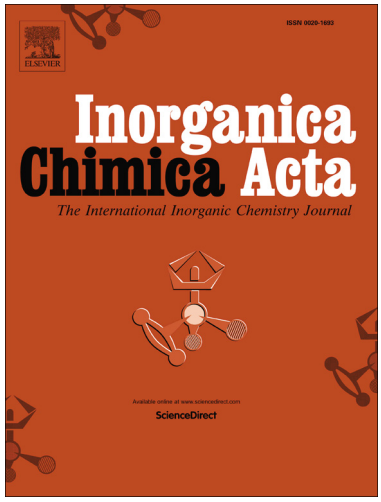

Research paper

New 4-vinylbenzyl-substituted bis(NHC)-Pd(II) complexes: Synthesis, characterization and the catalytic activity in the direct arylation reaction.

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New 4-vinylbenzyl-substituted bis(NHC)-Pd(II) complexes: Synthesis, characterization and the catalytic activity in the direct arylation reaction.

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Abstract

This study contains the synthesis of the new 4-vinylbenzyl substituted bis(NHC)-Pd(II) complexes and their catalytic activity in direct arylation reaction. The bis(NHC)-Pd(II) complexes have been prepared from Ag(I)NHC complexes by transmetallation method. The complexes have been characterized by using ^{1}H NMR, ^{13}C NMR, FTIR spectroscopy and elemental analysis techniques. Also, all the complexes showed excellent activity as catalysts in the direct arylation reaction.

Keywords: *N*-Heterocyclic carbenes; bis(NHC)-Pd(II) complexes; Direct arylation; Butylfuran; Butylthiophene; 2-isopropylthiazole.

Introduction

The N-heterocyclic carbenes (NHCs) are one of the most important ligands for metal-catalyzed reactions. NHCs have had unique properties such as stability to air and moisture, adjustability as electronically and sterically, and being strong σ-donor and weak π-acceptor [1-7]. Increasing the popularity of these ligands in organic and organometallic chemistry is due to the durability of the metal-carbene bond, as well as having thermal and oxidative stability [8, 9].

The metal-carbene complexes involving a wide variety of transition metals such as Au(I), Cu(I), Cu(II), Ni(II), Pd(II), Pt(II), Rh(I), Rh(III), Ir(I), Ir(III), Ru(II), Ru(III), and Ru(IV) are easily synthesized by the transmetalation method of the transfer agent Ag(I)NHC complexes [10-12]. Also, Pd-NHC complexes are easily synthesized by this method. In recent years, there have been numerous studies published in which Pd-NHC complexes are used as

active catalysts [13-15]. In particular, palladium-carbene complexes derived from imidazolium and benzimidazolium salts have been successfully synthesized as highly active catalysts in a wide variety of organic transformations including cross-coupling reactions of Suzuki, Kumada, Hiyama, Stille, Negishi, and Sonogashira [16-19].

In recent years some outstanding studies on the direct arylation reaction (C-H activation) of bis(NHC)-Pd(II) complexes have been published [20-24]. These studies have showed that the bis(NHC)-Pd(II) complexes exhibit very good catalytic activity. In our study, we have investigated the synthesis and the characterization of new bis(NHC)-Pd(II) complexes. Also, we investigated the catalytic activities of new bis(NHC)-Pd(II) complexes in direct arylation reactions, and they showed fairly good activity as catalysts in the direct arylation reaction.

Experimental

All synthesis involving bis(NHC)-Pd(II) 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 commercially available by 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 Perkin Elmer Spectrum 100 FT-IR spectrometer. Proton (^1H) and Carbon (^{13}C) NMR spectra were recorded using either a Bruker AS 300 Merkur spectrometer operating at 300 MHz (^1H), 75.47 MHz (^{13}C) in DMSO-d_6 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 of bis[1-methyl-3-(4-vinylbenzyl)benzimidazol-2-ylidene]dichloropalladium(II), 1a

To a solution of bis(benzonitrile)palladium(II) chloride [$PdCl_2(PhCN)_2$] (100 mg. 0.26 mmol) in dichloromethane (20 mL) was added chloro[1-methyl-3-(4-vinylbenzyl)benzimidazol-2-ylidene]silver(I) (204 mg. 0.52 mmol). The reaction mixture was stirred for 24 h at room temperature in the dark conditions. Then filtered through celite and the solvents were evaporated under vacuum to afford the product as a light yellow solid. The crude product was recrystallized from dichloromethane/diethyl ether (1:3) at room temperature. Yield: 85 % (145 mg). m.p: 206-207 ^{0}C; $\nu_{(CN)}$: 1446 cm^{-1}. Anal. Calc. for $C_{34}H_{22}N_4PdCl_2$: C: 60.59, H: 4.79, N: 8.31. Found: C:60.42, H:4.89, N:8.26. ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm) = 4.49 (s, 6H, C***H*****$_3$**); 5.25 and 5.96 (d, 4H, $CH_2C_6H_4CH$=C***H*****$_2$**, *J*: 10.8 Hz); 6.22 (s, 4H, C***H*****$_2$**C_6H_4CH=CH_2); 6.65 (dd, 2H, C_6H_4C***H***=CH_2, *J*: 4.5 Hz); 7.13-7.93 (m, 16H, Ar-***H***). ^{13}C NMR (75.47 MHz, DMSO-d_6) δ (ppm) = 34.7 (-***C***H_3); 51.2 (-***C***$H_2C_6H_4CH$=CH_2); 110.2, 111.2, 113.9, 114.2, 114.8, 123.1, 125.5, 126.0, 126.5, 126.7, 127.4, 127.7, 128.1, 128.8, 134.1, 135.3, 135.9, 136.4, 137.0, 138.3 (Ar-***C*** and -***C***H=***C***H_2); 181.5 (2-***C***-Pd).

