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N-Propylphthalimide-substituted bis-(NHC)PdX_2 complexes: synthesis, characterization and catalytic activity in direct arylation reactions

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Abstract Palladium-catalyzed direct arylation of heteroaromatics has become a popular method for producing carbon–carbon bonds via C–H bond activation. A wide diversity of heteroaromatics such as furan, thiophenes and thiazoles can be used for this reaction. This paper reports the synthesis of *N*-propylphthalimide-substituted bis-(NHC)PdX_2 complexes (NHC = *N*-heterocyclic carbene), and their catalytic activity in direct arylation reactions. The complexes have been prepared from Ag(I)NHC precursors by transmetallation and characterized by spectroscopy and elemental analysis. The bis-(NHC)PdX_2 complexes show excellent activity as catalysts in the direct arylation reactions of 2-*n*-butylfuran, 2-*n*-butylthiophene and 2-isopropylthiazole.

Introduction

Direct arylation of aromatic and heteroaromatic C–H bonds has become an important method of aryl C–C bond formation in organic chemistry. Some catalytic systems developed for C–H bond transformations can allow eco-friendly synthesis methods [1–6]. One of the most common methods used for the formation of aryl–aryl bonds is by transition metal complex-mediated reactions. Suzuki–Miyaura, Stille and Negishi couplings are among the most important examples of these methods [7, 8].

In recent years, palladium catalytic systems have attracted much attention in metal-catalyzed direct arylation reactions due to their selectivity, efficiency and versatility [9–11]. Many chemists have devoted time to the development of new Pd-catalyzed direct arylation reactions. To date, a wide range of electronically rich and poor (hetero)aromatic compounds have been successfully used in palladium-catalyzed direct arylation reactions [12–19], and this approach is one of the most effective methods to access aryl–heteroaryl derivatives [20–22].

Numerous studies have been carried out on the catalytic activities of Pd(II)-based complexes containing different ligands [23, 24]. In recent years, Pd–NHC complexes containing *N*-heterocyclic carbene (NHC) ligands have attracted great interest [25–27]. Complexes of NHC ligands have distinctive properties such as being strong σ-donors, weak π-acceptors and good resistance to heat, air and moisture [28–30].

In our work, we have investigated the synthesis and characterization of bis-(NHC)PdX_2 complexes. Also, we examined the catalytic activities of these complexes in direct arylation reactions. The complexes proved to have fairly good activity, even with low catalyst loadings, in direct arylation reactions with 2-*n*-butylfuran, 2-*n*-butylthiophene and 2-isopropylthiazole.

Experimental

All synthesis involving bis-(NHC)PdX_2 complexes **1a–i** were carried out under an inert atmosphere in flame-dried glassware using standard Schlenk techniques. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: Et_2O (Na/K alloy), CH_2Cl_2 (P_4O_{10}), hexane, toluene (Na). All other reagents were obtained commercially from Merck and Aldrich, and used without further purification. Melting points were measured in glass capillaries under air with an

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Electrothermal-9200 melting point apparatus. FTIR spectra were obtained in the range of 400–4000 cm^{-1} on a Perkin–Elmer Spectrum 100 FTIR spectrometer. Proton (^1H) and carbon (^{13}C) NMR spectra were recorded using a Varian AS 300 Merkur spectrometer operating at 300 MHz (^1H) or 75.47 MHz (^{13}C) in $CDCl_3$ with tetramethylsilane as an internal reference. Reaction products were assayed on an Agilent 6890 N GC system by GC-FID with an HP-5 column of 30 m length, 0.32 mm diameter and 0.25 µm film thickness. Column chromatography was performed using silica gel 60 (70–230 mesh). Elemental analyses were obtained by the İnönü University Scientific and Technological Research Center (Malatya, TURKEY). Crystallographic and physical data of all the complexes are summarized in Table 1.

