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2-methyl-1,4-benzodioxan-substituted bis(NHC)PdX$_2$ complexes: Synthesis, characterization and the catalytic activity in the direct arylation reaction of some 2-alkyl-heterocyclic compounds

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Abstract

Almost in all fields of chemistry, the C–C cross-coupling reactions such as the direct arylation reaction have attracted much attention and have advanced quickly in recent years due to the importance of environment-friendly properties. This study contains the synthesis of the 2-methyl-1,4-benzodioxan-substituted bis(NHC)PdX$_2$ complexes and their catalytic activity in direct arylation reaction. The bis(NHC)PdX$_2$ complexes have been prepared from the 2-methyl-1,4-benzodioxan-substituted Ag(I)NHC complexes via transmetallation method. The bis(NHC)PdX$_2$ complexes have been characterized using ^{1}H NMR, ^{13}C NMR, FT-IR spectroscopy and elemental analysis techniques. The bis(NHC)PdX$_2$ complexes have been examined as catalysts in the direct arylation reactions with 2-n-butylfuran, 2-n-butylthiophene and 2-isopropylthiazole, and have demonstrated excellent activity in these reactions.

Keywords *N*-Heterocyclic carbenes · Direct arylation · Butylfuran · Butylthiophene · 2-Isopropylthiazole

Introduction

The importance of NHC ligands in organic and organometallic chemistry is increasing day by day [1–4]. It is emphasized that the remarkable effect of NHC ligands on transition metal catalysis is because of the strong sigma donor character even in the oldest reviews [5–7]. It is believed that in the cross-coupling reactions, in particular, the strong M–NHC bond prevents the decomposition of the molecular catalysts [8], and stabilizes the higher oxidation states necessary in multiple catalytic contexts.

Metal–NHC complexes are unique organometallic compounds in which numerous studies have been carried out on both catalytic activity studies and medical applications. The NHC–palladium complexes are simply synthesized by means of different NHC salts with Pd(OAc)$_2$ [9–12] and using the transmetallation method [13–15] in which Ag–NHC complexes are used as the transfer agent with PdCl$_2$(PhCN)$_2$ [16] or PdCl$_2$(CH$_3$CN)$_2$ [17, 18]. From these complexes, medical

applications [19–21] of Pd(II)NHC complexes are known, but Pd(II)NHC complexes are more well-known for their unique catalytic properties [22–24].

In recent years, formation of carbon–carbon bonds via C–H bond activation has become a popular method for palladium-catalyzed arylation of heteroaromatics. For this reaction, most of the heteroaromatic compounds such as (benzo)thiophenes, (benzo)furans, pyrroles, indoles, oxazoles, imidazoles, pyrazoles or triazoles can be used [25]. In recent years important studies have been published on the catalytic properties of palladium-based complexes [26–30]. In particular, the catalytic activities on the direct arylation reactions of the palladium-based complexes containing NHC ligands are becoming more and more important [31–38]. Therefore, we researched the synthesis and the characterization of the 2-methyl-1,4-benzodioxan-substituted bis(NHC)PdX$_2$ complexes. Also, we investigated the catalytic activities of the 2-methyl-1,4-benzodioxan-substituted bis(NHC)PdX$_2$ complexes in direct arylation reactions, and they demonstrated quite good activity as catalysts in the direct arylation reactions with 2-n-butylfuran, 2-n-butylthiophene, and 2-isopropylthiazole.

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Experimental

All synthesis involving bis(NHC)PdX$_2$ complexes **1a–h** 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$_2$O (Na/K alloy), CH$_2$Cl$_2$ (P$_4$O$_{10}$), hexane, toluene (Na).

All other reagents were commercially available from Merck and Aldrich Chemical Co. and used without further purification. Melting points were identified in glass capillaries under air with an Electrothermal-9200 melting point apparatus. FT-IR spectra were saved in the range 400–4000 cm^{-1} on PerkinElmer Spectrum 100 FT-IR spectrometer. Proton (^{1}H) and Carbon (^{13}C) NMR spectra were recorded using either a Varian AS 300 Merkur spectrometer operating at 300 MHz (^{1}H), 75.47 MHz (^{13}C) in CDCl$_3$ with tetramethylsilane as an internal reference. All reactions were observed 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 performed by İnönü University Scientific and Technological Research Center (Malatya, TURKEY).

Synthesis

Synthesis of dibromo-bis[1-methyl-3-(2-methyl-1, 4-benzodioxan)benzimidazol-2-ylidene]palladium(II), 1a

Bromo[1-methyl-3-(2-methyl-1,4-benzodioxan)benzimidazol-2-ylidene]silver(I)) (234 mg·0.50 mmol) and bis(benzonitrile)palladium(II) chloride [PdCl$_2$(PhCN)$_2$] (95 mg·0.25 mmol) in dichloromethane (20 mL) were stirred for 24 h at room temperature in dark conditions. Then, they were filtered through celite and the solvents were evaporated under vacuum to make the product into a white or light yellow solid. The crude product was recrystallized from dichloromethane/diethyl ether (1:3) at room temperature. Yield: 84% (174 mg). Anal. Calc. for C$_{34}$H$_{32}$N$_4$O$_4$PdBr$_2$: C: 49.39, H: 3.90, N: 6.78. Found: C: 49.47, H: 4.83, N: 6.72. ^{1}H NMR (300 MHz, DMSO-d$_6$) δ (ppm) = 4.44 (m, 4H, –NC***H***$_2$CHOCH$_2$–); 4.46 (s, 6H, –C***H***$_3$); 5.28 (m, 4H, –OCHC***H***$_2$O–); 5.38 (m, 2H, –CH$_2$C***H***OCH$_2$–); 6.93–7.54 (m, 16H, Ar–***H***). ^{13}C NMR (75.47 MHz, DMSO–d$_6$) δ (ppm) = 34.5 (–***C***H$_3$); 47.8 (O***C***H$_2$CH(CH$_2$)O); 53.5 (OCH$_2$CH(***C***H$_2$)O); 72.6 (OCH$_2$***C***H(CH$_2$)O); 117.5, 117.6, 117.7, 121.7, 122.2, 123.5, 134.9 and 143.1(Ar–***C***); 181.8 (2-***C***–Pd).

