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Catalytic activities in the direct C5 arylation of novel palladium *N*-heterocyclic carbene complexes containing benzimidazol-2-ylidene nucleus

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ABSTRACT

New palladium *N*-heterocyclic carbene (NHC) complexes (**1a–e**) were synthesized in very good yields by the reaction of 1-phenyl-3-alkylbenzimidazolium salts with $Pd(OAc)_2$ in dimethyl sulfoxide. These synthesized complexes were fully characterized using elemental analyses, FT-IR, ^1H NMR, ^{13}C NMR and LC–MS (for **1a**, **1c** and **1e**) spectroscopy data. Also, the molecular structure of the bis[1-phenyl-3-(2-methyl-1,4-benzodioxane)benzimidazol-2-ylidene]dibromopalladium(II) complex (**1d**) was structurally characterized by single crystal X-ray diffraction study. The new Pd^{II} complexes (**1a–e**) were tested as catalysts in the direct C5 arylation of 2-*n*-butylfuran, 2-*n*-butylthiophene and 2-*n*-propylthiazole with various aryl bromides at 130 °C for 1 h. Also, some experiments were carried out by using aryl chlorides in order to be used for comparison. The results are reported herein. These complexes exhibited quite high catalytic activities under the given conditions.

1. Introduction

Metal *N*-heterocyclic carbene (NHC) complexes display perfect catalytic activities for various useful organic transformations such as C–H bond activation, C–C and C–N cross-coupling reactions [1–15]. Among the metal–NHC complexes, Pd-NHC complexes have been used for certain purposes such as for catalysis and for their biological activity as anticancer agents [4,16]. Two approaches to perform a coupling reaction are available to generate a catalytically active species: (i) a Pd^0 source combined with an ancillary ligand to generate the catalyst *in situ* is employed [17,18] and (ii) Pd^{II} complexes are mostly used as precatalysts [19]. The Pd-NHC complexes are prepared simply both by means of diverse salts with $Pd(OAc)_2$ and by Ag-NHC complexes with $PdCl_2(PhCN)_2$ or $PdCl_2(CH_3CN)_2$. In the formation of palladium-carbene, various palladium compounds can be employed, like $PdCl_2$ [4,20], $Pd(OAc)_2$ [4,21–23], $PdCl_2(PhCN)_2$ [4,24] and $PdCl_2(CH_3CN)_2$ [13,25]. Among them, palladium acetate is the most commonly used.

In the case of direct arylation of heteroaromatics by using challenging aryl bromides, it was observed that "ligandless" palladium catalysts are usually relatively inefficient. Therefore, we synthesized Pd-NHC complexes to find more efficient catalysts for the direct 5-arylation of 2-*n*-propylthiazole, 2-*n*-butylfuran and 2-*n*-butylthiophene with various aryl halides. The catalytic activities of the synthesized Pd^{II} complexes were found to be very high. These complexes were fully characterized by means of elemental analyses, ^1H NMR, ^{13}C NMR, LC–MS (for **1a**, **1c** and **1e**) and FT-IR spectroscopies. Also, the crystal structure of the bis[1-phenyl-3-(1,4-benzodioxane-2-methyl) benzimidazol-2-ylidene]dibromopalladium(II) complex (**1d**) is reported here.

2. Experimental

2.1. Materials and methods

For the preparation of **1a–e**, all reactions were carried out under argon in flame–dried glassware using standard Schlenk-type flasks and standard high vacuum-line techniques. Solvents such as dichloromethane and diethyl ether were of analytical grade. Prior to their use, they were dried under P_4O_{10} and Na in an inert atmosphere, respectively. All reagents were purchased from Aldrich, Fluka and Merck. All ^1H NMR and ^{13}C NMR analyses were

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performed in $CDCl_3$ and DMSO. The ^1H NMR and ^{13}C NMR spectra were recorded by using a Bruker AC300P FT spectrometer operating at 300.13 MHz (^1H) and 75.47 MHz (^{13}C). Chemical shifts (δ) were given in ppm according to relative tetramethylsilane. The coupling constants (J) were given in Hz. The FT-IR spectra were recorded on a Mattson 1000 spectrophotometer and wave numbers were recorded in cm^{-1}. LC–MS analyses of Pd-NHC complexes were made using an Agilent Technologies 1100 Series LC mass spectrometer. Melting points were measured in open capillary tubes with an Electrothermal-9200 melting point apparatus. Elemental analyses were performed by the Technological and Scientific Research Council of Turkey Microlab.

2.1.1. Bis[1-phenyl-3-(2-morpholinoethyl)benzimidazol-2-ylidene]-dichloropalladium(II), ***1a***

1-Phenyl-3-(2-morpholinoethyl)benzimidazol-2-ylidene salt (0.309 g, 0.9 mmol) and $Pd(OAc)_2$ (0.1 g, 0.45 mmol) in dimethyl sulfoxide (3–4 mL) were heated at 60 °C for 24 h, and then at 110–120 °C for 1 h. The solvent (DMSO) was then removed under reduced pressure. The crude product was crystallized from dichloromethane-hexane (2:1) at room temperature. The crystals were filtered, washed with diethyl ether (3 × 10 mL) and dried under vacuum. Yield: 86%; m.p. 255–256 °C. ^1H NMR (300.13 MHz, DMSO, 25 °C, TMS): δ = 2.47 [t, J: 4.0 Hz, 8 H, $NCH_2CH_2N(CH_2CH_2)_2O$]; 2.87 (t, J: 6.6 Hz, 4 H, $NCH_2CH_2NC_4H_8O$); 3.68 [t, J: 4.0 Hz, 8 H, $NCH_2CH_2N(CH_2CH_2)_2O$]; 4.69 (t, J: 6.6 Hz, 4 H, $NCH_2CH_2NC_4H_8O$); 7.11–8.03 (m, 18 H, Ar–*H*). ^{13}C NMR (75.47 MHz, DMSO, 25 °C, TMS): δ = 45.9, 54.0 and 57.8 ($NCH_2CH_2NC_4H_8O$); 67.1 ($NCH_2CH_2NC_4H_8O$); 111.1, 123.2, 127.3, 128.1, 128.7, 129.4, 134.6, 135.3 and 137.9 (Ar–*C*); 181.7 (2-*C*). FT-IR $\nu_{(NCN)}$: 1597.45 cm^{-1}. LC–MS calcd. for $C_{38}H_{42}N_6O_2PdCl_2$: m/z: 792.11; found (L_2PdCl_2-Cl): 757.1. *Anal.* Calc. for $C_{38}H_{42}N_6O_2PdCl_2$: C, 57.62; H, 5.34; N, 10.61. Found: C, 57.68; H, 5.25; N, 10.63%.

