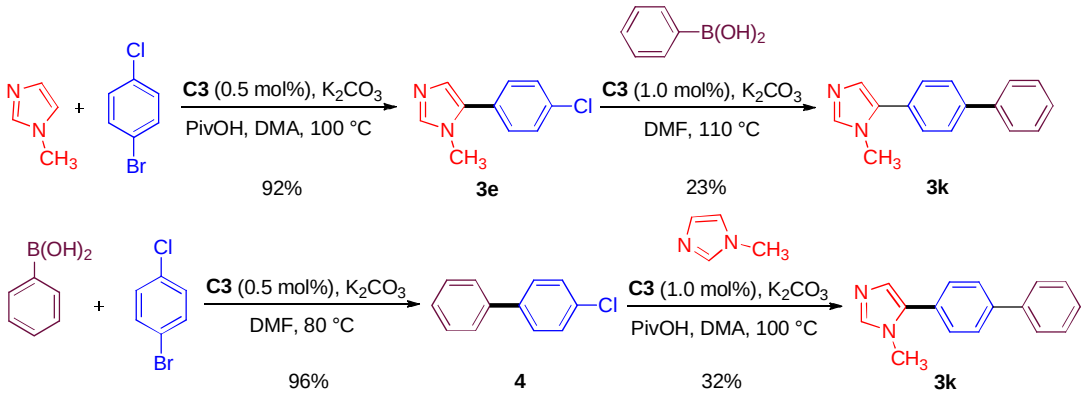
with high yields and greater regioselectivity. The yields for both 1,2-dimethyl-1*H*-imidazole and 1-methyl-1*H*-imidazole are in the same range. Using aryl chloride instead of the bromide derivative, decreased rate of the reaction (18 h) and gave desired cross-coupled product in moderate yield of 47% (Table 2, entry **3m** in parenthesis).

Table 2. Substrate scope of direct C-5 arylation[a]



[a]Reaction conditions: imidazole derivative (2.0 mmol), aryl bromide/chloride (1.0 mmol), PivOH (0.30 mmol), DMA (3 mL), **C3** (0.5 mol%), temp (100 °C), time (12 h), isolated yield; [b]1-chloro-4-nitrobenezene (1.0 mmol), **C3** (1.0 mol%), time (18 h).

We have also performed sequential C-H arylation and Suzuki-Miyaura coupling reaction to access biaryl motifs having two phenyl rings, which are important intermediates in many functional and biologically active molecules.[19] We were particularly interested in synthesizing imidazole-bearing biaryl moieties which have only few reported protocols in literature.[10a] We successfully synthesized these imidazole containing biaryl motifs in one step by reacting 1-methyl-1*H*-imidazole with 4-bromo-1,1'-biphenyl in 87% yield (Table 2, entry **3k**). We then attempted to synthesize these compounds by a sequential arylation and Suzuki coupling route (Scheme 3). Suzuki-Miyaura coupling reaction of compound **3e** with phenylboronic acid in presence of **C3** successfully resulted in imidazole containing biaryl motifs **3k** in moderate yield (23%). It was earlier reported that Suzuki-Miyaura coupling reactions of imidazole containing substituent are less feasible due to their deactivating nature.[10a] A reverse reaction sequence, where the Suzuki coupling reaction was performed first followed by the arylation reaction with 1-methyl-1*H*-imidazole gave 32% yield of **3k**.



Reaction conditions for C-H bond arylation: *N*-methyl imidazole (2.0 mmol), aryl bromide/chloride (1.0 mmol), PivOH (0.30 mmol), DMA (3 mL), time (12 h), isolated yields are given; **for Suzuki-Miyaura coupling**: Phenyl boronic acid (1.2 mmol), aryl bromide/chloride (1.0 mmol), DMF (3 mL), time (12 h), isolated yields are given.

Scheme 3. Sequential arylation and Suzuki-Miyaura reactions.

