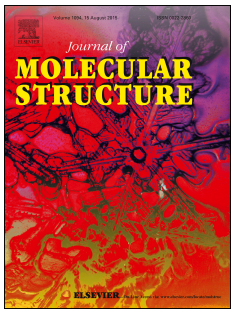

Palladium-carbene catalyzed direct arylation of five-membered heteroaromatics

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İlkay Yıldırım and Namık Özdemir: Software, Writing-Original Draft, Investigation.

İsmail Özdemir: Conceptualization, Resourches, Writing-Original Draft, Supervision, Funding Acquisition.

Palladium-Carbene Catalyzed Direct Arylation of Five-Membered Heteroaromatics

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ABSTRACT: Due to the industrial importance of bi(hetero)arenes, the synthesis of these compounds by homogeneous Pd-catalyzed direct arylation is an important research topic in modern organic chemistry. In this study, PEPPSI-type, (PEPPSI = Pyridine Enhanced Precatalyst Preparation Stabilization and Initiation), new Pd-catalysts with *N*-heterocyclic carbene ligand were synthesized, and they were used as catalysts in the synthesis of bi(hetero)arenes by direct arylation process. The structures of Pd-carbene complexes were elucidated by different spectroscopic and analytical techniques such as NMR, FT-IR and elemental analysis. The more detailed structural characterization of one of the complexes was determined by single-crystal X-ray diffraction study. Pd-carbene complexes were used as effective catalysts in the direct arylation of five-membered heteroaromatics such as thiophene, furan and thiazole derivatives with (hetero)aryl bromides for 1 h, in the presence of 1 mol% of catalyst loading, and successful results were obtained.

Keywords: *N*-Heterocyclic carbene, palladium, PEPPSI, direct arylation, heteroaromatics.

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1. Introduction

Bi(hetero)arenes are known as important units in the design of advanced materials, natural products, agrochemicals, pharmaceuticals and cosmetics.[1-6] Because of their applications in industrial area, the preparation of bi(hetero)arenes is an important research area in modern synthetic organic chemistry. To date, a number of strategies have been developed for the preparation of bi(hetero)arenes. The most common ones of among these strategies are, of course, the traditional cross-coupling reactions catalyzed by transition-metal (TM) catalysts. Suzuki,[7] Stille,[8] Negishi[9] or Kumada[10] type reactions are widely used in the TM-catalyzed synthesis of bi(hetero)arenes. However, the organometallic compounds used in such reactions are generally non-commercially available, or relatively expensive chemicals. In these reactions, the starting coupling partners should bear either a metal-containing functionality or a halogen atom and related groups. In this case in fact the preliminary preparation of two independent, expensive, starting materials is required. These processes have also some disadvantages such as generating stoichiometric amounts of waste materials and the use of unstable and corrosive chemicals etc. Therefore, there is a need for more environmentally attractive and atom economical methods in which total synthesis steps and by-product formation are minimized.

The direct arylation of bi(hetero)arenes by C-H bond activation provides an ideal alternative to traditional cross-coupling reactions in the synthesis of bi(hetero)arenes. This methodology is environmentally attractive, as the major reaction by-product is HX associated to a base, instead of the metallic salts mixture which is produced under the more classical Suzuki, Negishi or Stille cross-coupling reactions.[11,12] In this process, a variety of arylating reagents including aryl halides,[13] aryl organometallic reagents,[14] unactivated simple arenes,[15] and phenol derivatives such as triflates,[16] mesylates[17] and arene sulfonyl chlorides[18] have been employed. Particularly, aryl halides are the electrophilic reagents which are the most popular among the arylating reagents, due to their commercial availability and the variety of substrates. The Pd-catalyzed direct arylation of (hetero)arenes was firstly reported by Nakamura, Tajima and Sakai in 1982,[19] and by Ohta in 1985.[20] Since then, the Pd-catalyzed direct arylation of (hetero)arenes with aryl halides has proved to be a powerful method for the synthesis of a wide variety of arylated heteroaromatics. To date, Pd-catalyzed direct arylation of (hetero)arenes, especially five-membered heterocycles such as thiophene,[21] furan[22] and thiazole[23] has been largely described by a large number of researchers.

N-Heterocyclic carbenes (NHCs) are effective ligands that allow the preparation of the most suitable steric, electronic and chemically acceptable catalyst by altering the substituents on the nitrogen atom.[24] Due to these features, they have been successfully employed in different applications of organometallic chemistry[25], and they are a key ligand for metal complexes, because of their wide applicability in catalysis. Thanks to the strong σ-donor and weak π-acceptor property, NHCs do not dissociate easily from the metal center by interacting strongly with the coordinated metal. Due to activity, stability and selectivity of metal complexes containing NHC ligand, they have been widely used as highly reactive and rather selective catalysts for numerous reactions.[26] Recently, different-type of Pd-NHC complexes have been prepared by Caddick and Cloke,[27a] Bellemin-Laponnaz and Gade,[27b] Nolan,[27c] Herrmann,[27d] and Organ,[27e] (Figure 1). These different-type Pd-NHC complexes showed high levels of activity in a variety of cross-coupling reactions.[28]

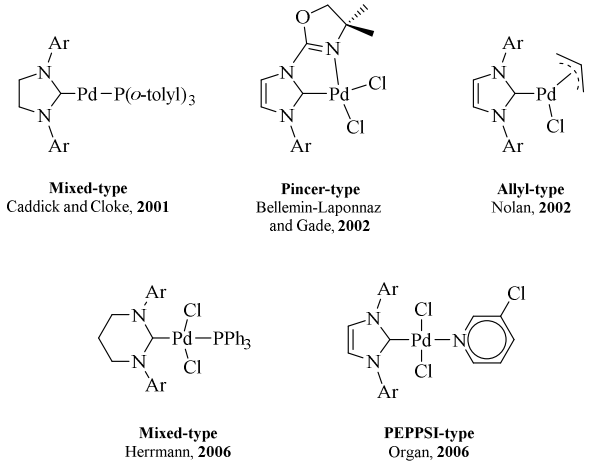


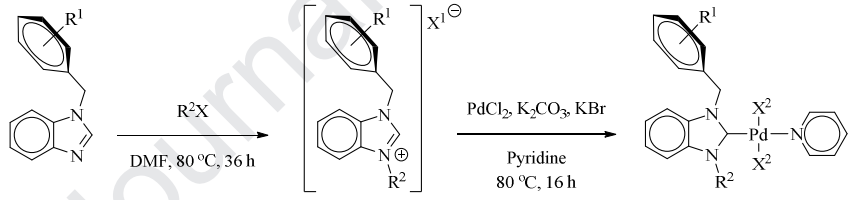
Figure 1. Examples of Pd-NHC species commonly used in cross-coupling reactions.

After the discovery of Organ's PEPPSI-type Pd-complexes in 2006,[27e] (PEPPSI = Pyridine Enhanced Precatalyst Preparation Stabilization and Initiation), these type complexes have shown remarkable catalytic activities towards various carbon-carbon and carbon-heteroatom cross-coupling reactions.[29] PEPPSI-type Pd-NHC complexes represent a class of Pd-NHC catalysts completely different from other Pd-NHC complexes. Unlike other types of Pd-NHC complexes, PEPPSI-type Pd-NHC complexes are easier to synthesize and use.[30] The high activity of PEPPSI-type Pd-complexes in catalysis has been based on to the presence of a loosely bound throw-away pyridine ligand that makes way for the incoming substrate.[31] In recent years, PEPPSI-type Pd-complexes have been used as effective catalysts in the direct arylation and successful results have been obtained.[32] In this context, recently we have also synthesized and characterized benzimidazole-based new PEPPSI-type Pd-NHC complexes, and have investigated catalytic activity of these complexes in the direct arylation reactions.[33] In view of the above information and the growing interest in catalytic activity of Pd-carbene complexes to act as an efficient catalyst in the direct arylation, in this article, we now report the preparation of PEPPSI-type five new Pd-NHC complexes (**2a**-**2e**) of the general formula [PdX_2(NHC)(pyridine)], (X = Cl, Br; NHC = 1,3-disubstituted benzimidazole-2-ylidene), and their characterization by different techniques such as ^{1}H NMR, ^{13}C NMR, FT-IR, and elemental analysis. The solid-state structure of one of the Pd-complexes {*trans*-dibromo-[1-(4-methylbenzyl)-3-(3-methoxylbenzyl)benzimidazole-2-ylidene]-(pyridine)-palladium(II)}, (**2c**) was established by single-crystal X-ray diffraction study. In the present study, the catalytic application of **2a**-**2e** Pd-carbene complexes have been tested in the direct arylation of five-membered heteroaromatics such as thiopene, furan and thiazole with (hetero)aryl bromides in presence of 1 mol% catalyst loading.