Synthesis of bis[1-ethyl-3-(4-vinylbenzyl)benzimidazol-2-ylidene]dichloropalladium(II), 1b

The synthesis of **1b** was carried out in the same way as that described for **1a**, but chloro[1-ethyl-3-(4-vinylbenzyl)benzimidazol-2-ylidene]silver(I) (210 mg. 0.52 mmol) was used instead of chloro[1-methyl-3-(4-vinylbenzyl)benzimidazol-2-ylidene]silver(I). Yield: 81% (148 g). m.p.: 198-200 ^{0}C; $\nu_{(CN)}$: 1443 cm^{-1}. Anal. Calc. for $C_{36}H_{36}N_4PdCl_2$ C: 61.59, H: 5.17, N: 7.98. Found: C: 61.48, H: 5.11, N: 8.03. ^{1}H NMR (300MHz, DMSO-d_6) δ (ppm) = 1.07 (t, 6H, -CH_2C***H*****$_3$**, J: 4.2 Hz); 5.26 (m, 4H, -C***H*****$_2$**CH_3); 6.18 (s, 4H, -C***H*****$_2$**C_6H_4CH=CH_2); 5.15 and 5.87 (m, 4H, -$CH_2C_6H_4CH$=C***H*****$_2$**); 6.25 (dd, 2H, $CH_2C_6H_4C$***H***=CH_2 J: 10.2 Hz); 6.65-7.98 (m, 16H, Ar-***H***). ^{13}C NMR (75.47 MHz, DMSO-d_6) δ (ppm) = 15.7 (-CH_2***C***H_3); 51.2 (-***C***H_2CH_3); 56.5 (-***C***$H_2C_6H_4CH$=CH_2); 111.4, 111.9, 114.9, 115.1, 123.6, 126.6, 126.8, 128.6, 133.7, 136.2 and 137.1. (Ar-***C*** and -***C***H=***C***H_2); 181.3 (2-**C**-Pd).

Synthesis of bis[1-butyl-3-(4-vinylbenzyl)benzimidazol-2-ylidene]dichloropalladium(II), 1c

The synthesis of **1c** was carried out in the same way as that described for **1a**, but chloro[1-butyl-3-(4-vinylbenzyl)benzimidazol-2-ylidene]silver(I) (225 mg. 0.52 mmol) was used

instead of chloro[1-methyl-3-(4-vinylbenzyl)benzimidazol-2-ylidene]silver(I). Yield: 83% (164 mg). m.p: 211-212 ^{0}C; $\nu_{(CN)}$: 1445 cm^{-1}. Anal. Calc. for $C_{40}H_{44}N_4PdCl_2$: C: 51.25, H: 4.95, N: 5.98. Found: C: 51.28, H: 4.91, N: 5.99. ^{1}H NMR (300MHz, DMSO-d_6) δ (ppm) = 0.70 (t, 6H, -$CH_2CH_2CH_2CH_3$, *J*: 4.5 Hz); 1.53 (m, 4H, -$CH_2CH_2CH_2CH_3$); 2.31 (m, 4H, -$CH_2CH_2CH_2CH_3$); 5.23 (t, 4H, -$CH_2CH_2CH_2CH_3$ *J*: 6.0 Hz); 5.82 and 6.01 (m, 4H, $CH_2C_6H_4CH=CH_2$); 6.21 (s, 4H, -$CH_2C_6H_4CH=CH_2$); 6.62 (dd, 2H, -$CH_2C_6H_4CH=CH_2$ *J*: 10.4 Hz); 7.22-7.81 (m, 16H, Ar-***H***). ^{13}C NMR (75.47 MHz, DMSO-d_6) δ (ppm) = 14.3 (-$CH_2CH_2CH_2CH_3$); 20.3 (-$CH_2CH_2CH_2CH_3$); 32.4 (-$CH_2CH_2CH_2CH_3$); 51.3 (-$CH_2CH_2CH_2CH_3$); 55.4 (-$CH_2C_6H_4CH=CH_2$); 111.5, 114.8, 123.5, 123.7, 124.6, 128.7, 133.4, 133.6, 134.4, 136.1 and 137.2 (Ar-***C*** and -***C***H=***C***H_2); 181.6 (2-**C**-Pd).

