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Catalytic activities in direct arylation of novel palladium *N*-heterocyclic carbene complexes

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Eight novel palladium *N*-heterocyclic carbene (Pd-NHC) complexes were synthesized by the reaction of chloro 1,3-dialkylbenzimidazolin-2-ylidene silver(I) complexes with bis(benzonitrile)palladium(II) chloride in dichloromethane. These eight Pd-NHC complexes are as follows: bis[1-phenyl-3-(2,4,6-trimethylbenzyl)benzimidazol-2-ylidene]dichloropalladium(II), bis[1-phenyl-3-(2,3,5,6-tetramethylbenzyl)benzimidazol-2-ylidene]dichloropalladium(II), bis[1-phenyl-3-(2,3,4,5,6-pentamethylbenzyl)benzimidazol-2-ylidene]dichloropalladium(II), bis[1-phenyl-3-(3,4,5-trimethoxybenzyl)benzimidazol-2-ylidene]dichloropalladium(II), bis[1-(2-diethylaminoethyl)-3-(3-methylbenzyl)benzimidazol-2-ylidene]dichloropalladium(II), bis[1-(2-diethylaminoethyl)-3-(2,3,5,6-tetramethylbenzyl)benzimidazol-2-ylidene]dichloropalladium(II), bis[1-(2-morpholinoethyl)-3-naphthalenomethylbenzimidazol-2-ylidene]dichloropalladium(II) and bis[1-(2-morpholinoethyl)-3-(2-methylbenzyl)benzimidazol-2-ylidene]dichloropalladium(II). Also, these synthesized complexes were fully characterized using Fourier transform infrared, ^{1}H NMR and ^{13}C NMR spectroscopic methods and elemental analysis techniques. These synthesized novel Pd-NHC complexes were tested as catalysts in the direct arylation of 2-*n*-butylthiophene, 2-*n*-butylfuran and 2-isopropylthiazole with various aryl bromides at 130°C for 1 h. The complexes showed very good catalytic activities in these reactions. Copyright © 2014 John Wiley & Sons, Ltd.

Keywords: *N*-heterocyclic carbene; palladium complex; direct arylation; aryl bromide

Introduction

N-heterocyclic carbenes (NHCs) have been widely used in both organometallic chemistry and coordination chemistry for years. Much attention has been focused on these compounds as ancillary ligands for a number of transition metal complexes since the discovery of stable NHCs in 1991.[1,2] Various metal complexes have been applied in many areas such as catalysis, medicine, magneto-structural chemistry, the dye and polymer industry, analytical chemistry, agriculture and enzyme modelling.[3–7] Among these metal complexes, NHC metal complexes which have high stability, strong σ-donating and weak π-accepting properties[8,9] are significant structural motifs in medicinal chemistry.[10–14] Also, these complexes are very significant for catalytic applications. Numerous saturated and unsaturated 1,3-disubstituted benzimidazol-2-ylidene palladium NHC (Pd-NHC) complexes have been successfully applied in various reactions in the area of catalytic C–C bond formation such as direct arylation and Suzuki–Miyaura, Mizoroki–Heck, Sonogashira, Hiyama and Kumada–Tamao–Corriu coupling reactions.[15–21] In homogeneous catalysis, NHCs as alternatives to phosphines[22,23] have also been used in olefin metathesis[24,25] and C–N coupling reactions.[26,27]

A significant aim in chemistry is to find ways for using less raw material and energy so that the use of renewable resources increases while the use of hazardous chemicals decreases or they are eliminated altogether in the development of environmentally friendly processes. Therefore, new catalytic systems are needed which are more active and selective for organic reactions. For this reason, in order to develop successful catalysts for the formation of aryl–aryl bonds, in the study reported here, eight novel pure Pd-NHC complexes (**2a–2h**) bearing two chlorine atoms were prepared by the interaction of benzimidazol-2-ylidene silver NHC complexes with bis(benzonitrile)palladium(II) chloride ($PdCl_2(PhCN)_2$) in dichloromethane at room temperature. Their structures were characterized using appropriate spectroscopic methods (NMR, FT-IR) and elemental analysis techniques. These metal carbene complexes were tested for their catalytic activities in direct arylation, being an effective method for forming sp^2–sp^2 C–C bonds. It was found that these complexes act as catalysts.

Experimental

Materials and Methods

The reactions for the synthesis of Pd-NHC complexes **2a–2h** were carried out under argon in flame-dried glassware using standard Schlenk-type flasks and standard high vacuum line techniques. Solvents 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. Some of the necessary reagents were synthesized in our laboratory and some others were purchased commercially. Reagents and solvents 2-methylbenzyl chloride, 3-methylbenzyl chloride, 2,4,6-trimethylbenzyl chloride, 2,3,5,6-tetramethylbenzyl chloride, 2,3,4,5,6-pentamethylbenzyl chloride, 3,4,5-trimethoxybenzyl chloride, bis(benzonitrile)palladium chloride, *N*,*N*-dimethylformamidedimethylacetal, hexane, dimethylformamide, dichloromethane and diethyl ether were purchased from commercial

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suppliers (Merck, Aldrich, Alfa-Aesar and Fluka). $CDCl_3$ and DMSO-d_6 were used as solvents in all ^{1}H NMR and ^{13}C NMR analyses.