2. Results and discussion

2.1. Synthesis

1a,[34] **1b**,[35] **1c**[36] and **1e**[37] benzimidazolium salts as NHC ligand precursors were synthesized as previously described in the literature. The general procedure for the benzimidazolium salts (**1a**-**1e**) and their corresponding PEPPSI-type Pd-NHC complexes (**2a**-**2e**) are shown in the Scheme 1. Also, some physical and spectroscopic data of all new compounds are summarized in Table 1.



	R^1	R^2	X^2
a,	H	*n*-Bu	Br
b,	$(Me)_5$-2,3,4,5,6	*n*-Bu	Cl
c,	(Me)-4	CH_2Ph(OMe)-3	Br
d,	$(Me)_3$-2,4,6	CH_2Ph(OMe)-3	Br
e,	$(Me)_4$-2,3,5,6	CH_2Ph(OMe)-3	Br

Scheme 1. Synthesis of the benzimidazolium salts (**1a**-**1e**) and their PEPPSI-type palladium-NHC complexes (**2a**-**2e**).

Table 1. Physical and spectroscopic properties of new compounds.

Compound	Molecular formula	Isolated yield (%)	M.p. (°C)	$\nu_{(CN)}$ (cm^{-1})	H(2) ^{1}H NMR (ppm)	C(2) ^{13}C NMR (ppm)
1d	$C_{25}H_{27}BrN_2O$	90	199-200	1553	11.74	144.2
2a	$C_{23}H_{25}Br_2N_3Pd$	78	202-203	1403	–	164.3
2b	$C_{28}H_{35}Cl_2N_3Pd$	71	196-197	1409	–	163.0
2c	$C_{28}H_{27}Br_2N_3OPd$	83	222-223	1409	–	164.2
2d	$C_{30}H_{31}Br_2N_3OPd$	75	247-248	1395	–	164.0
2e	$C_{31}H_{33}Br_2N_3OPd$	80	213-214	1405	–	163.9

2.2. Preparation of benzimidazolium salts

The benzimidazolium salts (**1a**-**1e**) were synthesized by the reaction of different *N*-(benzyl)-benzimidazoles with 3-methoxybenzyl chloride or *n*-butyl chloride in dimethylformamide (DMF) at 80 ^{o}C for 36 h (Scheme 1). The new **1d** benzimidazolium salt was characterized by different techniques. As shown in Table 1, the FT-IR data clearly indicated that the **1d** benzimidazolium salt exhibit a characteristic $\nu_{(CN)}$ band typically at 1553 cm^{-1}. In the ^{1}H NMR spectra, C(2)-*H* proton resonance was observed at δ = 11.74 ppm as sharp singlets. In the ^{13}C NMR spectra, *C*(2)-carbon resonance was observed at δ = 144.2 ppm as single signal. These downfield signals of the acidic C(2)-*H* proton and *C*(2)-carbon were support the formation of **1d** benzimidazolium salt. These spectroscopic data of **1d** benzimidazolium salt are consistent with the data observed for other benzimidazolium salts in the literature.[22f,33-37]

2.3. Preparation of PEPPSI-type palladium–NHC complexes

The PEPPSI-type Pd-NHC complexes (**2a-2e**) were synthesized in a similar manner to that reported by Organ[28]. The general procedure for the preparation of complexes is shown in Scheme 1. Five new Pd-carbene complexes were synthesized by reaction of the corresponding benzimidazolium salts (**1a-1e**) with $PdCl_2$ in the presence of pyridine. All Pd-carbene complexes were isolated as air-stable, yellow solids, and they were soluble in solvents such as dichloromethane, chloroform, toluene, and tetrahydrofuran and insoluble in non-polar solvents. All new Pd-carbene complexes were characterized by different techniques. In the ^{1}H NMR and ^{13}C NMR spectra of the Pd-carbene complexes, the absence of the characteristic signals of the acidic C(2)-*H* proton and *C*(2)-carbon of the benzimidazolium salts, suggests the formation of Pd-carbene bond. Also, the characteristic signals of aromatic hydrogens of pyridine ring were observed as downfield resonances in the ^{1}H NMR spectra between δ = 7.34-9.03 ppm. These signals suggest that the pyridine ring coordinated to the palladium centre to form a PEPPSI-type palladium complex. In the ^{13}C NMR spectra, the characteristic *C*(2)-carbene signals of **2a-2e** complexes are appear as singlet at δ = 164.3, 163.0, 164.2, 164.0, 163.9 ppm, respectively. Also, characteristic signals of the aromatic carbons of pyridine ring at approximately δ = 124, 137 and 152 ppm, support the formation of PEPPSI-type palladium complex. The NMR spectra also provide a potential tool to estimate the electronic properties of these Pd-carbene complexes. In the ^{13}C NMR spectra, due to the 2,4,6-trimethylbenzyl and 2,3,5,6-tetramethyl benzyl groups increasing the electron density of the NHC ring, the Pd-carbene signals of the complex **2c** (δ = 164.2 ppm) are shifted further downfield as compared to those of complexes **2d** and **2e**. This observation is in agreement with the downfield-shifted Pd-carbene signal of the complex **2a** (δ = 164.3 ppm) in comparison to that of complex **2b** in the ^{13}C NMR spectra. The FT-IR data clearly indicated that the PEPPSI-type Pd-NHC complexes exhibit a characteristic $\nu_{(CN)}$ band typically between 1395-1409 cm^{-1}. The FT-IR spectra of all five Pd-complexes show similar absorption bands with moderately shifted wavelengths (mostly less than 15 cm^{-1}). Due to the flow of electrons from the carbene ligand to the palladium centre, the C=N bond is weakened, and as a result, a decreasing in the $\nu_{(CN)}$ stretching frequency is observed. Therefore, in comparison to the **1a-1e** ligand precursors, **2a**-**2e** Pd-complexes give rise to obvious red-shifted absorption bands. These complexes show typical spectroscopic signatures, which are in line with those reported for other similar type Pd-complexes.[33] Also, additional elemental analysis results of these complexes are in agreement with the proposed molecular formula.

2.4. Description of the crystal structure

The complex consists of a 1-(3-methoxybenzyl)-3-(4-methylbenzyl)-2,3-dihydro-1*H*-benzo[*d*]imidazole ligand with a Pd^{II} metal center and two bromide ligands. The metal coordination environment features a square-planar geometry, in which the NHC and the pyridine are *trans* to each other. This reflects the tendency to avoid a sterically more crowded *cis*-configuration. The *cis*- angles varying from 87.51(17) to 92.60(16)° and the *trans*- angles changing from 175.82(3) to 178.1(2)° are a little off from the ideal values of 90 and 180°. The four-coordinate geometry index for the complex, τ_4,[38] is 0.04. In the case of an ideal square-planar geometry, the τ_4 value is equal to zero, while it becomes unity for a perfect tetrahedral geometry. Consequently, the value of τ_4 shows that the coordination polyhedron of the palladium atom is a slightly distorted square-planar. In the square-planar environment, the Pd atom is lying 0.0210(5) Å out the coordination plane defined by atoms Br1, Br2, N3 and C1.