Preparation of complex 1a

A mixture of bis(benzonitrile)palladium(II) chloride $[PdCl_2(PhCN)_2]$ (0.1g, 0.26 mmol) and bromo[1-methyl-3-(*N*-propylphthalimide)benzimidazol-2-ylidene]silver(I) (0.264 g, 0.52 mmol) in dichloromethane (20 mL) was stirred for 24 h at room temperature in the dark. The mixture was filtered through celite, and the solvents were evaporated under vacuum to afford the product as a white or light yellow solid. The crude product was recrystallized from dichloromethane/diethyl ether (1:3) at room temperature. Yield: 0.21 g (89%). Anal. Calc. for $C_{38}H_{34}N_6O_4PdBr_2$: C: 50.43, H: 3.79, N: 9.29. Found: C:50.47, H:3.83, N:9.26. ^1H NMR (300 MHz, DMSO-d_6) δ (ppm) = 2.59 (m, 4H, –(C_6H_4)NCH$_2$C***H***$_2$CH$_2$N–); 4.35 (t, 4H, –(C_6H_4)NCH$_2$CH$_2$C***H***$_2$N– *J*: 7.5 Hz); 4.44 (s, 6H, –C***H***$_3$); 5.01 (m, 4H, –(C_6H_4)NC***H***$_2$CH$_2$CH$_2$N–); 7.29–7.90 (m, 16H, Ar–***H***). ^{13}C NMR (75.47 MHz, DMSO-d_6) δ (ppm) = 29.2 (–(C_6H_4)NCH$_2$***C***H$_2$CH$_2$N–); 34.7 (–***C***H$_3$); 36.1 (–(C_6H_4)NCH$_2$CH$_2$***C***H$_2$N–); 55.6 (–(C_6H_4)N***C***H$_2$CH$_2$CH$_2$N–); 110.2, 110.3, 123.1, 123.2, 123.4, 132.1, 132.2, 133.8, 134.1 and 135.1 (Ar–***C***). 181.5 (2–***C***–Pd).

Preparation of complex 1b

According to the same procedure as for complex **1a,** complex **1b** was prepared from bromo[1-ethyl-3-(*N*-propylphthalimide)benzimidazol-2-ylidene]silver(I) (271 mg. 0.52 mmol). Yield: 0.15 g (60%). Anal. Calc. for $C_{40}H_{38}N_6O_4PdBr_2$: C: 51.49, H: 4.11, N: 9.01. Found: C: 51.46, H: 4.09, N: 9.03. ^1H NMR (300 MHz, DMSO-d_6) δ (ppm) = 1.65 (m, 6H, –CH$_2$C***H***$_3$); 2.51 (m, 4H, –(C_6H_4)NCH$_2$C***H***$_2$CH$_2$N–); 3.89 (m, 4H, –(C_6H_4)NCH$_2$CH$_2$C***H***$_2$N–); 4.72 (m, 4H, –C***H***$_2$CH$_3$); 4.92 (m, 4H, –(C_6H_4) NC***H***$_2$CH$_2$CH$_2$N–); 7.31–7.90 (m, 16H, Ar–***H***). ^{13}C NMR (75.47 MHz, DMSO-d_6) δ (ppm) = 15.2 (–CH$_2$***C***H$_3$); 28.8 (–(C_6H_4)NCH$_2$***C***H$_2$CH$_2$N–); 36.2 (–(C_6H_4)NCH$_2$CH$_2$***C***H$_2$N–); 46.2 (–***C***H$_2$CH$_3$); 55.4 (–(C_6H_4)N***C***H$_2$CH$_2$CH$_2$N–); 111.3, 123.5, 132.2, 132.3, 133.7, 133.8, 134.0, 134.1, 134.7 and 134.8 (Ar–***C***); 181.0 (2–***C***–Pd).

Preparation of complex 1c

According to the same procedure as for complex **1a,** complex **1c** was prepared from bromo[1-butyl-3-(*N*-propylphthalimide)benzimidazol-2-ylidene]silver(I) (285 mg. 0.52 mmol). Yield: 86% (221 mg). 0.22 g (86%). Anal. Calc. for $C_{44}H_{46}N_6O_4PdBr_2$: C: 53.43, H: 4.69, N: 8.50. Found: C: 53.39, H: 4.74, N: 8.47. ^1H NMR (300 MHz, DMSO-d_6) δ (ppm) = 1.09 (t, 3H, –CH$_2$CH$_2$CH$_2$C***H***$_3$, *J*: 6.9 Hz); 1.55 (m, 4H, –CH$_2$CH$_2$C***H***$_2$CH$_3$); 2.26 (m, 4H, –CH$_2$C***H***$_2$CH$_2$CH$_3$); 2.73 (m, 4H, –(C_6H_4)NCH$_2$C***H***$_2$CH$_2$N–); 3.96 (t, 4H, –(C_6H_4) NCH$_2$CH$_2$C***H***$_2$N, *J*: 6.9 Hz); 4.81 (m, 4H, –C***H***$_2$CH$_2$CH$_2$CH$_3$); 4.93 (m, 4H, –(C_6H_4)NC***H***$_2$CH$_2$CH$_2$N–); 7.27–7.89 (m, 16H, Ar–***H***). ^{13}C NMR (75.47 MHz, DMSO-d_6) δ (ppm) = 13.7 (–CH$_2$CH$_2$CH$_2$***C***H$_3$); 20.4 (–CH$_2$CH$_2$***C***H$_2$CH$_3$); 29.4 (–(C_6H_4)NCH$_2$***C***H$_2$CH$_2$N–); 35.1 (–(C_6H_4)NCH$_2$CH$_2$***C***H$_2$N–); 41.0 (–CH$_2$***C***H$_2$CH$_2$CH$_3$); 56.1 (–***C***H$_2$CH$_2$CH$_2$CH$_3$); 56.6 (–(C_6H_4)N***C***H$_2$CH$_2$CH$_2$N–); 110.9, 111.2, 123.0, 123.3, 123.4, 132.1, 133.1 and 134.1 (Ar–***C***); 181.2 (2–***C***–Pd).