A comparison of the performance of catalyst **C3** with previously reported literature using palladium catalysts for the arylation of imidazoles has been made. Palladium-PEPPSI complexes of imidazolium carbene ligands were reported as efficient catalyst for arylation of imidazole, however, they used a rather large catalyst loading (1.0 mol%, 33-98%).[1a] Recently, the same

group synthesized sterically bulky Pd-PEPPSI complexes of bis(imino)acenaphthene and used as catalysts for the direct arylation of azoles with aryl halides. Here, 0.5 mol% of the catalyst was required to achieve >90% yield of coupled product using comparable reaction times and at substantially higher temperatures (12 h at 130 °C).[10e] The *trans*-$[PdBr_2(CH_3CN)]_2$(μ -ditz) (140 °C, 2.5 mol%, 18 h, inert atm)[10c] and phosphine functionalized NHC palladium complexes (140 °C, 2.5 mol%, 18 h, inert atm)[10d] are less efficient compared to **C3**. A NHC Im-palladium complex was reported to be better for C-H arylation of benzimidazole and imidazole with aryl chlorides, but 2-4 mol% of catalyst is required to achieve acceptable yields under inert conditions.[10b] Palladium (II) complexes having both NHC and phosphine ligands were found to be efficient catalysts (140 °C, 2.5 mol%, 18 h) for arylation of imidazole.[10a] However, their protocol required higher catalyst loading, longer reaction times, and substantially higher reaction temperature compared to our optimized protocol. A tridentate C,N,O-donor palladium(II)-NHC was also reported to catalyze the direct C-H functionalization of heterocycles with aryl bromides. This protocol also required longer time, harsher conditions and a higher catalyst loading (2 mol%, 18 h, 140 °C).[20] Recently, palladium (II) complexes of organochalcogen bearing NHC ligands were used as efficient catalyst for the direct arylation of imidazoles. The catalyst loading was 0.5 mol% and good yields were obtained in 10 h and at a slightly lower reaction temperature than aforementioned studies (110 °C).[10f]

The reusability of **C3** was studied for arylation of 1-bromo-4-nitrobenzene (**2a**) with **1a**. After achieving maximum conversion in first reaction cycle, a fresh batch of **1a**, **2a**, K_2CO_3, and pivalic acid were added to the reaction pot (see experimental section in SI). The catalyst **C3** showed appreciable recyclability up to next five reaction cycles with minor decrease in efficiency later on**.** The results of this experiment are presented in Figure 5, which shows respective yields after each reaction cycle.

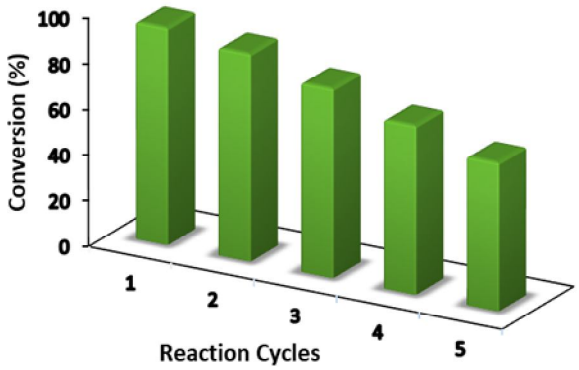


Figure 5. Results of reusability experiments of **C3** under standard reaction conditions.

Homogeneous vs heterogeneous catalysis.

To gain an insight about the type of catalytic process (homogeneous vs heterogeneous), PPh_3 and Hg poisoning experiments were performed.[21] The availability of excess amount of PPh_3 or Hg (5.0 mol% PPh_3 or Pd/Hg 1/300) under standard reactions conditions (Table 1, entry 18) showed negligible effect on the yield of desired product (see experimental section for procedure and results). This confirms the homogeneous nature of present catalytic process for the regioselective arylation of imidazole.