The ^{1}H NMR and ^{13}C NMR spectra were obtained using a Bruker AC300P FT spectrometer operating at 300.13 MHz (^{1}H) and 75.47 MHz (^{13}C). Chemical shifts were measured relative to tetramethylsilane. Coupling constants (*J*) were measured in Hz. The FT-IR spectra were recorded with a Mattson 1000 spectrophotometer and wavenumbers were recorded in cm^{-1}. Melting points were determined in open capillary tubes with an Electrothermal-9200 melting point device. GC analysis was conducted with an Agilent 6890N Network GC system using an HP-5 column (column length 30 m, column diameter 0.32 mm, column filler size 0.25 μm) and a temperature range from −60 to 325°C. Elemental analyses were performed using CHNS-932 LECO apparatus.

Syntheses

*Complexes **1a–1h***

1,3-Dialkyl-substituted silver NHC complexes **1a–1h** containing both electron-donating and electron-withdrawing moieties were synthesized from the deprotonation of benzimidazolium salts, as in our previous study.[28–30]

*Bis[1-phenyl-3-(2,4,6-trimethylbenzyl)benzimidazol-2-ylidene]dichloropalladium (II) complex (**2a**)*

Chloro [1-phenyl-3-(2,4,6-trimethylbenzyl)benzimidazol-2-ylidene] silver(I) complex (**1a**) (0.195 g, 0.42 mmol) and $PdCl_2(PhCN)_2$ (0.08g, 0.21 mmol) were dissolved in dried dichloromethane (4 ml) and then were stirred at room temperature for 18 h in a Schlenk-type flask. The flask was covered with aluminium foil to avoid light exposure. The resulting cream-brown solution was filtered over celite, silica gel and cotton. Then, the solvent was removed under reduced pressure. The resulting product was crystallized from dichloromethane–hexane mixture (2:1) at 25°C. Finally, the obtained crystals were washed twice with 10 ml of diethyl ether and dried under vacuum.

Light cream-coloured powder; yield 85%; m.p. 312–313°C; $\nu_{(CN)}$ = 1596.47 cm^{-1}. ^{1}H NMR (300.13 MHz, $CDCl_3$, δ, ppm): 2.31 (s, 12 H, $NCH_2C_6H_2(CH_3)_3$-2,6); 2.40 (s, 6 H, $NCH_2C_6H_2(CH_3)_3$-4); 5.89 (s, 4 H, $NCH_2C_6H_2(CH_3)_3$-2,4,6); 6.42 (s, 4 H, $NCH_2C_6H_2(CH_3)_3$-2,4,6); 6.95–7.28 (m, 8 H, C_6H_4); 7.32–8.09 (m, 10 H, NC_6H_5). ^{13}C NMR (75.47 MHz, $CDCl_3$, δ, ppm): 20.9 ($NCH_2C_6H_2(CH_3)_3$-2,6); 21.2 ($NCH_2C_6H_2(CH_3)_3$-4); 49.9 ($NCH_2C_6H_2(CH_3)_3$-2,4,6); 111.8 (NCCHCHCHCHCH-4); 122.8 (NCCHCHCHCHCH-2,6); 128.3 (NCCHCHCHCHCH-3,5); 138.7 (NCCHCHCHCHCH-1); 110.8, 123.2, 127.8, 128.9 (NCCH-CHCHCHCN); 134.2, 138.2 (NCCHCHCHCHCN); 128.7, 129.5, 135.6, 137.9 ($NCH_2C_6H_2(CH_3)_3$); 182.8 (*C*–Pd). Elemental analysis. Calcd for $C_{46}H_{44}N_4PdCl_2$ (830.19 g/mol) (%): C, 66.55; H, 5.34; N, 6.75. Found (%): C, 66.59; H, 5.27; N, 6.74.

*Bis[1-phenyl-3-(2,3,5,6-tetramethylbenzyl)benzimidazol-2-ylidene]dichloropalladium(II) complex (**2b**)*

Complex **2b**, using the same conditions and procedure as for **2a**, was prepared from chloro [1-phenyl-3-(2,3,5,6-tetramethylbenzyl) benzimidazol-2-ylidene]silver(I) complex (**1b**) (0.201 g, 0.42 mmol) and $PdCl_2(PhCN)_2$ (0.08 g, 0.21 mmol) in dichloromethane (4 ml).

