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N-Heterocyclic Carbenes: Useful Ligands for the Palladium-Catalysed Direct C5 Arylation of Heteroaromatics with Aryl Bromides or Electron-Deficient Aryl Chlorides

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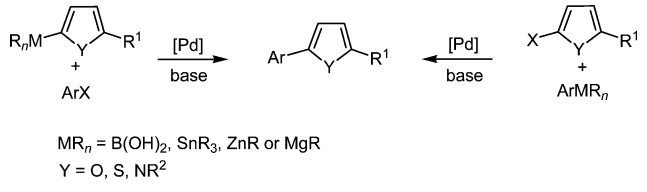
Keywords: Aryl halides / Atom economy / C–H activation / Carbenes / Heteroaromatics / Palladium

New Pd–N-heterocyclic carbene complexes have been prepared and employed for palladium-catalysed direct arylation of heteroaromatic derivatives by using aryl halides. These catalyst precursors promote the coupling of challenging aryl halides such as deactivated or congested aryl bromides and also activated aryl chlorides. This procedure employs only 1 mol-% of an air-stable palladium complex. This is a practical advantage over the procedures that employ palladium attached to air-sensitive phosphane ligands, which are often used to promote the coupling of such aryl halides.

Introduction

Due to their inherent biological activity, the synthesis of arylated heterocycles continues to attract the attention of synthetic organic chemists. Conventional methods for the synthesis of such compounds include metal-catalysed cross-coupling reactions such as Suzuki-, Stille-, Negishi- or Kumada-type reactions (Scheme 1).[1] They make possible either the coupling of aryl halides with organometallic derivatives of heterocycles or the coupling of heteroaryl halides with aryl–metal derivatives. Nevertheless, these procedures require the preliminary preparation of an organometallic derivative, and produce stoichiometric amounts of metallic salts as byproducts.



Scheme 1.

The direct regioselective couplings of heteroaromatics with aryl halides by means of C–H bond activation/functionalisation would provide cost-effective and environmentally attractive access to arylated heterocycles. The selective C2 or C5 arylation of heteroaromatics such as furans, thiophenes, thiazoles, oxazoles or indoles by means of a palladium-catalysed C–H bond activation has been largely described in recent years.[2–7] However, most of these reactions were performed by using reactive aryl halides such as aryl iodides or electron-deficient aryl bromides. Relatively few examples of couplings using deactivated aryl bromides[8,9] and especially aryl chlorides[10] have been reported so far. In most cases, the couplings with such challenging substrates were performed by using palladium attached to a phosphane ligand.[8,10] A few reactions have also been performed with $Pd(OH)_2$, $Pd(OAc)_2$ or Pd/C; however, in the presence of such a catalyst, the substrate scope is limited,[9] and the yields are low in some cases.[9a,9c]

Whereas the efficiency of phosphane ligands has been explored for these couplings, the influence of carbene ligands remains almost unexplored.[10e,11,12] One of the examples was reported by Sames and co-workers. They described in 2006 the use of imidazolylidene ligands of varying electronic and steric properties for the palladium-catalysed direct arylation of indoles or pyrroles using bromobenzene or aryl iodides.[11a] They observed that an important steric demand on the carbene ligand led to better results in terms of both rate and conversion. Fagnou and co-workers also employed quite congested N-heterocyclic carbene palladium catalysts to promote intramolecular direct arylations of arenes.[12] To the best of our knowledge, N-heterocyclic carbene ligands have not yet been employed for the palladium-catalysed direct arylation of furans, thiophenes or thiazoles.

N-Heterocyclic carbene (NHC) ligands show many interesting properties that make them valuable as ligands in palladium or ruthenium catalysis.[13–17] A combination of their powerful σ-donating and weak π-accepting character allows

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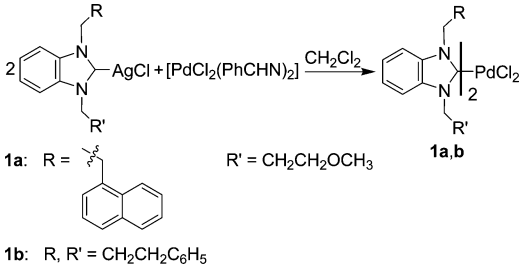
for the generation of a stronger bond to the metal atom than their phosphane homologues and leads to the formation of interestingly robust electron-rich metal complexes. Consequently, metal–NHC complexes tend to be air-stable, easy to handle and highly active in several catalytic transformations for which harsh conditions are required. *N*-Benzylimidazolinium and benzimidazolium salts have already been used to generate ruthenium–carbene complexes that have shown efficient catalytic properties in C–H bond activation[15] and allylic substitution.[16]