Synthesis of dibromo-bis[1-butyl-3-(2-methyl-1,4-benzodioxan)benzimidazol-2-ylidene]palladium(II), 1b

Using the same method for the synthesis of complex **1a**, the **1b** complex was prepared from bromo[1-butyl-3-(2-methyl-1,4-benzodioxan)benzimidazol-2-ylidene]silver(I) (255 mg·0.50 mmol) and bis(benzonitrile)palladium(II) chloride [PdCl$_2$(PhCN)$_2$] (95 mg·0.25 mmol). Yield: 79% (180 mg). Anal. Calc. for C$_{40}$H$_{44}$N$_4$O$_4$PdBr$_2$: C: 52.73, H: 4.87, N: 6.15. Found: C: 52.68, H: 4.82, N: 6.11. ^{1}H NMR (300 MHz, DMSO-d$_6$) δ (ppm) = 0.97 (t, 6H, –CH$_2$CH$_2$CH$_2$C***H***$_3$, *J*: 6.8 Hz); 1.53 (m, 4H, –CH$_2$CH$_2$C***H***$_2$CH$_3$); 2.31 (m, 4H, –CH$_2$C***H***$_2$CH$_2$CH$_3$); 4.37 (m, 4H, –NC***H***$_2$CHOCH$_2$–); 5.23 (t, 4H, –NC***H***$_2$CH$_2$CH$_2$CH$_3$ *J*: 6.0 Hz); 5.34 (m, 2H, –CH$_2$C***H***OCH$_2$–); 5.38 (d, 4H, –OCHC***H***$_2$O– *J*: 4.6 Hz); 7.05–7.49 (m, 16H, Ar–***H***). ^{13}C NMR (75.47 MHz, DMSO-d$_6$) δ (ppm) = 14.3 (–CH$_2$CH$_2$CH$_2$***C***H$_3$); 20.3 (–CH$_2$CH$_2$***C***H$_2$CH$_3$); 32.4 (–CH$_2$***C***H$_2$CH$_2$CH$_3$); 47.3 (O***C***H$_2$CH(CH$_2$)O); 51.3 (–***C***H$_2$CH$_2$CH$_2$CH$_3$); 53.2 (OCH$_2$CH(***C***H$_2$)O); 72.4 (OCH$_2$***C***H(CH$_2$)O); 117.2, 117.4, 117.5, 121.4, 122.0, 123.3, 135.0 (Ar–***C***); 181.6 (2-***C***–Pd).

Synthesis of dibromo-bis[1-(2-methoxyethyl)-3-(2-methyl-1, 4-benzodioxan) benzimidazol-2-ylidene]palladium(II), 1c

Using the same method for the synthesis of complex **1a**, the **1c** complex was prepared from bromo[1-(2-methoxyethyl)-3-(2-methyl-1,4-benzodioxan)benzimidazol-2-ylidene]silver(I) (256 mg·0.50 mmol) and bis(benzonitrile)palladium(II) chloride [PdCl$_2$(PhCN)$_2$] (95 mg·0.25 mmol). Yield: 87%. (200 mg). Anal. Calc. for C$_{38}$H$_{40}$N$_4$O$_6$PdBr$_2$: C: 49.88, H: 4.41, N: 6.12. Found: C: 49.91, H: 4.42, N: 6.14. ^{1}H NMR (300 MHz, DMSO-d$_6$) δ (ppm) = 3.38 (s, 6H, –CH$_2$CH$_2$OC***H***$_3$); 4.32 (t, 4H, –CH$_2$C***H***$_2$OCH$_3$ *J*: 7.2 Hz); 4.39 (m, 4H, –NC***H***$_2$CHOCH$_2$–); 4.42 (m, 4H, –C***H***$_2$CH$_2$OCH$_3$ *J*: 7.2 Hz); 5.40 (d, 4H, –OCHC***H***$_2$O–*J*: 4.6 Hz); 5.44 (m, 2H, –CH$_2$C***H***OCH$_2$–); 6.90–7.04 (m, 16H, Ar–***H***). ^{13}C NMR (75.47 MHz, DMSO-d$_6$) δ (ppm) = 28.6 (–CH$_2$CH$_2$O***C***H$_3$); 35.9 (–CH$_2$***C***H$_2$OCH$_3$); 47.5 (O***C***H$_2$CH(CH$_2$)O); 53.4 (–***C***H$_2$CH$_2$OCH$_3$); 58.5 (OCH$_2$CH(***C***H$_2$)O); 72.5 (OCH$_2$***C***H(CH$_2$)O); 117.5, 117.6, 117.7, 121.7, 122.1, 123.4, 134.7, 135.1, 142.3 and 143.2 2 (Ar–***C***); 182.4 (2-***C***–Pd).