Light yellow-coloured powder; yield 89%; m.p. 317–318°C; $\nu_{(CN)}$ = 1596.68 cm^{-1}. ^{1}H NMR (300.13 MHz, $CDCl_3$, δ, ppm): 2.39 (s, 12 H, $NCH_2C_6H(CH_3)_4$-2,6); 2.56 (s, 12 H, $NCH_2C_6H(CH_3)_4$-3,5); 5.99 (s, 4 H, $NCH_2C_6H(CH_3)_4$-2,3,5,6); 6.26 (s, 2 H, $NCH_2C_6H(CH_3)_4$-2,3,5,6); 6.98–7.40 (m, 8 H, C_6H_4); 7.50–8.09 (m, 10 H, NC_6H_5). ^{13}C NMR (75.47 MHz, $CDCl_3$, δ, ppm): 16.5 ($NCH_2C_6H(CH_3)_4$-2,6); 20.6 ($NCH_2C_6H(CH_3)_4$-3,5); 50.8 ($NCH_2C_6H(CH_3)_4$-2,3,5,6); 110.7, 128.6, 130.7, 132.3, 134.3, 135.0 (C_6H_4); 123.1, 128.3, 134.0, 135.6 ($NCH_2C_6H(CH_3)_4$); 111.9, 122.7, 128.9, 137.9 (NC_6H_5); 182.8 (*C*–Pd). Elemental analysis. Calcd for $C_{48}H_{48}N_4PdCl_2$ (858.25 g/mol) (%): C, 67.17; H, 5.64; N, 6.53. Found (%): C, 67.24; H, 5.54; N, 6.54.

*Bis[1-phenyl-3-(2,3,4,5,6-pentamethylbenzyl)benzimidazol-2-ylidene]dichloropalladium(II) complex (**2c**)*

Complex **2c**, using the same conditions and procedure as for **2a**, was prepared from chloro [1-phenyl-3-(2,3,4,5,6-pentamethylbenzyl) benzimidazol-2-ylidene]silver(I) complex (**1c**) (0.21 g, 0.42 mmol) and $PdCl_2(PhCN)_2$ (0.08 g, 0.21 mmol) in dichloromethane (4 ml).

Cream-coloured powder; yield 87%; m.p. 294–295°C; $\nu_{(CN)}$ = 1473.48 cm^{-1}. ^{1}H NMR (300.13 MHz, $CDCl_3$, δ, ppm): 2.29 (s, 12 H, $NCH_2C_6(CH_3)_5$-2,6); 2.36 (s, 6 H, $NCH_2C_6(CH_3)_5$-4); 2.45 (s, 12 H, $NCH_2C_6(CH_3)_5$-3,5); 6.27 (s, 4 H, $NCH_2C_6(CH_3)_5$-2,3,4,5,6); 6.79–7.62 (m, 18 H, NC_6H_5 and C_6H_4). ^{13}C NMR (75.47 MHz, $CDCl_3$, δ, ppm): 16.9 ($NCH_2C_6(CH_3)_5$-2,6); 17.3 ($NCH_2C_6(CH_3)_5$-4); 17.5 ($NCH_2C_6(CH_3)_5$-3,5); 53.3 ($NCH_2C_6(CH_3)_5$-2,3,4,5,6); 125.3, 126.1, 128.3, 137.3 (NC_6H_5); 122.4, 130.6, 131.8, 132.8, 134.8, 135.9 (C_6H_4); 127.7, 129.1, 133.9, 136.7 ($NCH_2C_6(CH_3)_5$); 166.2 (*C*–Pd). Elemental analysis. Calcd for $C_{50}H_{52}N_4PdCl_2$ (886.3 g/mol) (%): C, 67.76; H, 5.91; N, 6.32. Found (%): C, 67.70; H, 5.91; N, 6.32.

*Bis[1-phenyl-3-(3,4,5-trimethoxybenzyl)benzimidazol-2-ylidene]dichloropalladium(II) complex (**2d**)*

Complex **2d**, using the same conditions and procedure as for **2a**, was prepared from chloro [1-phenyl-3-(3,4,5-trimethoxybenzyl) benzimidazol-2-ylidene]silver(I) complex (**1d**) (0.22 g, 0.42 mmol) and $PdCl_2(PhCN)_2$ (0.08 g, 0.21 mmol) in dichloromethane (4 ml).

Cream-coloured powder; yield 83%; m.p. 305–306°C; $\nu_{(CN)}$ = 1590.51 cm^{-1}. ^{1}H NMR (300.13 MHz, $CDCl_3$, δ, ppm): 3.81, 3.91 (m, 18 H, $NCH_2C_6H_2(OCH_3)_3$-3,4,5); 5.86 (s, 4 H, $NCH_2C_6H_2(OCH_3)_3$-3,4,5); 6.65 (s, 4 H, $NCH_2C_6H_2(OCH_3)_3$-3,4,5); 7.06–8.04 (m, 18 H, NC_6H_5 and C_6H_4). ^{13}C NMR (75.47 MHz, $CDCl_3$, δ, ppm): 52.9 ($NCH_2C_6H_2(OCH_3)_3$-4); 56.8 ($NCH_2C_6H_2(OCH_3)_3$-3,5); 60.8 ($NCH_2C_6H_2(OCH_3)_3$-3,4,5); 105.3, 131.2, 134.0, 153.6 ($NCH_2C_6H_2(OCH_3)_3$-3,4,5); 111.4, 123.6, 127.2, 128.4, 129.1, 135.3, 137.7 (NC_6H_5 and C_6H_4); 182.1 (*C*–Pd). Elemental analysis. Calcd for $C_{46}H_{44}N_4O_6PdCl_2$ (926.19 g/mol) (%): C, 59.65; H, 4.79; N, 6.05. Found: C, 59.71; H, 4.78; N, 6.02.