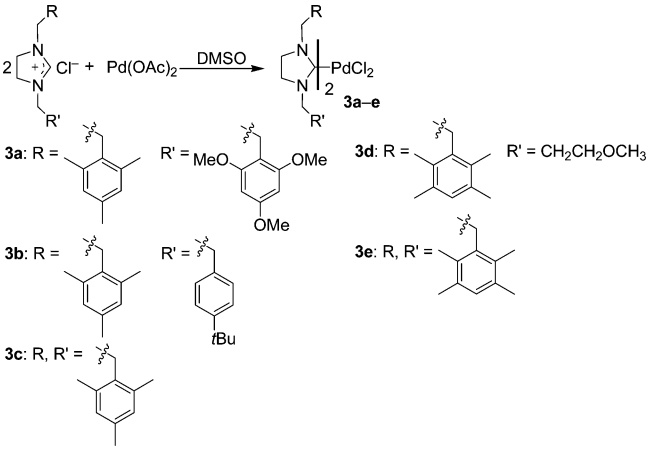
"Ligandless" palladium catalysts are generally relatively inefficient for the direct arylation of heteroaromatics by using challenging aryl bromides or aryl chlorides.[3d,4e,9] Therefore, the discovery of more efficient catalysts for the direct arylation of deactivated aryl bromides or aryl chlorides would provide environmentally attractive and industrially viable procedures. As carbene ligands have proved to be very useful for several palladium-catalysed reactions, we decided to explore their potential for the direct 5-arylation of thiophenes, furans or thiazoles.

Results and Discussion

First, we prepared a range of Pd–NHC complexes using a variety of carbene ligands. It is known that deviations from the accustomed structures of palladium–NHC complexes can be attributed to steric rather than to electronic factors.[14c] As the use of relatively congested carbene ligands had been found to be required for the direct arylation of indoles or pyrroles[11a] or arenes,[12] we decided to employ carbenes bearing relatively bulky *N*-substituents. The reaction of $[PdCl_2(PhCN)_2]$ with a silver complex of carbene ligands at room temperature gave **1a** and **1b** in 76 and 78% yields, respectively (Scheme 2). Complexes **2a**–**e** were prepared in 55–89% yields by the reaction of carbene salts with $PdCl_2$ in the presence of 3-chloropyridine and a base (Scheme 3). The reaction of benzimidazolium salts with $Pd(OAc)_2$ proceeded smoothly on heating at 60 °C for 3 h and then 110 °C for a further 2 h to give **3a**–**e**[11c] (Scheme 4).

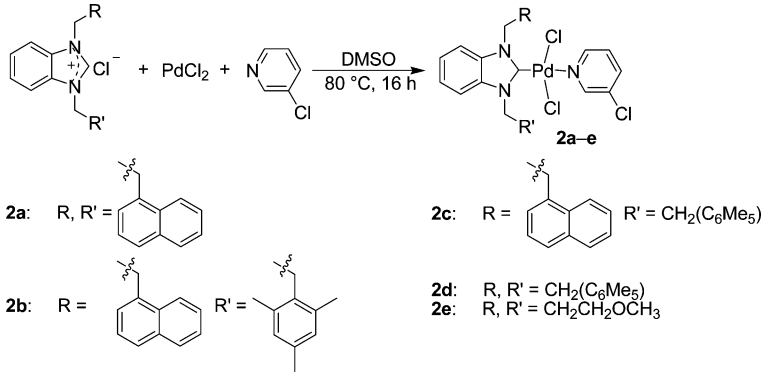


Scheme 2.

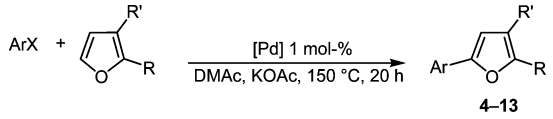


Scheme 4.

We initially directed our efforts towards the palladium-catalysed direct 5-arylation of 2-*n*-butylfuran with 4-bromoanisole using these Pd–NHC complexes (Scheme 5). We had previously observed that with this deactivated aryl bromide, a low yield of 12% was obtained in the presence of 1 mol-% $Pd(OAc)_2$ as the catalyst in the absence of ligand.[3c] At elevated temperature, when a high concentration of $Pd(OAc)_2$ is employed as the catalyst precursor (>1 mol-%), so-called "palladium black", which is generally inactive for such catalysed reactions, is formed quite rapidly. Consequently, in the absence of a stabilising agent such as phosphane or carbene ligands, the conversions of such challenging aryl bromides and the yields of coupling products are generally not increased by using a high catalyst loading (5–10 mol-%).



Scheme 3.

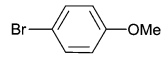
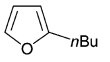
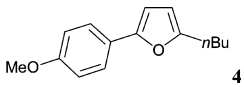
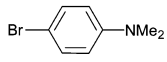
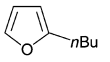
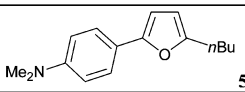
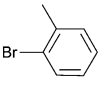
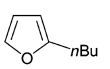
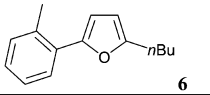
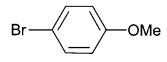
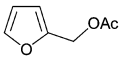
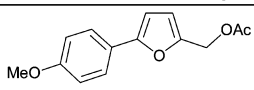
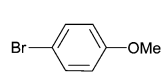
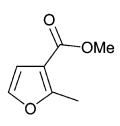
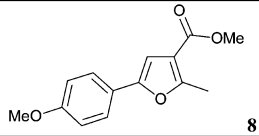
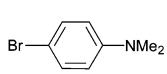
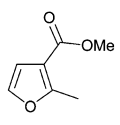
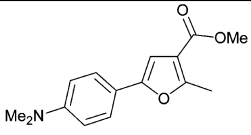


Scheme 5.