The Pd─$C_{carbene}$ bond distance [1.967(5) Å] is slightly smaller than the sum of the individual covalent radii of the palladium and carbon atoms (2.12 Å), while the Pd─$N_{pyridine}$ bond distance [2.110(5) Å] is almost equal to the sum of the covalent individual radii of the palladium and nitrogen atoms (2.10 Å).[39] The internal N─C─N ring angle at the carbene center is 108.2(5)°. Furthermore, the Pd─Br1 and Pd─Br2 bonds only differ by ca. 0.01 Å, and interestingly

bent toward NHC ligand rather than toward the nonbulky pyridine ligand. These values are in good agreement with those found in other Pd-NHC-Pyridine complexes.[33,40] The carbene ring is oriented almost perpendicularly to the $PdCNBr_2$ coordination plane with a dihedral angle of 81.28(19)°, which is typical for NHC complexes to relieve steric congestion. On the other hand, the pyridine ring is inclined at an angle of 48.8(3)° with the coordination plane. Finally, the NHC ring makes dihedral angles of 88.8(3) and 82.2(3)° with the methoxybenzene and methylbenzene rings, respectively.

The molecular structure of **2c** complex with the atom-labelling scheme is shown in Figure 3, while relevant bond distances and angles are reported in Table 2.

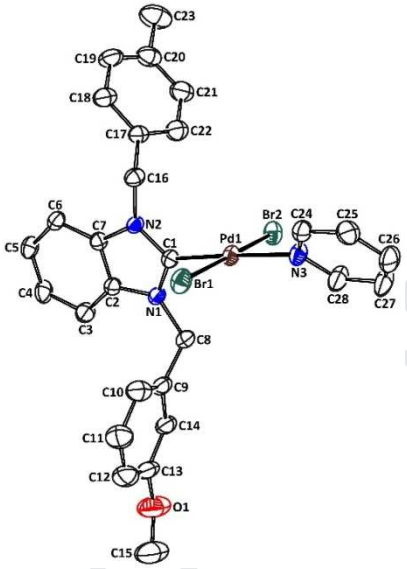


Figure 3. The molecule of **2c**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 20% probability level. For clarity purpose, hydrogens have been omitted and only the major part of disordered fragment is drawn.

Table 2. Selected geometric parameters for complex **2c**.

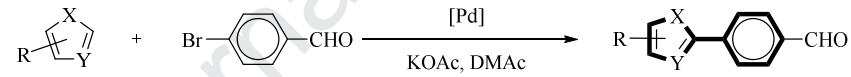
Bond lengths (Å)			
Pd1─C1	1.967(5)	N1─C2	1.391(7)
Pd1─N3	2.110(5)	N1─C8	1.470(7)
Pd1─Br1	2.4189(9)	N2─C1	1.339(6)
Pd1─Br2	2.4293(9)	N2─C7	1.389(7)
N1─C1	1.332(7)	N2─C16	1.463(6)
Bond angles (°)			
C1─Pd1─N3	178.1(2)	C1─N1─C2	109.9(4)
C1─Pd1─Br1	87.51(17)	C1─N1─C8	126.3(5)
N3─Pd1─Br1	91.39(16)	C2─N1─C8	123.7(5)
C1─Pd1─Br2	88.47(17)	C1─N2─C7	109.5(4)
N3─Pd1─Br2	92.60(16)	C1─N2─C16	125.6(5)
Br1─Pd1─Br2	175.82(3)	C7─N2─C16	124.9(4)
N1─C1─N2	108.2(5)		

2.5. Optimization of the reaction conditions for the direct arylation of heteroaromatics

Our first objective was to determine the most suitable reaction conditions. For this purpose, we first selected the complex **2e** as the model catalyst, 2-acetylthiophene, 2-furaldehyde and 4,5-dimethylthiazole as heteroaromatic substrates and the *p*-bromobenzaldehyde as model coupling partner (Table 3). We selected DMAc as the solvent, and KOAc as the base in this study, because the DMAc/KOAc combination has been commonly used for the direct arylation of heteroarenes.[21-23] In literature, it is known to difficult to achieve high selectivity in such direct arylation reactions without the use of stoichiometrically large amounts of heteroaromatic compound relative to amount of aryl halide.[23j] Since the 2-acetylthiophene and 2-furaldehyde have also other positions such as C3 and C4 to react with aryl bromide, so 1 equivalent of *p*-bromobenzaldehyde was used as the limiting reagent to prevent di- or tri-arylation. Thus

mono-arylation of the heteroaromatic compound was targeted. Firstly, the C5-arylation of 2-acetylthiophene with *p*-bromobenzaldehyde was carried out at 150 °C for 10 h without the addition of Pd-catalyst in order to examine the effect of catalyst on the reaction. As attempt, no products were formed without the addition of Pd-catalyst (Table 3, entry 1). Under the same conditions, when only **1e** NHC precursor was used as catalyst without any Pd-catalyst, no reaction takes place (Table 3, entry 2). In the direct arylation reaction of 2-acetylthiophene with *p*-bromobenzaldehyde, different Pd-salts such as $Pd(OAc)_2$ and $PdCl_2$ were tested using 1 mol% of catalyst loading at 150 °C for 10 h. Products were obtained in 45% and 28% yields with low conversions, respectively. When the reaction was carried out for 18 h in the presence of the same Pd-salts, we observed that conversion and yield increased (Table 3, entries 3 and 4). When *in situ* generated catalytic system with 1 mol% of **1e** NHC precursor and 1 mol% of $Pd(OAc)_2$ was used, 51% yield was observed (Table 3, entry 5). However, when the same conditions were used **2e** Pd-complex as catalysts, 90% yield was observed with full conversion in the reaction. When the reaction time was increased to 18 h as in the entries 3 and 4, we observed full conversion, but no significant difference in yield. (Table 3, entry 6). When the reaction time was reduced from 10 h to 5 h, 87% yield was observed in the reaction (Table 3, entry 7). When the reaction time was reduced from 5 h to 3 h or 3 h to 1 h at 150 °C, no noticeable effect on the yield was observed (Table 3, entries 8,9). When the reaction temperature was reduced from 150 °C to 120 °C, no noticeable effect on the yield was also observed (Table 3, entry 10), but when the reaction temperature was reduced from 120 °C to 90 °C, the yield dropped to 27% (Table 3, entry 11). When the catalyst loading was decreased to 0.5 mol% at 120 °C, yield was observed to decrease significantly (Table 3, entry 12). As a result of the optimisation experiments in the arylation of 2-acetylthiophene with *p*-bromobenzaldehyde, a very good yield (81%) with 96% conversion was obtained in DMAc/KOAc combination in the presence of 1 mol% **2e** Pd-catalyst at 120 °C for 1 h (Table 3, entry 10). For coupling of 2-furaldehyde with *p*-bromobenzaldehyde, the same reaction condition was found to be optimal. In this case a yield of 83% was observed with 97% conversion (Table 3, entry 13). When the arylation of 4,5-dimethylthiazole with *p*-bromobenzaldehyde was tested at the same condition, only 50% coupling product was obtained (Table 3, entry 14), so the temperature was increased up to 140 °C and reaction yield was up to %78 with 91 conversion (Table 3, entry 15).