*Bis[1-(2-diethylaminoethyl)-3-(3-methylbenzyl)benzimidazol-2-ylidene]dichloropalladium(II) complex (**2e**)*

Complex **2e**, using the same conditions and procedure as for **2a**, was prepared from chloro [1-(2-diethylaminoethyl)-3-(3-methylbenzyl)benzimidazol-2-ylidene]silver(I) complex (**1e**) (0.19 g, 0.41 mmol) and $PdCl_2(PhCN)_2$ (0.08 g, 0.21 mmol) in dichloromethane (4 ml).

Cream-coloured powder; yield 79%; $\nu_{(CN)}$ = 1523.17 cm^{-1}. ^{1}H NMR (300.13 MHz, DMSO, δ, ppm): 1.06 (t, 12 H, *J* = 7.6 Hz, $NCH_2CH_2N(CH_2CH_3)_2$); 2.28 (s, 6 H, $NCH_2C_6H_4CH_3$-3); 3.66 (m, 8 H, $NCH_2CH_2N(CH_2CH_3)_2$); 3.85 (m, 4 H, $NCH_2CH_2N(CH_2CH_3)_2$); 5.37 v (m, 4 H, $NCH_2CH_2N(CH_2CH_3)_2$); 6.22 (s, 4 H, $NCH_2C_6H_4CH_3$-3); 7.01–8.02 (m, 16 H, $NCH_2C_6H_4CH_3$-3 and C_6H_4). ^{13}C NMR (75.47 MHz, DMSO, δ, ppm): 12.9 ($NCH_2CH_2N(CH_2CH_3)_2$); 19.9 ($NCH_2C_6H_4CH_3$-3); 21.3 ($NCH_2CH_2N(CH_2CH_3)_2$); 46.5 ($NCH_2CH_2N(CH_2CH_3)_2$); 47.6 ($NCH_2CH_2N(CH_2CH_3)_2$); 50.6 ($NCH_2C_6H_4CH_3$-3); 124.2, 125.3, 128.0, 128.9, 133.9, 138.0, 138.4 ($NCH_2C_6H_4CH_3$-3 and C_6H_4); 183.2 (*C*–Pd). Elemental analysis. Calcd for $C_{42}H_{54}N_6PdCl_2$ (820.24 g/mol) (%): C, 61.50; H, 6.64; N, 10.25. Found (%): C, 61.59; H, 6.54; N, 10.25.

*Bis[1-(2-diethylaminoethyl)-3-(2,3,5,6-tetramethylbenzyl)benzimidazol-2-ylidene] dichloropalladium(II) complex (**2f**)*

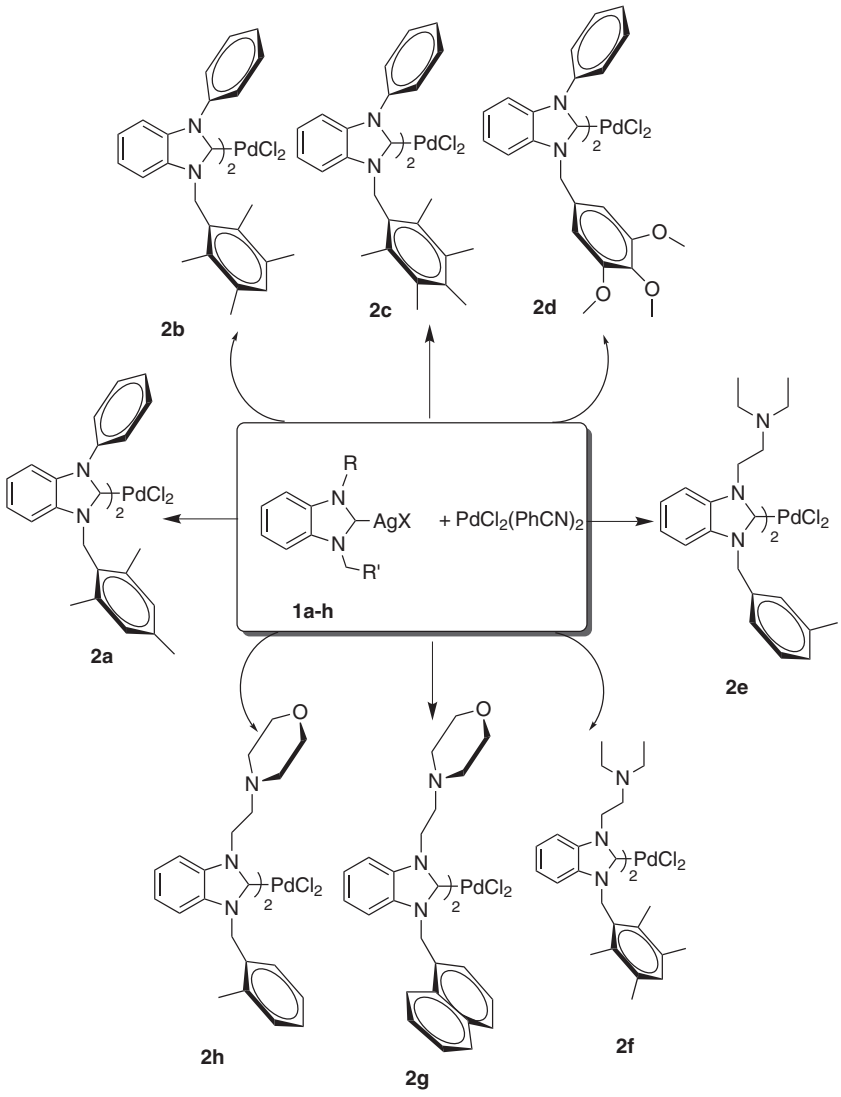
Complex **2f**, using the same conditions and procedure as for **2a**, was prepared from chloro [1-(2-diethylaminoethyl)-3-(2,3,5,6-tetramethylbenzyl)benzimidazol-2-ylidene]silver(I) complex (**1f**) (0.21 g, 0.42 mmol) and $PdCl_2(PhCN)_2$ (0.08 g, 0.21 mmol) in dichloromethane (4 ml).