2.1.2. Bis1-phenyl-3-(4-vinylbenzyl)benzimidazol-2-ylidene]dichloropalladium(II), ***1b***

1b compound, with a method similar to the one used in **1a** compound, was prepared from 1-phenyl-3-(4-vinylbenzyl)benzimidazolium salt (0.31 g, 0.89 mmol) and $Pd(OAc)_2$ (0.1 g, 0.45 mmol) in dimethyl sulfoxide (3–4 mL). Yield: 82%; m.p. 320–321 °C. ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C, TMS): δ = 5.32 (d, J: 10.86 Hz, 4 H, $C_6H_4CHCH_2$); 5.82 (s, 4 H, $NCH_2C_6H_4CHCH_2$); 6.77 (m, 2 H, $C_6H_4CHCH_2$); 7.14–8.02 (m, 26 H, Ar–*H*). ^{13}C NMR (75.47 MHz, $CDCl_3$, 25 °C, TMS): δ = 53.8 ($C_6H_4CHCH_2$); 108.5 ($NCH_2C_6H_4CHCH_2$); 110.8 ($C_6H_4CHCH_2$); 111.1, 123.4, 126.7, 127.5, 128.1, 129.1, 135.1, 137.3 and 137.7 (Ar–*C*); 181.2 (2-*C*). FT-IR $\nu_{(NCN)}$: 1597.34 cm^{-1}. *Anal.* Calc. for $C_{44}H_{36}N_4PdCl_2$: C, 66.22; H, 4.55; N, 7.02. Found: C, 66.29; H, 4.47; N, 7.00%.

2.1.3. Bis1-phenyl-3-(phthalimido-N-propyl)benzimidazol-2-ylidene]-dibromopalladium(II), ***1c***

1c compound, with a method similar to the one used in **1a** compound, was prepared from 1-phenyl-3-(phthalimido-*N*-propyl)benzimidazolium salt (0.38 g, 0.9 mmol) and $Pd(OAc)_2$ (0.1 g, 0.45 mmol) in dimethyl sulfoxide (3–4 mL). Yield: 85%; m.p. 330–331 °C. ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.64, 3.69 and 4.97 (m, 12 H, $NCH_2CH_2CH_2N$); 7.25–7.83 (m, 26 H, Ar–*H*). ^{13}C NMR (75.47 MHz, $CDCl_3$, 25 °C, TMS): δ = 26.7, 35.6 and 45.7 ($NCH_2CH_2CH_2N$); 111.1, 123.4, 123.8, 124.1, 129.5, 132.1, 132.8, 134.2, 134.8 and 136.9 (Ar–*C*); 168.2 (C=O); 173.0 (2-*C*). FT-IR $\nu_{(NCN)}$: 1596.32 cm^{-1}. LC–MS calcd. for $C_{48}H_{38}N_6O_4$ $PdBr_2$ m/z: 1029.08; found (L_2PdBr_2-Br): 949.1. *Anal.* Calc. for C_{48} $H_{38}N_6O_4PdBr_2$: C, 56.02; H, 3.72; N, 8.17. Found: C, 56.11; H, 3.68; N, 8.15%.

2.1.4. Bis1-phenyl-3-(1,4-benzodioxano-2-methyl)benzimidazol-2-ylidene]dibromopalladium(II), ***1d***

1d compound, with a method similar to the one used in **1a** compound, was prepared from 1-phenyl-3-(1,4-benzodioxano-2-methyl)benzimidazolium salt (0.34 g, 0.9 mmol) and $Pd(OAc)_2$ (0.1 g, 0.45 mmol) in dimethyl sulfoxide (3–4 mL). Yield: 89%; m.p. 328–329 °C. ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C, TMS): δ = 3.57 (m, 4 H, $NCH_2CHCH_2O_2C_6H_4$); 4.74 (m, 2 H, $NCH_2CHCH_2O_2C_6H_4$); 4.85 (m, 4 H, $NCH_2CHCH_2O_2C_6H_4$); 6.99–7.74 (m, 26 H, Ar–*H*). ^{13}C NMR (75.47 MHz, $CDCl_3$, 25 °C, TMS): δ = 48.7, 65.7 and 71.9 ($NCH_2CHCH_2O_2C_6H_4$); 111.0, 111.6, 117.4, 121.8, 123.6,

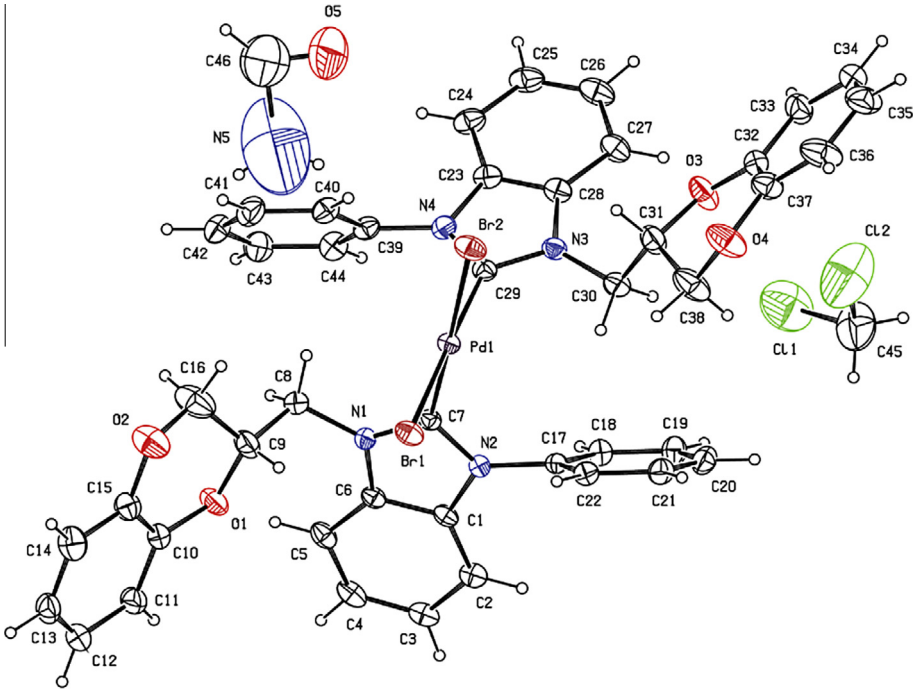


Fig. 1. Molecular structure of **1d** with displacement ellipsoids drawn at the 20% probability level.