■ Conclusions

Three moisture/air insensitive palladium(II) complexes, two of them bearing novel S,C_{NHC} half-pincer ligand and one bearing Se,C_{NHC},S type first pincer ligand, have been successfully synthesized in high yield and fully characterized with multinuclear NMR, HR-MS and FT-IR. Single crystal X-ray studies of the two Pd(II) complexes revealed the distorted square planar geometry around Pd in each complex. All three complexes were screened for the catalysis of regioselective C-H bond arylation of imidazole in open air conditions. Owing to the unique S,C_{NHC},Se pincer coordination mode, the air/moisture stable complex **C3** showed excellent activity and remarkable C-5 selectivity during C-H bond arylation of imidazoles derivatives with aryl bromides/chlorides, yet running under mild conditions with air and moisture tolerance. This work shows a promising outlook for the use of chalcogenated *N*-heterocyclic carbenes in catalysis by enabling unique selectivity paradigms. The catalyst showed high functional group tolerance and only 0.5 mol% of the catalyst loading was found to be sufficient in achieving

excellent yields. More importantly, the catalyst can also be reused efficiently up to five reaction cycles with minor decrease in the catalytic efficiency. Mercury and PPh_3 poisoning tests suggest homogeneous nature of the catalysis process.

■ E**xperimental section**

General. All the reactions to synthesize imidazolium salts (**L1**-**L3**) and carbene complexes (**C1**-**C3**) were performed under inert atmosphere using standard Schlenk techniques. Direct arylation reactions were cunducted in pressure tube under aerobic conditions. HPLC grade 1,2-dichloeoethane, EtOH, CH_2Cl_2, toluene, hexane, CH_3CN, THF, DMF, DMSO, NMP and 1,4-dioxane were used directly for the reactions. $CDCl_3$ (Sigma Aldrich), thiophenol (Spectrochem), diphenyldiselenide (TCI Ltd.), $NaBH_4$ (Fisher Scientific), Na_2SO_4 (EMD), $PdCl_2$ (Alfa Aesar, 99.9%), 1-methyl-1*H*-imidazole (Alfa Aesar), and 1,2-dimethyl-1*H*-imidazole (Alfa Aesar), were used as purchased. The other reagents used for arylation reaction were procured from local sources and used as purchased. The proton and carbon NMR spectra were obtained on Bruker 400 MHz instrument at ambient temperature. The solvent peaks are referenced as (δ, ppm): ^{1}H, $CHCl_3$ (7.26); $^{13}C\{^1H\}$, $CDCl_3$ (77.00). HRMS were recorded using Agilent Technologies 6545 Q-TOF LC/MS. The melting points of complexes were taken in open capillary and reported as it is. IR spectrums of all ligands and complexes were taken on a Nicolet Protége 460 FT-IR spectrometer on KBr pellets.

3-Benzyl-1-(2-phenylthio-ethyl)-3*H*-imidazolium bromide (L1). A round bottom reaction flask was used and filled with 1-(2-(phenylthio)ethyl)-1*H*-imidazole (0.408 g, 2.00 mmol), benzyl bromide (0.342 g, 2.00 mmol), and acetonitrile (4 mL) and attached with a condenser under inert atmosphere. The mixture was heated on refluxing for 48 h while stirring. After 48 h, the reaction was cooled to room temperature and solvent was removed using rotary evaporation. The residue was washed with *n*-pentane and dried to give L**1** as a dark red viscous oil (0.713 g, 1.90 mmol, 95%).

NMR ($CDCl_3$, δ/ppm): **^{1}H** (400 MHz) 10.21 (s, 1H, H_9), 7.53 – 7.52 (m, 1H, H_8), 7.45 – 7.42 (m, 2H, H_7 and H_3), 7.37 – 7.35 (m, 3H, H_3 and H_{12}), 7.32 – 7.29 (m, 2H, H_2), 7.27 – 7.18

(m, 4H, H_{13}, H_{14} and H_1), 5.49 (s, 2H, H_{10}), 4.51 (t, $^3J_{H-H}$ = 6.1 Hz, 2H, H_6), 3.47 (t, $^3J_{H-H}$ = 6.1 Hz, 2H, H_5); **$^{13}C\{^1H\}$** (100 MHz) 137.0 (s, C_9), 133.3 (s, C_4), 132.8 (s, C_{11}), 130.3 (s, C_3), 129.5 (s, C_1), 129.5 (s, C_{12}), 129.4 (s, C_2), 129.0 (s, C_{13}), 127.3 (s, C_{14}), 123.1 (s, C_7), 121.6 (s, C_8), 53.3 (s, C10), 49.2 (s, C6), 34.3 (s, C_5). **IR** (cm^{-1}, powder film): 3040 (w), 2963 (s), 1558 (s), 1265 (m), 1026 (m), 725 (s). **Mass** (CH_3CN) $[M - Br]^+$ (*m/z*) Found: 295.1261; Calc. value for $[C_{18}H_{19}N_2S]^+$: 295.1263.