Cream-coloured powder; yield 89%; m.p. 217–218°C; $\nu_{(CN)}$ = 1504.35 cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$, δ, ppm): 0.96 (t, 12 H, J = 7.2 Hz, $NCH_2CH_2N(CH_2CH_3)_2$); 2.30 (s, 12 H, $NCH_2C_6H(CH_3)_4$-2,6); 2.37 (s, 12 H, $NCH_2C_6H(CH_3)_4$-3,5); 2.68 (q, 8 H, J = 7.2 Hz, $NCH_2CH_2N(CH_2CH_3)_2$); 2.82 (t, 4 H, J = 7.5 Hz, $NCH_2CH_2N(CH_2CH_3)_2$); 3.33 (t, 4 H, J = 7.5 Hz, $NCH_2CH_2N(CH_2CH_3)_2$); 5.13 (s, 4 H, $NCH_2C_6H(CH_3)_4$-2,3,5,6); 6.31 (s, 2 H, $NCH_2C_6H(CH_3)_4$-2,3,5,6); 6.34–7.64 (m, 8 H, C_6H_4). ^{13}C NMR (75.47 MHz, $CDCl_3$, δ, ppm): 11.8 ($NCH_2CH_2N(CH_2CH_3)_2$); 15.9 ($NCH_2C_6H(CH_3)_4$-2,6); 16.6 ($NCH_2C_6H(CH_3)_4$-3,5); 20.5 ($NCH_2CH_2N(CH_2CH_3)_2$); 20.6 ($NCH_2CH_2N(CH_2CH_3)_2$); 46.4 ($NCH_2CH_2N(CH_2CH_3)_2$); 65.9 ($NCH_2C_6H(CH_3)_4$); 110.8, 111.9, 122.5, 122.9, 134.8, 135.3 (C_6H_4); 130.0, 130.9, 132.4, 134.2, ($NCH_2C_6H(CH_3)_4$-2,3,5,6); 182.0 (*C*–Pd). Elemental analysis. Calcd for $C_{48}H_{66}N_6PdCl_2$ (904.4 g/mol) (%): C, 63.75; H, 7.36; N, 9.29. Found (%): C, 63.84; H, 7.23; N, 9.31.

*Bis[1-(2-morpholinoethyl)-3-naphthalenomethylbenzimidazol-2-ylidene]dichloropalladium(II) complex (**2g**)*

Complex **2g**, using the same conditions and procedure as for **2a**, was prepared from chloro [1-(2-morpholinoethyl)-3-naphthalenomethyl)benzimidazol-2-ylidene]silver(I) complex (**1g**) (0.21 g, 0.41 mmol) and $PdCl_2(PhCN)_2$ (0.08 g, 0.21 mmol) in dichloromethane (4 ml).

Light cream-coloured powder; yield: 88%; m.p. 226–227°C; $\nu_{(CN)}$ = 1599.32 cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$, δ, ppm): 2.17, 2.85 (m, 16 H, $NCH_2CH_2N(CH_2CH_2)_2O$); 2.91, 4.78 (m, 8 H, $NCH_2CH_2N(CH_2CH_2)_2O$); 5.31 (s, 4 H, $NCH_2C_{10}H_7$); 6.39–7.51 (m, 8 H, C_6H_4); 7.55–7.81 (m, 14 H, $NCH_2C_{10}H_7$). ^{13}C NMR (75.47 MHz, $CDCl_3$, δ, ppm): 41.0 ($NCH_2CH_2N(CH_2CH_2)_2O$); 49.2 ($NCH_2CH_2N(CH_2CH_2)_2O$); 53.3 ($NCH_2CH_2N(CH_2CH_2)_2O$); 56.0 ($NCH_2CH_2N(CH_2CH_2)_2O$); 66.6 ($NCH_2C_{10}H_7$); 111.3, 112.9, 113.7, 122.5, 125.4, 126.6, 127.0, 127.8, 128.0, 128.5, 129.3, 130.6 131.4, 133.2, 133.9, 134.2, 144.5 ($NCH_2C_{10}H_7$ and C_6H_4); 182.3 (*C*–Pd). Elemental analysis. Calcd for $C_{48}H_{50}N_6O_2PdCl_2$ (920.28 g/mol) (%): C, 62.65; H, 5.48; N, 9.13. Found (%): C, 62.59; H, 5.48; N, 9.13.