Synthesis of dibromo-bis[1-(2-ethoxyethyl)-3-(2-methyl-1,4-benzodioxan) benzimidazol-2-ylidene]palladium(II), 1d

Using the same method for the synthesis of complex **1a**, the **1d** complex was prepared from bromo[1-(2-ethoxyethyl)-3-(2-methyl-1,4-benzodioxan)benzimidazol-2-ylidene]silver(I) (263 mg 0.50 mmol) and bis(benzonitrile)palladium(II) chloride [PdCl$_2$(PhCN)$_2$] (95 mg·0.25 mmol). Yield: 81% (234 mg). Anal. Calc.

for $C_{40}H_{44}N_4O_6PdBr_2$: C: 50.95, H: 4.70, N: 5.95. Found: C: 50.89, H: 4.68, N: 6.01. ^{1}H NMR (300 MHz, DMSO-d$_6$) δ (ppm) = 1.06 (t, 6H, –CH$_2$CH$_2$OCH$_2$C$\textbf{\textit{H}}_3$, J: 6.9 Hz); 3.48 (m 4H, –CH$_2$CH$_2$OC$\textbf{\textit{H}}_2$CH$_3$); 4.13 (m, 4H, –CH$_2$C$\textbf{\textit{H}}_2$OCH$_2$CH$_3$); 4.48 (m, 4H, –NC$\textbf{\textit{H}}_2$CHOCH$_2$–); 4.71 (m, 4H, –C$\textbf{\textit{H}}_2$CH$_2$OCH$_2$CH$_3$); 5.20 (d, 4H, –OCHC$\textbf{\textit{H}}_2$O– J: 4.6 Hz); 5.40 (m, 2H, –CH$_2$C$\textbf{\textit{H}}$OCH$_2$–); 6.82–7.78 (m, 16H, Ar–$\textbf{\textit{H}}$). ^{13}C NMR (75.47 MHz, DMSO-d$_6$) δ (ppm) = 15.3 (–CH$_2$CH$_2$OCH$_2$$\textbf{\textit{C}}H_3$); 35.9 (–CH$_2$$\textbf{\textit{C}}H_2OCH_2CH_3$); 47.5 (O$\textbf{\textit{C}}H_2$CH(CH$_2$)O); 53.6 (–CH$_2$$\textbf{\textit{C}}H_2OCH_2CH_3$); 66.3 (OCH$_2$CH($\textbf{\textit{C}}H_2$)O); 72.3 (–$\textbf{\textit{C}}H_2CH_2OCH_2CH_3$); 73.2 (OCH$_2$$\textbf{\textit{C}}$H(CH$_2$)O); 111.7, 112.2, 117.6, 117.8, 122.1, 122.3, 123.7, 134.8, 142.7 and 143.3 (Ar–$\textbf{\textit{C}}$); 182.0 (2-$\textbf{\textit{C}}$–Pd).

Synthesis of dichloro-bis[1-benzyl-3-(2-methyl-1,4-benzodioxan)benzimidazol-2-ylidene]palladium(II), 1e

Using the same method for the synthesis of complex **1a**, the **1e** complex was prepared from chloro[1-benzyl-3-(2-methyl-1,4-benzodioxan)benzimidazol-2-ylidene]silver(I) (250 mg·0.50 mmol) and bis(benzonitrile)palladium(II) chloride [PdCl$_2$(PhCN)$_2$] (95 mg·0.25 mmol). Yield: 86% (190 mg). Anal. Calc. for $C_{46}H_{40}N_4O_4PdCl_2$: C: 62.07, H: 4.53, N: 6.29. Found: C: 62.11, H: 4.56, N: 6.32. ^{1}H NMR (300 MHz, DMSO-d$_6$) δ (ppm) = 4.05 (d, 4H, –NC$\textbf{\textit{H}}_2$CHOCH$_2$– J: 9.9 Hz); 4.57 (d, 4H, –OCHC$\textbf{\textit{H}}_2$O– J: 9.9 Hz); 4.93 (m, 2H, –CH$_2$C$\textbf{\textit{H}}$OCH$_2$–); 5.21 (s, 4H, –NC$\textbf{\textit{H}}_2$C$_6$H$_5$); 6.68–7.67 (m, 26H, Ar–$\textbf{\textit{H}}$). ^{13}C NMR (75.47 MHz, DMSO-d$_6$) δ (ppm) = 48.1 (O$\textbf{\textit{C}}$H$_2$CH(CH$_2$)O); 52.5 (–$\textbf{\textit{C}}$H$_2$C$_6$H$_5$); 65.1 (OCH$_2$CH($\textbf{\textit{C}}$H$_2$)O); 72.6 (OCH$_2$$\textbf{\textit{C}}$H(CH$_2$)O); 111.1, 117.3, 117.7, 121.5, 121.9, 122.2, 123.5, 127.4, 127.8, 128.2, 128.7, 129.1, 133.9, 134.1, 135.2, 135.4, 142.3 and 143.2 (Ar–$\textbf{\textit{C}}$); 182.5(2-$\textbf{\textit{C}}$–Pd).

Synthesis of dichloro-bis[1-(4-methylbenzyl)-3-(2-methyl-1, 4-benzodioxan) benzimidazol-2-ylidene]palladium(II), 1f

Using the same method for the synthesis of complex **1a**, the **1f** complex was prepared from chloro[1-(4-methylbenzyl)-3-(2-methyl-1,4-benzodioxan)benzimidazol-2-ylidene]silver(I) (257 mg·0.50 mmol) and bis(benzonitrile)palladium(II) chloride [PdCl$_2$(PhCN)$_2$] (95 mg·0.25 mmol). Yield: 90% (207 mg). Anal. Calc. for $C_{48}H_{44}N_4O_4PdCl_2$: C: 62.79, H: 4.83, N: 6.10. Found: C: 62.82, H: 4.79, N: 6.12. ^{1}H NMR (300 MHz, DMSO-d$_6$) δ (ppm) = 2.29 (s, 6H, –CH$_2$C$_6$H$_4$(C$\textbf{\textit{H}}_3$)); 4.06 (d, 4H, –NC$\textbf{\textit{H}}_2$CHOCH$_2$– J: 10.8 Hz); 4.52 (m, 2H, –CH$_2$C$\textbf{\textit{H}}$OCH$_2$–); 4.96 (d, 4H, –OCHC$\textbf{\textit{H}}_2$O– J: 10.8 Hz); 5.33 (s, 4H, –NC$\textbf{\textit{H}}_2$C$_6$H$_4$(CH$_3$); 6.32–7.59 (m, 24H, Ar–$\textbf{\textit{H}}$). ^{13}C NMR (75.47 MHz, DMSO-d$_6$) δ (ppm) = 21.2 (–CH$_2$C$_6$H$_4$($\textbf{\textit{C}}$H$_3$)); 48.1 (O$\textbf{\textit{C}}$H$_2$CH(CH$_2$)O); 53.3 (–$\textbf{\textit{C}}$H$_2$C$_6$H$_4$(CH$_3$)); 65.8 (OCH$_2$CH($\textbf{\textit{C}}$H$_2$)O); 72.8 (OCH$_2$$\textbf{\textit{C}}$H(CH$_2$)O); 111.1, 117.3 117.7, 121.5, 121.7, 122.1, 123.3, 129.4, 129.7, 132.2,