3-Benzhydryl-1-(2-phenylthio)-ethyl)-3*H*-imidazolium bromide (L2). Acetonitrile (4 mL), 1-(2-(phenylthio)ethyl)-1*H*-imidazole (0.409 g, 2.00 mmol), and (bromomethylene)dibenzene (0.494 g, 2.00 mmol) were taken in a round bottom flask using procedure same as **L1**. A similar workup as **L1**, gave **L2** as a dark red viscous oil (0.834 g, 1.85 mmol, 92%).

NMR ($CDCl_3$, δ/ppm): **^1H** (400 MHz) 9.60 (s, 1H, H_9), 7.89 (s, 1H, H_7), 7.39 – 7.36 (m, 7H, H_3, H_{12} and H_8), 7.24 – 7.17 (m, 9H, H_1, H_2, H_{13}, and H_{14}), 7.11 (s, 1H, H_{10}), 4.57 (t, $^3J_{H-H}$ = 6.0 Hz, 2H, H_6), 3.49 (t, $^3J_{H-H}$ = 6.0 Hz, 2H, H_5); **$^{13}C\{^1H\}$** (100 MHz) 137.0 (s, C_9), 136.3 (s, C_{11}), 133.1 (s, C_4), 130.1 (s, C_3), 129.5 (s, C_2), 129.4 (s, C_{12}), 128.3 (s, C_{13}), 127.3 (s, C_{14} and C_1 merged), 123.5 (s, C_7), 121.4 (s, C_8), 66.8 (s, C_{10}), 49.0 (s, C_6), 34.2 (s, C_5); **IR** (cm^{-1}, powder film): 3078 (s), 2945 (m), 1551 (s), 1450 (s), 1327 (m), 1141 (s), 864 (s), 733 (s); **Mass** (CH_3CN) $[M - Br]^+$ (*m/z*) Found: 371.1566 ; Calc. value for $[C_{18}H_{19}N_2S]^+$: 371.1576.

Complex 1. Path A: A round bottom two necked flask taken to combine **L1** (0.454 g, 1.21 mmol), Ag_2O (0.280 g, 1.21 mmol), and CH_2Cl_2 (25 mL). The reaction mixture was stirred overnight at rt under nitrogen atmosphere. $Pd(CH_3CN)_2Cl_2$ (0.314 g, 1.21 mmol) in CH_2Cl_2 (5 mL) was then mixed in the reaction mixture and further stirred at rt. After 8 h, reaction mixture was passed through celite pad and filtrate was concentrated on a rotary evaporator. The remaining residue was then purified by using silica column (2 × 12 cm) with MeOH/CH_2Cl_2 (1:20 v/v) solvents. Complex **C1** was collected by removing solvent fractions containing product, using rotary evaporator. The **C1** was isolated as yellow solid (0.502 g, 1.06 mmol, 88%). mp: 192-194 °C.

Path B: A round bottom two necked flask taken to combine **L1** (0.454 g, 1.21 mmol), *t*-

BuOK (0.168 g, 1.50 mmol), $Pd(CH_3CN)_2Cl_2$ (0.314 g, 1.21 mmol) and THF (20 mL). The reaction mixture was stirred at reflux under nitrogen atmosphere. After 10 h, reaction mixture was passed through celite pad and filtrate was concentrated on a rotary evaporator. A similar workup as **C1** (Path A), gave **C1** as a yellow solid (0.371 g, 0.84 mmol, 65%).