Synthesis of bis[1-(2-methoxyethyl)-3-(4-vinylbenzyl)benzimidazol-2-ylidene]dichloro palladium(II), 1d

The synthesis of **1d** was carried out in the same way as that described for **1a**, but chloro[1-(2-methoxyethyl)-3-(4-vinylbenzyl)benzimidazol-2-ylidene]silver(I) (227 mg. 0.52 mmol) was used instead of chloro[1-methyl-3-(4-vinylbenzyl)benzimidazol-2-ylidene]silver(I). Yield: 78%. (155 mg). m.p.: 221-222 ^{0}C; $\nu_{(CN)}$: 1444 cm^{-1}. Anal. Calc. for $C_{38}H_{40}N_4O_2PdCl_2$ C: 59.89, H: 5.29, N: 7.35. Found: C: 59.73, H: 5.22, N: 7.42. ^{1}H NMR (300MHz, DMSO-d_6) δ (ppm) = 3.18 (s, 6H, -$CH_2CH_2OCH_3$); 5.13 (m, 4H, -$CH_2CH_2OCH_3$); 5.29 (t, 4H, -$CH_2CH_2OCH_3$ *J*: 8.4 Hz); 5.67 and 6.31 (m, 4H, -$CH_2C_6H_4CH=CH_2$); 6.12 (s, 4H, -$CH_2C_6H_4CH=CH_2$); 6.86 (m, 2H, -$CH_2C_6H_4CH=CH_2$); 7.22-7.91 (m, 16H, Ar-***H***). ^{13}C NMR (75.47 MHz, DMSO-d_6) δ (ppm) = 48.1(-$CH_2CH_2OCH_3$); 51.9 (-$CH_2CH_2OCH_3$); 59.2 (-$CH_2C_6H_4CH=CH_2$); 72.1 (-$CH_2CH_2OCH_3$); 110.9, 111.2, 113.9, 114.1, 123.1, 126.5, 127.8, 133.8, 135.2, 136.3, 136.4 and 137.3 (Ar-***C*** and -***C***H=***C***H_2); 181.9 (2-**C**-Pd).

Synthesis of bis[1-(2-ethoxyethyl)-3-(4-vinylbenzyl)benzimidazol-2-ylidene]dichloro palladium(II), 1e

The synthesis of **1e** was carried out in the same way as that described for **1a**, but chloro[1-(2-ethoxyethyl)-3-(4-vinylbenzyl)benzimidazol-2-ylidene]silver(I) (234 mg. 0.52 mmol) was used instead of chloro[1-methyl-3-(4-vinylbenzyl)benzimidazol-2-ylidene]silver(I). Yield: 84% (173 mg). m.p.: 229-230 ^{0}C; $\nu_{(CN)}$: 1443 cm^{-1}. Anal. Calc. for $C_{40}H_{44}N_4O_2PdCl_2$: C:

60.80, H: 5.61, N: 8.97. Found: C: 60.87, H: 5.64, N: 9.02. ^{1}H NMR (300MHz, DMSO-d_6) δ (ppm) = 1.16 (t, 6H, -$CH_2CH_2OCH_2C\boldsymbol{H_3}$, *J*: 4.6 Hz); 3.53 (m, 4H, -$CH_2CH_2OC\boldsymbol{H_2}CH_3$); 4.09 (t, 4H, -$CH_2C\boldsymbol{H_2}OCH_2CH_3$, *J*: 4.4 Hz); 5.98 (m, 4H, -$C\boldsymbol{H_2}CH_2OCH_2CH_3$); 5.63 and 6.28 (m, 4H, -$CH_2C_6H_4CH=C\boldsymbol{H_2}$); 6.19 (s, 4H, -$C\boldsymbol{H_2}C_6H_4CH=CH_2$); 6.84 (m, 2H, -$CH_2C_6H_4C\boldsymbol{H}=CH_2$); 7.21-7.86 (m, 16H, Ar-***H***). ^{13}C NMR (75.47 MHz, DMSO-d_6) δ (ppm) = 15.2 (-$CH_2CH_2OCH_2C\boldsymbol{H_3}$); 48.2 (-$CH_2CH_2OC\boldsymbol{H_2}CH_3$); 51.9 (-$CH_2C\boldsymbol{H_2}OCH_2CH_3$); 66.6 (-$C\boldsymbol{H_2}CH_2OCH_2CH_3$); 69.9 (-$\boldsymbol{C}H_2C_6H_4CH=CH_2$); 110.9, 111.2, 113.8, 114.1, 114.2, 126.7, 126.9, 127.8, 130.8, 134.0, 135.2, 136.4, 137.1 and 137.3. (Ar-***C*** and -$\boldsymbol{C}H=\boldsymbol{C}H_2$); 181.9 (2-**C**-Pd).

Synthesis of bis[1-benzyl-3-(4-vinylbenzyl)benzimidazol-2-ylidene] dichloropalladium(II), 1f

The synthesis of **1f** was carried out in the same way as that described for **1a**, but chloro[1-benzyl-3-(4-vinylbenzyl)benzimidazol-2-ylidene]silver(I) (243 mg. 0.52 mmol) was used instead of chloro[1-methyl-3-(4-vinylbenzyl)benzimidazol-2-ylidene]silver(I). Yield: 82 % (176 mg). m.p: 236-237 ^{0}C; $\nu_{(CN)}$: 1447 cm^{-1}. Anal. Calc. for $C_{46}H_{40}N_4PdCl_2$: C: 66.87, H: 4.88, N: 6.78. Found: C: 66.73, H: 4.92, N: 6.75. ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm) = 5.22 and 5.71 (d, 4H, -$CH_2C_6H_4CH=C\boldsymbol{H_2}$, *J*: 8.1 Hz); 6.01 (s, 4H, -$C\boldsymbol{H_2}C_6H_5$); 6.10 (s, 4H, -$C\boldsymbol{H_2}C_6H_4CH=CH_2$); 6.62 (dd, 2H, -$C_6H_4C\boldsymbol{H}=CH_2$, *J*: 8.4 Hz); 7.08-7.72 (m, 26H, Ar-**H**). ^{13}C NMR (75.47 MHz, DMSO-d_6) δ (ppm) = 40.4 (-$C\boldsymbol{H_2}C_6H_5$); 51.8 (-$C\boldsymbol{H_2}C_6H_4CH=CH_2$); 111.2,113.9, 114.5, 123.1, 125.5, 125.8, 126.5, 127.1, 127.7, 127.9, 128.4, 128.8, 134.5, 135.1, 135.3, 135.9, 136.4, 137.1 and 138.1 (Ar-***C*** and -$\boldsymbol{C}H=\boldsymbol{C}H_2$); 182.4 (2-***C***-Pd).