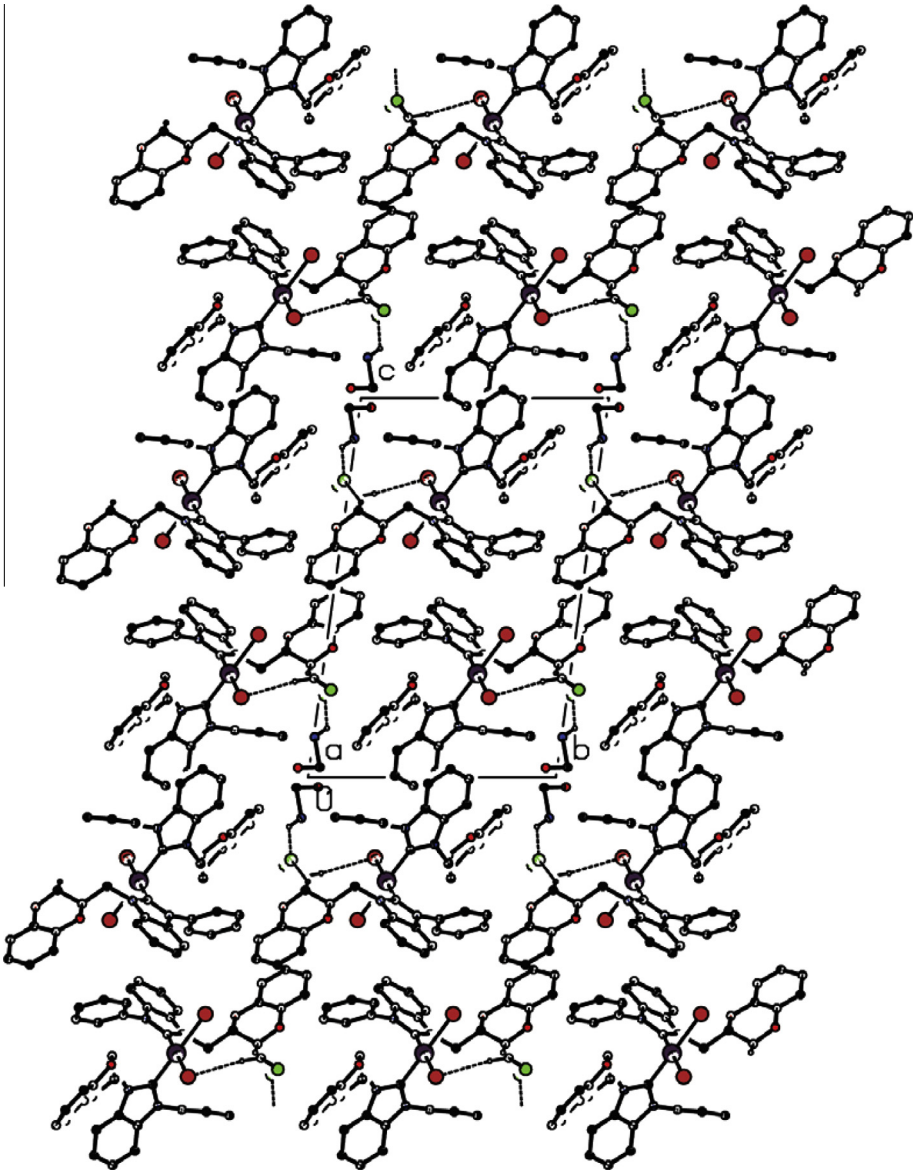


Fig. 2. The molecular packing of **1d** viewed down the *a*-axis.

128.8, 129.6, 134.7, 136.1, 137.5, 142.4 and 143.3 (Ar–*C*); 182.1 (2-*C*). FT-IR $\nu_{(NCN)}$: 1594.49 cm^{-1}. *Anal.* Calc. for $C_{44}H_{36}N_4O_4PdBr_2$: C, 55.57; H, 3.82; N, 5.89. Found: C, 55.65; H, 3.75; N, 5.90%.

2.1.5. Bis1-phenyl-3-naphthalenomethylbenzimidazol-2-ylidene]-dichloropalladium(II), ***1e***

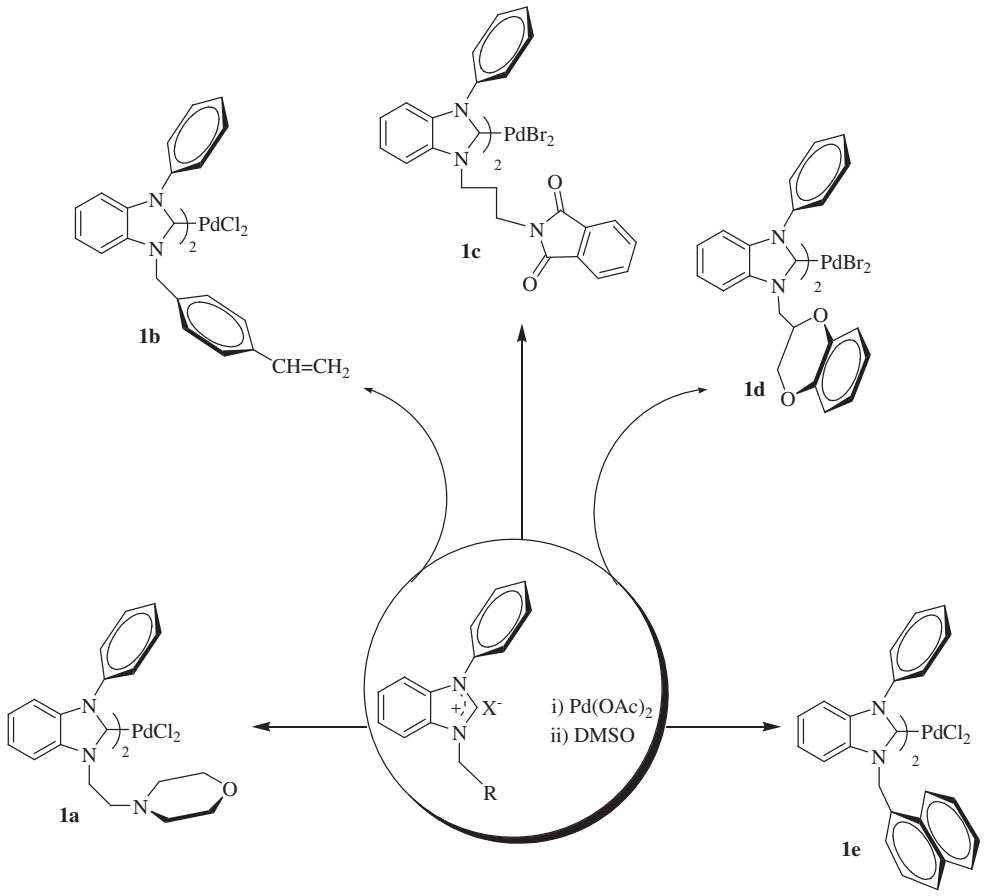
1e compound, with a method similar to the one used in **1a** compound, was prepared from 1-phenyl-3-naphthalenomethylbenzimidazolium salt (0.33 g, 0.9 mmol) and $Pd(OAc)_2$ (0.1 g, 0.45 mmol) in dimethyl sulfoxide (3–4 mL). Yield: 83%; m.p. 294–295 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$, 25 °C, TMS): δ = 6.25 (s, 4 H, $NCH_2C_{10}H_7$); 6.47–8.30 (m, 32 H, Ar–*H*). ^{13}C NMR (75.47 MHz, $CDCl_3$, 25 °C, TMS): δ = 49.5 ($NCH_2C_{10}H_7$); 111.1, 112.5, 123.4, 123.8, 125.6, 125.9, 126.6, 127.3, 128.3, 128.8, 129.2, 130.6, 133.4, 133.7, 134.1, 135.2, 137.2 (Ar–*C*); 182.9 (2-*C*). FT-IR $\nu_{(NCN)}$: 1500.08 cm^{-1}. LC–MS calcd. for $C_{48}H_{36}N_4PdCl_2$ *m*/*z*: 846.15; found (L_2PdCl_2-Cl): 811.2. *Anal.* Calc. for $C_{48}H_{36}N_4PdCl_2$: C, 68.13; H, 4.29; N, 6.62. Found: C, 68.21; H, 4.35; N, 6.64%.