133.9, 134.2, 135.4, 137.5, 142.2 and 143.2 (Ar–$\textbf{\textit{C}}$); 182.3 (2-$\textbf{\textit{C}}$–Pd).

Synthesis of dichloro-bis[1-(2,4,6-trimethylbenzyl)-3-(2-methyl-1,4-benzodioxan) benzimidazol-2-ylidene] palladium(II), 1g

Using the same method for the synthesis of complex **1a**, the **1g** complex was prepared from chloro[1-(2,4,6-trimethylbenzyl)-3-(2-methyl-1,4-benzodioxan)benzimidazol-2-ylidene]silver(I) (271 mg·0.50 mmol) and bis(benzonitrile)palladium(II) chloride [PdCl$_2$(PhCN)$_2$] (95 mg·0.25 mmol). Yield: 80% (195 mg). Anal. Calc. for $C_{52}H_{52}N_4O_4PdCl_2$: C: 64.10, H: 5.38, N: 5.75. Found: C: 64.08, H: 5.35, N: 5.77. ^{1}H NMR (300 MHz, DMSO-d$_6$) δ (ppm) = 2.31 and 2.41 (s, 18H, –CH$_2$C$_6$H$_2$(C$\textbf{\textit{H}}_3$)$_3$); 4.50 (d, 4H, –OCHC$\textbf{\textit{H}}_2$O– J: 6.6 Hz); 5.23 (d, 4H, –NC$\textbf{\textit{H}}_2$CHOCH$_2$– J: 9.9 Hz); 5.32 (s, 4H, –C$\textbf{\textit{H}}_2$C$_6$H$_2$(CH$_3$)$_3$), 5.48 (m, 2H, –CH$_2$C$\textbf{\textit{H}}$OCH$_2$–); 6.03–7.51 (m, 20H, Ar–$\textbf{\textit{H}}$). ^{13}C NMR (75.47 MHz, DMSO-d$_6$) δ (ppm) = 21.0 and 21.2 (–CH$_2$C$_6$H$_2$($\textbf{\textit{C}}$H$_3$)$_3$); 47.9 (O$\textbf{\textit{C}}$H$_2$CH(CH$_2$)O); 51.1 (–$\textbf{\textit{C}}$H$_2$C$_6$H$_2$(CH$_3$)$_3$); 65.1 (OCH$_2$CH($\textbf{\textit{C}}$H$_2$)O); 72.3 (OCH$_2$$\textbf{\textit{C}}$H(CH$_2$)O); 110.4, 111.7, 112.1, 117.3, 117.7, 121.5, 121.9, 122.2, 122.9, 123.3, 127.8, 129.7, 134.5, 135.3, 138.6, 138.8, 142.3 and 143.2 (Ar–$\textbf{\textit{C}}$); 182.4 ($\textbf{\textit{C}}$–Pd).

Synthesis of dichloro-bis[1-(2-methyl-1,4-benzodioxan)-3-(4-vinylbenzyl)benzimidazol-2-ylidene] palladium(II), 1h

Using the same method for the synthesis of complex **1a**, the **1h** complex was prepared from chloro[1-(2-methyl-1,4-benzodioxan)-3-(4-vinylbenzyl)benzimidazol-2-ylidene] silver(I) (263 mg·0.50 mmol) and bis(benzonitrile) palladium(II) chloride [PdCl$_2$(PhCN)$_2$] (95 mg·0.25 mmol). Yield: 84% (198 mg). Anal. Calc. for $C_{50}H_{44}N_4O_4PdCl_2$: C: 63.74, H: 4.71, N: 5.95. Found: C: 63.76, H: 4.74, N: 5.92. ^{1}H NMR (300 MHz, DMSO-d$_6$) δ (ppm) = 4.07 (d, 4H, –NC$\textbf{\textit{H}}_2$CHOCH$_2$– J: 7.2 Hz); 4.32 (m, 2H, –CH$_2$C$\textbf{\textit{H}}$OCH$_2$–); 4.57 (d, 4H, –OCHC$\textbf{\textit{H}}_2$O– J: 7.2 Hz); 5.23 and 5.75 (d, 4H, CH$_2$C$_6$H$_4$CH=C$\textbf{\textit{H}}_2$, J: 7.5 Hz); 5.84 (s, 4H, C$\textbf{\textit{H}}_2$C$_6$H$_4$CH=CH$_2$); 6.60 (dd, 2H, C$_6$H$_4$C$\textbf{\textit{H}}$=CH$_2$, J: 7.5 Hz); 6.74–7.67 (m, 24H, Ar–$\textbf{\textit{H}}$). ^{13}C NMR (75.47 MHz, DMSO-d$_6$) δ (ppm) = 48.3 (O$\textbf{\textit{C}}$H$_2$CH(CH$_2$) O); 51.4 (–$\textbf{\textit{C}}$H$_2$C$_6$H$_4$CH=CH$_2$); 65.4 (OCH$_2$CH($\textbf{\textit{C}}$H$_2$)O); 71.6 (OCH$_2$$\textbf{\textit{C}}$H(CH$_2$)O); 111.3, 113.8, 115.2, 117.5, 117.8, 123.5, 126.6, 126.8, 127.1, 127.8, 128.2, 128.7, 131.1, 132.2, 135.9, 136.3 and 138.4 (Ar–$\textbf{\textit{C}}$ and –$\textbf{\textit{C}}$H=$\textbf{\textit{C}}$H$_2$); 182.1 (2-$\textbf{\textit{C}}$–Pd).