We examined the influence of our Pd–N-heterocyclic carbene complexes for this coupling reaction (Table 1, Entries 1–11). In all cases, the presence of such ligands on palladium was found to be beneficial. With several ligands, a complete conversion of 4-bromomoanisole was observed. Moreover, the yields in the target product **4** were generally high (Table 1, Entries 2, 5 and 11). The use of a hemilabile *N*-substituent[18] on the carbene in complexes **1a** and **3d**, which had been found to be beneficial for some catalysed reactions, did not improve the yield (Table 1, Entries 1, 2, 10 and 11). We also compared the efficiency of this reaction of the complexes containing an annullated N-heterocyclic carbene (**1a**, **1b** and **2a**–**e**) with complexes **3a**–**e**. Annullated N-heterocyclic carbenes are less electron-rich ligands than imidazolidinylenes.[16,19] However, we did not observe significant differences using these two types of carbene ligands (Table 1, Entries 1–11). Then, we examined the scope and limitations of some of these catalysts using a variety of aryl bromides and furan derivatives (Table 1, Entries 12–28). The reaction of strongly deactivated aryl bromide, 4-bromo-*N*,*N*-dimethylaniline with 2-*n*-butylfuran gave **5** in 69% in the presence of 1 mol-% of complex **1b** (Table 1, Entry 13). It should be noted that, in the presence of $Pd(OAc)_2$ as the catalyst, only traces of **5** had been obtained.[3c] The coupling of the congested aryl bromide, 2-bromotoluene, with 2-*n*-butylfuran also proceeded to give **6**. However, a moderate yield of 41% was obtained in the presence of catalyst **1b** due to the formation of unidentified side-products (Table 1, Entry 16). Again, the use of $Pd(OAc)_2$ as the catalyst gave only traces of **6**.[3c] Two functionalised furan derivatives have also been arylated in moderate to good yields by using 4-bromoanisole or 4-bromo-*N*,*N*-dimethylaniline (Table 1, Entries 17–28). Starting from methyl 2-methylfuran-3-carboxylate, the use of carbene ligands substituted by a hemilabile ether functionality on one side chain (complexes **1a** and **3d**) gave the highest yields (Table 1, Entries 21–26).

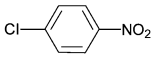
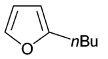
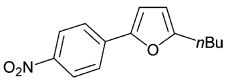
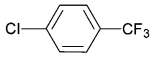
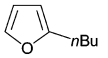
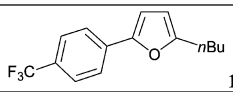
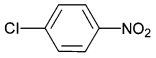
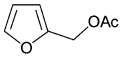
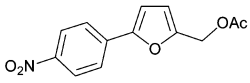
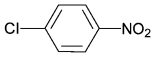
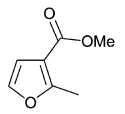
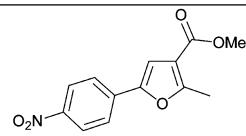
The direct coupling of aryl chlorides to heteroaromatics, and especially with furans, is still a very challenging reaction. To the best of our knowledge, only one example of coupling of a furan derivative (benzofuran) with an aryl chloride has been reported,[10b] and there is no report on the use of Pd–N-heterocyclic carbene complexes for this reaction. We observed that the reaction of 4-chloronitrobenzene with three furan derivatives gave **10**, **12** and **13** in good yields (Table 2, Entries 1–4 and 6–12). On the other hand,

Table 1. Pd-catalysed direct arylation of furan derivatives by using aryl bromides (Scheme 5).[a]

Entry	Aryl bromide	Furan derivative	Major product	Catalyst	Conv. (%)	Yield (%)
1			 **4**	**1a**	96	74
2				**1b**	100	79
3				**2a**	96	69
4				**2b**	100	59
5				**2c**	100	76
6				**2d**	94	64
7				**3a**	99	66
8				**3b**	100	63
9				**3c**	80	61
10				**3d**	83	58
11				**3e**	100	71
12			 **5**	**1a**	99	65
13				**1b**	100	69
14				**3a**	77	31
15			 **6**	**1a**	98	39
16				**1b**	100	41
17			 **7**	**1a**	99	46
18				**1b**	100	76
19				**2a**	98	63
20				**2c**	100	64
21			 **8**	**1a**	91	66
22				**1b**	95	53
23				**2b**	91	42
24				**3a**	93	57
25				**3b**	84	28
26				**3d**	97	79
27			 **9**	**2b**	40	25
28				**3a**	80	44

[a] Conditions: [Pd] (0.01 mmol), aryl bromide (1 mmol), furan derivative (2 mmol), KOAc (2 mmol), *N*,*N*-dimethylacetamide (DMAc; 3 mL), 150 °C, 20 h, conversion of the aryl bromide determined by GC and NMR spectroscopy, isolated yields.