2.2. General procedure for the direct C5 arylations

The heteroaryl derivative (2 mmol), aryl halide (1 mmol), Pd complexes **1a–e** (0.005 mmol), KOAc (1 mmol) and DMAc (2 mL) were added into a Schlenk tube equipped with a magnetic stirring bar. The Schlenk tube was purged several times with argon and was placed in a preheated oil bath at 130 °C. The reactants were stirred for 1 h (with aryl bromides) and for 20 h (with aryl chlorides). The solvent was removed by heating the reaction vessel under vacuum. The products were eluted by using an appropriate ratio of diethyl ether/pentane (1:3). The reaction mixture was purified by flash chromatography on silica gel. The purity of compounds was checked by GC and NMR. Yields were based on aryl halides (aryl bromide and aryl chloride).

*2.2.1. 2-Acetophenyl-5-n-propylthiazole (****2****)*

Corresponding product **2** was obtained in 85%, 51%, 50%, 88% and 81% conversions by the reaction of 2-*n*-propylthiazole



Scheme 1. The synthesis of [1-phenyl-3-alkylbenzimidazol-2-ylidene]dihalidepalladium(II) complexes (**1a–e**).

(0.26 g, 2 mmol), 4-bromoacetophenone (0.2 g, 1 mmol), KOAc (0.1 g, 1 mmol) and **1a–e** (0.005 mmol).

*2.2.2. 2-(4-Methoxyphenyl)-5-n-propylthiazole (**3**)*

Corresponding product **3** was obtained in 100%, 79%, 94%, 100% and 100% conversions by the reaction of 2-*n*-propylthiazole (0.26 g, 2 mmol), 4-bromoanisole (0.19 g, 1 mmol), KOAc (0.1 g, 1 mmol) and **1a–e** (0.005 mmol).

*2.2.3. 2-(4-Methylphenyl)-5-n-propylthiazole (**4**)*

Corresponding product **4** was obtained in 100%, 61%, 94%, 100% and 81% conversions by the reaction of 2-*n*-propylthiazole (0.26 g, 2 mmol), 4-bromotoluene (0.17 g, 1 mmol), KOAc (0.1 g, 1 mmol) and **1a–e** (0.005 mmol).

*2.2.4. 2-Phenyl-5-n-propylthiazole (**5**)*

Corresponding product **5** was obtained in 100%, 66%, 96%, 86% and 89% conversions by the reaction of 2-*n*-propylthiazole (0.25 g, 2 mmol), bromobenzene (0.16 g, 1 mmol), KOAc (0.1 g, 1 mmol) and **1a–e** (0.005 mmol).

*2.2.5. 2-n-Butyl-5-acetophenylthiophene (**6**)*

Corresponding product **6** was obtained in 98%, 100%, 99%, 91% and 96% conversions by the reaction of 2-*n*-butylthiophene (0.27 g, 2 mmol), 4-bromoacetophenone (0.2 g, 1 mmol), KOAc (0.1 g, 1 mmol) and **1a–e** (0.005 mmol).

*2.2.6. 2-n-Butyl-5-(4-methoxyphenyl)thiophene (**7**)*

Corresponding product **7** was obtained in 92%, 99%, 97%, 94% and 100% conversions by the reaction of 2-*n*-butylthiophene (0.28 g, 2 mmol), 4-bromoanisole (0.19 g, 1 mmol), KOAc (0.1 g, 1 mmol) and **1a–e** (0.005 mmol).

*2.2.7. 2-(4-Methylphenyl)-5-n-butylthiophene (**8**)*

Corresponding product **8** was obtained in 94%, 80%, 97%, 99% and 96% conversions by the reaction of 2-*n*-butylthiophene (0.28 g, 2 mmol), 4-bromotoluene (0.17 g, 1 mmol), KOAc (0.1 g, 1 mmol) and **1a–e** (0.005 mmol).

*2.2.8. 2-Phenyl-5-n-butylthiophene (**9**)*

Corresponding product **9** was obtained in 85%, 71%, 62%, 93% and 88% conversions by the reaction of 2-*n*-butylthiophene (0.28 g, 2 mmol), bromobenzene (0.16 g, 1 mmol), KOAc (0.1 g, 1 mmol) and **1a–e** (0.005 mmol).

*2.2.9. 2-n-Butyl-5-acetophenylfuran (**10**)*

Corresponding product **10** was obtained in 97%, 92%, 100%, 74% and 79% conversions by the reaction of 2-*n*-butylfuran (0.25 g, 2 mmol), 4-bromoacetophenone (0.2 g, 1 mmol), KOAc (0.1 g, 1 mmol) and **1a–e** (0.005 mmol).

*2.2.10. 2-n-Butyl-5-(4-methoxyphenyl)furan (**11**)*

Corresponding product **11** was obtained in 92%, 54%, 87%, 86% and 70% conversions by the reaction of 2-*n*-butylfuran (0.25 g, 2 mmol), 4-bromoanisole (0.19 g, 1 mmol), KOAc (0.1 g, 1 mmol) and **1a–e** (0.005 mmol).

*2.2.11. 2-n-Butyl-5-(4-methylphenyl)furan (**12**)*

Corresponding product **12** was obtained in 88%, 70%, 91%, 95% and 89% conversions by the reaction of 2-*n*-butylfuran (0.25 g,

Table 1
Crystallographic data and collection parameters for **1d**.

Formula	$C_{44}H_{36}Br_2N_4O_4Pd{\cdot}CH_2Cl_2{\cdot}CH_3NO$
Molecular weight	1080.94
Crystal size (mm)	0.18 × 0.20 × 0.35
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	9.3581 (3)
b (Å)	12.3362 (5)
c (Å)	19.0523 (7)
α (°)	81.881 (2)
β (°)	87.575 (2)
γ (°)	85.186 (2)
V (Å3)	2168.70 (14)
Z	2
Calculated density (g cm−3)	1.655
μ (mm−1)	2.45
Absorption correction	multi-scan
Transmission factor range	0.561–0.644
Reflections measured	32335
R_{int}	0.038
Mean $\sigma(I)/I$	
θ_{max}	27.1
Independent reflections	9522
Weighting scheme	$w = 1/[\sigma 2(F_o 2) + (0.0553P)2 + 1.3897P]$ where $P = (F_o 2 + 2F_c 2)/3$
Reflections used in refinement [$I > 2\sigma(I)$]	6354
Parameters	552
$R(F_{obs})$	0.046
$R_w(F2)$	0.121
S	1.02
Shift/error$_{max}$	0.001
Maximum electron density (e Å−3)	0.64
Minimum electron density (e Å−3)	−0.86
CCDC	894210

2 mmol), 4-bromotoluene (0.17 g, 1 mmol), KOAc (0.1 g, 1 mmol) and **1a–e** (0.005 mmol).