Results and discussion

### Synthesis of bis(NHC)PdX$_2$ synthetic route complexes (1a–h)

The parent 2-methyl-1,4-benzodioxan-substituted bis(NHC)PdX$_2$ complexes **1a–h** were synthesized using the common silver carbene transfer method. The silver complexes were directly used for transmetalation to palladium(II) in a 2/1 ratio to afford the desired bis(NHC) PdX$_2$ complexes which have been illustrated in Scheme 1. The bis(NHC)PdX$_2$ complexes **1a–h** were prepared by mixing [PdCl$_2$(PhCN)$_2$] with 0.5 equivalents of chloro(or bromo)[1-alkyl(or aryl)-3-(2-methyl-1,4-benzodioxan) benzimidazol-2-ylidene]silver(I) in dichloromethane (20 mL), then the reaction mixture was stirred at room temperature for 24 h in dark conditions. The bis(NHC) PdX$_2$ complexes were obtained as a light yellow and white solid in 79–89% yield. The air- and moisture-stable bis(NHC)PdX$_2$ complexes were soluble in solvents such as dimethylformamide and dimethylsulfoxide. The bis(NHC)PdX$_2$ complexes were less soluble in halogens such as chloroform and dichloromethane. The formation of the 2-methyl-1,4-benzodioxan-substituted complexes was confirmed by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopic methods and elemental analysis techniques. These spectra are consistent with the proposed formulate. This condition indicated the successful transmetallation and confirmed the formation of the expected bis(NHC)PdX$_2$ complexes. In the ^{13}C NMR spectra, the Pd-C$_{carbene}$ resonances of this bis(NHC)PdX$_2$ complexes in the ^{13}C NMR spectra appeared highly downfield when it shifted at δ 181.8, 181.60, 181.4, 182.0, 182.5, 182.3, 182.4, and 182.1 ppm for **1a–h**, respectively. The results of the elemental analysis, which is one of the most analytical techniques used to prove the synthesis of compounds, were evaluated and it was observed that the calculated values were very close to the found values. The FT-IR data clearly indicated the presence of ν(CN) at 1452, 1444, 1455, 1454, 1445, 1447, 1445, and 1447 cm^{-1} for the bis(NHC)PdX$_2$ complexes (**1a–i**), respectively. Crystallographic and physical data of all compounds are summarized in Table 1.

Proposed catalytic cycle for bis(NHC)PdX$_2$ complexes

The proposed general catalytic pathway is shown in Scheme 2. In this cycle, first the oxidative addition of the aryl halide to the pre-activated bis(NHC)PdX$_2$ complex takes place. It is believed that oxidative addition occurs more readily in the presence of the NHC complex thanks to strong sigma donor properties [39, 40]. Then, the ligand exchange occurs with the effect of the base. The character of the base in this step has important due to both oxidative addition and reductive elimination. Then, the 2-substituted furan/thiophene molecule is added to the complex. In this

Scheme 1 Synthesis of 2-methyl-1,4-benzodioxan-substituted bis(NHC)PdX$_2$ complexes **1a–h**
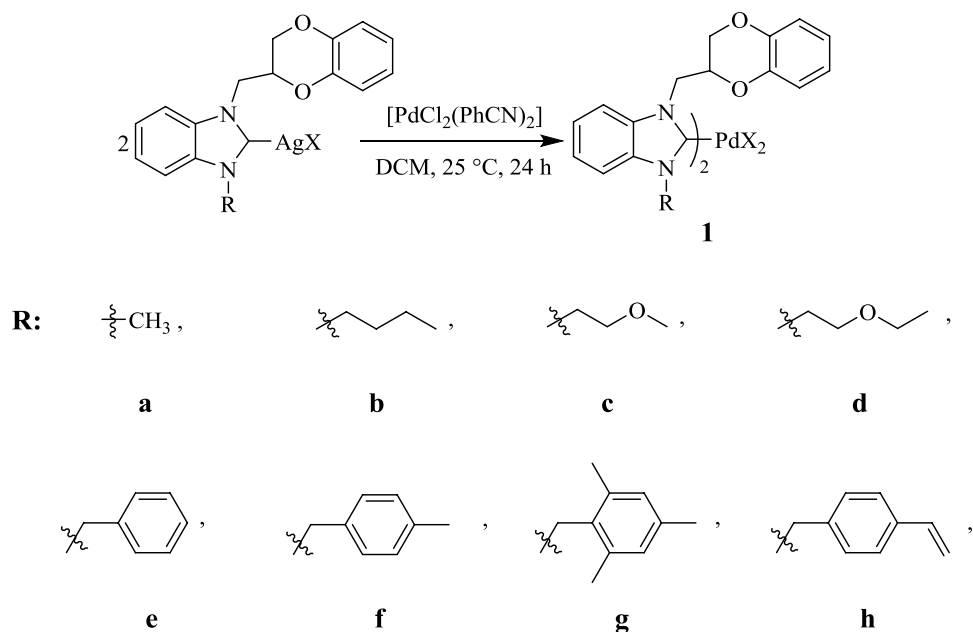
X: Cl, Br