Synthesis of bis[1-(2-methylbenzyl)-3-(4-vinylbenzyl)benzimidazol-2-ylidene] dichloropalladium(II), 1g

The synthesis of **1g** was carried out in the same way as that described for **1a**, but chloro[1-(2-methylbenzyl)-3-(4-vinylbenzyl)benzimidazol-2-ylidene]silver(I) (250 mg. 0.52 mmol) was used instead of chloro[1-methyl-3-(4-vinylbenzyl)benzimidazol-2-ylidene]silver(I). Yield: 76% (170 mg). m.p: 265-266 ^{0}C; $\nu_{(CN)}$: 1439 cm^{-1}. Anal. Calc. for $C_{48}H_{44}N_4PdCl_2$: C: 67.49, H: 5.19, N: 6.56. Found: C: 67.35, H: 5.11, N: 6.47. ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm) = 2.27 (s, 6H, -$CH_2C_6H_4C\boldsymbol{H_3}$); 5.23 and 5.69 (d, 4H, -$CH_2C_6H_4CH=C\boldsymbol{H_2}$, *J*: 8.4 Hz); 5.88 (s, 4H, -$C\boldsymbol{H_2}C_6H_4CH_3$); 6.02 (s, 4H, -$C\boldsymbol{H_2}C_6H_4CH=CH_2$); 6.72 (m, 2H, -$CH_2C_6H_4C\boldsymbol{H}=CH_2$); 6.95-

7.51 (m, 24H, Ar-***H***). ^{13}C NMR (75.47 MHz, DMSO-d_6) δ (ppm) = 19.4 (-$CH_2C_6H_4$***C***H_3); 49.5 (-***C***$H_2C_6H_4CH_3$), 51.9 (-***C***$H_2C_6H_4CH{=}CH_2$); 110.9, 111.2, 113.9, 123.1, 126.4, 126.6, 127.2, 127.4, 127.9, 130.1, 133.6, 134.2, 134.7, 135.1, 135.4, 136.5 and 137.1 (Ar-***C*** and -***C***H=***C***H_2); 182.7. (2-***C***-Pd).

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

The synthesis of **1h** was carried out in the same way as that described for **1a**, but chloro[1-(4-methylbenzyl)-3-(4-vinylbenzyl)benzimidazol-2-ylidene]silver(I) (250 mg. 0.52 mmol) was used instead of chloro[1-methyl-3-(4-vinylbenzyl)benzimidazol-2-ylidene]silver(I). Yield: 82% (182 mg). m.p: 244-245 ^{0}C; $\nu_{(CN)}$: 1436 cm^{-1}. Anal. Calc. for $C_{48}H_{44}N_4PdCl_2$: C: 67.49, H: 5.19, N: 6.56. Found: C: 67.42, H: 5.14, N: 6.48. ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm) = 2.35 (s, 6H, -$CH_2C_6H_4C$***H₃***); 5.35 and 5.83 (m, 4H, -$CH_2C_6H_4CH{=}C$***H₂***); 5.65 (s, 4H, -***H₂***$C_6H_4CH_3$); 6.05 (s, 4H, -***H₂***$C_6H_4CH{=}CH_2$); 6.71 (dd, 2H, C_6H_4C***H***$=CH_2$, *J*: 7.5 Hz); 7.04-7.45 (m, 24H, Ar-***H***). ^{13}C NMR (75.47 MHz, DMSO-d_6) δ (ppm) = 21.2 (-$CH_2C_6H_4$***C***H_3); 52.1 (-***C***$H_2C_6H_4CH_3$); 54.0 (-***C***$H_2C_6H_4CH{=}CH_2$); 111.2, 112.2, 113.9, 114.8, 123.0, 124.4, 126.6, 127.4, 127.8, 129.8, 131.7, 132.7, 133.9, 134.5, 135.9, 136.5, 137.4, 137.9 and 138.6 (Ar-***C*** and -***C***H=***C***H_2); 182.1 (2-***C***-Pd).