Table 3. Influence of the reaction conditions on the Pd-catalyzed direct arylation of five-membered heteroaromatics with *p*-bromobenzaldehyde.[a]



X = O or S
Y = H or N
R = Me, CHO or COMe

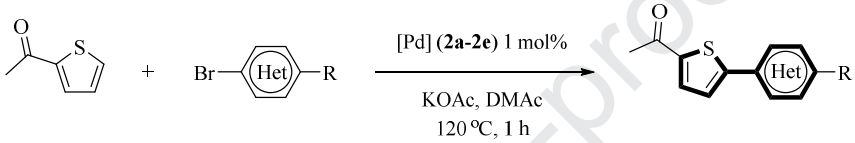
Entry	Heteroaromatics	[Pd] (mol%)	Time (h)	Temperature	Conversion (%)[b]	Yield (%)[c]
1	2-Acetylthiophene	–	10	150	–	–
2[d]	2-Acetylthiophene	–	10	150	–	–
3[e]	2-Acetylthiophene	$Pd(OAc)_2$ (1)	10	150	56 (90)	45 (76)
4[e]	2-Acetylthiophene	$PdCl_2$ (1)	10	150	45 (74)	28 (61)
5[f]	2-Acetylthiophene	$Pd(OAc)_2$ (1)	10	150	60	51
6[e]	2-Acetylthiophene	**2e** (1)	10	150	100 (100)	90 (91)
7	2-Acetylthiophene	**2e** (1)	5	150	100	87
8	2-Acetylthiophene	**2e** (1)	3	150	99	85
9	2-Acetylthiophene	**2e** (1)	1	150	97	83
10	**2-Acetylthiophene**	**2e (1)**	**1**	**120**	96	**81**
11	2-Acetylthiophene	**2e** (1)	1	90	46	27
12	2-Acetylthiophene	**2e** (0.5)	1	120	42	30
13	**2-Furaldehyde**	**2e (1)**	**1**	**120**	97	**83**
14	4,5-Dimethylthiazole	**2e** (1)	1	120	72	50
15	**4,5-Dimethylthiazole**	**2e (1)**	**1**	**140**	91	**78**

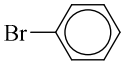
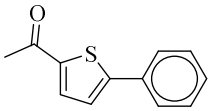
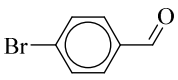
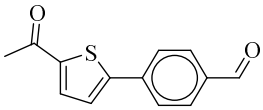
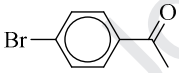
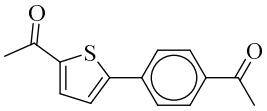
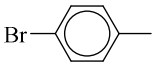
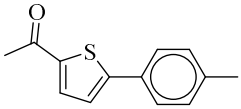
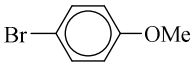
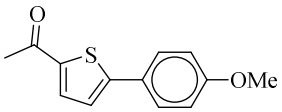
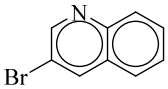
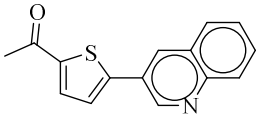
[a] Conditions: 2-acetylthiophene (2.0 mmol), *p*-bromobenzaldehyde (1.0 mmol), KOAc (1.5 mmol), DMAc (2 mL).
[b] Conversions were calculated with respect to *p*-bromobenzaldehyde from the results of GC spectrometry with dodecane as internal standard.
[c] GC yields.
[d] Without any palladium catalyst, only **1e** NHC precursor was used as catalyst.
[e] Results obtained at 18 h are shown in parentheses.
[f] *In situ* generated catalytic system with **1e** NHC precursor and $Pd(OAc)_2$ was used.

After successful results summarized in Table 3, we tried to evaluate the scope and limitations of the Pd-complexes **2a-2e** for the direct arylation of 2-acetylthiophene, 2-furaldehyde and 4,5-dimethylthiazole with different (hetero)aryl bromides. All reactions we performed for this purpose worked smoothly to give the desired arylated

products in moderate to high yields (see Table 4-6). Firstly, under the optimal condition, the direct arylation of 2-acetylthiophene with various (hetero)aryl bromides were examined and the C(5)-arylated thiophene derivatives were obtained with moderate to high yield. When 2-acetylthiophene was arylated with *p*-substituted aryl bromides and 3-bromoquinoline, arylated products were obtained with 54-92% yields by using only 1 mol% Pd-complexes (**2a**-**2e**) as a catalyst (Table 4). The reaction of 2-acetylthiophene with bromobenzene generated the 5-phenyl-2-acetylthiophene[21i] in 80% and 82% yield in the presence of **2d** and **2e** catalysts, respectively (Table 4, entries 4,5). The reaction of 2-acetylthiophene with *p*-bromobenzaldehyde gave the expected product[7c] in 81% yield in the presence of **2e** catalyst (Table 4, entry 9). Moderate to high yields of 5-(4-acetylphenyl)-2-acetylthiophene[21g] were obtained for the coupling with *p*-bromoacetophenone (Table 4, entries 11-15). The reaction of 2-acetylthiophene with *p*-bromotoluene gave the expected product[21h] in 86% and 90% yield in the presence of **2d** and **2e** catalysts, respectively (Table 4, entries 19,20). At among reaction arylated with bromobenzene, *p*-bromoanisole and *p*-bromotoluene using 1 mol% of catalyst, the reaction of the electron-rich *p*-bromoanisole with 2-acetylthiopene gave lower C5-arylated product[21g] (Table 4, entries 21-25). Pyridines are π-electron-deficient heterocycles. Therefore, their reactivity is quite similar to electron-deficient aryl bromides. As expected, using 3-bromoquinoline, we obtained the 3-(2-acetylthiophene-5-yl)quinoline[33a] in moderate to high yield (Table 4, entries 26-30).

Table 4. Palladium-catalyzed direct C(5)-arylation of 2-acetylthiophene with (hetero)aryl bromides.[a]



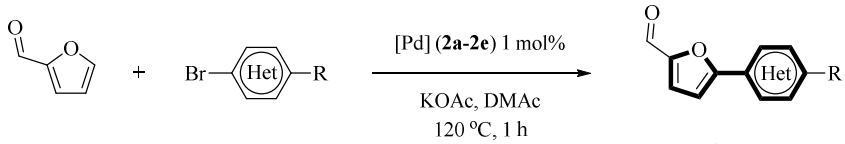
Entry	Aryl bromide	[Pd]	Product	Yield (%)[b]
1		**2a**		78
2		**2b**		76
3		**2c**		68
4		**2d**		80
5		**2e**		82
6		**2a**		73
7		**2b**		69
8		**2c**		64
9		**2d**		71
10		**2e**		81
11		**2a**		62
12		**2b**		59
13		**2c**		72
14		**2d**		75
15		**2e**		80
16		**2a**		83
17		**2b**		79
18		**2c**		68
19		**2d**		86
20		**2e**		90
21		**2a**		66
22		**2b**		54
23		**2c**		64
24		**2d**		70
25		**2e**		68
26		**2a**		69
27		**2b**		81
28		**2c**		75
29		**2d**		86
30		**2e**		92

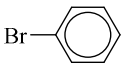
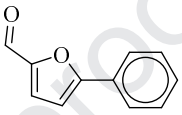
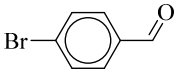
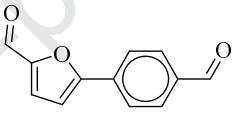
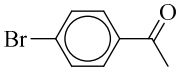
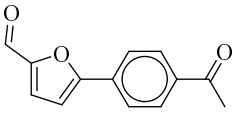
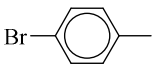
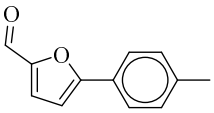
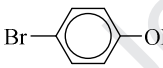
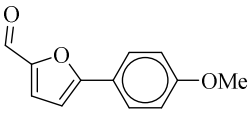
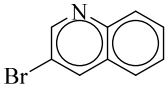
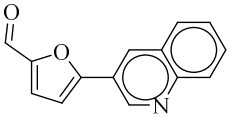
[a] Conditions: [Pd] **2a-2e** (0.01 mmol), 2-acetylthiophene (2.0 mmol), aryl bromide (1.0 mmol), KOAc (1.5 mmol), DMAc (2 mL), 120 °C, 1 h.
[b] GC yields were calculated with respect to aryl bromide from the results of GC spectrometry with dodecane as internal standard.