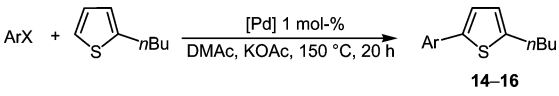
Table 2. Pd-catalysed direct arylation of furan derivatives by using aryl chlorides (Scheme 5).[a]

Entry	Aryl bromide	Furan derivative	Major product	Catalyst	Conv. (%)	Yield (%)
1			 **10**	**1a**	97	51
2				**1b**	98	50
3				**2a**	100	71
4				**3a**	100	69
5			 **11**	**1a**	100	19
6			 **12**	**1a**	92	70
7				**1b**	100	48
8				**2c**	100	73
9				**3a**	100	66
10			 **13**	**2a**	98	78
11				**2b**	100	52
12				**3a**	95	59

[a] Conditions: [Pd] (0.01 mmol), aryl chloride (1 mmol), furan derivative (2 mmol), KOAc (2 mmol), DMAc (3 mL), 150 °C, 20 h, conversion of the aryl chloride determined by GC and NMR spectroscopy, isolated yields.

1-chloro-4-(trifluoromethyl)benzene was found to be less reactive, and **11** was obtained in only 19% yield (Table 2, Entry 5).

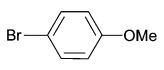
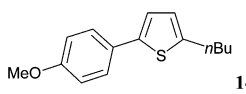
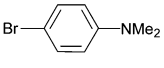
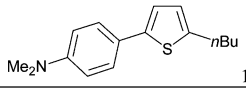
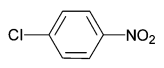
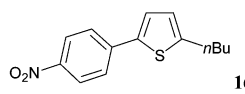
Next, we examined the reactivity of 2-*n*-butylthiophene in the presence of these Pd–N-heterocyclic carbene complexes (Scheme 6, Table 3). High yields of **14** were obtained for the coupling with 4-bromoanisole by using catalysts **1a**, **1b** or **3a** (Table 3, Entries 1, 2 and 6). Even 4-bromo-*N*,*N*-dimethylaniline was successfully coupled with 2-*n*-butylthiophene in the presence of 1 mol-% of catalyst **1b** to give **15** in 69% yield (Table 3, Entry 8). It should be noted that for this reaction the use of $Pd(OAc)_2$ without addition of ligands gave no coupling product.[4e] Several complexes were employed for the coupling of 1-chloro-4-nitrobenzene; however, only moderate yields of **16** were obtained (Table 3, Entries 11–18). The best yields were obtained in the presence of the benzimidazolylidene-containing carbene complexes **2c**, **2d** and **2e**, whereas imidazolidinium ligand based complexes **3a** and **3c** gave very poor yields (Table 3, Entries 14–18). It should be noted that no example of direct arylation of thiophenes with aryl halides by using Pd–N-heterocyclic carbene complexes have been reported so far.



Scheme 6.

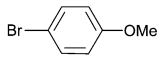
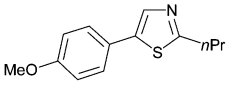
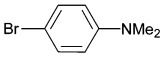
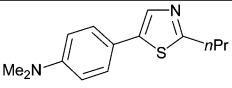
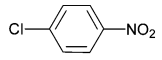
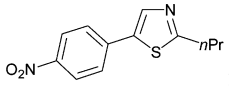
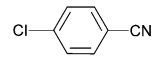
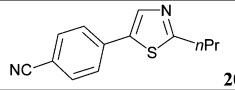
Finally, we studied the reactivity of a thiazole derivative with these Pd–carbene complexes (Table 4). As expected, good yields of product **17** were obtained in the presence of 2-*n*-propylthiazole and 4-bromoanisole (Table 4, Entries 1–6). The use of more challenging substrate 4-bromo-*N*,*N*-dimethylaniline reacted with 2-*n*-propylthiazole gave the target compound **18** in high yield (Table 4, Entries 7 and 8).

Table 3. Pd-catalysed direct arylation of 2-*n*-butylthiophene by using aryl halides (Scheme 6).[a]

Entry	Aryl bromide	Major product	Catalyst	Conv. (%)	Yield (%)
1		 **14**	**1a**	94	80
2			**1b**	100	77
3			**2a**	75	45
4			**2c**	100	56
5			**2e**	59	10
6			**3a**	100	81
7			**3b**	93	32
8		 **15**	**1b**	89	69
9			**2a**	40	21
10			**3b**	57	28
11		 **16**	**1b**	57	23
12			**2a**	98	40
13			**2b**	100	31
14			**2c**	100	50
15			**2d**	84	45
16			**2e**	97	51
17			**3a**	62	23
18			**3c**	93	15

[a] Conditions: [Pd] (0.01 mmol), aryl halide (1 mmol), 2-*n*-butylthiophene (2 mmol), KOAc (2 mmol), DMAc (3 mL), 150 °C, 20 h, conversion of the aryl halide determined by GC and NMR spectroscopy, isolated yields.

Table 4. Pd-catalysed direct arylation of 2-*n*-propylthiazole by using aryl halides (Scheme 7).[a]

Entry	Aryl bromide	Major product	Catalyst	Conv. (%)	Yield (%)
1		 **17**	**1a**	100	82
2			**1b**	100	80
3			**2a**	96	89
4			**2b**	100	85
5			**2d**	100	92
6			**3a**	100	75
7		 **18**	**1a**	89	71
8			**2a**	94	82
9		 **19**	**1a**	65	35
10			**1b**	92	39
11			**2a**	99	62
12			**2b**	99	65
13			**2d**	99	60
14			**3a**	100	68
15			**3b**	100	72
16			**3c**	76	39
17		 **20**	**2d**	82	41
18			**3b**	66	37

[a] Conditions: [Pd] (0.01 mmol), aryl halide (1 mmol), 2-*n*-propylthiazole (2 mmol), KOAc (2 mmol), DMAc (3 mL), 150 °C, 20 h, conversion of the aryl halide determined by GC and NMR spectroscopy, isolated yields.