Synthesis of bis[1-(2,3,5,6-tetramethylbenzyl)-3-(4-vinylbenzyl)benzimidazol-2-ylidene] dichloropalladium(II), 1i

The synthesis of **1i** was carried out in the same way as that described for **1a**, but chloro[1-(2,3,5,6-tetramethylbenzyl)-3-(4-vinylbenzyl)benzimidazol-2-ylidene]silver(I) (272 mg. 0.52 mmol) was used instead of chloro[1-methyl-3-(4-vinylbenzyl)benzimidazol-2-ylidene]silver(I). Yield: 83% (202 mg). m.p: 248-249 ^{0}C; $\nu_{(CN)}$: 1455 cm^{-1}. Anal. Calc. for $C_{54}H_{56}N_4PdCl_2$: C: 69.12, H: 6.02, N: 5.97. Found: C: 69.19, H: 6.06, N: 5.91. ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm) = 2.28 and 2.39 (s, 24H, -C_6H(C***H₃***)$_4$); 5.21 and 5.67 (d, 4H, *J*: 7.5 Hz -$C_6H_4CH{=}C$***H₂***); 6.37 (s, 4H, -***H₂***$C_6H(CH_3)_4$); 6.55 (dd, 2H, *J*: 7.2 Hz -C_6H_4C***H***$=CH_2$); 6.86-7.55 (m, 18H, Ar-***H***). ^{13}C NMR (75.47 MHz, DMSO-d_6) δ (ppm) = 15.3, 16.7, 20.6 and 29.7 (-C_6H(***C***$H_3)_4$); 50.8 (-***C***$H_2C_6H(CH_3)_4$); 51.8 (-***C***$H_2C_6H_4CH{=}CH_2$); 110.7, 111.9, 113.7,

122.6, 123.0, 127.8, 131.1, 132.2, 134.2, 134.4, 134.5, 134.6, 134.8, 135.3, 135.5, 136.9 and 137.0. (Ar-***C*** and -***C***H=***C***H_2); 182.3 (2-***C***-Pd).

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

Compound	Formula	Yield (%)	m.p. (^{o}C)	^{13}C 2-*C*-Pd (δ)	IR: $\nu_{(CN)}$ (cm^{-1})
1a	$C_{34}H_{22}N_4PdCl_2$	85	206-207	181.5	1446
1b	$C_{36}H_{36}N_4PdCl_2$	81	198-200	181.3	1443
1c	$C_{40}H_{44}N_4PdCl_2$	83	211-212	181.6	1445
1d	$C_{38}H_{40}N_4O_2PdCl_2$	78	221-222	181.9	1444
1e	$C_{40}H_{44}N_4O_2PdCl_2$	84	229-230	181.9	1443
1f	$C_{46}H_{40}N_4PdCl_2$	82	236-237	182.4	1447
1g	$C_{48}H_{44}N_4PdCl_2$	76	265-266	182.7	1439
1h	$C_{48}H_{44}N_4PdCl_2$	82	244-245	182.1	1436
1i	$C_{54}H_{56}N_4PdCl_2$	83	248-249	182.3	1455

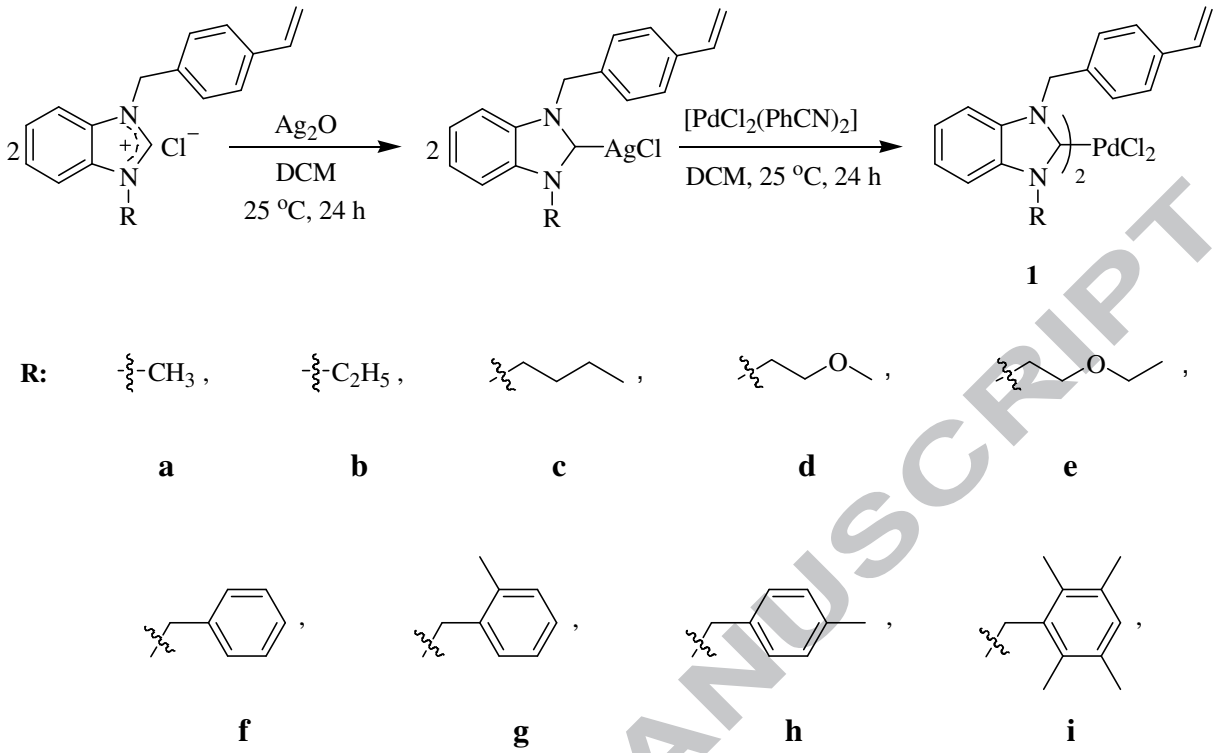
General Method for Direct Arylation of Furan and Thiophene With Aryl Bromides

The aryl bromide derivatives (4-bromo acetophenone, 4-bromoanisole, 4-bromotoluene and 4-bromobenzene) (1 mmol) and heteroaryl derivatives (2-*n*-butylfuran, 2-*n*-butylthiophene and 2-isopropylthiazole) (2 mmol), KOAc (1 mmol) and bis(NHC)-Pd(II) 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 [23]. The reaction mixture was stirred in an oil bath at 130 ^{0}C for 1 hour. 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) by 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.