*2.2.12. 2-n-Butyl-5-phenylfuran (**13**)*

Corresponding product **13** was obtained in 95%, 92%, 82%, 92% and 94% conversions by the reaction of 2-*n*-butylfuran (0.25 g, 2 mmol), bromobenzene (0.16 g, 1 mmol), KOAc (0.1 g, 1 mmol) and **1a–e** (0.005 mmol).

*2.2.13. 2-n-Butyl-5-acetophenylthiophene (**14**)*

Corresponding product **14** was obtained in 60% conversion by the reaction of 2-*n*-butylthiophene (0.25 g, 2 mmol), 4-chloroacetophenone (0.14 g, 1 mmol), KOAc (0.09 g, 1 mmol) and **1a** (0.005 mmol).

Table 2
Bond lengths (Å) for **1d**.

Pd1–Br1	2.4796 (5)	O5–C46	1.19 (2)
Pd1–Br2	2.4892 (6)	N1–C8	1.462 (6)
Pd1–C7	2.002 (4)	N1–C7	1.349 (5)
Pd1–C29	1.986 (4)	N1–C6	1.397 (5)
Cl1–C45	1.748 (10)	N2–C17	1.429 (5)
Cl2–C45	1.626 (10)	N2–C7	1.350 (5)
O1–C10	1.373 (6)	N2–C1	1.403 (5)
O1–C9	1.440 (7)	N3–C28	1.394 (5)
O2–C16	1.378 (8)	N3–C30	1.472 (6)
O2–C15	1.374 (6)	N3–C29	1.360 (5)
O3–C31	1.432 (7)	N4–C23	1.406 (6)
O3–C32	1.376 (7)	N4–C39	1.428 (6)
O4–C38	1.410 (7)	N4–C29	1.347 (5)
O4–C37	1.379 (7)	N5–C46	1.58 (4)

*2.2.14. 2-n-Butyl-5-(4-methylphenyl)thiophene (**15**)*

Corresponding product **15** was obtained in 70% conversion by the reaction of 2-*n*-butylthiophene (0.25 g, 2 mmol), 4-chlorotoluene (0.11 g, 1 mmol), KOAc (0.09 g, 1 mmol) and **1c** (0.005 mmol).

*2.2.15. 2-n-Butyl-5-acetophenylfuran (**16**)*

Corresponding product **16** was obtained in 78% conversion by the reaction of 2-*n*-butylfuran (0.25 g, 2 mmol), 4-chloroacetophenone (0.16 g, 1 mmol), KOAc (0.1 g, 1 mmol) and **1a** (0.005 mmol).

*2.2.16. 2-n-Butyl-5-(4-methylphenyl)furan (**17**)*

Corresponding product **17** was obtained in 65% conversion by the reaction of 2-*n*-butylfuran (0.25 g, 2 mmol), 4-chlorotoluene (0.13 g, 1 mmol), KOAc (0.1 g, 1 mmol) and **1d** (0.005 mmol).

2.3. Crystal structure determinations

X-ray data for **1d** were collected on a Bruker Kappa APEXII CCD diffractometer using Mo Kα radiation ($\lambda = 0.71073$ A) at $T = 296(2)$ K. The structure was solved by SIR-97 [26] and refined by full-matrix least-squares refinement on F^2 using SHELXL-97 [27]. All H atoms were placed geometrically with N–H = 0.86 Å, C–H = 0.93 Å (aromatic), 0.97 Å (methylene) and 0.98 Å (methine), and refined using a riding model with $U_{iso}(H) = 1.2U_{eq}(C, N)$. Five poorly fitted reflections, (001), (−1−11), (012), (−104), and (−110), were omitted from the refinement. The ORTEP and packing diagrams (Figs. 1 and 2) of **1d** were drawn using PLATON [28].

3. Results and discussion

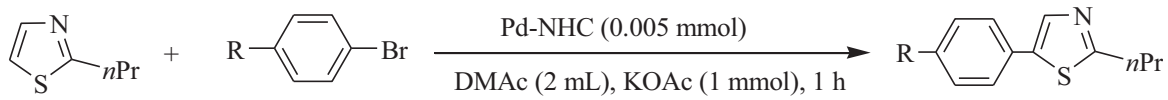
3.1. Synthesis of palladium N-heterocyclic carbene complexes (Pd-NHC)

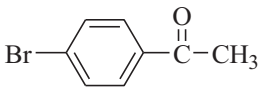
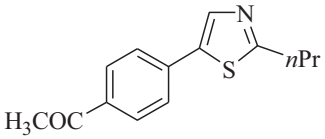
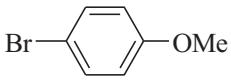
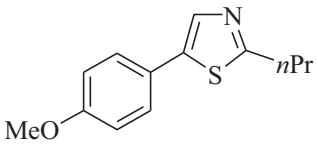
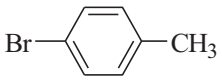
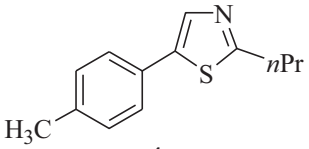
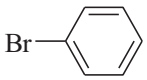
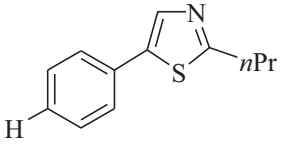
The synthetic route for phenyl substituted palladium complexes described in this study is given in Scheme 1. According to the method described in the literature, the 1-phenyl-3-alkyl benzimidazolium salts were prepared by the quaternization of *N*-phenylbenzimidazole with a variety of alkyl halides in dimethylformamide (DMF) [29–31]. The Pd-NHC complexes (**1a–e**) were

Table 3
Bond Angles (°) for **1d**.