Using the same reaction conditions, we investigated the reactivity of 2-furaldehyde in Pd-catalyzed direct arylation. As shown in Table 5, high yield C(5)-arylated products were obtained. Very close yields (65-84%) were observed for 2-furaldehyde using the neutral aryl bromide such as bromobenzene[22a] (Table 5, entries 1-5). The coupling of 2-furaldehyde with electron-poor aryl bromide such as *p*-bromobenzaldehyde proceeds nicely. *p*-Bromobenzaldehyde gave the C(5)-arylated product[22f] with 65-83% yields (Table 5, entries 6-10). The electron-poor *p*-

bromoacetophenone was also a good substrate to afford the corresponding products 5-(4-acetylphenyl)-2-furaldehyde[22f] at between 61-79% yields (Table 5, entries 11-15). When the reaction of 2-furaldehyde with electron-rich aryl bromides such as *p*-bromotoluene and *p*-bromoanisole was investigated, the yields were at between 75-80% for 4-bromotoluene with 2-furaldehyde[22a] (Table 5, entries 16-20). *p*-Bromoanisole gave also the 5-(4-methoxyphenyl)-2-furaldehyde[22a] with 69-77% yields (Table 5, entries 21-25). 3-Bromoquinoline was found to be very reactive in DMAc at 1 h (Table 5, entries 26-30). 3-(2-Furaldehyde-5-yl)quinoline[9b] was obtained in 87% yield in the presence of **2d** catalysts (Table 5, entry 29).

Table 5. Palladium-catalyzed direct C(5)-arylation of 2-furaldehyde with (hetero)aryl bromides.[a]



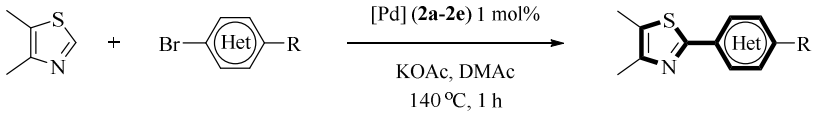
Entry	Aryl bromide	[Pd]	Product	Yield (%)[b]
1		**2a**		75
2		**2b**		70
3		**2c**		65
4		**2d**		75
5		**2e**		84
6		**2a**		65
7		**2b**		72
8		**2c**		80
9		**2d**		76
10		**2e**		83
11		**2a**		61
12		**2b**		69
13		**2c**		76
14		**2d**		73
15		**2e**		79
16		**2a**		75
17		**2b**		78
18		**2c**		80
19		**2d**		81
20		**2e**		80
21		**2a**		70
22		**2b**		69
23		**2c**		72
24		**2d**		74
25		**2e**		77
26		**2a**		71
27		**2b**		76
28		**2c**		80
29		**2d**		87
30		**2e**		83

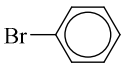
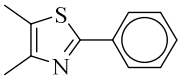
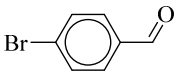
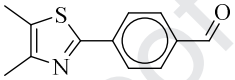
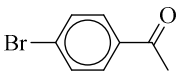
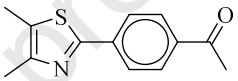
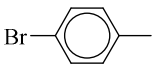
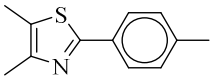
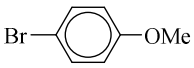
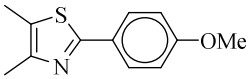
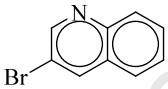
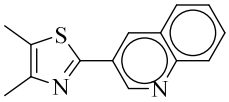
[a] Conditions: [Pd] **2a-2e** (0.01 mmol), 2-furaldehyde (2.0 mmol), aryl bromide (1.0 mmol), KOAc (1.5 mmol), DMAc (2 mL), 120 °C, 1 h.
[b] GC yields were calculated with respect to aryl bromide from the results of GC spectrometry with dodecane as internal standard.

Finally, the scope of the direct arylation reaction was extended to 4,5-dimethylthiazole. The C2-position of 4,5-dimethylthiazole was arylated because of blocked its C4- and C5-positions. We also found 4,5-dimethylthiazole to be a suitable reactant for this reaction. In the direct arylation of 4,5-dimethylthiazole with *p*-substituted aryl bromides and 3-bromoquinoline, a very high yield C(2)-arylated products were obtained at 140 °C for 1 h (Table 6). Best yields were obtained in the presence of **2d** and **2e** catalysts when bromobenzene[8c] was used (Table 6, entries 4,5). When *p*-bromobenzaldehyde and *p*-bromoacetophenone were used, generally C(2)-arylated products[37] were obtained in moderate to high yield with all catalysts. (Table 6, entries 6-15). When *p*-bromotoluene was used, (4-methylphenyl)-4,5-dimethylthiazole[23g] product was obtained in 84% yield in the presence of **2e** catalyst (Table 6, entry 20). Moderate yields of 2-(4-methoxyphenyl)-4,5-dimethylthiazole[23i] were obtained for the coupling with *p*-bromoanisole (Table 6, entries 21-25) with little variance between the Pd-complexes. We also tested the coupling with the 3-bromoquinoline. This heteroaryl bromide gave the expected 3-(4,5-dimethylthiazol-2-yl)quinoline[23i] in very good yields (Table 6, entries 26-30). Generally, the reactivity of 4,5-dimethylthiazole was similar to 2-acetylthiophene and 2-furaldehyde,

and the yields for substrates containing electron-withdrawing groups were lower than those for substituents containing electron-donating group.

Table 6. Palladium-catalyzed direct C(2)-arylation of 4,5-dimethylthiazole with (hetero)aryl bromides.[a]



Entry	Aryl bromide	[Pd]	Product	Yield (%)[b]
1		**2a**		78
2		**2b**		70
3		**2c**		74
4		**2d**		84
5		**2e**		88
6		**2a**		65
7		**2b**		74
8		**2c**		68
9		**2d**		74
10		**2e**		78
11		**2a**		69
12		**2b**		76
13		**2c**		72
14		**2d**		76
15		**2e**		79
16		**2a**		63
17		**2b**		73
18		**2c**		70
19		**2d**		75
20		**2e**		84
21		**2a**		57
22		**2b**		72
23		**2c**		69
24		**2d**		73
25		**2e**		78
26		**2a**		72
27		**2b**		65
28		**2c**		82
29		**2d**		85
30		**2e**		88

[a] Conditions: [Pd] **2a-2e** (0.01 mmol), 4,5-dimethylthiazole (2.0 mmol), aryl bromide (1.0 mmol), KOAc (1.5 mmol), DMAc (2 mL), 140 °C, 1 h.
[b] GC yields were calculated with respect to aryl bromide from the results of GC spectrometry with dodecane as internal standard.

The role of the steric and electronic effects plays on the catalytic activity for NHC ligands was investigated using a variety of techniques in the literature.[41] Even though benzimidazol-2-ylidenes have received limited attention as NHC ligands, they provide a suitable platform for tuning the electron density on the carbene carbon. It is known that by introducing electronically different substituents at the C5- and C6-positions of the benzimidazol-2-ylidene ligand, it is possible to remotely change the electronic property of the Pd center without altering the steric environment in the metal.[29a] Also, altering the *N*-substituent would allow the topography around the metal to be tuned to ensure the required steric bulk for reductive elimination is in place. Therefore, we preferred benzimidazol-2-ylidene ligands with oxygen-donor and/or sterically bulky benzyl substituents. Of the Pd-complexes **2c**-**2e** with 3-methoxybenzyl substituent, progressively better results were seen as the number of methyl groups of the *N*-benzyl rings were increased from mono-methyl to tri-methyl to tetra-methyl. In contrast, in aliphatic *n*-butyl substituted Pd-complexes **2a** and **2b**, it appears that complex **2a** containing benzyl ring gives better results than complex **2b** containing sterically bulky 2,3,4,5,6-pentamethylbenzyl ring. Since the σ-donor abilities of carbene ligands of **2c**-**2e** complexes are similar, steric factors are likely at work in the improved performance of **2e** complex. However, for **2a** and **2b** complexes which bearing *n*-butyl substituent, the steric effects have not significant effect on the catalytic activity. As a result, we believe that such substituents on the NHC ligands provides the steric and electronic effects to confer the Pd center the appropriate properties to make optimum to key steps of the catalytic cycles.