Results and Discussion

Synthesis of Bis(NHC)-Pd(II) Parent Complexes. (1a-i)

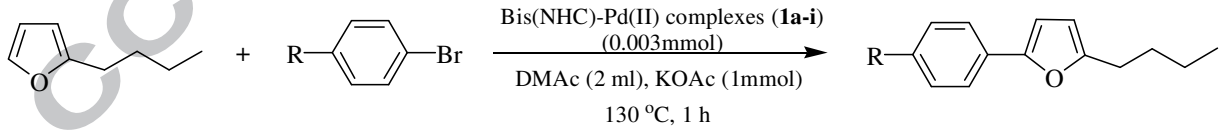
The parent 4-vinylbenzyl substituted bis(NHC)-Pd(II) complexes described in this work have been seen in Scheme 1. The new bis(NHC)-Pd(II) complexes **1a-i** were prepared from the synthesized Ag(I)NHC complexes via transmetallation method. The new bis(NHC)-Pd(II) complexes **1a-i** were prepared by mixing chloro[1-alkyl(or aryl)-3-(4-vinylbenzyl) benzimidazol-2-ylidene]silver(I) with 0.5 equivalents of $[PdCl_2(PhCN)_2]$ in dichloromethane (20 mL). Then the reaction mixture was stirred at room temperature for 24 h. in dark condition. The new bis(NHC)-Pd(II) complexes were obtained as a light yellow solid in 76 % to 85 % yield. The air and moisture stable the new bis(NHC)-Pd(II) complexes were soluble in solvents such as toluene, dichloromethane, and chloroform. The formations of the nonsymmetrical substituted complexes were confirmed by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopic methods and elemental analysis techniques. These spectra are consistent with the proposed formula. In the ^{13}C NMR spectra, the Pd-$C_{carbene}$ resonances of these new bis(NHC)-Pd(II) complexes in the ^{13}C NMR spectra appeared highly downfield shifted at δ 181.5, 181.3, 181.6, 181.9, 181.9, 182.4, 182.7, 182.1 and 182.3 ppm for **1a-i**, respectively. The results of the elemental analysis, which is one of the 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 1446, 1443, 1445, 1444, 1443, 1447, 1439, 1436 and 1455 cm^{-1} for the new bis(NHC)-Pd(II) complexes (**1a–i**), respectively.



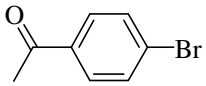
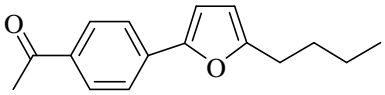
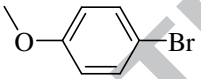
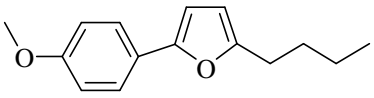
Scheme 1. Synthesis of 4-vinylbenzyl substituted bis(NHC)-Pd(II) Complexes **1a-i**.

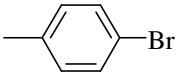
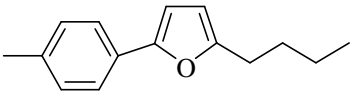
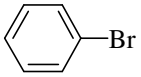
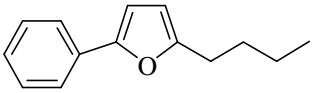
Direct Arylation of 2-*n*-butylfuran, 2-*n*-butylthiophene and 2-isopropylthiazole with Various Aryl Bromides

Table 2. Bis(NHC)-Pd(II) complexes (**1a-i**) catalysed direct arylation of 2-*n*-butylfuran by using aryl bromides.



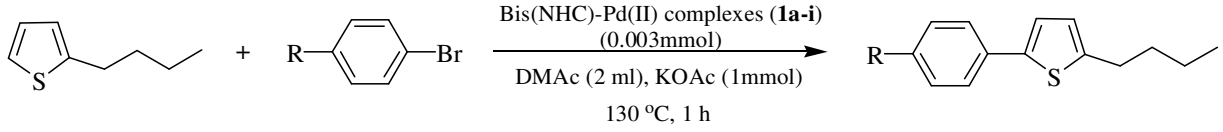
Entry	Ar-Br	Pd(II)NHC	Product	% Conv.
1		**1a**		94
2		**1b**		96

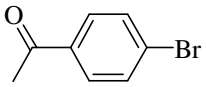
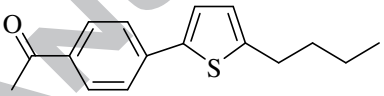
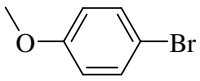
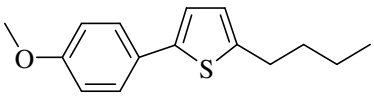
3		**1c**	93
4		**1d**	95
5		**1e**	 99
6		**1f**	96
			2
7		**1g**	98
8		**1h**	96
9		**1i**	99
10		**1a**	80
11		**1b**	74
12		**1c**	75
13		**1d**	79
14		**1e**	 88
15		**1f**	84
			3
16		**1g**	79
17		**1h**	87
18		**1i**	89
19		**1a**	82
20		**1b**	81
21		**1c**	85