We had previously observed that $Pd(OAc)_2$ catalyses this reaction in moderate yield.[9d] Up to 72% of product **19** was obtained for the coupling of 1-chloro-4-nitrobenzene in the presence of catalyst **3b** (Table 4, Entry 15).

Conclusion

We have demonstrated that N-heterocyclic carbene ligands attached to a palladium(II) centre generate useful catalyst precursors for the direct regioselective C5 arylation of furans, thiophenes or thiazoles using some deactivated aryl bromides. We also report the first examples of direct arylations of heteroaromatics using aryl chlorides as coupling partners in the presence of Pd–N-heterocyclic carbene complexes. Our procedure employs only 1 mol-% of air-stable palladium complexes.[20] This is a practical advantage over the procedures using palladium attached to air-sensitive phosphane ligands.[10b,10d,10e,10f] Finally, this procedure is environmentally attractive, as the major byproducts are AcOK together with HBr instead of the metal salts that result from using more classical coupling procedures.

Experimental Section

General Remarks: All chemical reactants were obtained from commercial sources and used without further purification. NHC–Pd and NHC–$PdCl_2$–3-chloropyridine complexes were prepared according to known methods.[16] DMAc analytical grade (99%) was not distilled before use. KOAc (99%+) was employed. All reactions were carried out under argon by using vacuum lines with Schlenk tubes and oven-dried glassware. ^1H (200 MHz) and ^{13}C (50 MHz) spectra were recorded in $CDCl_3$. Chemical shifts (δ) are reported in ppm relative to $CDCl_3$. Flash chromatography was performed on silica gel (230–400 mesh).

Synthesis of the Benzimidazol-2-ylidene–Pd Complexes 1: Benzimidazolin-2-ylidene–Ag complex (2 mmol) and $[PdCl_2(PhCN)_2]$ (1 mmol) were dissolved in CH_2Cl_2 (20 mL) and stirred at room temperature for 24 h. The reaction mixture was purified through a short pad of Celite. The solvent was removed under reduced pressure. The solid was washed with diethyl ether (3 × 10 mL) and dried under vacuum. The crude product was then crystallised from CH_2Cl_2/Et_2O (1:2) (Scheme 2).

Dichloridobis[1-(2-methoxyethyl)-3-(naphthalen-1-ylmethyl)benzimidazol-2-ylidene]palladium(II) (1a): Yield: 0.616 g, 76%; m.p. 237–238 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.46 (s, 6 H, $CH_2CH_2OCH_3$), 4.65 (m, 8 H, $CH_2CH_2OCH_3$), 6.20 (s, 4 H, $CH_2C_{10}H_7$), 6.89–8.45 (m, 22 H, Ar-*H*) ppm. ^{13}C NMR (75.7 MHz, $CDCl_3$): δ = 47.9 49.5, 58.6, 71.8, 110.6, 111.2, 122.3, 122.9, 125.2, 125.5, 126.0, 126.8, 128.1, 128.3, 130.3, 133.2, 134.3, 135.3, 182.5 ppm. $C_{42}H_{40}Cl_2N_4O_2Pd$ (810.12): calcd. C 62.27, H 4.98, N 6.92; found C 62.28, H 4.95, N 6.89.

Bis[1,3-bis(2-phenylethyl)benzimidazol-2-ylidene]dichloridopalladium(II) (1b): Yield: 0.648 g, 78%; m.p. 278–279 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.46 (m, 16 H, $CH_2CH_2C_6H_5$), 7.07–7.73 (m, 28 H, Ar-*H*) ppm. ^{13}C NMR (75.7 MHz, $CDCl_3$): δ = 50.4, 55.4, 112.5, 124.3, 127.1, 129.0, 129.3, 133.5, 138.1, 183.9 ppm. $C_{46}H_{44}Cl_2N_4Pd$ (830.19): calcd. C 66.55, H 5.34, N 6.75; found C 66.54, H 5.34, N 6.76.

Synthesis of the NHC–$PdCl_2$–3-Chloropyridine Complexes 2a–e: In air, a vial was charged with $PdCl_2$ (1.0 mmol), benzimidazolidinium salt (1.1 mmol), K_2CO_3 (5 mmol) and a stirrer bar. 3-Chloropyridine (4.0 mL) was added and the mixture heated with vigorous stirring at 80 °C for 16 h. After cooling to room temperature, the reaction mixture was diluted with CH_2Cl_2 and filtered through a short pad of silica gel covered with a pad of Celite eluting with CH_2Cl_2 until the product was completely recovered. Most of the CH_2Cl_2 was removed, and the 3-chloropyridine was then vacuum-distilled and saved for reuse. The pure complexes **2a**–**e** were isolated after triturating with hexane, decanting the supernatant and drying under high vacuum (Scheme 3).