Table 1 Physical properties and spectroscopic analysis of the complexes

Compound	Formula	Yield (%)	m.p. (°C)	^{13}C 2-*C*-Pd (δ)	IR: $\nu_{(CN)}$ (cm^{-1})
1a	$C_{38}H_{34}N_6O_4PdBr_2$	89	228–230	181.5	1442
1b	$C_{40}H_{38}N_6O_4PdBr_2$	60	244–246	181.0	1464
1c	$C_{44}H_{46}N_6O_4PdBr_2$	86	218–220	181.2	1465
1d	$C_{42}H_{42}N_6O_6PdBr_2$	75	292–294	181.9	1462
1e	$C_{44}H_{46}N_6O_6PdBr_2$	65	248–250	181.6	1454
1f	$C_{52}H_{46}N_6O_4PdCl_2$	81	204–205	182.1	1432
1 g	$C_{52}H_{46}N_6O_4PdCl_2$	78	254–255	181.9	1440
1 h	$C_{56}H_{54}N_6O_4PdCl_2$	87	276–277	182.0	1426
1i	$C_{58}H_{46}N_6O_4PdCl_2$	84	225–227	182.6	1432

Preparation of complex 1d

According to the same procedure as for complex **1a,** complex **1d** was prepared from bromo[1-(2-methoxyethyl)-3-(*N*-propylphthalimide)benzimidazol-2-ylidene]silver(I) (287 mg. 0.52 mmol). Yield: 0.19 g (75%). Anal. Calc. for $C_{42}H_{42}N_6O_6PdBr_2$: C: 50.80, H: 4.26, N: 8.46. Found: C: 50.73, H: 5.22, N: 8.42. ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm) = 3.26 (s, 6H, –$CH_2CH_2OCH_3$); 3.90 (m, 4H, –$CH_2CH_2OCH_3$); 4.97 (m, 4H, –$CH_2CH_2OCH_3$); 2.51 (m, 4H, –$(C_6H_4)NCH_2CH_2CH_2N$); 4.26 (m, 4H, –$(C_6H_4)NCH_2CH_2CH_2N$); 4.99 (m, 4H, –$(C_6H_4)NCH_2CH_2CH_2N$); 7.37–7.91 (m, 16H, Ar–***H***).^{13}C NMR (75.47 MHz, DMSO-d_6) δ (ppm) = 29.4 (–$(C_6H_4)NCH_2CH_2CH_2N$); 35.2 (–$(C_6H_4)NCH_2CH_2CH_2N$); 56.6 (–$(C_6H_4)NCH_2CH_2CH_2N$); 29.1 (–$CH_2CH_2OCH_3$); 36.2 (–$CH_2CH_2OCH_3$); 58.9 (–$CH_2CH_2OCH_3$); 123.4, 123.5, 132.2, 132.3, 134.7 and 134.8 (Ar–***C***); 181.9 (2–***C***–Pd).