Table 1 Physical properties of compounds and their results of spectroscopic analysis

Compound	Formula	Yield (%)	m.p. (°C)	^{13}C 2-C–Pd (δ)	IR: $\nu_{(CN)}$ (cm^{-1})
1a	$C_{34}H_{32}N_4O_4PdBr_2$	84	280–282	181.8	1452
1b	$C_{40}H_{44}N_4O_4PdBr_2$	79	221–223	181.6	1444
1c	$C_{38}H_{40}N_4O_6PdBr_2$	87	232–234	181.4	1455
1d	$C_{40}H_{44}N_4O_6PdBr_2$	81	234–236	182.0	1454
1e	$C_{46}H_{40}N_4O_4PdCl_2$	86	237–238	182.5	1445
1f	$C_{48}H_{44}N_4O_4PdCl_2$	90	146–147	182.3	1447
1g	$C_{52}H_{52}N_4O_4PdCl_2$	80	288–289	182.4	1445
1h	$C_{50}H_{44}N_4O_4PdCl_2$	84	230–231	182.1	1447
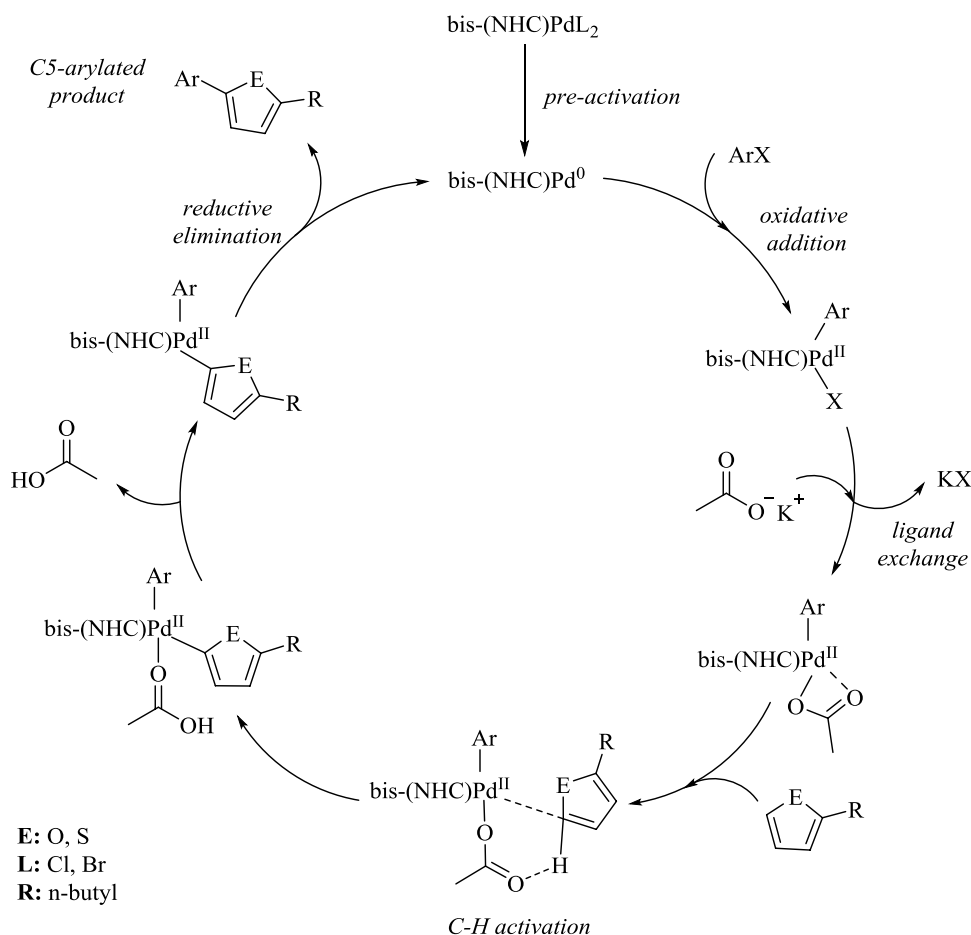
Scheme 2 Proposed catalytic cycle for the direct C–H bond arylation for bis(NHC)PdX$_2$ complexes

step, activation of C–H occurs at position 5. In the course of C–H activation, the NHC ligand contributes to stabilizing of the occurring complex. Lastly, C5-arylated furan/thiophene product has been obtained by the result of reductive elimination. In this step, the steric bulk of the bis(NHC)PdX$_2$ complex facilitates elimination of arylated furan/thiophene product.

In the bis(NHC)PdX$_2$ complexes, the electronic properties provided by the alkyl substituents attached to the N atom provide the stability of the complex in the catalytic cycle, while the steric bulk of the ligand facilitating reductive elimination in the catalytic cycle. Therefore, we used ligands with different electronic and steric properties on the bis(NHC)PdX$_2$ complexes.

General method for direct arylation of furan and thiophene with aryl halides

The heteroaryl derivatives (2-*n*-butylfuran, 2-*n*-butylthiophene and 2-isopropylthiazole) (2 mmol), the aryl halide derivatives (4-chloroacetophenone, 4-chloroanisole, 4-iodotoluene, 4-bromoacetophenone, 4-bromoanisole, 4-bromotoluene and 4-bromobenzene) (1 mmol), KOAc (1 mmol) and bis(NHC)PdX$_2$ complexes **1a–h** (0.003 mmol) were dissolved in *N,N*-dimethylacetamide (DMAc) (2 mL) in a small Schlenk tube under argon as described in the literature [9]. The reaction mixture was stirred in an oil bath at 130 °C for 1 h, and then was cooled to room temperature and the solvent was removed under vacuum. The obtained 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 purity of the compounds was checked by gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS). Conversions were calculated by taking into account the conversion of aryl bromides to products.

Direct arylation of 2-*n*-butylfuran, 2-*n*-butylthiophene and 2-isopropylthiazole with various aryl bromides

We performed some experiments for the parameters of direct arylation reaction of para-substituted aryl bromides with 2-*n*-butylfuran, 2-*n*-butylthiophene and 2-isopropylthiazole (for **1a–d**) in the presence of **1a–h** as catalyst. Conversions of the products for 2-*n*-butylfuran are between 59 and 99%, for 2-*n*-butylthiophene are between 74 and 98%, and for 2-isopropylthiazole are between 76 and 99% (Tables 2, 3, 4).

First, we examined the coupling of 2-*n*-butylfuran with 4-bromoacetophenone, 4-bromoanisole, 4-bromotoluene, and 4-bromobenzene using complexes **1a–h** as the catalyst. When the effect of **1a–h** in the formation of the products **2, 3, 4** and **5** was analyzed, conversions of 86–99%, 59–96%, 75–93% and 73–96% were observed, respectively (Table 2). In the case of using 2-*n*-butylfuran with 4-bromoacetophenone and 4-bromobenzene, the desired coupling product is obtained in a better conversion, whereas when the 2-*n*-butylfuran was used with 4-bromoanisole and 4-bromotoluene, the desired coupling product is obtained in a lower conversion (Table 2). In general, the conversion at the reaction that used groups containing the electron donating substrates is lower, while the conversion at the reaction that used groups

containing the electron withdrawing substrates is higher (Table 2).

Second, we examined the coupling of 2-*n*-butylthiophene with 4-bromoacetophenone, 4-bromoanisole, 4-bromotoluene and 4-bromobenzene with complexes **1a–h** as the catalyst. When the effect of **1a–h** in the formation of product **6, 7, 8** and **9** was analyzed, conversions of 89–98%, 75–97%, 74–96% and 89–98% were observed, respectively (Table 3). The use of 4-bromoacetophenone with 2-*n*-butylthiophene gave the desired coupling product for different complexes (**1c** and **1d**) as catalysts in better conversion than the others, such as 98 and 98%, respectively (Table 3). The use of 4-bromobenzene with 2-*n*-butylthiophene gave the desired coupling product for different complexes (**1a** and **1c**) as catalysts in better excellent conversion than the others, such as 98% and 99%, respectively (Table 3). The 2-*n*-butylthiophene was bound with 4-bromoanisole to give the arylated products **7** in less conversions. When 4-bromoacetophenone, 4-bromotoluene and 4-bromobenzene with 2-*n*-butylthiophene were utilized in the direct arylation reaction, conversions of the products (**6, 8** and **9**) were obtained and observed to be better than the product **7** (Table 3).

Then, we investigated the coupling of 2-isopropylthiazole with 4-bromoacetophenone, 4-bromoanisole, 4-bromotoluene and 4-bromobenzene with complexes **1a–d** as the catalyst. When the effect of **1a–d** in the formation of product **10, 11, 12** and **13** was analyzed, conversions of 98–99%, 85–92%, 80–94% and 76–98% were observed, respectively (Table 4). The use of 4-bromoacetophenone with 2-isopropylthiazole gave the desired coupling product for all complexes **1a–d** as catalysts in better excellent conversion than the others, such as 99%, 98%, 99%, and 99%, respectively (Table 4). When 4-bromoacetophenone, 4-bromotoluene and 4-bromobenzene with 2-isopropylthiazole were utilized in the direct arylation reaction, conversions of the products (**10, 11** and **12**) were obtained and observed to be better than the product **13** (Table 4). The 2-isopropylthiazole was bound with 4-bromoanisole to give the arylated products **13** in less conversions (Table 4).

Then, we used the chloride substrates, which are more difficult to bind than the bromide substrates. We examined the catalytic activities of 4-chloroacetophenone and 4-chloroanisole substrates in the presence 2-*n*-butylfuran and 2-*n*-butylthiophene with catalysts **1d** and **1h** at 16 h and 130 °C. As expected from the experiment, the conversions of coupling of 4-chloroacetophenone with 2-*n*-butylfuran and 2-*n*-butylthiophene (product 2 and 6) are higher than the

Table 2 Bis(NHC) PdX$_2$ complexes (**1a–h**) catalyzed direct arylation of 2-*n*-butylfuran using aryl bromides
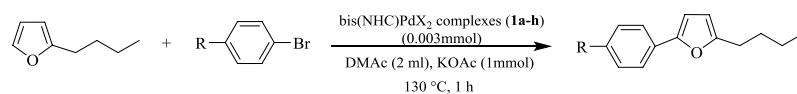
Entry	R	Pd(II)NHC	Product	% Conv.
1		1a		95
2		1b		86
3		1c		92
4	-COCH$_3$	1d		99
5		1e		95
6		1f	**2**	86
7		1g		92
8		1h		92
9		1a		96
10		1b		64
11		1c		92
12	-OCH$_3$	1d		59
13		1e		96
14		1f		64
15		1g	**3**	70
16		1h		59
17		1a		79
18		1b		82
19		1c		75
20		1d		81
21	-CH$_3$	1e		93
22		1f	**4**	82
23		1g		82
24		1h		75
25		1a		96
26		1b		91
27		1c		87
28	-H	1d		73
29		1e		87
30		1f	**5**	89
31		1g		88
32		1h		90

Reaction conditions 2-*n*-butylfuran (2 mmol), aryl bromide (1 mmol), bis(NHC)PdX$_2$ complexes (**1a–h**) (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 aryl bromide