[1,3-Bis(naphthalen-1-ylmethyl)benzimidazol-2-ylidene]dichlorido[(3-chloropyridine-*N*)palladium(II) (2a): Yield: 0.613 g, 89%; m.p. 170–171 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 6.77 (s, 4 H, CH_2Ar), 7.05–8.91 (m, 22 H, Ar-*H*) ppm. ^{13}C NMR (75.7 MHz, $CDCl_3$): δ

= 50.5, 115.5, 122.9, 123.6, 124.7, 125.2, 125.6, 126.0, 126.1, 126.9, 128.8, 129.0, 130.2, 130.8, 132.5, 133.8, 134.7, 138.1, 149.2, 150.3, 164.8, 197.3 ppm. $C_{34}H_{26}Cl_3N_3Pd$ (689.37): calcd. C 59.24, H 3.80, N 6.10; found C 59.23, H 3.82, N 6.11.

Dichlorido(3-chloropyridine-*N*)[1-(naphthalen-1-ylmethyl)-3-(2,3,4,5,6-pentamethylbenzyl)benzimidazol-2-ylidene]palladium(II) (2b): Yield: 0.582 g, 82%; m.p. 135–136 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.42 (m, 15 H, C_6Me_5), 6.33 (s, 2 H, CH_2Ar), 6.71 (s, 2 H, CH_2Ar), 6.80–8.91 (m, 15 H, Ar-*H*) ppm. ^{13}C NMR (75.7 MHz, $CDCl_3$): δ = 17.7, 18.0, 18.1, 50.7, 51.8, 103.9, 111.6, 114.4, 123.4, 123.7, 126.1, 126.2, 127.2, 129.5, 135.0, 136.5, 138.5, 149.6, 150.6, 157.9, 164.0, 175.5 ppm. $C_{35}H_{34}Cl_3N_3Pd$ (709.44): calcd. C 59.25, H 4.83, N 5.92; found C 59.25, H 4.86, N 5.94.

Dichlorido(3-chloropyridine-*N*)[1-(naphthalen-1-ylmethyl)-3-(2,4,6-trimethylbenzyl)benzimidazol-2-ylidene]palladium(II) (2c): Yield: 0.600 g, 88%; m.p. 154–155 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.43 (s, 9 H), 5.57 (s, 2 H, Ar), 5.92 (s, 2 H, CH_2Ar), 6.31 (s, 2 H, CH_2Ar), 6.50–8.32 (m, 15 H, Ar-*H*) ppm. ^{13}C NMR (75.7 MHz, $CDCl_3$): δ = 20.8, 20.9, 21.0, 49.1, 50.2, 110.5, 111.2, 122.3, 122.8, 123.1, 124.7, 125.1, 126.1, 126.7, 127.5, 127.9, 128.3, 128.5, 129.1, 129.7, 130.4, 131.2, 132.5, 133.1, 133.7, 134.6, 137.6, 138.1, 138.9, 149.2, 163.8, 182.6 ppm. $C_{33}H_{30}Cl_3N_3Pd$ (681.39): calcd. C 58.17, H 4.44, N 6.17; found C 58.15, H 4.45, N 6.17.

Dichlorido(3-chloropyridine-*N*)[1,3-bis(2,3,4,5,6-pentamethylbenzyl)-benzimidazol-2-ylidene]palladium(II) (2d): Yield: 0.576 g, 79%; m.p. 340 °C (decomp). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.36 (m, 30 H, C_6Me_5), 6.28 (s, 4 H, C$H_2C_6Me_5$), 6.40–8.87 (m, 8 H, Ar-*H*) ppm. ^{13}C NMR (75.7 MHz, $CDCl_3$): δ = 17.7, 17.9, 18.0, 51.8, 111.6, 123.0, 125.1, 128.3, 133.5, 133.6, 135.1, 136.3, 138.4, 148.0, 149.5 150.5, 159.6, 164.4, 175.6 ppm. $C_{36}H_{42}Cl_3N_3Pd$ (729.52): calcd. C 59.27, H 5.80, N 5.76; found C 59.30, H 5.20, N 5.75.

[1,3-Bis(2-methoxyethyl)benzimidazol-2-ylidene]dichlorido(3-chloropyridine-*N*)palladium(II) (2e): Yield: 0.289 g, 55%; m.p. 104–105 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.36 (s, 6 H, $NCH_2CH_2OCH_3$), 5.07 (m, 8 H, $NCH_2CH_2OCH_3$), 6.40–8.87 (m, 8 H, Ar-*H*) ppm. ^{13}C NMR (75.7 MHz, $CDCl_3$): δ = 48.6, 59.2, 71.7, 111.3, 123.2, 124.9, 132.7, 135.2, 138.2, 149.2, 150.3, 161.5, 186.5 ppm. $C_{18}H_{22}Cl_3N_3O_2Pd$ (525.16): calcd. C 41.17, H 4.22, N 8.00; found C 41.18, H 4.23, N 8.01.

The complexes **3a**, **3c**, **3d** and **3e** were synthesised according to a literature procedure.[20a]

Synthesis of Bis[1-(4-*tert*-butylbenzyl)-3-(2,4,6-trimethylbenzyl)-imidazolin-2-ylidene]dichloridopalladium(II) (3b): A stirred solution of 1,3-dialkylimidazolidinium salt (2 mmol) and $Pd(OAc)_2$ (1 mmol) in DMSO (10 mL) was heated at 60 °C for 3 h and then at 110 °C for a further 2 h, during which time the reaction solution changed from being initially orange. The solvent was then removed in vacuo to give pale yellow solid **3b**. The crude product was crystallised from CH_2Cl_2/Et_2O (1:2). The crystals were filtered, washed with diethyl ether (3 × 10 mL) and dried under vacuum (Scheme 7). Yield: 0.568 g, 65%; m.p. 230 °C (decomp). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.32 (s, 18 H, *t*Bu), 2.41 (m, 18 H, Me), 3.18 (m, 4 H, CH_2CH_2), 3.40 (m, 4 H, CH_2CH_2), 5.35 (s, 8 H, CH_2Ar), 6.87 (s, 4 H, Ar), 7.29 (d, *J* = 8.4 Hz, 4 H, Ar), 7.45 (d, *J* = 8.4 Hz, 4 H, Ar) ppm. ^{13}C NMR (75.7 MHz, $CDCl_3$): δ = 20.7, 20.9, 21.0, 54.5, 125.8, 127.5, 128.5, 129.3, 131.6, 138.1, 138.4, 151.2, 174.6 ppm. $C_{48}H_{64}Cl_2N_4Pd$ (874.37): calcd. C 65.93, H 7.38, N 6.41; found C 65.94, H 7.37, N 6.42.

General Procedure for Direct Arylations: In a typical experiment, the aryl halide (1 mmol), heteroaryl derivative (2 mmol) and KOAc (2 mmol) were introduced into a Schlenk tube equipped with a magnetic stirring bar. The Pd complex (0.01 mmol, see Tables 1–4) and DMAc (3 mL) were added, and the Schlenk tube was purged several times with argon. The Schlenk tube was placed in a pre-heated oil bath at 150 °C, and the reactants were stirred for 20 h. Then, the reaction mixture was analysed by gas chromatography to determine the conversion of the aryl halide. The solvent was removed by heating of the reaction vessel under vacuum, and the residue was charged directly onto a silica gel column. The products were eluted by using an appropriate ratio of diethyl ether/pentane.

2-*n*-Butyl-5-(4-methoxyphenyl)furan (4):[3c] The reaction of 4-bromoanisole (0.187 g, 1 mmol), 2-*n*-butylfuran (0.248 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with **1a** (8.00 mg, 0.01 mmol) afforded the corresponding product **4** in 74% (0.170 g) yield.

2-*n*-Butyl-5-[4-(dimethylamino)phenyl]furan (5): The reaction of 4-bromo-*N*,*N*-dimethylaniline (0.200 g, 1 mmol), 2-*n*-butylfuran (0.248 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with **1a** (8.00 mg, 0.01 mmol) afforded the corresponding product **5** in 65% (0.158 g) yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.95 (t, *J* = 7.3 Hz, 3 H, $H_3CCH_2CH_2CH_2$), 1.46 (m, 2 H, $H_3CCH_2CH_2CH_2$), 1.46 (m, 2 H, $H_3CCH_2CH_2CH_2$), 2.69 (t, *J* = 7.3 Hz, 2 H, $H_3CCH_2CH_2CH_2$), 2.99 [s, 6 H, $C_6H_4N(CH_3)_2$], 6.04 (d, *J* = 3.2 Hz, 2 H, furan), 6.35 (d, *J* = 3.2 Hz, 2 H, furan), 6.75 (d, *J* = 8.9 Hz, Ar), 7.54 (d, *J* = 8.9 Hz, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.3, 22.7, 28.4, 30.5, 40.8, 101.3, 111.9, 112.7, 113.6, 125.5, 126.8, 145.6, 146.5 ppm. $C_{16}H_{21}NO$ (243.34): calcd. C 78.97, H 8.70, N 5.76; found C 78.95, H 8.72, N 5.77.

2-*n*-Butyl-5-(2-methylphenyl)furan (6):[8l] The reaction of 2-bromotoluene (0.171 g, 1 mmol), 2-*n*-butylfuran (0.248 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with **1a** (8.00 mg, 0.01 mmol) afforded the corresponding product **6** in 39% (0.084 g) yield.

[5-(4-Methoxyphenyl)furan-2-yl]methyl Acetate (7):[8e] The reaction of 4-bromoanisole (0.187 g, 1 mmol), furfuryl acetate (0.280 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with **1b** (8.30 mg, 0.01 mmol) afforded the corresponding product **7** in 76% (0.187 g) yield.

Methyl 2-(4-Methoxyphenyl)-5-methylfuran-3-carboxylate (8):[8e] The reaction of 4-bromoanisole (0.187 g, 1 mmol), methyl 2-methylfuran-3-carboxylate (0.280 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with **1a** (8.00 mg, 0.01 mmol) afforded the corresponding product **8** in 66% (0.163 g) yield.

Methyl 2-[4-(Dimethylamino)phenyl]-5-methylfuran-3-carboxylate (9): The reaction of 4-bromo-*N*,*N*-dimethylaniline (0.200 g, 1 mmol), methyl 2-methylfuran-3-carboxylate (0.280 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with **3a** (10.4 mg, 0.01 mmol) afforded the corresponding product **9** in 44% (0.114 g) yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.65 (s, 3 H, CH_3), 3.00 [s, 6 H, $N(CH_3)_2$], 3.86 (s, 3 H, OCH_3), 6.59 (s, 1 H, furan), 6.75 (d, *J* = 8.8 Hz, 2 H, Ar), 7.54 (d, *J* = 8.8 Hz, 2 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 40.9, 51.7, 57.9, 102.6, 112.7, 114.5, 123.2, 125.3, 126.8, 140.8, 143.5, 164.5 ppm. $C_{15}H_{17}NO_3$ (259.30): calcd. C 69.48, H 6.61, N 5.40; found C 69.49, H 6.63, N 5.38.