Br1–Pd1–Br2	92.62 (2)	N1–C8–C9	114.8 (3)
Br1–Pd1–C7	87.43 (11)	O1–C9–C8	106.6 (4)
Br1–Pd1–C29	177.14 (11)	O1–C9–C16	113.0 (5)
Br2–Pd1–C7	179.10 (11)	O1–C10–C15	121.3 (4)
Br2–Pd1–C29	85.22 (11)	O1–C10–C11	119.1 (4)
C7–Pd1–C29	94.75 (15)	O2–C15–C10	122.1 (4)
C9–O1–C10	113.4 (4)	O2–C15–C14	119.0 (4)
C15–O2–C16	114.7 (5)	O2–C16–C9	113.9 (6)
C31–O3–C32	115.0 (4)	N2–C17–C18	118.4 (3)
C37–O4–C38	113.2 (5)	N2–C17–C22	121.1 (4)
C6–N1–C7	110.4 (3)	N4–C23–C28	106.1 (3)
C6–N1–C8	124.7 (3)	N4–C23–C24	130.8 (4)
C7–N1–C8	124.9 (3)	N3–C28–C27	132.5 (4)
C1–N2–C7	110.3 (3)	N3–C28–C23	106.6 (4)
C1–N2–C17	123.0 (3)	Pd1–C29–N3	126.8 (3)
C7–N2–C17	126.6 (3)	Pd1–C29–N4	127.0 (3)
C28–N3–C29	110.6 (4)	N3–C29–N4	106.0 (3)
C28–N3–C30	125.9 (4)	N3–C30–C31	114.0 (4)
C29–N3–C30	123.5 (4)	O3–C31–C38	110.1 (5)
C23–N4–C29	110.7 (4)	O3–C31–C30	106.8 (4)
C23–N4–C39	123.4 (3)	O3–C32–C33	117.6 (5)
C29–N4–C39	125.6 (3)	O3–C32–C37	122.5 (5)
N2–C1–C6	106.2 (3)	O4–C37–C32	121.6 (5)
N2–C1–C2	131.1 (4)	O4–C37–C36	119.3 (5)
N1–C6–C1	106.4 (3)	O4–C38–C31	111.3 (5)
N1–C6–C5	132.0 (4)	N4–C39–C44	119.4 (4)
Pd1–C7–N2	126.0 (3)	N4–C39–C40	119.7 (4)
Pd1–C7–N1	127.3 (3)	Cl1–C45–Cl2	108.9 (6)
N1–C7–N2	106.6 (3)	O5–C46–N5	89.4 (15)

Table 4
In Pd-NHC catalysts (**1a–e**), direct C5 arylation of 2-*n*-propylthiazole by using aryl bromides.[a,b,c]



Entry	Aryl bromide	Pd-NHC	Product	Conversion (%)
1		**1a**	 **2**	85
2		**1b**		51
3		**1c**		50
4		**1d**		88
5		**1e**		81
6		**1a**	 **3**	100
7		**1b**		79
8		**1c**		94
9		**1d**		100
10		**1e**		100
11		**1a**	 **4**	100
12		**1b**		61
13		**1c**		94
14		**1d**		100
15		**1e**		81
16		**1a**	 **5**	100
17		**1b**		66
18		**1c**		96
19		**1d**		86
20		**1e**		89

[a] Reaction condition: 2-*n*-propylthiazole (2 mmol), aryl bromide (1 mmol), Pd-NHC (**1a–e**) (0.005 mmol), KOAc (1 mmol), *N*,*N*-dimethylacetamide (2 mL), 130 °C, 1 h.
[b] Product purity was checked by GC and NMR.
[c] Conversions were calculated according to aryl bromide.

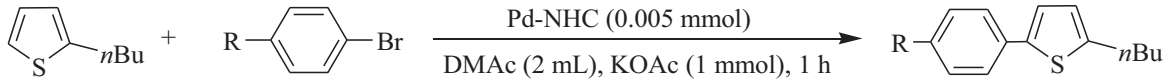
obtained by the treatment of 1-phenyl-3-alkyl benzimidazolium salts with 1 equivalent of $Pd(OAc)_2$ in the presence of dimethyl sulfoxide in 82–89% yields (Scheme 1). The reaction mixture was heated at 60 °C for 24 h and at 110–120 °C for 1 h. The air and moisture stable Pd-NHC complexes were soluble in halogenated solvents such as chloroform and dichloromethane. The five new Pd-NHC complexes were characterized by spectroscopic methods (^{1}H NMR, ^{13}C NMR, LC–MS and FT-IR) and elemental analysis techniques which support the proposed structures. Furthermore, the solid state structure of **1d** was analyzed by single crystal X-ray diffraction. The ^{1}H NMR and ^{13}C NMR spectra are consistent with the proposed formulae and appear to be spectroscopically pure. The ^{1}H NMR spectra of the heterocyclic salts containing the benzimidazolium further supported the assigned structures; the resonance for C(2)–H was observed as sharp singlets at 11.42, 12.08, 11.21, 11.41 and 11.70 ppm for benzimidazolium salts [31,39]. The ^{1}H NMR spectra of the Pd-NHC complexes showed the absence of any signal of the acidic benzimidazolium C2–H between 9 and 12 ppm. This condition indicated the successful deprotonation of benzimidazolium salts and confirmed the formation of the expected Pd-NHC complexes. In the ^{13}C NMR spectra, there is one signal for the carbenic carbons (NCN) at δ ca. 181.7, 181.2, 173.0, 182.1 and 182.9 ppm for **1a–e**, respectively. Therefore, these complexes are not cis/trans mixtures. The FT-IR data for Pd-NHC complexes exhibit a characteristic $\nu_{(NCN)}$ band at 1597.45, 1597.34, 1596.32, 1594.49 and 1500.08 for **1a–e**, respectively. Also, the resulting LC–MS spectrums confirmed the synthesized complexes, too.

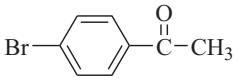
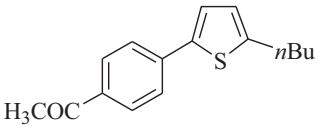
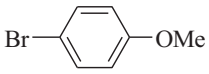
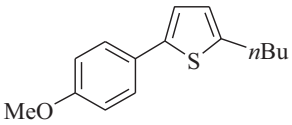
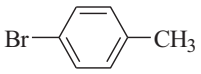
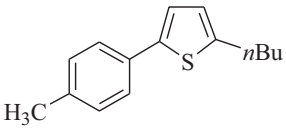
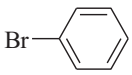
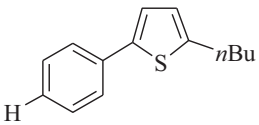
3.2. X-ray analysis

A single crystal of the representative complex **1d** was obtained for X-ray analysis by slow diffusion of CH_2Cl_2 into NH_2CHO solutions at ambient temperature. The lattice held organic solvent molecules, such as CH_2Cl_2, NH_2CHO, appear in the unit cells of the determined structure in **1d**. The molecular structure of **1d** was confirmed by single crystal X-ray structure determination; the atom-numbering scheme is shown in Fig. 1. The palladium center in the **1d** complex is coordinated by two NHC ligands and two bromo ligands in a cis fashion.