Scheme 1. Synthesis of [1,3-dialkylbenzimidazol-2-ylidene]dichloridopalladium(II) complexes (**2a–2h**).

*Bis[1-(2-morpholinoethyl)-3-(2-methylbenzyl) benzimidazol-2-ylidene]dichloropalladium(II) complex (**2h**)*

Complex **2h**, using the same conditions and procedure as for **2a**, was prepared from chloro [1-(2-morpholinoethyl)-3-(2-methylbenzyl)benzimidazol-2-ylidene]silver(I) complex (**1h**) (0.19 g, 0.40 mmol) and $PdCl_2(PhCN)_2$ (0.08 g, 0.21 mmol) in dichloromethane (4 ml).

Dark cream-coloured powder; yield 83%; m.p. 200–201°C; $\nu_{(CN)}$ = 1413.16 cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$, δ, ppm): 2.25 (m, 8 H, $NCH_2CH_2N(CH_2CH_2)_2O$); 2.42 (s, 6 H, $NCH_2C_6H_4CH_3$-2); 2.87 (t, 8 H, J = 8.4 Hz, $NCH_2CH_2N(CH_2CH_2)_2O$); 3.07 (m, 4 H, $NCH_2CH_2N(CH_2CH_2)_2O$); 4.46 (t, 4 H, J = 9 Hz, $NCH_2CH_2N(CH_2CH_2)_2O$); 5.31 (s, 4 H, $NCH_2C_6H_4CH_3$-2); 7.01–7.87 (m, 16 H, $NCH_2C_6H_4CH_3$-2 and C_6H_4). ^{13}C NMR (75.47 MHz, $CDCl_3$, δ, ppm): 19.8 ($NCH_2C_6H_4CH_3$-2); 43.4 ($NCH_2CH_2N(CH_2CH_2)_2O$); 49.9 ($NCH_2CH_2N(CH_2CH_2)_2O$); 53.2 ($NCH_2CH_2N(CH_2CH_2)_2O$); 53.5 ($NCH_2CH_2N(CH_2CH_2)_2O$); 66.2 ($NCH_2C_6H_4CH_3$-2); 111.2, 113.2, 113.7, 123.7, 126.9, 128.5, 129.5, 130.6, 131.4, 133.9, 134.9, 136.6, 144.6 ($NCH_2C_6H_4CH_3$ and C_6H_4); 183.1 (*C*–Pd). Elemental analysis. Calcd for $C_{42}H_{50}N_6O_2PdCl_2$ (848.21 g/mol) (%): C, 59.47; H, 5.84; N, 9.91. Found (%): C, 59.41; H, 5.96; N, 9.90.

*2-n-Butyl-5-acetophenylfuran (**3**)*

^1H NMR (300.13 MHz, $CDCl_3$, δ, ppm): 0.98 (t, 3 H, J = 7.5 Hz, $CCH_2CH_2CH_2CH_3$); 1.43 (m, 2 H, $CCH_2CH_2CH_2CH_3$); 1.71 (tt, 2 H, J = 7.5 Hz, J = 7.5 Hz, $CCH_2CH_2CH_2CH_3$); 2.73 (t, 2 H, J = 7.5 Hz, $CCH_2CH_2CH_2CH_3$); 2.62 (s, 3 H, $O{=}CCH_3$); 6.13–7.99 (m, 6 H, Ar–*H*).

General Procedure for Direct Arylation

Heteroaryl derivative (2-*n*-butylfuran, 2-*n*-butylthiophene and 2-isopropylthiazole) (2 mmol), aryl bromide (4-bromoacetophenone, 4-bromoanisole, 4-bromotoluene and bromobenzene) (1 mmol), Pd-NHC complexes **2a–2h** (0.005 mmol), KOAc (1 mmol) and *N*,*N*-dimethylacetamide (DMAc; 2 ml) were added into a Schlenk tube equipped with a magnetic stirring bar as indicated in the literature.[20,31] The Schlenk tube was heated in an oil bath at 130°C for 1 h. The ambient solvent was removed by heating the reaction vessel under vacuum. The product was eluted using a pentane–diethyl ether mixture (3:1). The reaction mixture was purified by flash chromatography on silica gel. The purity of compounds was checked using GC and NMR. Conversions were based on aryl bromides.

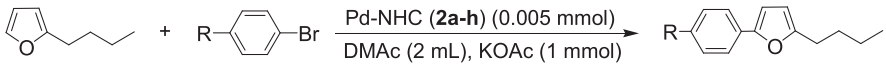
Results and Discussion

Synthesis of Pd-NHC Complexes

Various 1,3-dialkylbenzimidazolium salts were synthesized by the quaternization of *N*-alkylbenzimidazole with alkyl halides in DMF according to the method reported in the literature.[8,32,33] Silver NHC complexes **1a–1h** were obtained by the reaction of benzimidazolium salts with silver oxide in CH_2Cl_2 at room temperature for 24 h.[28–30] Eight novel Pd-NHC complexes **2a–2h** were synthesized using complexes **1a–1h** as the carbene transfer reagent with $PdCl_2(PhCN)_2$ in the presence of CH_2Cl_2 at 25°C for 24 h in 79–89% yields (Scheme 1). The obtained Pd-NHC complexes are stable against air and moisture.

The Pd-NHC complexes were characterized using both spectroscopic methods and elemental analysis techniques. ^{1}H NMR and ^{13}C NMR spectra which appear to be spectroscopically pure are consistent with the proposed formulae. In each ^{13}C NMR spectrum, there is one signal for the carbenic carbon (NCN) at *ca* 182.8, 182.8, 166.2, 182.1, 183.2, 182.0, 182.3 and 183.1 ppm for **2a–2h**, respectively. The FT-IR spectrum of each Pd-NHC complex exhibits a characteristic $\nu_{(NCN)}$ band at 1596.47, 1596.68, 1473.48, 1590.51, 1523.17, 1504.35, 1599.32 and 1413.16 cm^{-1} for **2a–2h**, respectively. When results of the elemental analysis, which is one of the analytical techniques that verifies synthesis of the compounds, are evaluated, it is observed that calculated values are very close to found values. Unfortunately, we

Table 1. Arylation of 2-*n*-butylfuran with various aryl bromides[a]



Entry	R	Pd-NHC	Product	Conversion (%)[b]
1	*p*-$COCH_3$	**2a**		75
2		**2b**		65
3		**2c**		98
4		**2d**	3	66
5		**2e**		88
6		**2f**		100
7		**2g**		100
8		**2h**		99
9	*p*-OCH_3	**2a**		66
10		**2b**		83
11		**2c**		93
12		**2d**	4	69
14		**2f**		81
15		**2g**		66
16		**2h**		97
17	*p*-CH_3	**2a**		93
18		**2b**		85
19		**2c**		84
20		**2d**	5	100
22		**2f**		97
23		**2g**		95
24		**2h**		96
25	H	**2a**		83
26		**2b**		88
27		**2c**		89
28		**2d**	6	63
30		**2f**		89
31		**2g**		75
32		**2h**		97

[a]Reaction conditions: 2-*n*-butylfuran (2 mmol), aryl bromide (1 mmol), Pd-NHC (**2a–2h**) (0.005 mmol), KOAc (1 mmol), DMAc (2 ml), 130°C, 1 h. Product purity was checked using GC and NMR.
[b]Conversions were calculated according to aryl bromide.

were unable to obtain an appropriate single crystal from these new complexes for X-ray diffraction.

Direct Arylation of 2-*n*-Butylfuran/2-*n*-Butylthiophene/2-Isopropylthiazole with Various Aryl Bromides

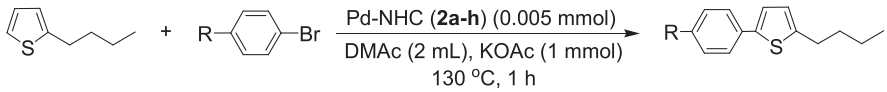
Generally, Pd(II)-catalysed direct arylation of furan, thiazole or thiophene gives arylated products at the 2- or 5-positions in high conversions.[34–37]

For example, Pd(II)-catalysed direct arylation of unsubstituted heteroaromatic groups such as thiazole and furan together with aryl bromides is developed at the C2 position and it generally takes shape at the C5 position in the presence of 2-substituted heteroaromatic compound.[20,38] Direct arylation at the C2 or C5 position of aryl halides and heteroaromatic compounds provides an important and easy way for the formation of aryl–heteroaryl bonds, that is, the synthesis of biaryls.

Our aim is to obtain the best conversions under the most appropriate conditions by decreasing the quantities of synthesized novel complexes (**2a–2f**) as catalysts. To achieve this, the **3–14** bound patterns from couplings of 2-*n*-butylfuran/2-*n*-butylthiophene/2-isopropylthiazole with various aryl bromides are obtained in high conversions by using just 0.005 mmol% catalyst (Tables 1–3). Conversions of products are between 45 and 100% for the **3–14** matching patterns in the most appropriate conditions of solvent, base and temperature. The best results for the examination of the temperature are acquired at approximately 130°C.

Initially, we studied the coupling of 2-*n*-butylfuran with 4-bromoacetophenone in the presence of KOAc as base and complex **2a** as catalyst (Table 1, entry 1). Product **3** is obtained in 75% conversion. Different tests for the obtained coupling product **3** were also done using other Pd-NHC complexes. Lower conversion for product **3** is obtained when **2b** is used. When the effects of **2c–2h** in the formation of product **3** are analysed, conversions of 66–100% are seen. The best results are obtained when complexes **2c** and **2f–2h** are used. Then, the effects of 2-*n*-butylfuran with 4-bromoanisole, 4-bromotoluene and bromobenzene were investigated in the presence of **2a–2h**, as a result of which products **4–6** are obtained in 63–100% conversions (Table 1). Very good conversions are obtained from the direct arylation at the 5-position of 4-bromoacetophenone containing electron-attracting group and 4-bromotoluene containing electron-donating group with 2-*n*-butylfuran.

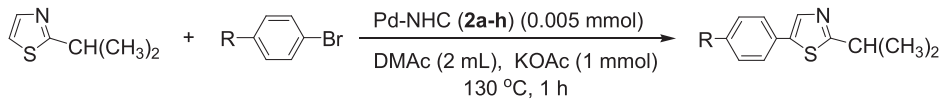
Table 2. Arylation of 2-*n*-butylthiophene with various aryl bromides[a]



Entry	R	Pd-NHC	Product	Conversion (%)[b]
1	*p*-$COCH_3$	**2a**		100
2		**2b**		97
3		**2c**		100
4		**2d**	7	100
5		**2e**		96
6		**2f**		97
7		**2g**		100
8		**2h**		100
9	*p*-OCH_3	**2a**		88
10		**2b**		96
11		**2c**		96
12		**2d**	8	79
14		**2f**		100
15		**2g**		97
16		**2h**		100
17	*p*-CH_3	**2a**		89
18		**2b**		72
19		**2c**		93
20		**2d**	9	89
21		**2e**		86
23		**2g**		97
24		**2h**		82
25	H	**2a**		79
26		**2b**		45
27		**2c**		83
28		**2d**	10	71
30		**2f**		75
31		**2g**		93
32		**2h**		87

[a]Reaction conditions: 2-*n*-butylthiophene (2 mmol), aryl bromide (1 mmol), Pd-NHC (**2a–2h**) (0.005 mmol), KOAc (1 mmol), DMAc (2 ml), 130°C, 1 h. Product purity was checked using GC and NMR.
[b]Conversions were calculated according to aryl bromide.

Table 3. Arylation of 2-isopropylthiazole with various aryl bromides[a]



Entry	R	Pd-NHC	Product	Conversion (%)[b]
1	*p*-$COCH_3$	**2a**		97
2		**2b**		98
3		**2c**		98
4		**2d**	11	88
5		**2e**		87
6		**2f**		72
7		**2g**		89
8		**2h**		88
9	*p*-OCH_3	**2a**		96
10		**2b**		91
11		**2c**		90
12		**2d**	12	97
14		**2f**		100
15		**2g**		98
16		**2h**		100
17	*p*-CH_3	**2a**		93
18		**2b**		95
19		**2c**		79
20		**2d**	13	99
22		**2f**		100
23		**2g**		97
24		**2h**		100
25	H	**2a**		91
26		**2b**		100
27		**2c**		83
28		**2d**	14	94
30		**2f**		88
31		**2g**		90
32		**2h**		89

[a]Reaction conditions: 2-isopropylthiazole (2 mmol), aryl bromide (1 mmol), Pd-NHC (**2a–2h**) (0.005 mmol), KOAc (1 mmol), DMAc (2 ml), 130°C, 1 h. Product purity was checked using GC and NMR.
[b]Conversions were calculated according to aryl bromide.

Finally, 2-*n*-butylthiophene was coupled with 4-bromoacetophenone and 4-bromoanisole to give the arylated products **7** and **8** in excellent conversions. When 4-bromotoluene and bromobenzene with 2-*n*-butylthiophene are utilized in the direct arylation reaction, conversions of the obtained products **9** and **10** are seen to be lower than those of products **7** and **8** (Table 2). With four different aryl bromides, 4-bromoacetophenone containing electron-attracting group gives the best conversions in direct arylation of 2-*n*-butylthiophene. It is found that the most effective catalyst in the direct arylation of thiophene is **2g** containing both morpholinoethyl and naphthalenomethyl groups. Also, 2-isopropylthiazole reacts with 4-bromoanisole leading to the desired product **12** in 90–100% conversions (Table 3). Generally, good results are obtained when aryl bromides together with heteroaromatic groups are used in reaction. Almost all catalysts (**2a**, **2b**, **2d**, **2f**, **2g** and **2h**) are highly effective in the direct arylation of 2-isopropylthiazole. As this study also illustrates, catalytic activities in direct arylation at the 5-position of different homogeneous Pd-NHC complexes were investigated by our research group previously.[20] Similar catalytic activity results were obtained in this study, too.

Conclusions

To summarize the research findings of this study, benzimidazole-based Pd-NHC complexes **2a–2h**, which are stable against air and moisture, were synthesized using silver NHC complexes. Characterization of these complexes was done using NMR and FT-IR spectroscopic and elemental analysis techniques. The catalytic activities of the eight novel Pd-NHC complexes were investigated in direct arylation, which is an efficient method for sp^2–sp^2 C–C bond formation, of 2-*n*-butylfuran/2-*n*-butylthiophene/2-isopropylthiazole with 4-bromoacetophenone/4-bromoanisole/4-bromotoluene/bromobenzene at the 5-position. Desired C_{Ar}–C_{Ar} bond formation was achieved efficiently with high regioselectivity. The 5-arylated compounds (**3–14**) were obtained in high conversions in the presence of KOAc as base, DMAc as solvent and complexes **2a–2h** as catalysts.

Acknowledgements

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