Table 3 Bis(NHC) PdX$_2$ complexes (**1a–h**) catalyzed direct arylation of 2-*n*-butylthiophene using aryl bromides
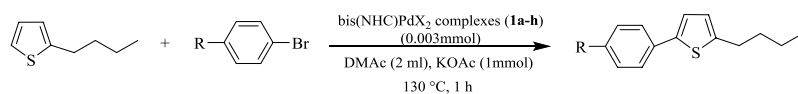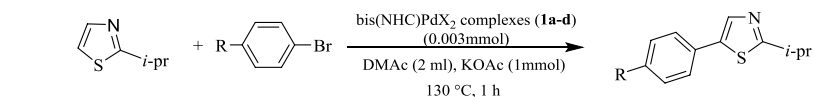

Entry	R	Pd(II)NHC	Product	% Conv.
1		1a		93
2		1b		93
3		1c		98
4	-COCH$_3$	1d	**6**	98
5		1e		93
6		1f		93
7		1g		91
8		1h		89
9		1a		97
10		1b		96
11		1c		82
12	-OCH$_3$	1d	**7**	91
13		1e		75
14		1f		96
15		1g		82
16		1h		91
17		1a		96
18		1b		91
19		1c		74
20		1d		92
21	-CH$_3$	1e	**8**	94
22		1f		91
23		1g		96
24		1h		90
25		1a		97
26		1b		98
27		1c		89
28	-H	1d	**9**	98
29		1e		96
30		1f		97
31		1g		96
32		1h		95

Reaction conditions 2-*n*-butylthiophene (2 mmol), aryl bromide (1 mmol), bis(NHC)PdX$_2$ (**1a–h**) (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 aryl bromide

Table 4 Bis(NHC) PdX$_2$ complexes (**1a–d**) catalyzed direct arylation of 2-isopropylthiazole using aryl bromides

Reaction scheme: 2-isopropylthiazole + R–C$_6$H$_4$–Br, bis(NHC)PdX$_2$ complexes (**1a-d**) (0.003 mmol), DMAc (2 ml), KOAc (1 mmol), 130 °C, 1 h → arylated product

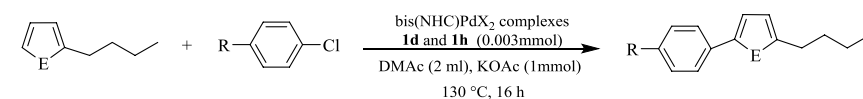| Entry	R	Pd(II)NHC	Product	% Conv.
1		1a		99
2	-COCH$_3$	1b		98
3		1c	**10**	99
4		1d		99
5		1a		90
6	-OCH$_3$	1b		85
7		1c	**11**	90
8		1d		92
9		1a		94
10	-CH$_3$	1b		80
11		1c	**12**	90
12		1d		85
13		1a		83
14	-H	1b		76
15		1c	**13**	87
16		1d		98

Reaction conditions 2-isopropylthiazole (2 mmol), aryl bromide (1 mmol), bis(NHC)PdX$_2$ (**1a–d**) (0.003 mmol), KOAc (1 mmol), DMAc (2 mL), 130 °C, 1 h, product purity was checked by GC, conversions were calculated according to aryl bromide

conversions of coupling of 4-chloroanisol with 2-*n*-butyl-furan and 2-*n*-butylthiophene (product 3 and 7) (Table 5). The use of catalyst **1h** that containing aromatic substituent gave the desired coupling product in better conversion than the catalyst **1d** that containing the aliphatic substituent. We can say reductive elimination may be easier for aromatic compounds. However, 4-iodotoluene, which easily bonded with 2-*n*-butylfuran and 2-*n*-butylthiophene (product 4 and 8) was obtained at low temperature (80 °C) and in a short time (30 min) in the high conversion (Table 6). All the above catalytic studies, when compared with the similar studies in the recent [31, 35, 39–41], the bis(NHC)PdX$_2$ **1a–h** complexes appeared to be highly active catalysts in direct arylation reactions.

Conclusions

Conclusively, we reported the synthesis of the 2-methyl-1,4-benzodioxan-substituted bis(NHC)PdX$_2$ complexes **1a–h**. The bis(NHC)PdX$_2$ **1a–h** complexes were prepared from the Ag(I)NHC complexes via transmetallation method. The catalytic activity of this 2-methyl-1,4-benzodioxan-sub-stituted bis(NHC)PdX$_2$ complexes have been investigated as they are more efficient and stable catalysts for the direct arylation reactions of 2-*n*-butylfuran 2-*n*-butylthiophene and 2-isopropylthiazole with aryl halide.

Table 5 Bis(NHC)PdX$_2$ complex (**1d** and **1 h**) catalyzed direct arylation of 2-*n*-butylfuran and 2-*n*-butylthiophene using aryl chlorides

Entry	R	E	Pd(II)NHC	Product	% Conv.
1	-COCH$_3$	O	**1d**	**2**	93
2		O	**1h**		96
3	-OCH$_3$	O	**1d**	**3**	75
4		O	**1h**		81
5	-COCH$_3$	S	**1d**	**6**	90
6		S	**1h**		94
7	-OCH$_3$	S	**1d**	**7**	71
8		S	**1h**		77

Table 6 Bis(NHC)PdX$_2$ complex (**1d** and **1 h**) catalyzed direct arylation of 2-*n*-butylfuran and 2-*n*-butylthiophene using 4-iodotoluene
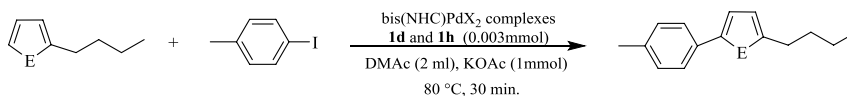
Entry	E	Pd(II)NHC	Product	% Conv.
1	O	**1d**	**4**	98
2	O	**1h**		99
3	S	**1d**	**8**	96
4	S	**1h**		99

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