As shown in Fig. 1, the Pd atom of the **1d** compound has a distorted square-planar coordination environment defined by two imidazole C atoms derived from a chelating 1-(2,3-dihydro-1,4-benzodioxane-2-ylmethyl)-3-phenyl-2,3-dihydro-1H-benzimidazole ligand and two Br atoms. The N1/N2/C1–C7 and N3/N4/C23–C29 benzimidazole ring systems in **1d** are planar with the maximum deviations of −0.040(3) Å for N1 and −0.029(4) Å for C29, respectively. While the benzimidazole and phenyl rings make a dihedral angle of 61.98(18) and 66.6(2)° with each other, they are rotated with respect to the coordination plane of the metal

Table 5
In Pd-NHC catalysts (**1a–e**), direct arylation of 2-*n*-butylthiophene by using aryl bromides.[a,b,c]



Entry	Aryl bromide	Pd-NHC	Product	Conversions (%)
1		**1a**		98
2		**1b**		100
3		**1c**		99
4		**1d**		91
5		**1e**		96
			6	
6		**1a**		92
7		**1b**		99
8		**1c**		97
9		**1d**		94
10		**1e**		100
			7	
11		**1a**		94
12		**1b**		80
13		**1c**		97
14		**1d**		99
15		**1e**		96
			8	
16		**1a**		85
17		**1b**		71
18		**1c**		62
19		**1d**		93
20		**1e**		88
			9	

[a] Reaction condition: 2-*n*-butylthiophene (2 mmol), aryl bromide (1 mmol), Pd-NHC (**1a–e**) (0.005 mmol), KOAc (1 mmol), *N*,*N*-dimethylacetamide (2 mL), 130 °C, 1 h.
[b] Product purity was checked by GC and NMR.
[c] Conversions were calculated according to aryl bromide.

by 83.93(11), 70.11(16)°, 76.55(13) and 70.58(18)°, respectively. The 1,4 dioxane rings of the 2,3-dihydro-1,4-benzodioxane groups almost adopt a distorted half-chair conformation [the puckering parameters [32] are Q_T = 0.394(6) Å, θ = 131.0(9)°, ϕ = 268.1(10)° for O1/O2/C9/C10/C15/C16 and Q_T = 0.453(6) Å, θ = 128.9(8)°, ϕ = 278.8(8)° for O3/O4/C31C32/C37/C38].

The molecular packing along the *a*-axis of **1d** is shown in Fig. 2. Weak C–H···π interactions and π–π stacking interactions [Cg6···Cg6 (2 − *x*, −*y*, 1 − *z*) = 3.842(3) Å and Cg8···Cg8(1 − *x*, 1 − *y*, 2 − *z*) = 3.804(3) Å, where Cg6 and Cg8 are the centroids of the C10–C15 and C23–C28 rings, respectively] also help in the stabilization of the crystal packing. The crystal data and collection parameters are listed in Table 1.

The Pd–Br bond lengths are 2.4796(5) and 2.4892(6) Å, and the Pd–C bond lengths are 2.002(4) and 1.986(4) Å. The Br–Pd–Br and C–Pd–C bond angles are 92.62(2) and 94.75(15)°, respectively. The values of all bond lengths and bond angles (Tables 2 and 3) are normal and are comparable with the reported values of similar structures [33,34].

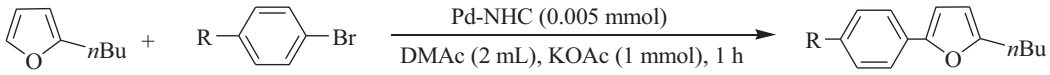
3.3. Catalytic applications of Pd-NHC complexes (*1a–e*) in arylation reactions

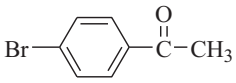
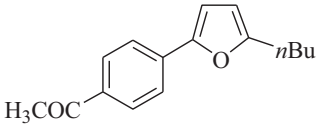
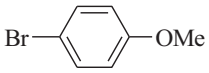
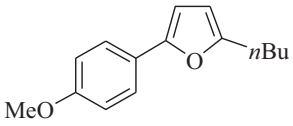
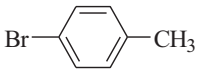
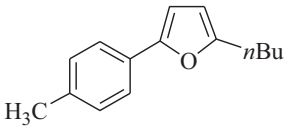
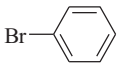
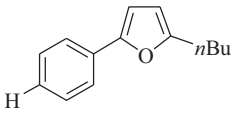
The selective C2 or C5 arylation of heteroaromatics such as thiazole, oxazole thiophene, pyrrole, imidazole, pyrazole, triazole, pyridine, furan or indole has been extensively described through palladium-catalyzed C–H bond activation in recent years [8–12]. However, a few examples of couplings using deactivated aryl bromides have been reported [35,36]. We achieved very good results even though we conducted the arylation reaction for a short period of 1 h and at a low temperature. We performed a study focusing on the catalytic activity of direct arylation in 5 situations using 2-*n*-propylthiazole, 2-*n*-butylthiophene and 2-*n*-butylfuran rings with diverse aryl halides (4-bromoacetophenone, 4-bromoanisole, 4-bromotoluene, bromobenzene, 4-chloroacetophenone and 4-chlorotoluene). The reactions cannot proceed at 3- and 4-positions. This is because the charge density at 3- and 4-positions are less than charge density at 5-position. Also, C5 arylation is highly selective because 2-position (C2) is blocked. The reaction was achieved by using Pd-NHC, aryl bromide, thiazole/thiophene/furan and KOAc in DMAc by heating in an oil bath at 130 °C for 1 h. The desired product was obtained in more than 50% yield when KOAc was used as a base. The time of reactions which were conducted by using aryl chlorides was limited to 20 h and lower conversions were obtained. When the reactions were completed, the products were purified by flash chromatography on silica gel. The purity of the compounds was checked by using GC and NMR. The conversion of starting material to product was determined by GC.

3.3.1. In Pd-NHC catalysts, direct arylation of 2-n-propylthiazole

Miura and Nomura studied the arylation reaction of thiazoles. The palladium-catalyzed direct arylation of arylbromides with 2-*n*-propylthiazole in dimethylformamide has been described by them [37,38]. The influence of the five new synthesized Pd-NHC

Table 6
In Pd-NHC catalysts (**1a–e**), direct C5 arylation of 2-butylfuran by using aryl bromides.[a,b,c]



Entry	Aryl bromide	Pd-NHC	Product	Conversion (%)
1		**1a**		97
2		**1b**		92
3		**1c**		100
4		**1d**		74
5		**1e**		79
			10	
6		**1a**		92
7		**1b**		54
8		**1c**		87
9		**1d**		86
10		**1e**		70
			11	
11		**1a**		88
12		**1b**		70
13		**1c**		91
14		**1d**		95
15		**1e**		89
			12	
16		**1a**		95
17		**1b**		92
18		**1c**		82
19		**1d**		92
20		**1e**		94
			13	

[a] Reaction condition: 2-*n*-butylfuran (2 mmol), aryl bromide (1 mmol), Pd-NHC (**1a–e**) (0.005 mmol), KOAc (1 mmol), *N*,*N*-dimethylacetamide (2 mL), 130 °C, 1 h.
[b] Product purity was checked by GC and NMR.
[c] Conversions were calculated according to aryl bromide.

complexes was successively investigated in this coupling reaction. The results in the desired product are usually very high. The obtained results are given in Table 4.

Firstly, we investigated the direct 5-arylation of 2-*n*-propylthiazole with 4-bromoacetophenone using these five new palladium complexes. A high conversion of the coupling product **2** was obtained with 4-bromoacetophenone and Pd-NHC complexes (**1a**, **1d** and **1e**) (Table 4, entries 1–6). Then, to assure this tendency, 4-bromoanisole, 4-bromotoluene and bromobenzene were reacted with 2-*n*-propylthiazole by using these five new complexes (Table 4, entries 6–20). For this transformation, complexes **1a**, **1c** and **1d** were found to be effective catalysts. When Table 4 is examined, it is seen that the results of the arylation coupling reaction are between 50 and 100. In arylation coupling reactions conducted using 2-*n*-propylthiazole, it appears that higher conversions were obtained using electron-rich rather than electron-deficient rings. Also, for 4-bromoanisole, the best results were achieved with catalysts **1a**, **1d** and **1e** to give **3** in 100% for three complexes (Table 4, entries 6, 9 and 10). The best conversions were obtained with catalysts **1a** and **1d** for 4-bromotolune and **1a** for bromobenzene to give **4** and **5** in 100%.

3.3.2. In Pd-NHC catalyst, direct arylation of 2-n-butylthiophene

It should be noted that just a few examples of the direct arylation of aryl halides with 2-*n*-butylthiophene by using Pd-NHC complexes have been reported [4]. We investigated the reactivity of 2-*n*-butylthiophene using different aryl bromides in the presence of Pd-NHC complexes. The obtained results are given in Table 5.

The reactivity of 2-*n*-butylthiophene was similar to 2-*n*-propylthiazole (Table 5). In the Pd-NHC (**1a–e**) catalysts, arylation coupling products were obtained as a result of the reaction of 4-bromoacetophenone, 4-bromoanisole, 4-bromotoluene and bromobenzene with 2-*n*-butylthiophene. When Table 5 is examined, it is seen that the results of the arylation coupling reaction are between 62% and 99%. The activities of the complexes are close to each other, but the best results are obtained in the presence of the **1d** complex.

3.3.3. In Pd-NHC catalysts, direct arylation of 2-n-butylfuran

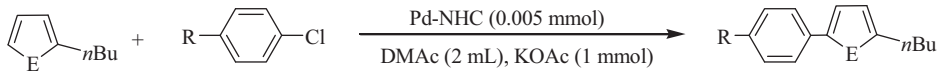
We analyzed the reactivity of 2-*n*-butylfuran with four aryl bromides in Pd-NHC (**1a–e**) catalysts for this coupling reaction and the results are given in Table 6.

The arylation coupling conversions of aryl bromides with 2-*n*-butylfuran were obtained in the Pd-NHC (**1a–e**) catalysts. When Table 6 is examined, it is seen that the results of the arylation coupling reaction are between 74% and 100%. In general, the catalytic activities of the palladium complexes are quite similar, with only small differences that can be attributed to the substituents present on the ligands. It was observed that the **1a** complex is more active than the other complexes. Good conversions in **10** were achieved with complexes **1a–c** for the coupling with 4-bromoacetophenone.

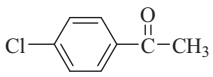
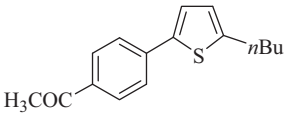
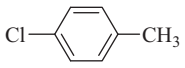
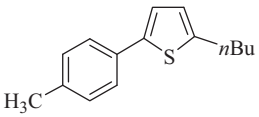
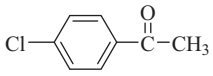
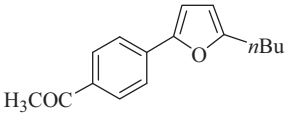
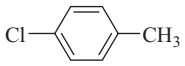
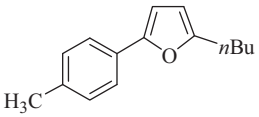
3.3.4. In Pd-NHC catalysts, direct arylation of heteroarenes by using aryl chlorides

Finally, we investigated the reactivity of 2-*n*-butylfuran and 2-*n*-butylthiophene with aryl chlorides (4-chloroacetophenone

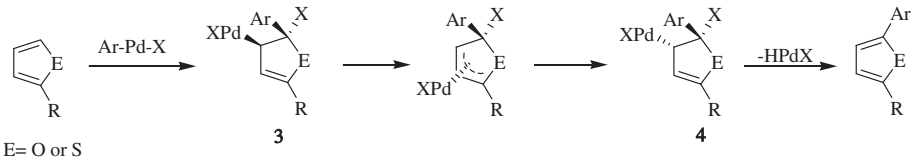
Table 7
In Pd-NHC catalysts, direct arylation of heteroarenes by using aryl chlorides.[a,b,c]



E: S or O

Entry	Aryl chloride	Pd-NHC	Product	Conversions (%)
1		**1a**	 **14**	70
2		**1c**	 **15**	72
3		**1a**	 **16**	78
4		**1d**	 **17**	69

[a] Reaction condition: Heteroarene (2 mmol), aryl chloride (1 mmol), Pd-NHC (0.005 mmol), KOAc (1 mmol), *N*,*N*-dimethylacetamide (2 mL), 130 °C, 20 h.
[b] Product purity was checked by GC and NMR.
[c] Conversions were calculated according to aryl chloride.



Scheme 2. Stereomutation to allow elimination.

and 4-chlorotoluene) in Pd-NHC (**1a**, **1c** and **1d**) catalysts at 130 °C for 20 h and the obtained conversions are given in Table 7.

The arylation coupling reactions conducted by using aryl chlorides such as p-chloroacetophenone and p-chlorotoluene were acquired by heating the mixture at 130 °C for 20 h. These reactions were obtained in good conversions (Table 7, entries 1–4). However, when the results of these reactions conducted using aryl chlorides are examined, lower conversions are observed with respect to reactions conducted using aryl bromides. In other words, they were found to be less reactive.

3.4. Mechanism of furan and thiophene direct arylation

A mechanism similar to that of the Heck reaction for the arylation of thiophenes and furans was suggested by Sharp [40]. Such a mechanism would require either the stereomutation or elimination of **3**–**4** prior to elimination [41] (Scheme 2).

4. Conclusion

To conclude, in this study, five new Pd-NHC complexes (**1a–e**) which were confirmed by elemental analyses, FT-IR, LC–MS (for **1a**, **1c** and **1e**), ^{1}H NMR and ^{13}C NMR were synthesized from various 1-phenyl-3-alkylbenzimidazolium salts with $Pd(OAc)_2$ in dimethyl sulfoxide in very excellent yields. The complex **1d** was also characterized by single crystal X-ray diffraction studies. We have found out that these new palladium complexes are practical catalysts for the direct regioselective C5 arylation of 2-*n*-butylfuran, 2-*n*-butylthiophene and 2-*n*-propylthiazole using both electron-deficient and electron-rich aryl halides as coupling partners. Better results were obtained from reactions which were conducted by using aryl bromides.

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Appendix A. Supplementary material

CCDC 894210 contains the supplementary crystallographic data for **1d**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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