The Pd-catalyzed direct arylation of five-membered heteroaromatics with various arylating reagents has been reported in some previous studies.[21-23,32,33] In these previous studies, similar substrates were used with higher catalyst

loading (1-20 mol%) and higher reaction times (1-48 h) were preferred for the direct arylation of heteroaromatics in the presence of Pd-catalysts. In the present work, 1 mol% catalyst loading was used, and the reaction time was shortened to 1 h. Moreover, five-membered heteroaromatics such as thiophene, furan and thiazole derivatives could be efficiently and selectively arylated at the C(5)- or C(2)-position. In this study, satisfactory results were obtained as compared to previously reported similar studies using (hetero)aryl bromides.[32,33a] Finally, the catalytic activities of the new **2a**-**2e** Pd-complexes were investigated in the direct C(5)- or C(2)-arylation of five-membered heteroaromatics. In all cases, except in a few cases with complex **2d** and **2e**, high yields of the (hetero)aryl bromides were observed. Only a minor effect of the NHC ligand on the Pd-complex was observed for the coupling of (hetero)aryl bromide with heteroaromatics. Surprisingly, similar conversions were obtained for the coupling of each (hetero)aryl bromides. We can say that there is no significant difference between these complexes on the catalytic activity of direct arylation of heteroaromatics by (hetero)aryl bromides. The only significant difference between **2a-2e** complexes indicates that electronic and steric effects are also playing some role in these processes.

3. Conclusion

In summary, we prepared a series of five new PEPPSI-type Pd-NHC complexes. These complexes were characterized using different techniques. The catalytic activities of the new Pd-complexes were investigated in the direct C(5)- or C(2)-arylation of five-membered heteroaromatics with (hetero)aryl bromides. It was found that the new Pd-complexes were effective catalysts for the direct arylation reactions. Overall except in a few cases, satisfactory results were obtained in all trials. Surprisingly, similar yields were obtained for the coupling of each (hetero)aryl bromides. Since the NHC ligands used were similar to each other, no significant difference was observed between the catalytic activities of Pd-complexes. This study was performed by using 1 mol% of palladium catalyst. Therefore, this low catalyst loading procedure was economically attractive. In this study, only AcOH and HBr were formed as a by-products by the use of direct arylation method and thus the by-product formation was minimized compared to the multi-step traditional transition metal-catalyzed reactions. Also, this study contributes both organometallic synthesis and the literature in the preparation of bi(hetero)aryl derivatives.

4. Experimental

4.1. General procedure for the preparation of benzimidazolium salts (1a-1e)

N-(Benzyl)-benzimidazole derivative (5.0 mmol) was dissolved in degassed DMF (3 mL) and alkyl halide (5.0 mmol) was added at room temperature. The reaction mixture was stirred at 80 °C for 36 h under argon. After completion of the reaction, the solvent was removed by vacuum and Et_2O (15 mL) was added to obtain a white crystalline solid, which was filtered off. The solid was washed with Et_2O (3×10 mL) and dried under vacuum. The crude product was recrystallized from EtOH/Et_2O mixture (1:5, *v/v*) at room temperature, and completely dried under vacuum. All benzimidazolium salts (**1a-1e**) were isolated as air- and moisture-stable white solids in high yields. For the ^{1}H NMR, ^{13}C NMR and FT-IR spectrums of the new **1d** benzimidazolium salt see SI, pp. S1-S2.

4.1.1. 1-(Benzyl)-3-(*n*-butyl)-benzimidazolium bromide, (1a)

This benzimidazolium salt was synthesized according to a published procedure.[34]

4.1.2. 1-(2,3,4,5,6-Pentamethylbenzyl)-3-(*n*-butyl)-benzimidazolium chloride, (1b)

This benzimidazolium salt was synthesized according to a published procedure.[35]

4.1.3. 1-(4-Methylbenzyl)-3-(3-methoxybenzyl)-benzimidazolium bromide, (1c)

This benzimidazolium salt was synthesized according to a published procedure.[36]

4.1.4. 1-(2,4,6-Trimethylbenzyl)-3-(3-methoxybenzyl)-benzimidazolium bromide, (1d)

Yield 90%, 1.83 g; m.p. 199─200 ^{o}C; white solid; FT-IR $\nu_{(CN)}$ = 1553 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ (ppm) = 2.22 and 2.26 (s, 9H, $NCH_2Ph(CH_3)_3$-2,4,6); 3.73 (s, 3H, $NCH_2Ph(OCH_3)$-3); 5.82 (s, 4H, $NCH_2Ph(CH_3)_3$-2,4,6 and $NCH_2Ph(OCH_3)$-3); 6.77-7.19 (m, 5H, arom. *H*s of benzimidazole and 3-methoxybenzyl); 7.21 (s, 2H, arom. *H*s of 2,4,6-trimethylbenzyl); 7.32-7.52 (m, 3H, arom. *H*s of benzimidazole and 3-methoxybenzyl); 11.74 (s, 1H,

NC*H*N). ^{13}C NMR (101 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ (ppm) = 20.3 and 21.1 ($NCH_2Ph(CH_3)_3$-2,4,6); 47.5 ($NCH_2Ph(CH_3)_3$-2,4,6); 51.4 ($NCH_2Ph(OCH_3)$-3); 55.6 ($NCH_2Ph(OCH_3)$-3); 113.6, 113.7, 113.8, 114.8, 120.1, 125.1, 127.0, 127.1, 130.2, 130.4, 131.5, 134.4, 137.9, 139.7 and 160.3 (arom. *C*s of benzimidazole, 2,4,6-trimethylbenzyl and 3-methoxybenzyl); 144.2 (N*C*HN). Elemental analysis calcd. (%) for $C_{25}H_{27}BrN_2O$: C 66.52, H 6.03, N 6.21; found (%): C 66.96, H 6.22, N 6.31.

4.1.5. 1-(2,3,5,6-Tetramethylbenzyl)-3-(3-methoxybenzyl)-benzimidazolium bromide, (1e)

This benzimidazolium salt was synthesized according to a published procedure.[37]

4.2. General procedure for the preparation of palladium complexes (2a-2e)

Benzimidazolium salts (**1a-1e**) (1.0 mmol) were converted with high yields into the PEPPSI-type palladium-NHC complexes (**2a-2e**) by reaction with $PdCl_2$ (1.0 mmol) in refluxing pyridine in the presence of K_2CO_3 (5.0 mmol) as a base at 80 ^{o}C for 16 h. Volatiles were removed in vacuo, and the residue was washed with *n*-pentane (2×5 mL). The crude product was dissolved with CH_2Cl_2 then filtered through a pad of celite and silica gel (70-230 mesh) to remove the unreacted $PdCl_2$ and benzimidazolium salt. Then, the crude complex was crystallized from CH_2Cl_2/*n*-pentane mixture (1:5, *v/v*) at room temperature and, completely dried under vacuum. Since the **1c**-**1e** benzimidazolium salts have the bromide anion, the synthesized Pd-complexes could be formed as mixtures containing bromine and chlorine. We were synthesized only bromine-containing **2c**-**2e** Pd-complexes by adding a large excess of KBr in the reaction to prevent the formation of the different anions-containing Pd-complex mixtures. All Pd-complexes were isolated as air- and moisture-stable yellow solids in 71%-83% yields. For the ^{1}H NMR, ^{13}C NMR and FT-IR spectrums of the new **2a**-**2e** complexes see SI, pp. S3-S12.