NMR (Path A) ($CDCl_3$, δ/ppm): **^{1}H** (400 MHz) 7.52 – 7.33 (m, 14H) 5.69 – 5.41 (m, 2H, H_6), 4.59 (br s, 2H, H_5); **^{13}C{^{1}H}** (100 MHz) 137.1 (s, C_9), 136.6 (s, C_4), 132.9 (s, C_{11}), 130.9 (s, C_3), 130.0 (s, C_1), 129.2 (s, C_{12}), 129.1 (s, C_2), 128.9 (s, C_13), 128.6 (s, C_{14}), 123.7 (s, C_7, C_8), 53.7 (C_{10}), 49.7 (s, C_6), 23.5 (s, C_5). **IR** (cm^{-1}, powder film): 3095 (w), 2924 (m), 1419 (s), 1211 (m), 717 (s); **Mass** (CH_3CN) $[(M + H) – PdCl_2]^+$ (*m/z*) Found: 295.1260; Calc. value for $[C_{18}H_{19}N_2S]^+$: 295.1263.

Complex 2. Path A. CH_2Cl_2 (25 mL), **L2** (0.546 g, 1.21 mmol), Ag_2O (0.280 g, 1.21 mmol) and $Pd(CH_3CN)_2Cl_2$ (0.314 g, 1.21 mmol) were taken in a round bottom flask by using procedure same as **C1 (Path A)**. A similar workup as **C1**, gave **C2** as a yellow solid (0.523 g, 0.96 mmol, 79%). mp: 196-198 °C.

Path B: THF (20 mL), **L2** (0.546 g, 1.21 mmol), *t*-BuOK (0.168 g, 1.50 mmol), and $Pd(CH_3CN)_2Cl_2$ (0.314 g, 1.21 mmol) were taken in a round bottom flask by using procedure same as **C1 (Path B)**. A similar workup as **C1 (Path A)**, gave **C2** as a yellow solid (0.411 g, 0.75 mmol, 62%).

NMR (Path A) ($CDCl_3$, δ/ppm): **^{1}H** (400 MHz) 7.84 – 7.08 (m, 18H), 4.85 – 4.36 (m, 2H), 3.82 – 3.50 (m, 2H); **^{13}C{^{1}H}** (100 MHz) 138.8 (s, C_9), 138.6 (s, C_{11}), 134.9 (s, C_4), 130.1 (s, C_3), 129.9 (s, C_2), 129.3 (s, C_{12}), 127.9 (s, C_{13}), 126.5 (s, C_1), 124.1 (s, C_7), 121.8 (s, C_8), 67.2 (s, C_{10}), 49.8 (s, C_6), 31.9 (s, C_5). **IR** (cm^{-1}, powder film): 3094 (m), 2924 (m), 2854 (m), 1411 (m), 1072 (s), 879 (w), 732 (m); **Mass** (CH_3CN) $[M – Cl]^+$ (*m/z*) Found: 511.0207; Calc. value for $[C_{24}H_{22}ClN_2PdS]^+$: 511.0222, $[M – 2Cl]^+$ (*m/z*) Found: 475.045; Calc. value for $[C_{24}H_{22}N_2PdS]^{2+}$: 476.0539.

1-(2-(phenylselanyl)ethyl)-3-(2-(phenylthio)ethyl)-3*H*-imidazolium bromide (L3). Acetonitrile (4 mL), 1-(2-(phenylselanyl)ethyl)-1*H*-imidazole (0.502 g, 2.00 mmol), and (2-

bromoethyl)(phenyl)sulfane (0.434 g, 2.00 mmol) were taken in a round bottom flask using procedure same as **L1**. A similar workup as **L1**, gave **L3** as a off white viscous oil (0.829 g, 1.77 mmol, 88%).

NMR ($CDCl_3$, δ/ppm): **^{1}H** (400 MHz) 9.65 (s, 1H, H_9), 7.43 (br s, 2H, H_7, H_8), 7.38 – 7.36 (m, 2H, H_3), 7.25 (d, $^3J_{H–H}$ = 7.5 Hz, 2H, H_{13}), 7.18 – 7.05 (m, 6H, H_{14}, H_{15}, H_1, and H_2), 4.43 (t, $^3J_{H–H}$ = 6.3 Hz, 2H, H_6), 4.37 (t, $^3J_{H–H}$ = 6.0 Hz, 2H, H_{10}), 3.38 (t, $^3J_{H–H}$ = 6.0 Hz, 2H, H_5), 3.31 (d, $^3J_{H–H}$ = 2H, H_{11}); **^{13}C{^{1}H}** (100 MHz) 136.5 (s, C_9), 133.5 (s, C_4), 132.9 (s, C_3), 130.1 (s, C_{13}), 129.5 (s, C_2), 129.4 (s, C_{14}), 127.9 (s, C_{12}), 127.7 (s, H_1), 127.1 (s, H_{15}), 122.8 (s, C_7), 122.5 (s, C_8), 49.9 (s, C_6), 49.1 (s, C_{10}), 33.9 (C_5), 27.1 (s, C_{11}). **IR** (cm^{-1}, powder film): 3042 (w), 2951 (s), 2845 (s), 1442 (m), 1264 (m), 1028 (s), 732 (m); **Mass** (CH_3CN) $[M - Br]^+$ (*m/z*) Found: 389.0557 ; Calc. value for $[C_{19}H_{21}N_2SSe]^+$: 389.0585.

Complex 3. CH_2Cl_2 (15 mL), CH_3CN (10 mL), **L3** (0.567 g, 1.21 mmol), Ag_2O (0.280 g, 1.21 mmol) and $Pd(CH_3CN)_2Cl_2$ (0.314 g, 1.21 mmol) were taken in a round bottom flask by using procedure same as **C1**. The reaction mixture was stirred overnight under reflux in nitrogen atmosphere. Thereafter, the reaction mixture was cooled to rt and filtered through G4 crucible. Solid $AgBF_4$ (0.233 g, 1.21 mmol) was added to the filtrate and the reaction mixture was further stirred under reflux in N_2 atm. After 2 h, reaction mixture was passed through celite pad to remove the precipitate of AgCl and filtrate was concentrated on a rotary evaporator. The remaining residue was then purified by using silica column with 5% CH_3OH in CH_2Cl_2. Complex **C3** was collected by removing solvent fractions containing product, using rotary evaporator. The **C3** was isolated as an off white solid (0.567 g, 0.92 mmol, 76%). mp: 215-217 °C.

NMR ($CDCl_3$, δ/ppm): **^{1}H** (400 MHz) 7.96 (d, $^3J_{H–H}$ = 7.3 Hz, 3H, H_3, and H_{13}), 7.62 (s, 2H, C_7, and C_8), 7.60 – 7.41 (m, 6H, C_1, C_2, C_{14}, and C_{15}), 4.86 – 4.35 (m, 4H, C_{10}, and C_6), 3.32 (s, 2H, C_5), 3.08 (s, 2H, C_{11}); **^{13}C{^{1}H}** (100 MHz) 148.3 (s, C_9), 134.7 (s, C_3), 134.2 (s, C_{13}), 131.3 (s, C_4), 131.2 (s, C_1), 130.8 (s, C_{15}), 130.4 (s, C_2), 130.2 (s, C_{14}), 128.9 (s, C_{12}), 124.1 (s, C_7), 124.1 (s, C_8), 49.6 (s, C_6), 48.8 (s, C_{10}), 37.3 (s, C_5), 32.5 (s, C_{11}) . **IR** (cm^{-1}, powder film):

3007 (m), 2947 (s), 1439 (m), 1048 (s), 868 (w), 744 (m); **Mass** (CH_3CN) $[M - BF_4]^+$ (*m/z*) Found: 528.9227 ; Calc. value for $[C_{19}H_{20}ClN_2PdSSe]^+$: 528.9236.

General procedure for arylation reaction. A 10 mL pressure tube is taken to combine imidazole derivatives (2.0 mmol), additive (0.30 mmol), aryl bromide/chloride (1.0 mmol), catalyst (**C1-C3**), base (2.00 mmol), and solvents (3 mL). The reaction mixture was stirred and heated at 100 °C in open air conditions for 12 h. The progress of reaction was monitored by using TLC to achieve the maximum conversion of product. After that, the reaction mixture was cooled to rt and 25 mL distilled water was added. The mixture was washed with CH_2Cl_2 (2 ×20 mL) and dried with Na_2SO_4 (anhyd.). The solvent was then removed using rotary evaporator and mixture was purified using silica gel column (1 × 12 cm) chromatography with CH_2Cl_2/MeOH (20:1 v/v) solvents. The products as isolated were then authenticated with the help of proton and carbon NMR spectroscopy and data are presented in SI.

Reusability experiment of C3. In a 10 mL pressure tube, 1-methyl-1*H*-imidazole (2.0 mmol), 1-bromo-4-nitrobenzene (1.0 mmol), **C3** (0.5 mol %), PivOH (0.30 mmol), DMA (3 mL), and K_2CO_3 (2.0 mmol), were combined. The tube was then stirred for 12 h at 100 °C. After 12 h, the mixture was cooled to rt and an aliquot (60 μL) was pipette out for ^{1}H NMR analysis. Thereafter, a fresh batch of reactants was added without catalyst and mixture was allowed to stir for 12 h under similar reaction conditions. This procedure was repeated for three more times and the results were summarized in the Figure 5.

Triphenylphosphine poisoning test. In a pressure tube, 1-methyl-1*H*-imidazole (2.0 mmol), 1-bromo-4-nitrobenzene (1.0 mmol), PivOH (0.30 mmol), K_2CO_3 (2.0 mmol), and DMA (3 mL) were combined. Thereafter, catalyst **C3** (0.5 mol%) and triphenylphosphine (PPh_3/Pd, 1:5) were added into the reaction mixture. Mixture was stirred for 12 h under optimal reaction conditions. The analogues workup of reaction mixture resulted in 89% of **3a**.

Hg poisoning test. In a pressure tube, 1-methyl-1*H*-imidazole (2.0 mmol), 1-bromo-4-nitrobenzene (1.0 mmol), K_2CO_3 (2.0 mmol), PivOH (0.30 mmol), and DMA (3 mL) were combined. Thereafter, an excess of Hg and catalyst **C3** (0.5 mol%, Hg/Pd 300/1) were added into

the reaction mixture. Mixture was stirred for 12 h under optimal reaction conditions. The analogues workup of reaction mixture resulted in 86% of **3a**.

Notes

The authors declare no competing financial interest.

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Supplementary Information (SI)

CCDC 1963719 and 1963720 contain the supplementary crystallographic data for **C1** and **C2** respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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TOC

Palladium Complexes of Thio/Seleno-Ether Containing *N*-Heterocyclic Carbenes: Efficient and Reusable Catalyst for Regioselective C-H Bond Arylation

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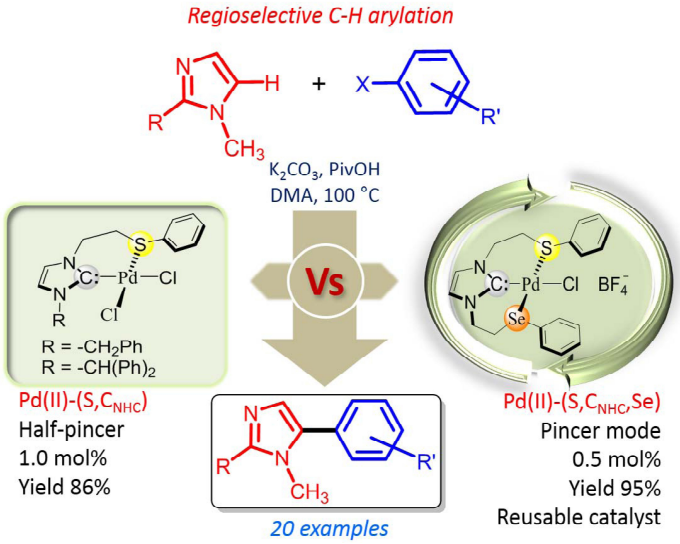

Three Pd(II) catalysts, two bearing S,C_{NHC} half-pincer and one bearing Se,C_{NHC},S type pincer, have been synthesized and applied in the regioselective C-H bond arylation of imidazole. All the complexes were found to be efficient under mild conditions. The Se,C_{NHC},S pincer ligated Pd(II) complex, which is the first example of this type, was found to be utmost effective amongst them.