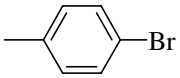
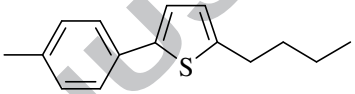
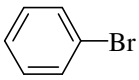
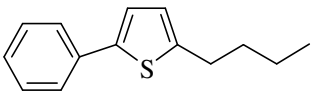
22		**1d**		82
23		**1e**		92
24		**1f**	**4**	91
25		**1g**		88
26		**1h**		90
27		**1i**		89
28		**1a**		96
29		**1b**		98
30		**1c**		95
31		**1d**		96
32		**1e**	**5**	96
33		**1f**		97
34		**1g**		91
35		**1h**		95
36		**1i**		93

Reaction conditions: 2-*n*-butylfuran (2 mmol), aryl bromide (1 mmol), bis(NHC)-Pd(II) complexes (**1a-i**) (0.003 mmol), KOAc (1 mmol), DMAc (2 mL), 130 ^{o}C, 1 h, product purity was checked by GC and NMR, conversions were calculated according to aryl bromide.

Table 3. Bis(NHC)-Pd(II) complexes (**1a-i**) catalysed direct arylation of 2-*n*-butylthiophene by using aryl bromides.



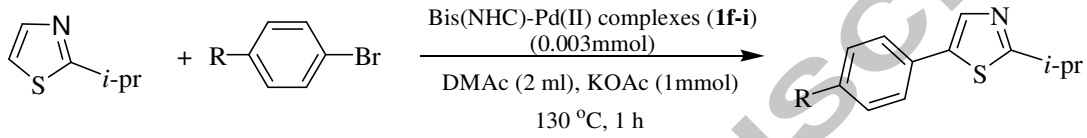
Entry	Ar-Br	Pd(II)NHC	Product	% Conv.
1		**1a**		96
2		**1b**		96
3		**1c**		94
4		**1d**		97
5		**1e**		95
6		**1f**	**6**	96
7		**1g**		98
8		**1h**		96
9		**1i**		98
10		**1a**		79
11		**1b**		74
12		**1c**		72
13		**1d**		77
14		**1e**		85
15		**1f**	**7**	71
16		**1g**		79

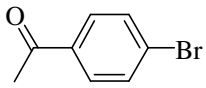
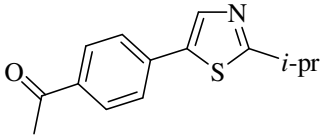
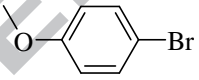
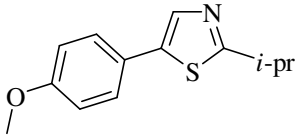
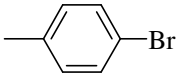
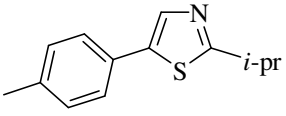
17		**1h**	69
18		**1i**	75
19		**1a**	88
20		**1b**	87
21		**1c**	90
22		**1d**	92
23		**1e**	 94
24		**1f**	87
		8	
25		**1g**	91
26		**1h**	89
27		**1i**	90
28		**1a**	97
29		**1b**	95
30		**1c**	93
31		**1d**	96
32		**1e**	 98
33		**1f**	95
		9	
34		**1g**	94
35		**1h**	97

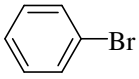
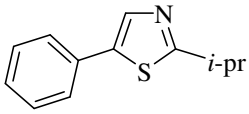
36	**1i**		93

Reaction conditions: 2-*n*-butylthiophene (2 mmol), aryl bromide (1 mmol), bis(NHC)-Pd(II) (**1a-i**) (0.003 mmol), KOAc (1 mmol), DMAc (2 mL), 130 ^{o}C, 1 h, product purity was checked by GC and NMR, conversions were calculated according to aryl bromide.

Table 4. Bis(NHC)-Pd(II) complexes (**1a-i**) catalysed direct arylation of 2-isopropylthiazole by using aryl bromides.



Entry	Ar-Br	Pd(II)NHC	Product	% Conv.
1		**1f**		96
2		**1g**		99
3		**1h**		99
4		**1i**	**10**	99
5		**1f**		90
6		**1g**		87
7		**1h**		92
8		**1i**	**11**	83
9		**1f**		94
10		**1g**		91
11		**1h**		96

12	**1i**	**12**	92
13	**1f**		93
14 	**1g**		91
15	**1h**		96
16	**1i**	**13**	95

Reaction conditions: 2-isopropylthiazole (2 mmol), aryl bromide (1 mmol), bis(NHC)-Pd(II) (**1f-i**) (0.003 mmol), KOAc (1 mmol), DMAc (2 mL), 130 ^{o}C, 1 h, product purity was checked by GC, conversions were calculated according to aryl bromide.

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 **1f-i**) in the presence of **1a-i** as catalyst.

Conversions of the products for 2-*n*-butylfuran are between 74% and 99%, for 2-*n*-butylthiophene are between 71% and 98%, and for 2-isopropylthiazole are between 83% and 99% (Table 2-4). When 4-bromoacetophenone was used, the best conversion was obtained. However, when we used 4-bromoanisole, it was obtained at fewer conversion (Table 2-4).

Initially, we investigated the binding of 2-*n*-butylfuran with 4-bromoacetophenone, 4-bromoanisole, 4-bromotoluene and 4-bromobenzene by using complexes **1a-i** as catalyst. When the effects of **1a-i** in the formation of the products **2-5** were analysed, conversions of 93–99%, 74–89%, 81–92% and 91–98% were observed respectively (Table 2). The use of 4-bromoacetophenone with 2-*n*-butylfuran gave the desired coupling product for different complexes (**1e**, **1g** and **1i**) as catalysts in better excellent conversion than the others, such as 99%, 98% and 99%, respectively (Table 2). When 4-bromoacetophenone, 4-bromotoluene and 4-bromobenzene with 2-*n*-butylfuran were utilized in the direct arylation reaction, conversions of the products (**2**, **4** and **5**) were obtained and observed to be better than the product **3** (Table 2). Then, we investigated the binding of 2-*n*-butylthiophene with 4-bromoacetophenone, 4-bromoanisole, 4-bromotoluene and 4-bromobenzene with complexes **1a-i** as the catalyst.

When the effects of **1a-i** in the formation of products **6**-**9** were analyzed, conversions of 94–98%, 71–85%, 87–94% and 93–98% were observed respectively (Table 3). The use of 4-bromoacetophenone with 2-*n*-butylthiophene gave the desired coupling product for different complexes (**1g** and **1i**) as catalysts in better excellent conversion than the others, such as 98% and 98%, respectively (Table 3). The 2-*n*-butylthiophene was bound with 4-bromoanisole to give the arylated products **7** in fewer 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). Finally, we investigated the binding of 2-isopropylthiazole with 4-bromoacetophenone, 4-bromoanisole, 4-bromotoluene and 4-bromobenzene with complexes **1f-i** as the catalyst. When the effects of **1f-i** in the formation of products **10**-**13** were analyzed, conversions of 96–99%, 83–92%, 91–96% and 91–96% were observed respectively (Table 4). The use of 4-bromoacetophenone with 2-isopropylthiazole gave the desired coupling product for different complexes (**1g**, **1h** and **1i**) as catalysts in better excellent conversion than the others, such as 99%, 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**, **12** and **13)** were obtained and observed to be better than the product **11** (Table 4). The 2-isopropylthiazole was bound with 4-bromoanisole to give the arylated products **11** in fewer conversions (Table 4). When compared to similar studies [25, 26] published recently, bis(NHC)-Pd(II) complexes that we have synthesized to have appeared highly active catalysts. Also, as compared to the bis(NHC)-Pd(II) complexes **1a-e** containing aliphatic substituents, when the bis(NHC)-Pd(II) complexes **1f-i** containing aromatic substituents are used, the conversion is somewhat more efficient (Table 2-4).

Conclusions

Consequently, our study is containing the synthesis of the new 4-vinylbenzyl substituted bis(NHC)-Pd(II) complexes **1a-i**. The bis(NHC)-Pd(II) **1a-i** complexes were prepared from the Ag(I)NHC complexes via transmetallation route. The catalytic effects of this new 4-vinylbenzyl substituted bis(NHC)-Pd(II) complexes have been investigated that they are more efficient and stable catalysts for the direct arylation reactions of 2-*n*-butylfuran 2-*n*-butylthiophene and 2-isopropylthiazole with aryl bromide.

Acknowledgment

This work was financially supported by Inönü University Research Fund (IUBAP 2012/02) and the authors acknowledge İnönü University Scientific and Technology Center for the elemental analyses of the compounds.

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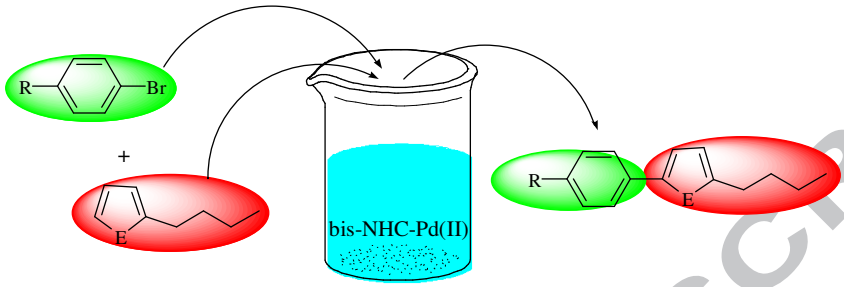
Highlight

1. The bis(NHC)$PdCl_2$ complexes have been prepared from the 4-vinylbenzyl substituted Ag(I)NHC complexes via transmetallation method.

2. The bis(NHC)$PdCl_2$ complexes have been characterized by using ^{1}H NMR, ^{13}C NMR, FTIR spectroscopy and elemental analysis techniques.

3. The bis(NHC)$PdCl_2$ 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.

Graphical Abstract



This study contains the synthesis of the new 4-vinylbenzyl substituted bis(NHC)-Pd(II) complexes and their catalytic activity in direct arylation reaction. The bis(NHC)-Pd(II) complexes have been prepared from Ag(I)NHC complexes by transmetallation method. The complexes have been characterized by using ^{1}H NMR, ^{13}C NMR, FTIR spectroscopy and elemental analysis techniques. Also, all the complexes showed excellent activity as catalysts in the direct arylation reaction.