4.2.1. Dibromo-[1-(benzyl)-3-(*n*-butyl)-benzimidazole-2-ylidene]-(pyridine)-palladium(II), (2a)

Yield 78%, 0.406 g; mp = 202─203 ^{o}C; yellow solid; FT-IR $\nu_{(CN)}$ = 1403 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ (ppm) = 1.01 (t, *J* = 7.3 Hz, 3H, $NCH_2CH_2CH_2CH_3$); 1.51 (hext, *J* = 7.4 Hz, 2H, $NCH_2CH_2CH_2CH_3$); 2.15 (pent, *J* = 7.4 Hz, 2H, $NCH_2CH_2CH_2CH_3$); 4.86 (t, *J* = 7.8 Hz, 2H, $NCH_2CH_2CH_2CH_3$); 6.23 (s, 2H, NCH_2Ph); 6.99-7.02, 7.05-7.09, 7.14-7.23 and 7.27-7.34 (m, 11H, arom. *H*s of benzimidazole, benzyl and pyridine); 7.70 (tt, *J* = 7.5, 1.5 Hz, 1H, arom. *H* of pyridine); 8.89 (dd, *J* = 6.5, 1.5 Hz, 2H, arom. *H*s of pyridine). ^{13}C NMR (101 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ (ppm) = 13.9 ($NCH_2CH_2CH_2CH_3$); 20.4 ($NCH_2CH_2CH_2CH_3$); 31.7 ($NCH_2CH_2CH_2CH_3$); 48.6 ($NCH_2CH_2CH_2CH_3$); 49.1 (NCH_2Ph); 110.5, 111.1, 123.0, 123.2, 128.9, 130.6, 130.8, 134.2, 134.9 and 138.1 (arom. *C*s of benzimidazole and benzyl); 124.5, 137.4 and 151.3 (arom. *C*s of pyridine); 164.3 (Pd-$C_{carbene}$). Elemental analysis calcd. (%) for $C_{23}H_{25}Br_2N_3Pd$: C 45.31, H 4.13, N 6.89; found (%): C 47.28, H 3.82, N 7.11.

4.2.2. Dichloro-[1-(2,3,4,5,6-pentamethylbenzyl)-3-(*n*-butyl)-benzimidazole-2-ylidene]-(pyridine)-palladium(II), (2b)

Yield 71%, 0.419 g; mp = 196─197 ^{o}C; yellow solid; FT-IR $\nu_{(CN)}$ = 1409 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ (ppm) = 1.09 (t, *J* = 7.4 Hz, 3H, $NCH_2CH_2CH_2CH_3$); 1.61 (hext, *J* = 7.5 Hz, 2H, $NCH_2CH_2CH_2CH_3$); 2.23 (pent, *J* = 7.4 Hz, 2H, $NCH_2CH_2CH_2CH_3$); 2.23, 2.30 and 2.31 (s, 15H, $NCH_2Ph(CH_3)_5$-2,3,4,5,6); 4.91 (t, *J* = 7.8 Hz, 2H, $NCH_2CH_2CH_2CH_3$); 6.27 (s, 2H, $NCH_2Ph(CH_3)_5$-2,3,4,5,6); 6.38 (d, *J* = 8.6 Hz, 1H arom. *H* of benzimidazole), 6.90-6.94 (m, 1H arom. *H* of benzimidazole), 7.12-7.16 (m, 1H arom. *H* of benzimidazole), 7.34-7.38 (m, 3H, arom. *H*s of benzimidazole and pyridine); 7.78 (tt, *J* = 7.7, 1.6 Hz, 1H, arom. *H* of pyridine); 8.98 (dd, *J* = 6.5, 1.5 Hz, 2H, arom. *H*s of pyridine). ^{13}C NMR (101 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ (ppm) = 13.9 ($NCH_2CH_2CH_2CH_3$); 16.9, 17.3 and 17.4 ($NCH_2Ph(CH_3)_5$-2,3,4,5,6); 20.4 ($NCH_2CH_2CH_2CH_3$); 31.7 ($NCH_2CH_2CH_2CH_3$); 48.4 ($NCH_2CH_2CH_2CH_3$); 51.3 ($NCH_2Ph(CH_3)_5$-2,3,4,5,6); 110.1, 111.7, 122.5, 122.9, 127.8, 133.1, 134.5, 134.6, 134.8 and 135.9 (arom. *C*s of benzimidazole and 2,3,4,5,6-pentamethylbenzyl); 124.5, 138.1 and 151.2 (arom. *C*s of pyridine); 162.9 (Pd-$C_{carbene}$). Elemental analysis calcd. (%) for $C_{28}H_{35}Cl_2N_3Pd$: C 56.91, H 5.97, N 7.11; found (%): C 56.96, H 5.86, N 7.10.

4.2.3. *Trans*-Dibromo-[1-(4-methylbenzyl)-3-(3-methoxylbenzyl)-benzimidazole-2-ylidene]-(pyridine)-palladium(II), (2c)

Yield 83%, 0.570 g; mp = 222─223 ^{o}C; yellow solid; FT-IR $\nu_{(CN)}$ = 1409 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ (ppm) = 2.32 (s, 3H, $NCH_2Ph(CH_3)$-4); 3.75 (s, 3H, $NCH_2Ph(OCH_3)$-3); 6.18 (s, 4H, $NCH_2Ph(CH_3)$-4 and $NCH_2Ph(OCH_3)$-4); 6.86 (d, *J* = 7.4 Hz, 1H arom. *H* of 4-methylbenzyl), 7.03-7.31 (m, 11H, arom. *H*s of

benzimidazole, 3-methoxylbenzyl and 4-methylbenzyl); 7.50 (d, *J* = 7.9 Hz, 2H, arom. *H*s of pyridine); 7.72 (tt, *J* = 7.7, 1.6 Hz, 1H, arom. *H* of pyridine); 9.02 (dd, *J* = 6.5, 1.5 Hz, 2H, arom. *H*s of pyridine). ^{13}C NMR (101 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ (ppm) = 21.2 ($NCH_2Ph(\mathit{C}H_3)$-4); 53.5 ($N\mathit{C}H_2Ph(CH_3)$-4); 53.7 ($N\mathit{C}H_2Ph(OCH_3)$-4); 55.7 ($NCH_2Ph(O\mathit{C}H_3)$-4); 111.5, 111.6, 113.1, 114.7, 120.4, 123.1, 128.0, 129.5, 129.7, 131.8, 134.7, 134.8, 136.6, 137.8 and 160.2 (arom. *C*s of benzimidazole, 3-methoxylbenzyl and 4-methylbenzyl); 124.5, 137.9 and 153.0 (arom. *C*s of pyridine); 164.2 (Pd-$C_{carbene}$). Elemental analysis calcd. (%) for $C_{28}H_{27}Br_2N_3OPd$: C 48.90, H 3.96, N 6.11; found (%): C 49.22, H 3.94, N 6.17.