2-*n*-Butyl-5-(4-nitrophenyl)furan (10):[3d] The reaction of 1-chloro-4-nitrobenzene (0.157 g, 1 mmol), 2-*n*-butylfuran (0.248 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with **3a** (10.4 mg, 0.01 mmol) afforded the corresponding product **10** in 69% (0.169 g) yield.

2-*n*-Butyl-5-[4-(trifluoromethyl)phenyl]furan (11):[3d] The reaction of 1-chloro-4-(trifluoromethyl)benzene (0.181 g, 1 mmol), 2-*n*-butylfuran (0.248 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with **1a** (8.00 mg, 0.01 mmol) afforded the corresponding product **11** in 19% (0.051 g) yield.

[5-(4-Nitrophenyl)furan-2-yl]methyl Acetate (12):[8e] The reaction of 1-chloro-4-nitrobenzene (0.157 g, 1 mmol), (furan-2-yl)methyl acetate (0.280 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with **1a** (8.00 mg, 0.01 mmol) afforded the corresponding product **12** in 70% (0.183 g) yield.

Methyl 2-Methyl-5-(4-nitrophenyl)furan-3-carboxylate (13):[3d] The reaction of 1-chloro-4-nitrobenzene (0.157 g, 1 mmol), methyl 2-methylfuran-3-carboxylate (0.280 g, 2 mmol) with **2a** (6.90 mg, 0.01 mmol) afforded the corresponding product **13** in 78% (0.204 g) yield.

2-*n*-Butyl-5-(4-methoxyphenyl)thiophene (14):[4e] The reaction of 4-bromoanisole (0.187 g, 1 mmol), 2-*n*-butylthiophene (0.280 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with **1a** (8.00 mg, 0.01 mmol) afforded the corresponding product **14** in 80% (0.197 g) yield.

2-*n*-Butyl-5-[4-(dimethylamino)phenyl]thiophene (15):[4e] The reaction of 4-bromo-*N*,*N*-dimethylaniline (0.200 g, 1 mmol), 2-*n*-butylthiophene (0.280 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with **1b** (8.30 mg, 0.01 mmol) afforded the corresponding product **15** in 69% (0.179 g) yield.

2-*n*-Butyl-5-(4-nitrophenyl)thiophene (16): The reaction of 1-chloro-4-nitrobenzene (0.157 g, 1 mmol), 2-*n*-butylthiophene (0.280 g, 2 mmol) with **2a** (6.90 mg, 0.01 mmol) afforded the corresponding product **16** in 40% (0.104 g) yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.98 (t, J = 7.4 Hz, 3 H, $H_3CCH_2CH_2CH_2$), 1.45 (m, 2 H, $H_3CCH_2CH_2CH_2$), 1.75 (m, 2 H, $H_3CCH_2CH_2CH_2$), 2.88 (t, J = 7.4 Hz, 2 H, $H_3CCH_2CH_2CH_2$), 6.92 (d, J = 3.7 Hz, 1 H, thiophene), 7.19 (d, J = 8.9 Hz, Ar), 8.17 (d, J = 3.7 Hz, 1 H, thiophene), 8.23 (d, J = 8.9 Hz, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.1, 22.7, 30.5, 34.1, 122.3, 123.2, 123.6, 124.7, 135.5, 139.8, 145.4, 148.7 ppm. $C_{14}H_{15}NO_2S$ (261.34): calcd. C 64.34, H 5.79, N 12.24; found C 64.36, H 5.80, N 12.23.

2-(4-Methoxyphenyl)-5-*n*-propylthiazole (17):[9d] The reaction of 4-bromoanisole (0.187 g, 1 mmol), 2-*n*-propylthiazole (0.254 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with **1a** (8.00 mg, 0.01 mmol) afforded the corresponding product **17** in 82% (0.191 g) yield.

2-[4-(Dimethylamino)phenyl]-5-*n*-propylthiazole (18):[9d] The reaction of 4-bromo-*N*,*N*-dimethylaniline (0.200 g, 1 mmol), 2-*n*-propylthiazole (0.254 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with **1a** (8.00 mg, 0.01 mmol) afforded the corresponding product **18** in 71% (0.175 g) yield.

2-(4-Nitrophenyl)-5-*n*-propylthiazole (19):[9d] The reaction of 1-chloro-4-nitrobenzene (0.157 g, 1 mmol), 2-*n*-propylthiazole (0.254 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with **3a** (10.4 mg, 0.01 mmol) afforded the corresponding product **19** in 68% (0.169 g) yield.

5-(4-Cyanophenyl)-2-*n*-propylthiazole (20):[9d] The reaction of 4-chlorobenzonitrile (0.138 g, 1 mmol), 2-*n*-propylthiazole (0.254 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with **2d** (7.30 mg, 0.01 mmol) afforded the corresponding product **20** in 41% (0.094 g) yield.

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