Preparation of complex 1e

According to the same procedure as for complex **1a,** complex **1e** was prepared from bromo[1-(2-ethoxyethyl)-3-(*N*-propylphthalimide)benzimidazol-2-ylidene]silver(I) (294 mg. 0.52 mmol). Yield: 0.17 g (65%). Anal. Calc. for $C_{44}H_{46}N_6O_6PdBr_2$: C: 51.76, H: 4.54, N: 8.23. Found: C: 51.87, H: 4.64, N: 8.27. ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm) = 1.24 (t, 6H, –$CH_2CH_2OCH_2CH_3$, *J*: 7.2 Hz); 2.64 (m 4H, –$(C_6H_4)NCH_2CH_2CH_2N$–); 3.50 (m 4H, –$CH_2CH_2OCH_2CH_3$); 4.12 (m, 4H, –$(C_6H_4)NCH_2CH_2CH_2N$–); 4.14 (t, 4H, –$CH_2CH_2OCH_2CH_3$, *J*: 7.2 Hz); 4.71 (m, 4H, –$CH_2CH_2OCH_2CH_3$); 5.15 (m, 4H, –$(C_6H_4)NCH_2CH_2CH_2N$–); 7.28–7.91 (m, 16H, Ar–***H***). ^{13}C NMR (75.47 MHz, DMSO-d_6) δ (ppm) = 15.2 (–$CH_2CH_2OCH_2CH_3$); 28.9 (–$(C_6H_4)NCH_2CH_2CH_2N$–); 36.3 (–$(C_6H_4)NCH_2CH_2CH_2N$–); 46.2 (–$CH_2CH_2OCH_2CH_3$); 66.8 (–$(C_6H_4)NCH_2CH_2CH_2N$–); 69.8 (–$CH_2CH_2OCH_2CH_3$); 70.2 (–$CH_2CH_2OCH_2CH_3$); 109.9, 110.2, 111.6, 112.1, 123.2, 123.3, 132.1, 132.2, 133.8 and 134.1 (Ar–***C***); 181.6 (2–***C***–Pd).

Preparation of complex 1f

According to the same procedure as for complex **1a,** complex **1f** was prepared from chloro[1-(3-methylbenzyl)-3-(*N*-propylphthalimide)benzimidazol-2-ylidene]silver(I) (288 mg. 0.52 mmol). Yield: 0.21 g (81%). Anal. Calc. for $C_{52}H_{46}N_6O_4PdCl_2$: C: 62.69, H: 4.65, N: 8.44. Found: C: 62.65, H: 4.61, N: 8.38. ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm) = 2.32 (s, 6H, –$CH_2C_6H_4(CH_3)$); 2.81 (m, 4H, –$(C_6H_4)NCH_2CH_2CH_2N$–); 4.19 (t, 4H, –$(C_6H_4)NCH_2CH_2CH_2N$, *J*: 7.2 Hz); 5.14 (t, 4H, –$(C_6H_4)NCH_2CH_2CH_2N$, *J*: 7.2 Hz); 5.97 (s, 4H, –$CH_2C_6H_4(CH_3)$); 6.99–7.83 (m, 24H, Ar–***H***). ^{13}C NMR (75.47 MHz, DMSO-d_6) δ (ppm) = 21.3 (–$CH_2C_6H_4(CH_3)$); 29.0 (–$(C_6H_4)NCH_2CH_2CH_2N$); 36.3 (–$(C_6H_4)NCH_2CH_2CH_2N$); 46.3 (–$(C_6H_4)NCH_2CH_2CH_2N$); 52.7 (–$CH_2C_6H_4(CH_3)$); 110.2, 111.4, 123.1, 124.7, 124.9, 128.4, 128.7, 132.1, 133.9, 134.2, 134.3, 134.5, 135.4, 135.6, 138.3 and 138.6 (Ar–***C***); 168.2 (**C**=O); 182.1(2–***C***–Pd).

Preparation of complex 1g

According to the same procedure as for complex **1a,** complex **1g** was prepared from chloro[1-(4-methylbenzyl)-3-(*N*-propylphthalimide)benzimidazol-2-ylidene]silver(I) (288 mg. 0.52 mmol). Yield: 0.20 g (78%). Anal. Calc. for $C_{52}H_{46}N_6O_4PdCl_2$: C: 62.69, H: 4.65, N: 8.44. Found: C: 62.75, H: 4.69, N: 8.48. ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm) = 2.27 (s, 6H, –$CH_2C_6H_4(CH_3)$); 2.59 (m, 4H, –$(C_6H_4)CH_2CH_2CH_2N$–); 3.71 (t, 4H, –$(C_6H_4)CH_2CH_2CH_2N$, *J*: 7.2 Hz); 4.91 (t, 4H, –$(C_6H_4)CH_2CH_2CH_2N$–, *J*: 7.2 Hz); 5.96 (s, 4H, –$(C_6H_4)CH_2C_6H_4(CH_3)$); 7.02–7.86 (m, 24H, Ar–***H***). ^{13}C NMR (75.47 MHz, DMSO-d_6) δ (ppm) = 21.1 (–$CH_2C_6H_4(CH_3)$); 28.9 (–$(C_6H_4)CH_2CH_2CH_2N$–); 36.3 (–$(C_6H_4)CH_2CH_2CH_2N$–); 46.1 (–$(C_6H_4)CH_2CH_2CH_2N$–); 52.3 (–$CH_2C_6H_4(CH_3)$); 110.2, 110.5, 111.5, 123.0, 123.3, 127.6, 127.8, 129.3, 132.1, 132.5, 132.7, 133.9, 134.2, 134.3, 134.5, 137.3 ve 137.5 (Ar–***C***); 167.9 and 168.2 (***C***=O); 181.9 (2–***C***–Pd).

Preparation of complex 1h

According to the same procedure as for complex **1a,** complex **1h** was prepared from chloro[1-(2,4,6-trimethylbenzyl)-3-(*N*-propylphthalimide)benzimidazol-2-ylidene]silver(I) (302 mg. 0.52 mmol). Yield: 0.23 g (87%). Anal. Calc. for $C_{56}H_{54}N_6O_4PdCl_2$: C: 63.91, H: 5.17, N: 7.99. Found: C: 64.01, H: 5.20, N: 8.04. ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm) = 2.77 (m, 4H, –$(C_6H_4)CH_2CH_2CH_2N$–); 4.16 (t, 4H, –$(C_6H_4)CH_2CH_2CH_2N$–, *J*: 7.5 Hz); 5.23 (t, 4H, –$(C_6H_4)CH_2CH_2CH_2N$–, *J*: 7.5 Hz); 2.27 and 2.35 (s, 18H,$CH_2C_6H_2(CH_3)_3$); 6.18 (s, 4H, –$CH_2C_6H_2(CH_3)_3$), 6.38–7.82 (m, 20H, Ar–***H***). ^{13}C NMR (75.47 MHz, DMSO-d_6) δ (ppm) = 20.9 and 21.1 (–$CH_2C_6H_2(CH_3)_3$); 29.0 (–$(C_6H_4)CH_2CH_2CH_2N$); 36.3 (–$(C_6H_4)CH_2CH_2CH_2N$); 46.3 (–$(C_6H_4)CH_2CH_2CH_2N$); 49.6 (–$CH_2C_6H_2(CH_3)_3$); 110.3, 111.8, 122.8, 123.2, 128.2, 129.6, 132.0, 132.2, 133.8, 134.3, 134.5, 138.2, 138.5 ve 138.9 (Ar–**C**); 168.1 (**C**=O); 182.0 (**C**–Pd).

Preparation of complex 1i

According to the same procedure as for complex **1a,** complex **1i** was prepared from chloro[1-naftalenomethyl-3-(*N*-propylphthalimide)benzimidazol-2-ylidene] silver(I)

(306 mg. 0.52 mmol). Yield: 0.23 g (84%). Anal. Calc. for $C_{58}H_{46}N_6O_4PdCl_2$: C: 65.21, H: 4.34, N: 7.87. Found: C: 65.14, H: 4.32, N: 7.85. ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm) = 2.83 (m, 4H, (–(C_6H_4)CH_2C***H***$_2$$CH_2$N–); 4.21 (t, 4H, –($C_6H_4$)$CH_2CH_2$C***H***$_2$N–, *J*: 7.2 Hz); 5.18 (t, 4H, –(C_6H_4)C***H***$_2CH_2CH_2$N–, *J*: 7.2 Hz); 6.19 (s, 4H, –C***H***$_2C_{10}H_7$); 6.72–7.88 (m, 30H, Ar–***H***). ^{13}C NMR (75.47 MHz, DMSO-d_6) δ (ppm) = 29.1 (–(C_6H_4)CH_2***C***H_2CH_2N–); 36.3 (–(C_6H_4)CH_2CH_2***C***H_2N–); 46.3 (–(C_6H_4)***C***$H_2CH_2CH_2$N–); 49.5 (***C***$H_2C_{10}H_7$); 110.4, 111.3, 122.3, 123.2, 125.2, 125.9, 126.2, 126.8, 128.3, 128.9, 130.3, 130.9, 132.3, 133.1, 133.9, 134.7 ve 134.8 (Ar–***C***); 168.3 (***C***=O); 182.6 (2–***C***–Pd).

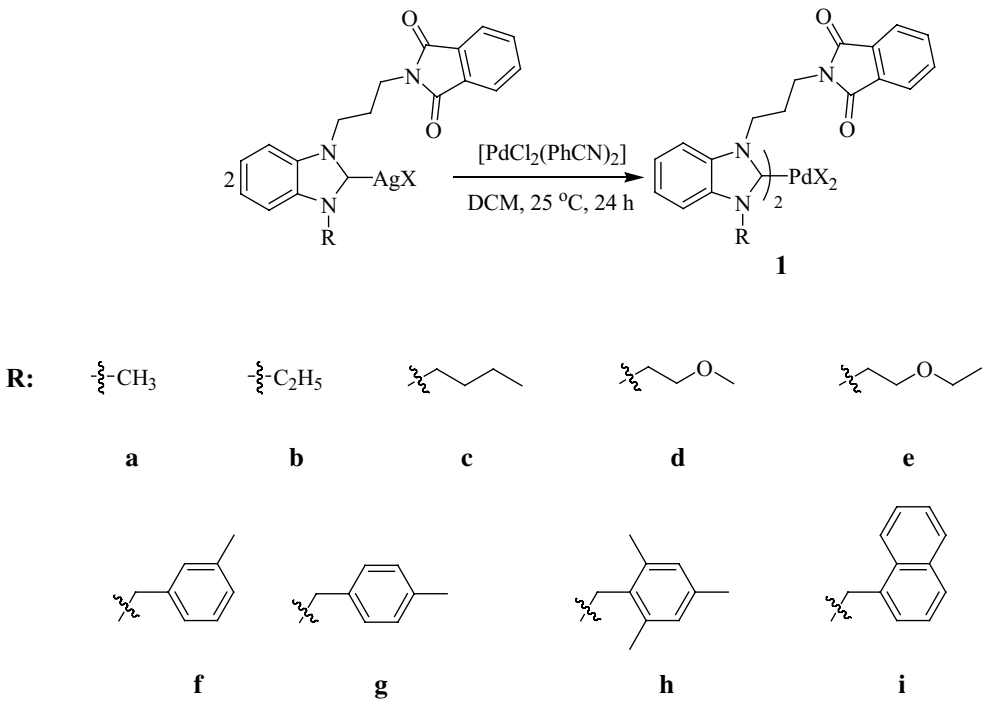
Procedure for arylation of furan, thiophene and thiazole

The heteroaryl derivatives (2-*n*-butylfuran, 2-*n*-butylthiophene and 2-isopropylthiazole) (2 mmol), the aryl bromide derivatives (4-bromo acetophenone, 4-bromoanisole, 4-bromotoluene and 4-bromobenzene) (1 mmol), KOAc (1 mmol) and bis-(NHC)PdX_2 complexes **1a–i** (0.003 mmol) were dissolved in *N*,*N*-dimethylacetamide (DMAc) (2 mL) in a small Schlenk tube under argon as described in the literature [31]. The mixture was stirred in an oil bath at 130 °C for 1 h, then cooled to room temperature, and the solvent was removed under vacuum. The residue was purified by column chromatography (silica gel 60–120 mesh) using diethyl ether/*n*-hexane (1:5) as eluent to afford the pure product. The purities of the compounds were checked by GC and GC–MS. Conversions were calculated based on the aryl bromide.

Results and discussion

Synthesis of bis-(NHC)PdX_2 parent complexes (1a–i)

The synthetic route for the *N*-propylphthalimide substituted bis-(NHC)PdX_2 complexes is illustrated in Scheme 1. The bis-(NHC)PdX_2 complexes **1a-i** were prepared from the corresponding *N*-propylphthalimide substituted Ag(I) NHC complexes via transmetallation, as reported in the literature [32]. The bis-(NHC)PdX_2 complexes were obtained as light yellow solids in 60–89% yields. Resistant to air and moisture, the complexes are soluble in solvents such as DMF and DMSO, but less soluble in halogenated solvents such as chloroform and dichloromethane. Formation of the *N*-propylphthalimide substituted complexes was confirmed by FTIR, ^{1}H NMR and ^{13}C NMR spectroscopy and by elemental analysis. The ^{13}C NMR spectra of the complexes reveal the Pd–C(carbene) signal as a singlet between at 181.0 and 182.6 ppm [33], instead of the Ag–C(carbene) singlet observed between 188 and 190 ppm for the Ag(I)NHC complexes [34], confirming the successful



Scheme 1 Synthesis of *N*-propylphthalimide substituted bis-(NHC)PdX_2 complexes **1a–i**. X = Cl or Br

Table 2 Catalysis of the direct arylation of 2-*n*-butylfuran with aryl bromides by complexes **1a–i** (see Scheme 2)

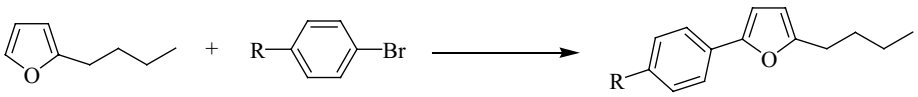
Entry	R	Pd(II)NHC	% Conv.
1	$-COCH_3$	**1a**	77
2	$-COCH_3$	**1b**	84
3	$-COCH_3$	**1c**	93
4	$-COCH_3$	**1d**	83
5	$-COCH_3$	**1e**	94
6	$-COCH_3$	**1f**	77
7	$-COCH_3$	**1g**	84
8	$-COCH_3$	**1h**	93
9	$-COCH_3$	**1i**	97
10	$-OCH_3$	**1a**	75
11	$-OCH_3$	**1b**	96
12	$-OCH_3$	**1c**	96
13	$-OCH_3$	**1d**	88
14	$-OCH_3$	**1e**	78
15	$-OCH_3$	**1f**	93
16	$-OCH_3$	**1g**	75
17	$-OCH_3$	**1h**	84
18	$-OCH_3$	**1i**	60
19	$-CH_3$	**1a**	61
20	$-CH_3$	**1b**	80
21	$-CH_3$	**1c**	89
22	$-CH_3$	**1d**	84
23	$-CH_3$	**1e**	99
24	$-CH_3$	**1f**	74
25	$-CH_3$	**1g**	80
26	$-CH_3$	**1h**	86
27	$-CH_3$	**1i**	84
28	–H	**1a**	81
29	–H	**1b**	74
30	–H	**1c**	70
31	–H	**1d**	85
32	–H	**1e**	85
33	–H	**1f**	76
34	–H	**1g**	83
35	–H	**1h**	80
36	–H	**1i**	77

Reaction conditions 2-*n*-butylfuran (2 mmol), aryl bromide (1 mmol), complexes **1a–i** (0.003 mmol), KOAc (1 mmol), DMAc (2 mL), 130 °C, 1 h. Product purity was checked by GC and NMR, conversions were calculated according to the aryl bromide

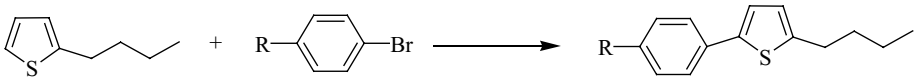
Table 3 Catalysis of the direct arylation of 2-*n*-butylthiophene with aryl bromides by complexes **1a–i** (see Scheme 3)

Entry	R	Pd(II)NHC	% Conv.
1	$-COCH_3$	**1a**	94
2	$-COCH_3$	**1b**	93
3	$-COCH_3$	**1c**	99
4	$-COCH_3$	**1d**	97
5	$-COCH_3$	**1e**	98
6	$-COCH_3$	**1f**	94
7	$-COCH_3$	**1g**	93
8	$-COCH_3$	**1h**	92
9	$-COCH_3$	**1i**	98
10	$-OCH_3$	**1a**	81
11	$-OCH_3$	**1b**	68
12	$-OCH_3$	**1c**	72
13	$-OCH_3$	**1d**	57
14	$-OCH_3$	**1e**	78
15	$-OCH_3$	**1f**	51
16	$-OCH_3$	**1g**	68
17	$-OCH_3$	**1h**	74
18	$-OCH_3$	**1i**	57
19	$-CH_3$	**1a**	94
20	$-CH_3$	**1b**	76
21	$-CH_3$	**1c**	61
22	$-CH_3$	**1d**	76
23	$-CH_3$	**1e**	79
24	$-CH_3$	**1f**	93
25	$-CH_3$	**1g**	85
26	$-CH_3$	**1h**	98
27	$-CH_3$	**1i**	63
28	–H	**1a**	98
29	–H	**1b**	96
30	–H	**1c**	99
31	–H	**1d**	97
32	–H	**1e**	95
33	–H	**1f**	93
34	–H	**1g**	96
35	–H	**1h**	94
36	–H	**1i**	91

Reaction conditions 2-*n*-butylthiophene (2 mmol), aryl bromide (1 mmol), complex **1a–i** (0.003 mmol), KOAc (1 mmol), DMAc (2 mL), 130 °C, 1 h. Product purity was checked by GC and NMR, conversions were calculated according to the aryl bromide



Scheme 2 The direct arylation reaction of 2-*n*-butylfuran with aryl bromides by complexes **1a–i**



Scheme 3 The direct arylation reaction of 2-*n*-butylthiophene with aryl bromides by complexes **1a**–**i**

Table 4 Catalysis of the direct arylation of 2-isopropylthiazole with aryl bromides by complexes **1a**–**e** (see Scheme 4)

Entry	R	Pd(II)NHC	% Conv.
1	$-COCH_3$	**1a**	94
2	$-COCH_3$	**1b**	99
3	$-COCH_3$	**1c**	96
4	$-COCH_3$	**1d**	99
5	$-COCH_3$	**1e**	98
6	$-OCH_3$	**1a**	71
7	$-OCH_3$	**1b**	89
8	$-OCH_3$	**1c**	92
9	$-OCH_3$	**1d**	91
10	$-OCH_3$	**1e**	80
11	$-CH_3$	**1a**	99
12	$-CH_3$	**1b**	99
13	$-CH_3$	**1c**	89
14	$-CH_3$	**1d**	87
15	$-CH_3$	**1e**	84
16	–H	**1a**	96
17	–H	**1b**	73
18	–H	**1c**	78
19	–H	**1d**	77
20	–H	**1e**	81

Reaction conditions 2-isopropylthiazole (2 mmol), aryl bromide (1 mmol), complex **1a**–**e** (0.003 mmol), KOAc (1 mmol), DMAc (2 mL), 130 °C, 1 h. Product purity was checked by GC, conversions were calculated according to the aryl bromide

transmetallation reaction. The results of the elemental analysis were in good agreement with the theoretical values. The FTIR spectra of all of the complexes **1a–i** show a strong band at 1426–1465 cm^{-1} for ν(CN) (Table 1). Unfortunately, despite all our efforts, we could not obtain a single crystal from these new complexes for X-ray diffraction studies.

Direct arylation of 2-*n*-butylfuran, 2-*n*-butylthiophene and 2-isopropylthiazole

We have investigated the direct arylation of para-substituted aryl bromides with 2-*n*-butylfuran, 2-*n*-butylthiophene and 2-isopropylthiazole in the presence of **1a–i** as catalyst. Product conversions for 2-*n*-butylfuran were between 60 and 99%, for 2-*n*-butylthiophene between 51 and 99%, and for 2-isopropylthiazole between 71 and 99% (Tables 2, 3 and 4).

Initially, we investigated the reactions of 2-*n*-butylfuran with 4-bromoacetophenone, 4-bromoanisole, 4-bromotoluene and 4-bromobenzene using complexes **1a–i** as catalysts. Conversions of 77–97%, 60–96%, 61–99% and 70–85% were observed for R = $-COCH_3$, $-OCH_3$, $-CH_3$ and –H, respectively (Table 2). Generally, the conversions for substrates containing electron-withdrawing groups were higher than those for substituents containing electron-donating groups.

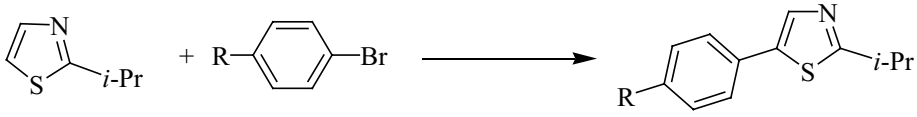
Next, we investigated the reactions of 2-*n*-butylthiophene with 4-bromoacetophenone, 4-bromoanisole, 4-bromotoluene and 4-bromobenzene using complexes **1a–i** as catalysts. Conversions of 92–99%, 51–81%, 61–94% and 91–99% were observed R=$-COCH_3$, $-OCH_3$, $-CH_3$ and –H, respectively (Table 3).

Finally, we investigated the reactions of 2-isopropylthiazole with 4-bromoacetophenone, 4-bromoanisole, 4-bromotoluene and 4-bromobenzene using complexes **1a–e** as catalysts. Conversions of 96–99%, 71–92%, 84–99% and 73–96% were observed R = $-COCH_3$, $-OCH_3$, $-CH_3$ and –H, respectively (Table 4). When compared to similar studies [32, 35] published recently, the bis-(NHC)PdX_2 complexes that we have synthesized in this work appear to be highly active catalysts.

Conclusions

We have reported the synthesis of *N*-propylphthalimide substituted bis-(NHC)PdX_2 complexes from the corresponding Ag(I)NHC complexes via transmetallation. The catalytic activities of these *N*-propylphthalimide substituted bis-(NHC)PdX_2 complexes show that they are efficient and stable catalysts for the direct arylation reactions of 2-*n*-butylfuran, 2-*n*-butylthiophene and 2-isopropylthiazole with aryl bromides.

Scheme 4 The direct arylation reaction of 2-isopropylthiazole with aryl bromides by complexes **1a**–**e**



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