4.2.4. Dibromo-[1-(2,4,6-trimethylbenzyl)-3-(3-methoxylbenzyl)-benzimidazole-2-ylidene]-(pyridine)-palladium(II), (2d)

Yield 75%, 0.536 g; mp = 247─248 ^{o}C; yellow solid; FT-IR ν_{CN} = 1395 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ (ppm) = 2.35 and 2.37 (s, 9H, $NCH_2Ph(C\mathit{H}_3)_3$-2,4,6); 3.75 (s, 3H, $NCH_2Ph(OC\mathit{H}_3)$-3); 6.19 (s, 4H, $NC\mathit{H}_2Ph(CH_3)_3$-2,4,6 and $NC\mathit{H}_2Ph(OCH_3)$-4); 6.85-6.89 and 6.98-7.30 (m, 8H, arom. *H*s of benzimidazole and 3-methoxylbenzyl); 6.95 (s, 2H arom. *H*s of 2,4,6-trimethylbenzyl), 7.34 (t, *J* = 7.6 Hz, 2H, arom. *H*s of pyridine); 7.75 (tt, *J* = 7.5, 1.5 Hz, 1H, arom. *H* of pyridine); 9.03 (dd, *J* = 7.5, 1.5 Hz, 2H, arom. *H*s of pyridine). ^{13}C NMR (101 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ (ppm) = 21.0 and 21.1 ($NCH_2Ph(\mathit{C}H_3)_3$-2,4,6); 51.1 ($N\mathit{C}H_2Ph(CH_3)_3$-2,4,6); 53.8 ($N\mathit{C}H_2Ph(OCH_3)$-4); 55.7 ($NCH_2Ph(O\mathit{C}H_3)$-4); 111.3, 113.1, 114.6, 120.3, 122.7, 123.1, 127.5, 129.6, 129.7, 134.6, 135.2, 136.6, 137.9, 139.0 and 160.2 (arom. *C*s of benzimidazole, 3-methoxylbenzyl and 2,4,6-trimethylbenzyl); 124.5, 138.7 and 152.6 (arom. *C*s of pyridine); 164.0 (Pd-$C_{carbene}$). Elemental analysis calcd. (%) for $C_{30}H_{31}Br_2N_3OPd$: C 50.34, H 4.37, N 5.87; found (%): C 49.71, H 4.43, N 5.83.

4.2.5. Dibromo-[1-(2,3,5,6-tetramethylbenzyl)-3-(3-methoxybenzyl)-benzimidazole-2-ylidene]-(pyridine)-palladium(II), (2e)

Yield 80%, 0.583 g; mp = 213─214 ^{o}C; yellow solid; FT-IR $\nu_{(CN)}$ = 1405 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ (ppm) = 2.31 (s, 12H, $NCH_2Ph(C\mathit{H}_3)_4$-2,3,5,6); 3.79 (s, 3H, $NCH_2Ph(OC\mathit{H}_3)$-3); 6.22 (s, 2H, $NC\mathit{H}_2Ph(CH_3)_4$-2,3,5,6); 6.26 (s, 2H, $NC\mathit{H}_2Ph(OCH_3)$-4); 6.85-7.31 (m, 11H, arom. *H*s of benzimidazole, 3-methoxylbenzyl and 2,3,5,6-tetramethylbenzyl); 7.36 (t, *J* = 7.5 Hz, 2H, arom. *H*s of pyridine); 7.78 (tt, *J* = 7.5, 1.5 Hz, 1H, arom. *H* of pyridine); 9.03 (dd, *J* = 6.5, 1.5 Hz, 2H, arom. *H*s of pyridine). ^{13}C NMR (101 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ (ppm) = 16.8 and 20.6 ($NCH_2Ph(\mathit{C}H_3)_4$-2,3,5,6); 51.6 ($N\mathit{C}H_2Ph(CH_3)_4$-2,3,5,6); 53.9 ($N\mathit{C}H_2Ph(OCH_3)$-4); 55.7 ($NCH_2Ph(O\mathit{C}H_3)$-4); 111.3, 113.1, 114.6, 120.4, 122.6, 123.1, 129.7, 130.5, 132.6, 134.4, 134.5, 135.2, 135.4, 137.9 and 160.2 (arom. *C*s of benzimidazole, 3-methoxylbenzyl and 2,3,5,6-tetramethylbenzyl); 124.5, 136.7 and 152.6 (arom. *C*s of pyridine); 163.9 (Pd-$C_{carbene}$). Elemental analysis calcd. (%) for $C_{31}H_{33}Br_2N_3OPd$: C 51.02, H 4.56, N 5.76; found (%): C 52.95, H 5.06, N 5.71.

4.3. General procedure for the direct arylation of five-membered heteroaromatics

In a typical experiment, an oven dried 10 mL Schlenk tube was charged with 1 mol% Pd-complex, (0.01 mmol), as catalyst, five-membered heteroaromatic compound (2.0 mmol), (hetero)aryl bromide (1.0 mmol), KOAc (1.5 mmol) as a base, and DMAc (2 mL) as solvent under an argon atmosphere. The reaction mixture was stirred at 120 ^{o}C or 140 ^{o}C for 1 h (see Table 4-6). After completion of the reaction, the solvent was evaporated under vacuum and the residue was solved with CH_2Cl_2 (2 mL). The chemical characterizations of the products were undertaken with GC and GC-MS spectrometry. GC yields were calculated with respect to aryl bromide from the results of GC spectrometry with dodecane as internal standard.

4.4. X-ray Analysis

Intensity data of **2c** were collected on a STOE IPDS II diffractometer at room temperature using graphite-monochromated Mo Kα radiation by applying the ω-scan method. Data collection and cell refinement were carried out using X-AREA[42] while data reduction was applied using X-RED32[42]. The structure was solved by a dual-space algorithm using SHELXT-2018[43] and refined with full-matrix least-squares calculations on F^2 using SHELXL-2018[44] implemented in WinGX[45] program suit. All carbon-bound H atoms were located in difference electron-density map and then treated as riding atoms in geometrically idealized positions, with C─H = 0.93 (aromatic), 0.97 (CH_2) and 0.96 Å (CH_3), and with U_{iso}(H) = kU_{eq}(C), where k = 1.5 for the methyl groups and 1.2 for all other H atoms. In the compound, the methoxy moiety was disordered over two positions, and the refined site-occupancy factors of the disordered parts, viz. O1A─C15A and O1B─C15B, are 0.673(15) and 0.327(15)%, respectively. In the final difference

Fourier map of the compound, the maximum residual densities being higher than 1 e $Å^{-3}$ were observed around the palladium and essentially meaningless. The crystallographic data and refinement parameters are summarized in Table 7. Molecular graphic was created by using ORTEP-3.[45]

Table 7. Crystal data and structure refinement parameters for **2c**.

CCDC depository	1910749
Color/shape	Colorless/plate
Chemical formula	$[PdBr_2(C_{23}H_{22}N_2O)(C_5H_5N)]$
Formula weight	687.74
Temperature (K)	296
Wavelength (Å)	0.71073 Mo Kα
Crystal system	Monoclinic
Space group	$P2_1/n$ (No. 14)
Unit cell parameters	
a, b, c (Å)	12.0678(6), 11.2435(6), 20.8956(10)
α, β, γ (°)	90, 106.548(4), 90
Volume ($Å^3$)	2717.8(2)
Z	4
$D_{calc.}$ (g/cm^3)	1.681
μ (mm^{-1})	3.649
Absorption correction	Integration
$T_{min.}$, $T_{max.}$	0.1835, 0.8479
F_{000}	1360
Crystal size (mm^3)	0.48 × 0.41 × 0.03
Diffractometer/measurement	STOE IPDS II/rotation (ω scan)
Index ranges	$-15 \le h \le 15$, $-14 \le k \le 14$, $-27 \le l \le 27$
θ range for data collection (°)	$2.033 \le \theta \le 27.692$
Reflections collected	26986
Independent/observed	6342/3458
$R_{int.}$	0.110
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6342/41/339
Goodness-of-fit on F^2	0.955
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0568$, $wR_2 = 0.1163$
R indices (all data)	$R_1 = 0.1177$, $wR_2 = 0.1374$
$\Delta\rho_{max.}$, $\Delta\rho_{min.}$ ($e/Å^3$)	1.11, −0.40

Appendix A. Supplementary data

CCDC 1910749 for **2c** complex contains the supplementary crystallographic data for the compound reported in this article. These data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk, https://www.ccdc.cam.ac.uk/structures/].

Supplementary data related to this article can be found at https://

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Highlights

- Benzimidazole-based PEPPSI-type palladium-complexes were synthesized.
- The structures of palladium-complexes were characterized by different techniques.
- The complexes were tested as catalysts in the direct arylation of five-membered heteroaromatics.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: