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REGULAR ARTICLE

Novel 2-hydroxyethyl substituted *N*-coordinate-Pd(II)(NHC) and bis(NHC)Pd(II) complexes: Synthesis, characterization and the catalytic activity in the direct arylation reaction

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Abstract. The direct arylation reaction has attracted attention in recent years especially because of its environment-friendly properties. In this study, we researched the synthesis of 2-hydroxyethyl substituted bis(NHC)Pd(II) complexes and also the synthesis of *N*-coordinate-Pd(II)(NHC) complexes containing *N*-bound benzimidazolium from palladium acetate ($[Pd(CH_3COO)_2]$) with 1,3-disubstituted benzimidazolium halides in DMSO. All the complexes have been characterized by using ^{1}H NMR, ^{13}C NMR, FTIR spectroscopy and elemental analysis techniques. The molecular and crystal structure of one of the complexes is confirmed by using single-crystal X-ray diffraction. These complexes have been examined as the catalyst in the direct arylation reaction with 2-*n*-butylfuran and 2-*n*-butylthiophene and have demonstrated excellent activity in this reaction.

Keywords. Bis(NHC)Pd(II) complex; butylfuran; butylthiophene; direct arylation; *N*-coordinate-Pd(II)(NHC) complexes; *N*-heterocyclic carbene.

1. Introduction

The *N*-Heterocyclic carbenes (NHCs) were first reported by the independent works of Öfele and Wanzlick at the beginning of the 1960s,[1] and after a long time, in 1991 NHCs were reported as stable compounds that could be isolated by Arduengo *et al.*[2] NHCs are very versatile ligands in catalysis and organometallic chemistry[3–6] which can be readily synthesized by the deprotonation of 1,3-diazonium salts.[7,8] They have tremendous potentials in organic synthesis and catalysis[9–11] because of their extremely strong σ-donor and weak π-acceptor properties.[12,13] Especially in the last decade, NHCs have become increasingly popular as they are suitable ligands for the synthesis of coordination compounds. Furthermore, organometallic chemists have been interested in NHCs due to their stability to air and moisture and capability of complexing with transition metals for half a century.

The palladium complexes containing NHC ligands that are easily tunable as sterically and electronically have thermal and oxidative stability and they are long-lived active catalysts.[14,15] The efficient applications of Pd-NHC complexes have been published in the field of organometallic chemistry and catalysts for many years.[16–21] Also, medical applications of NHC precursors[22–27] and Pd-NHC complexes[28] have been examined.

Two different products can be obtained in the synthesis of bis(NHC)Pd(II) complexes. In particular, it is known that cis and trans isomeric products form depending on the experimental conditions.[29–31] Recently, unusually, Han *et al.,* performed a synthesis of a new type of bis(NHC)Pd(II) complexes from 1,3-disubstituted NHC precursor containing bulky substituents in DMSO.[32] This complex contains both the NHC (carbene) ligand and the N-bound (NHC precursor) ligand. Also, Landaeta *et al.,* used different solvents for the synthesis of bis(NHC)Pd(II) complexes and obtained significant results. In that study, when the DMSO was used as the solvent, a balance is observed between the carbene ligand and N-bound carbene precursor ligand as the result of the kinetic control.[33]

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The palladium-based metal-catalyzed direct arylation reaction that has been used is quite common because of its high activity, selectivity, efficiency, and versatility. Various catalysts using in this reaction have been developed for environment-friendly syntheses. Numerous research groups have used the NHC-Pd metal catalysts in the formation of a C-C bond. Recently, the Pd-based NHC complexes have been applied in organic chemistry for important C-C bond formations such as the Suzuki,[34] Heck,[34] Negishi,[35] Stille,[36] Hiyama coupling,[37] Sonogashira coupling,[38] Kumada coupling[39] and Buchwald-Hartwig amination[40] reactions.

In our last studies, we have published bis(NHC)Pd(II) complexes that are effective catalysts for direct arylation reactions.[41–43] In this study, we have investigated the synthesis and characterization of the 2-hydroxyethyl substituted *N*-coordinate-Pd(II)(NHC) and bis(NHC)Pd(II) complexes, and examined their catalytic activities in the direct arylation reactions. Also, we have found that the catalytic activities of these complexes are more efficient and stable catalysts for the direct arylation reactions of 2-*n*-butylfuran and 2-*n*-butylthiophene with aryl chloride or aryl bromide.

2. Experimental

All synthesis including 2-hydroxyethyl substituted *N*-coordinate-Pd(II)(NHC) complexes **1a–b** and bis(NHC)Pd(II) complexes **2a–g** were prepared in the air using standard Schlenk techniques. The solvents and all other reagents were commercially available 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 (^{1}H) and Carbon (^{13}C) NMR spectra were recorded using either a Bruker AS 400 Merkur spectrometer operating at 400 MHz (^{1}H), 100 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. Elemental analyses were performed by İnönü University Scientific and Technological Research Center (Malatya, TURKEY).

X-ray single-crystal diffraction data for complex **1b** was collected at room temperature on a Rigaku-Oxford Xcalibur diffractometer with an EOS-CCD detector using graphite-monochromated MoKα radiation (λ= 0.71073 Å) with CrysAlis^{Pro} software.[44] Data reduction and analytical absorption correction were performed by CrysAlis^{Pro} program.[45] Utilizing Olex2,[46] structure was solved using the *Intrinsic Phasing* method with SHELXT[47] and refined by full-matrix least-squares on F^2 in SHELXL.[48] Anisotropic thermal parameters were applied to all non-hydrogen atoms. All hydrogen atoms were placed using standard geometric models and with their thermal parameters riding on those of their parent atoms (C–H = 0.93, 0.96 and 0.97 Å, O–H = 0.82 Å). Some positional disorders were observed for hydroxyethyl groups in the structure, and to ensure satisfactory refinement of these disordered hydroxyethyl groups, constraint and restraint instructions such as EADP, DFIX, SIMU and RIGU were applied. A summary of crystal data, experimental details, and refinement results for the complex **1b** are given in Table 1.

2.1 *Synthesis*

2.1a *Synthesis of dichloro[1-(2-hydroxyethyl)-3-methylbenzimidazol-2-ylidene)]-[1-(2-hydroxyethyl) benzimidazole]palladium(II), 1a*: 1-(2-hydroxyethyl)-3-methylbenzimidazolium chloride (106 mg. 0.50 mmol) and Palladium(II)acetate (56 mg, 0.25 mmol) in dimethyl sulfoxide (4 mL) were stirred for 4 h at room temperature, 4 h at 50 °C, 4 h at 80 °C, 10 h at 100 °C and 2 h at 120 °C. The excess of the solvent was removed by evaporation under vacuum. The dichloromethane was added to the residue. Then the residue was passed through a silica gel column (1 cm thick) by using dichloromethane solvent. The dichloromethane was evaporated under vacuum to allow the product as a white or light yellow solid. The crude product was recrystallized from dichloromethane/diethyl ether (1:3) at room temperature. Yield: 62% (86 mg). M.p. 236–237 °C; $\nu_{(CN)(for\ carbene)}$: 1400 cm^{-1}; $\nu_{(CN)}$:$_{(carbene\ precursor)}$ 1517 cm^{-1}; $\nu_{(O-H)}$: 3412 cm^{-1}. Anal. Calc. for $C_{19}H_{22}Cl_2N_4O_2Pd$: C: 44.25; H: 4.30; N: 10.86. Found: C: 44.22; H: 4.32; N: 10.85. ^{1}H NMR (400 MHz, $CDCl_3$); δ 1.63 and 4.41 (s, 2H, –NCH_2CH_2OH); 3.84 (s, 3H, –NCH_3); 4.50 (m, 4H, –NCH_2CH_2OH); 5.10 (t, 4H, *J* = 6 Hz –NCH_2CH_2OH); 7.26–8.33 (m, 8H, Ar–*H*); 8.50 (d, 1H, *J* = 7.0 Hz, 2-C*H*). ^{13}C NMR (100 MHz, $CDCl_3$); δ 31.6 and 34.9 (–NCH_2CH_2OH); 50.6 (–NCH_3); 61.4 and 61.6 (–NCH_2CH_2OH); 109.8–110.1–110.4–110.6–120.7–123.4–123.5–123.8–124.2–133.6–134.8, 135.0 and 140.4 (Ar-*C*); 144.3. (2-*C*H). 164.4 (2-*C*-Pd).

2.1b *Synthesis of dibromo[1-(2-hydroxyethyl)-3-ethylbenzimidazol-2-ylidene)]-[1-(2-hydroxyethyl)benzimidazole]palladium(II), 1b*: This compound was prepared with the same procedure as that for **1a**. But the complex **1b** was prepared by using 1-ethyl-3-(2-hydroxyethyl) benzimidazolium bromide (136 mg. 0.50 mmol) instead of 1-(2-hydroxyethyl)-3-methylbenzimidazolium chloride. Yield: 67% (117 mg). M.p.: 176–177 °C; $\nu_{(CN)(for\ carbene)}$: 1416 cm^{-1}; $\nu_{(CN)}$:$_{(carbene\ precursor)}$ 1517 cm^{-1}; $\nu_{(O-H)}$: 3404 cm^{-1}. Anal. Calc. for $C_{20}H_{24}Br_2N_4O_2Pd$: C: 38.83; H: 3.91; N: 9.06. Found: C: 38.87; H: 3.88; N: 9.03. ^{1}H NMR (400 MHz, $CDCl_3$); δ 1.78 (t, 3H, *J* = 6 Hz –NCH_2CH_3); 1.66 and 2.59 (s, 2H, –NCH_2CH_2OH); 4.24 (q, 2H, –NCH_2CH_3); 4.50 and 4.92 (t, 4H, *J* = 4 and 4 Hz, –NCH_2CH_2OH); 4.57 and 4.99 (t, m, 4H, *J* = 4 Hz –NCH_2CH_2OH); 7.26–8.52 (m,

Table 1. Crystal data and experimental details for the complex **1b**.

Empirical Formula	$C_{20}H_{24}Br_2N_4O_2Pd$
Formula Weight	618.65
Temperature (K)	293(2)
Crystal System, space group	Triclinic, *P-1*
a, b, c (Å)	8.6912(5), 8.7380(5), 14.9619(8)
α, β, γ (°)	79.057(5), 85.805(4), 81.429(5)
V (Å^3)	1101.96(11) 81.429(5)
Z	2
Density (calculated) (g/cm^3)	1.864
Absorption coefficient (μ, mm^{-1})	4.492
F(000)	608
Crystal size (mm^3)	0.364 × 0.189 × 0.151
Radiation	MoKα (λ = 0.71073)
2θ range for data collection (°)	6.264–51.362
Index ranges	$-10 \leq h \leq 8, -10 \leq k \leq 9, -13 \leq l \leq 18$
Reflections collected	5705
Independent reflections	4147 [R_{int} = 0.023, R_{sigma} = 0.063]
Restraints/Parameters	28/253
Goodness-of-fit on F^2	1.025
Final *R* indices [$I \geq 2\sigma(I)$]	R_1 = 0.053, wR_2 = 0.116
R indices	R_1 = 0.092, wR_2 = 0.136
Largest diff. peak/hole (eÅ^{-3})	1.11/− 0.82

8H, Ar-*H*); 9.06 and 9.10 (dd, 1H, *J* = 6.4 and 6.4 Hz, 2-C*H*). ^{13}C NMR (100 MHz, $CDCl_3$); δ 14.4 and 14.9 (–NCH_2CH_3); 40.8 and 43.9 (–NCH_2CH_2OH); 50.8 (–NCH_2CH_3); 61.2 and 65.8 (–NCH_2CH_2OH); 110.0–110.1–110.3–110.4–110.8–110.9–123.1–123.2–124.6–124.7–132.8–134.0–134.3–135.6–138.0, 138.1 and 140.8 (Ar-*C*); 143.8 (2-*C*H); 161.5 and 163.9. (2-*C*-Pd).

2.1c *Synthesis of cis/trans-dibromobis[1-(2-hydroxyethyl)-3-isopropylbenzimidazol-2-ylidene]palladium(II), 2a*: This compound was prepared with the same procedure as that for **1a**. But the complex **2a** was prepared by using 1-(2-hydroxyethyl)-3-isopropylbenzimidazolium bromide (143 mg. 0.50 mmol) instead of 1-(2-hydroxyethyl)-3-methylbenzimidazolium chloride. Yield: 79% (133 mg). M.p.: 169–170 °C; $\nu_{(CN)}$: 1403 cm^{-1}; $\nu_{(O-H)}$: 3381 cm^{-1}. Anal. Calc. for $C_{24}H_{32}Br_2N_4O_2Pd$: C: 42.72; H: 4.78; N: 8.30. Found: C: 42.68; H: 4.80; N: 8.32. ^{1}H NMR (400 MHz, $CDCl_3$); δ 1.65 and 2.61 (s, 2H, –NCH_2CH_2OH); 1.80 and 1.82 (d, d, 12H, *J* = 4 and 4 Hz –$NCH(CH_3)_2$); 4.33 and 4.43 (t, 4H, *J* = 6 and 6 Hz –NCH_2CH_2OH); 4.84 and 4.93 (m, 4H, –NCH_2CH_2OH); 5.92 and 6.07 (m, 1H, Hz –$NCH(CH_3)_2$); 7.26–7.60 (m, 8H, Ar-*H*). ^{13}C NMR (100 MHz, $CDCl_3$); δ 20.4 ve 20.6 (–$NCH(CH_3)_2$); 50.8 and 51.4 (–$NCH(CH_3)_2$); 54.5 and 55.0 (–NCH_2CH_2OH); 60.8 and 61.2 (–NCH_2CH_2OH); 110.3–110.6–110.9–111.0–112.5–112.6–122.6–122.8–122.7–122.8–132.5–132.6–132.7–135.1–135.7–136.3 and 136.8 (Ar-*C*); 178.9 and 180.9 (2-*C*-Pd).

2.1d *Synthesis of cis/trans-dichlorobis[1-benzyl-3-(2-hydroxyethyl)benzimidazol-2-ylidene]palladium(II), 2b*: This compound was prepared with the same procedure as that for **1a**. But the complex **2b** was prepared by using 1-benzyl-3-(2-hydroxyethyl)benzimidazolium chloride (144 mg. 0.50 mmol) instead of 1-(2-hydroxyethyl)-3-methylbenzimidazolium chloride. Yield: 75% (128 mg). M.p. 156–157 °C; $\nu_{(CN)}$: 1411 cm^{-1}; $\nu_{(O-H)}$: 3423 cm^{-1}. Anal. Calc. for $C_{32}H_{32}Cl_2N_4O_2Pd$: C: 56.36; H: 4.73; N: 8.22. Found: C: 56.40; H: 4.72; N: 8.27. ^{1}H NMR (400 MHz, $CDCl_3$); δ 1.68 and 2.60 (s, 2H, –NCH_2CH_2OH); 3.86 and 4.21 (m, 4H, –NCH_2CH_2OH); 4.91 and 5.14 (s, 4H, –NCH_2CH_2OH); 6.04 and 6.34 (s, 4H, –$NCH_2(C_6H_5)$); 7.23–8.49 (m, 18H, Ar-*H*). ^{13}C NMR (100 MHz, $CDCl_3$); δ 47.8 and 48.3 (–NCH_2CH_2OH); 52.2 and 53.1 (–$NCH_2(C_6H_5)$; 60.7 and 61.4 (–NCH_2CH_2OH); 110.5–110.7–111.3–111.5–123.1–123.2–123.4–127.4–127.6–127.7–127.8–128.1–128.7–128.8–128.9–129.2–133.0–134.0–134.3–134.4–134.6–135.3–135.4 and 135.7. (Ar-*C*); 181.3 and 182.0 (2-*C*-Pd).

2.1e *Synthesis of cis/trans-dichlorobis[1-(2-hydroxyethyl)-3-(2-methylbenzyl)benzimidazol-2-ylidene]palladium(II), 2c*: This compound was prepared with the same procedure as that for **1a**. But the complex **2c** was prepared by using 1-(2-hydroxyethyl)-3-(2-methylbenzyl)benzimidazolium chloride (151 mg. 0.50 mmol) instead of 1-(2-hydroxyethyl)-3-methylbenzimidazolium chloride. Yield: 69% (122 mg). M.p.: 227–228 °C; $\nu_{(CN)}$: 1401 cm^{-1}; $\nu_{(O-H)}$: 3404 cm^{-1}. Anal. Calc. for $C_{34}H_{36}Cl_2N_4O_2Pd$: C: 57.52; H: 5.11; N: 7.89. Found: C: 57.50; H: 5.08; N: 7.90. ^{1}H NMR (400 MHz, $CDCl_3$); δ 1.77 and 2.60 (s, 2H, –NCH_2CH_2OH); 2.22 and 2.32 (s, 6H, –$NCH_2(C_6H_4)CH_3$); 3.73 and 3.87 (m, 4H, –NCH_2CH_2OH); 4.23 and 4.54 (m, 4H, –NCH_2CH_2OH); 5.78 and 5.91 (s, 4H, –$NCH_2C_6H_4(CH_3)$); 6.76–7.64 (m, 16H, Ar-*H*). ^{13}C NMR

(100 MHz, $CDCl_3$); δ 19.5 and 19.6 (–$NCH_2(C_6H_4)CH_3$); 50.3 and 50.6 (–NCH_2CH_2OH); 52.0 (–$NCH_2(C_6H_5)$; 60.1 and 60.7 (–NCH_2CH_2OH); 111.0–112.5–112.9–113.0–121.9–122.5–122.7–124.4–124.8–126.6–126.7–126.9–127.1–128.2–128.3–128.7–130.9–131.0–131.3–134.1–134.2–134.8–136.2–136.9 and 137.1. (Ar-*C*); 189.8 and 190.0 (2-*C*-Pd).

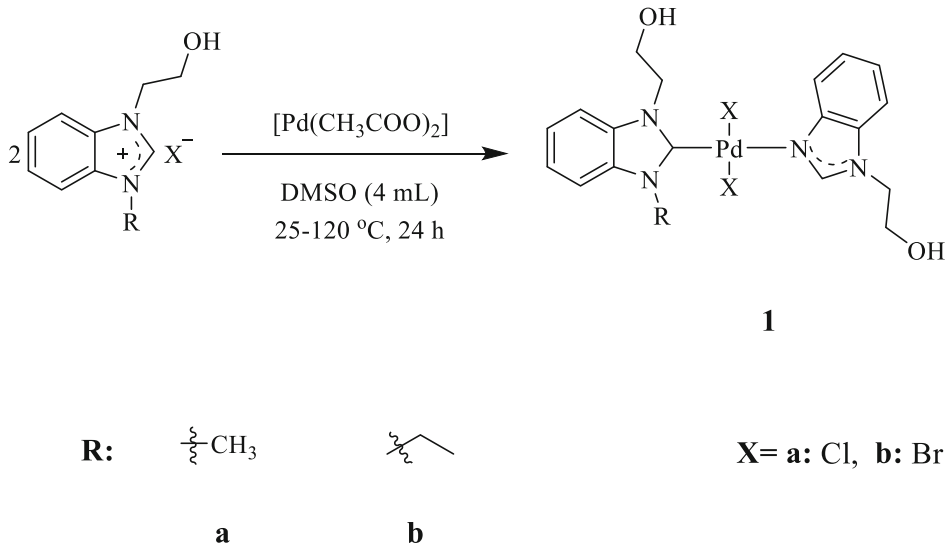
2.1f *Synthesis of cis/trans-dichlorobis[1-(2-hydroxyethyl)-3-(3-methylbenzyl)benzimidazol-2-ylidene]palladium(II), 2d*: This compound was prepared with the same procedure as that for **1a**. But the complex **2d** was prepared by using 1-(2-hydroxyethyl)-3-(3-methylbenzyl)benzimidazolium chloride (151 mg. 0.50 mmol) instead of 1-(2-hydroxyethyl)-3-methylbenzimidazolium chloride. Yield: 74% (131 mg). M.p. 175–176 °C; $\nu_{(CN)}$: 1410 cm^{-1}; $\nu_{(O\text{-}H)}$: 3404 cm^{-1}. Anal. Calc. for $C_{34}H_{36}Cl_2N_4O_2Pd$: C: 57.52; H: 5.11; N: 7.89. Found: C: 57.56; H: 5.14; N: 7.92. ^{1}H NMR (400 MHz, $CDCl_3$); δ 1.65 and 2.60 (s, 2H, –NCH_2CH_2OH); 2.55 and 2.59 (s, 6H, –$NCH_2(C_6H_4)CH_3$); 3.47 and 3.82 (m, 4H, –NCH_2CH_2OH); 5.17 and 5.29 (s, 4H, –NCH_2CH_2OH); 5.83 and 6.32 (s, 4H, –$NCH_2C_6H_4(CH_3)$); 6.93–7.66 (m, 16H, Ar-*H*). ^{13}C NMR (100 MHz, $CDCl_3$); δ 19.8 and 22.3 (–$NCH_2(C_6H_4)CH_3$); 31.6 and 34.1 (–NCH_2CH_2OH); 47.8 and 50.4 (–$NCH_2(C_6H_5)$; 60.6 and 61.3 (–NCH_2CH_2OH); 111.3–112.5–123.4–123.5–126.6–126.9–127.8–127.9–128.1–128.3–128.8–130.4–130.7–133.1–133.3–134.4–134.6–135.1 and 135.5. (Ar-*C*); 180.3 and 180.7 (2-*C*-Pd).

2.1g *Synthesis of cis/trans-dichlorobis[1-(2-hydroxyethyl)-3-(4-methylbenzyl)benzimidazol-2-ylidene]palladium(II), 2e*: This compound was prepared with the same procedure as that for **1a**. But the complex **2e** was prepared by using 1-(2-hydroxyethyl)-3-(4-methylbenzyl)benzimidazolium chloride (151 mg. 0.50 mmol) instead of 1-(2-hydroxyethyl)-3-methylbenzimidazolium chloride. Yield: 70% (124 mg). M.p. 224–225 °C; $\nu_{(CN)}$: 1407 cm^{-1}; $\nu_{(O\text{-}H)}$: 3431 cm^{-1}. Anal. Calc. for $C_{34}H_{36}Cl_2N_4O_2Pd$: C: 57.52; H: 5.11; N: 7.89. Found: C: 57.51; H: 5.13; N: 7.86. ^{1}H NMR (400 MHz, $CDCl_3$); δ 1.65 and 2.60 (s, 2H, –NCH_2CH_2OH); 2.27 and 2.34 (s, 6H, –$NCH_2(C_6H_4)CH_3$); 4.22 and 4.32 (m, 4H, –NCH_2CH_2OH); 4.93 and 5.14 (s, 4H, –NCH_2CH_2OH); 5.92 and 6.18 (s, 4H, –$NCH_2C_6H_4(CH_3)$); 7.03–7.55 (m, 16H, Ar-*H*). ^{13}C NMR (100 MHz, $CDCl_3$); δ 21.1 and 21.2 (–$NCH_2(C_6H_4)CH_3$); 50.3 and 50.4 (–NCH_2CH_2OH); 52.2 and 52.4 (–$NCH_2(C_6H_5)$; 61.5 and 61.7 (–NCH_2CH_2OH); 110.3–110.5–120.7–111.5–111.6–111.9–123.1–123.3–123.7–127.3–127.7–129.4–129.6–132.4–132.5–134.3–134.4–134.6–134.9–137.6 and 137.8. (Ar-*C*); 181.0 and 181.2 (2-*C*-Pd).

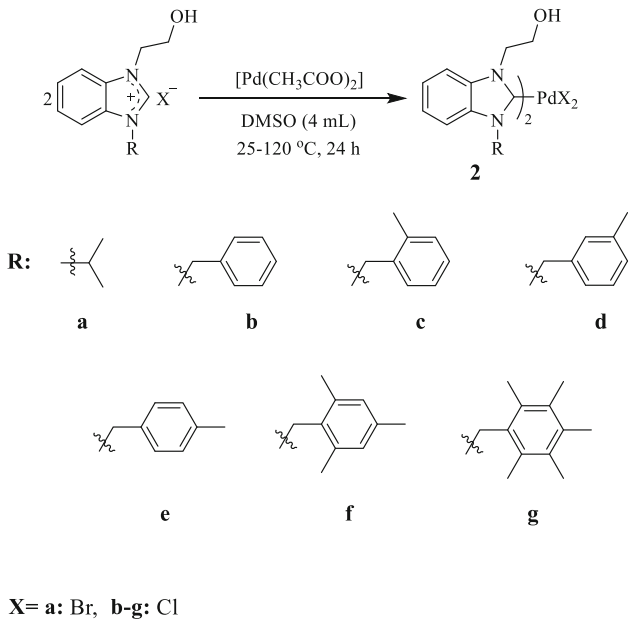
2.1h *Synthesis of cis/trans-dichlorobis[1-(2-hydroxyethyl)-3-(2,4,6-trimethylbenzyl)benzimidazol-2-ylidene]palladium(II), 2f*: This compound was prepared with the same procedure as that for **1a**. But the complex **2f** was prepared by using 1-(2-hydroxyethyl)-3-(2,4,6-trimethylbenzyl)benzimidazolium chloride (165 mg. 0.50 mmol) instead of 1-(2-hydroxyethyl)-3-methylbenzimidazolium chloride. Yield: 76% (146 mg). M.p.: 236–238 °C; $\nu_{(CN)}$: 1399 cm^{-1}; $\nu_{(O\text{-}H)}$: 3423 cm^{-1}. Anal. Calc. for $C_{38}H_{44}Cl_2N_4O_2Pd$: C: 59.57 H: 5.79; N: 7.31. Found: C: 59.63; H: 5.82; N: 7.36. ^{1}H NMR (400 MHz, $CDCl_3$); δ 1.76 and 2.59 (s, 2H, –NCH_2CH_2OH); 2.25–2.29 and 2.32–2.39 (s, 9H, –$NCH_2C_6H_2(CH_3)_3$); 4.02 and 4.28 (m, 4H, –NCH_2CH_2OH); 5.10 and 5.18 (t, 4H, *J* = 6 and 6 Hz –NCH_2CH_2OH); 5.29 and 5.32 (s, 4H, –$NCH_2C_6H_2(CH_3)_3$); 6.33–7.39 (m, 12H, Ar-*H*). ^{13}C NMR (100 MHz, $CDCl_3$); δ 20.9–21.0 and 22.3 (–$NCH_2C_6H_2(CH_3)_3$); 30.4 and 34.1 (–NCH_2CH_2OH); 49.6 and 50.2 (–$NCH_2C_6H_4(CH_3)_3$); 61.2 and 61.5 (–NCH_2CH_2OH); 110.2–110.4–111.3–112.5–111.9–122.8–123.0–123.3–123.7–127.5–128.0–128.1–128.3–128.5–134.2–134.5–134.7–138.4 and 138.5. (Ar-*C*); 180.9 and 182.3 (2-*C*-Pd).

2.1i *Synthesis of cis/trans-dichlorobis[1-(2-hydroxyethyl)-3-(2,3,4,5,6-pentamethylbenzyl)benzimidazol-2-ylidene]palladium(II), 2g*: This compound was prepared with the same procedure as that for **1a**. But the complex **2g** was prepared by using 1-(2-hydroxyethyl)-3-(2,3,4,5,6-pentamethylbenzyl)benzimidazolium chloride (180 mg. 0.50 mmol) instead of 1-(2-hydroxyethyl)-3-methylbenzimidazolium chloride. Yield: 71% (145 mg). M.p.: 245–246 °C; $\nu_{(CN)}$: 1396 cm^{-1}; $\nu_{(O\text{-}H)}$: 3457 cm^{-1}. Anal. Calc. for $C_{42}H_{52}Cl_2N_4O_2Pd$: C: 61.35; H: 6.37; N: 6.81. Found: C: 61.39; H: 6.40; N: 6.84. ^{1}H NMR (400 MHz, $CDCl_3$); δ 1.67 and 2.61 (s, 2H, –NCH_2CH_2OH); 2.11–2.13–2.20–2.23 and 2.27 (s, 30H, –$NCH_2C_6(CH_3)_5$); 3.75 and 4.44 (m, 4H, –NCH_2CH_2OH); 5.10 and 5.18 (t, 4H, *J* = 6 and 6 Hz –NCH_2CH_2OH); 6.22 and 6.32 (s, 4H, –$NCH_2C_6(CH_3)_5$); 6.94–7.81 (m, 8H, Ar-*H*). ^{13}C NMR (100 MHz, $CDCl_3$); δ 16.5–16.6–16.8–17.0–17.1 and 17.2 (–$NCH_2C_6(CH_3)_5$); 49.7 and 50.0 (–NCH_2CH_2OH); 64.7 and 64.8 (–$NCH_2C_6(CH_3)_5$); 61.0 and 61.2 (–NCH_2CH_2OH); 110.9–111.8–122.5–122.5–122.8–127.8–128.2–132.5–132.7–132.9–133.3–133.4–133.7–135.0–135.1 and 135.4. (Ar-*C*); 181.8 and 181.9 (2-*C*-Pd).

2.1j *General method for direct arylation of 2-n-butylfuran and 2-n-butylthiophene with aryl halides*: The derivatives of heteroaryl (2-*n*-butylfuran and 2-*n*-butylthiophene) (2 mmol), the derivatives of aryl chloride/bromide (4-chloroacetophenone, 4-chloroanisole, 4-bromoacetophenone, 4-bromoanisole) (1 mmol), KOAc (1 mmol) and the *N*-coordinate-Pd(II)(NHC) complexes **1a**–**b** or bis(NHC)Pd(II) complexes **2a**–**g** (0.3% mmol) were dissolved in *N*,*N*-dimethylacetamide (DMAc) (2 mL) in a small Schlenk tube as described in the literature.[42,43,52] The reaction mixture was stirred in an oil bath at 130 °C for 1 h/16 h. The solvent was removed under vacuum. The mixture was purified by using the column chromatography (silica gel 60–120 mesh) with ethylacetat/*n*-hexane (1:5) as eluent to obtain the pure product. The purity of the



Scheme 1. Synthesis of 2-hydroxyethyl substituted *N*-coordinate-Pd(II)(NHC) complexes **1a**–**b**.



Scheme 2. Synthesis of 2-hydroxyethyl substituted bis(NHC)Pd(II) complexes **2a**–**g**.

compounds was checked by gas chromatography (GC). The conversions were calculated by taking into account the conversion of the aryl bromides to the products.

3. Results and Discussion

3.1 *Synthesis of N-coordinate-Pd(II)(NHC) complexes (**1a-b**) and bis(NHC)Pd(II) Complexes (**2a-g**)*

The 2-hydroxyethyl substituted *N*-coordinate-Pd(II)(NHC) complexes **1a–b** and bis(NHC)Pd(II) complexes **2a–g** were synthesized from the reaction of NHC precursors and palladium acetate. The 2-hydroxyethyl substituted NHC precursors and palladium acetate [$Pd(CH_3COO)_2$] were used to obtain all the desired complexes that have been illustrated in Schemes 1 and 2. The *N*-coordinate-Pd(II)(NHC) complexes **1a–b** and bis(NHC)Pd(II) complexes **2a–g** were prepared by mixing 1-alkyl(or aryl)-3-(2-hydroxyethyl)benzimidazolium salts with 0.5 equivalents palladium acetate [$Pd(CH_3COO)_2$] in dimethylsulfoxide (4 mL). The reaction mixture was stirred at 25–120 °C temperature for 24 h. All the complexes (**1a–b** and **2a–g)** were obtained as a yellow and white solid in 69% to 78% yield. The air and moisture stable complexes (**1a–b** and **2a–g)** are soluble both in polar solvents such as dimethylformamide, dimethylsulfoxide and in halogenated solvents such as dichloromethane and chloroform. The formations of the 2-hydroxyethyl substituted complexes (**1a–b** and **2a–g)** were confirmed by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopic methods and elemental analysis techniques. The conditions of this experiment indicated the formation of the unexpected novel *N*-coordinate-Pd(II)(NHC) complexes.[32,33] In the ^{1}H NMR spectra, a characteristic proton peak at the 2-position (NCHN) of the 2-hydroxyethyl substituted N-coordinate-Pd(II)(NHC) complexes **1a–b** was detected, which appeared highly downfield shifted singleds δ 8.50 and 9.06–9.10 ppm in the ^{1}H NMR spectra, respectively. In the ^{13}C NMR spectra, the 2-C*H* resonances of the novel *N*-coordinate-Pd(II)(NHC) complexes appeared highly downfield shifted at 144.3 and 143.8 ppm for **1a–b**, respectively. Also, the conditions of this experiment indicated the formation of the expected

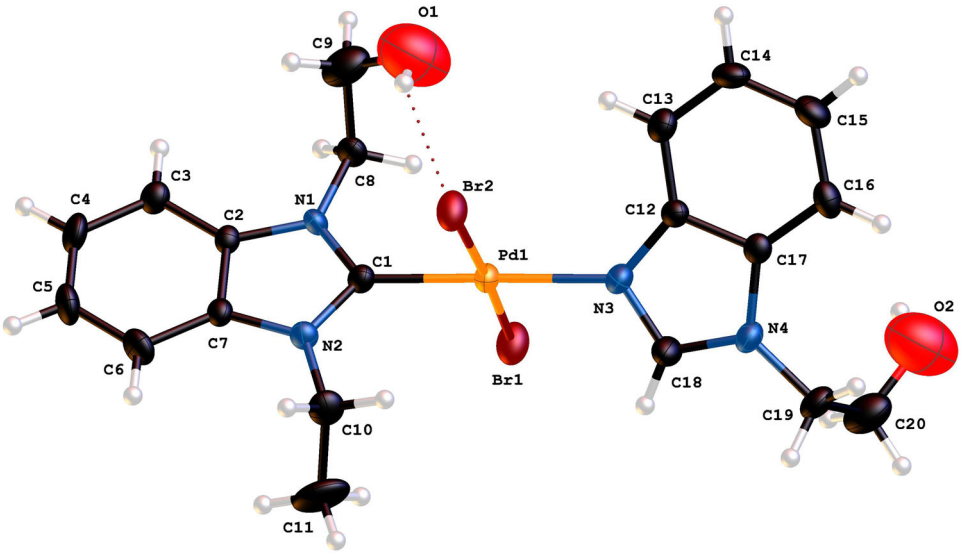


Figure 1. Molecular structure of complex **1b** with ellipsoids drawn at 30% probability level. Selected bond lengths (Å) and angles (°): Pd1–Br1 2.4260(11), Pd1–Br2 2.4426(11), Pd1–C1 1.959(7), Pd1–N3 2.080(6), O1–C9 1.398(9), O2–C20 1.386(8); Br1–Pd1–Br2 176.73(4), N3–Pd1–C1 177.9(3), Br1–Pd1–C1 91.0(2), Br1–Pd1–N3 90.48(18), Br2–Pd1–C1 85.8(2), Br2–Pd1–N3 92.75(18), C1–N1–C8 125.5(6), N1–C8–C9 113.2(8), O1–C9–C8 111.1(11), C1–N2–C10 125.9(6), N2–C10–C11 112.8(7), N4–C19–C20 113.6(7), O2–C20–C19 110.4(12).

bis(NHC)Pd(II) complexes. In the ^{13}C NMR spectra, the Pd-$C_{carbene}$ resonances of the bis(NHC)Pd(II) complexes appeared highly downfield shifted at δ 178.9–180.9, 181.3–182.0, 189.8–190.0, 180.3–180.7, 181.0–181.2, 180.9–182.3 and 181.8–181.9 ppm for **2a–g**, respectively. It was observed that the chemical shifts of carbene peaks in the ^{13}C NMR spectra of the *N*-coordinate-Pd(II)(NHC) complexes **1a-b** and the bis(NHC)Pd(II) complexes **2a–g** were different. FT-IR data clearly indicated the presence of ν(CN) (for $C_{carbene}$) at 1458 and 1448 of ν(CN) (for $C_{NHCprecursor}$) at 1517 and 1517 cm^{-1} for the *N*-coordinate-Pd(II)(NHC) complexes (**1a–b**), respectively. The FT-IR data clearly indicated the presence of ν(CN) (for $C_{carbene}$) at 1400 and 1416 cm^{-1} for the *N*-coordinate-Pd(II)(NHC) complexes (**1a–b**), respectively. The FT-IR data clearly indicated the presence of ν(CN) at 1403, 1411, 1401, 1410, 1407, 1399 and 1396 cm^{-1} for the bis(NHC)Pd(II) complexes (**2a–g**), respectively. The FT-IR data clearly indicated the presence of ν(OH) at 3412, 3404, 3381, 3423, 3404, 3404, 3430, 3423 and 3457 cm^{-1} for all complexes (**1a–b**) and (**2a–g**), 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. These spectroscopic data are consistent with the literature.[41] In this study, the single crystal of the synthesized novel *N*-coordinate-Pd(II)(NHC) complex **1b** was obtained by the X-ray diffraction method. Thus, the structure of the complex **1b** was confirmed.

3.2 *Structural description of 1b*

Complex **1b** crystallizes in the triclinic crystal system with $P\bar{1}$ space group. Figure 1 presents the molecular and crystal structure of the complex along with the number of the atoms. The palladium centre has a typical *square planar* geometry with a slight tetrahedral distortion. The environment of the metal centre consists of two bromide atoms in the *trans*-positions and two NHC ligands, coordinated to the palladium *via* nitrogen and carbon atoms. Also, two disordered hydroxyethyl groups are bound to the NHC ligands. Trans angles [176.73(4) and 177.9(3)°] around the Pd atom prove the distortion from the regular *square planar* coordination. The $PdBr_2CN$ coordination plane is almost planar with an r.m.s. deviation of 0.018 Å. The Pd–Br distances are compatible with the many other *trans*-$PdBr_2$ complexes.[28,49–51]

In the crystal structure of the complex, molecules connect to each other through the intermolecular C18–H18...O1^{i} hydrogen bonds to form an infinite chain along the *a*-axis. On the *c* axis, molecules stack as sheets *via* the C15–H15...O2^{ii} hydrogen bonding interactions. The intramolecular O1–H1...Br2 hydrogen bond is also responsible for the stabilization of the

Table 2. The intra- and intermolecular hydrogen bonds of the complex **1b** (Å, °).

D–H···A	D–H	H···A	D···A	D–H···A
O1–H1···Br2	0.82	2.71	3.434(14)	148
C18–H18···O1^{i}	0.93	2.59	3.438(17)	151
C15–H15···O2^{ii}	0.93	2.78	3.706(14)	175

Symmetry codes: (i) 1 + x, y, z; (ii) 1 − x, − y, 1 − z.

crystal structure (Table 2). Within the sheets, by means of these hydrogen-bonding interactions $R_6^6(32)$, $R_4^4(36)$, $R_2^2(16)$, S(8) loops and C(7), C(9) chains are apparent in Figure 2.[51]

3.3 *Proposed catalytic cycle for N-coordinate-Pd(II)(NHC) and Bis(NHC)Pd(II) complexes*

The proposed general catalytic cycle is illustrated in Scheme 3. In here, the catalytic cycle begins with pre-activation of the complex. Firstly, the oxidative addition of the aryl chloride/bromide to the pre-activated complex takes place. Then, the ligand exchange occurs by using the base (K_2CO_3). In this step is considerable the character of the base. Then, 2-*n*-butylfuran or 2-*n*-butylthiophene molecules are added to the Pd-(NHC) complexes for activation of C-H at position 5. Finally, C5-arylated furan/thiophene product has been obtained by the result of reductive elimination. In the final step, the steric bulk of the Pd-(NHC) complex facilitates the formation of the arylated furan/thiophene product.[53,54]

The electronic properties of Pd-(NHC) complexes have been provided by the alkyl substituents attached to the N atom. This effect provides the stability of the occurring complex in the catalytic cycle. Also, the steric bulk of the ligand facilitates the reductive elimination in the catalytic cycle. In this study; the catalytic activities of bis(NHC)Pd(II) complexes were higher than the catalytic activities of *N*-coordinate-Pd(II)(NHC) complexes due to the steric bulk of bis(NHC)Pd(II) complexes that it may facilitate reductive elimination in the catalytic cycle.

3.4 *Direct arylation of 2-n-butylfuran and 2-n-butylthiophene with various aryl halides*

All complexes (**1a–b** and **2a–g**) that contain 2-hydroxyethyl substituent may increase the solubility in the polar solvent (DMAc). Moreover, the electronic effects of the hydroxyl (OH) group may increase the

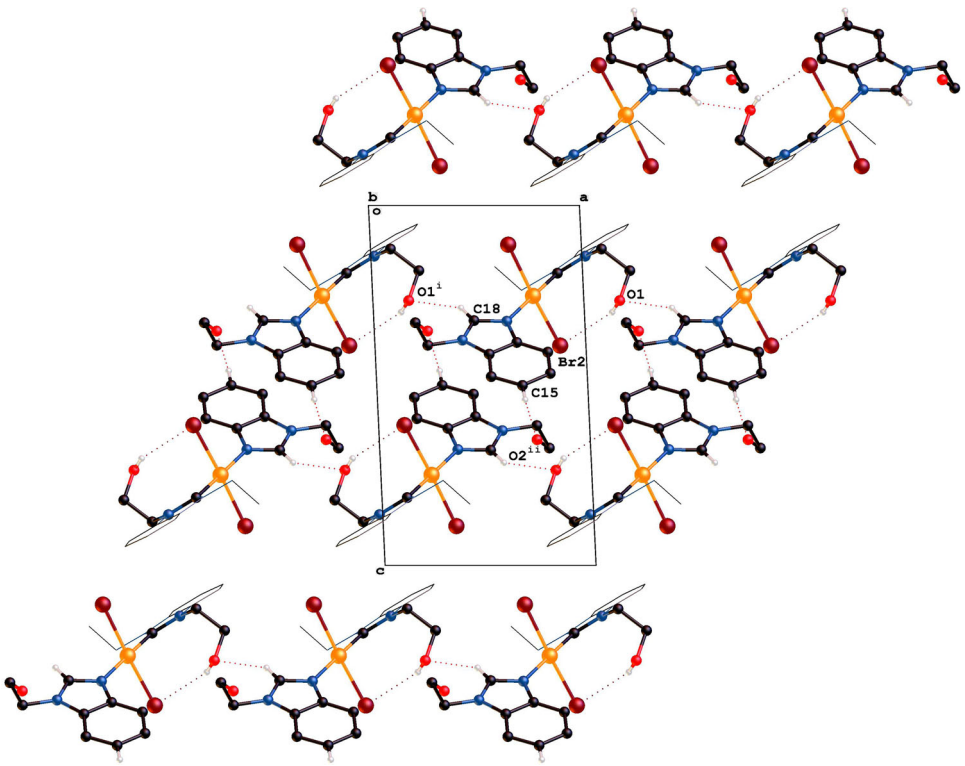
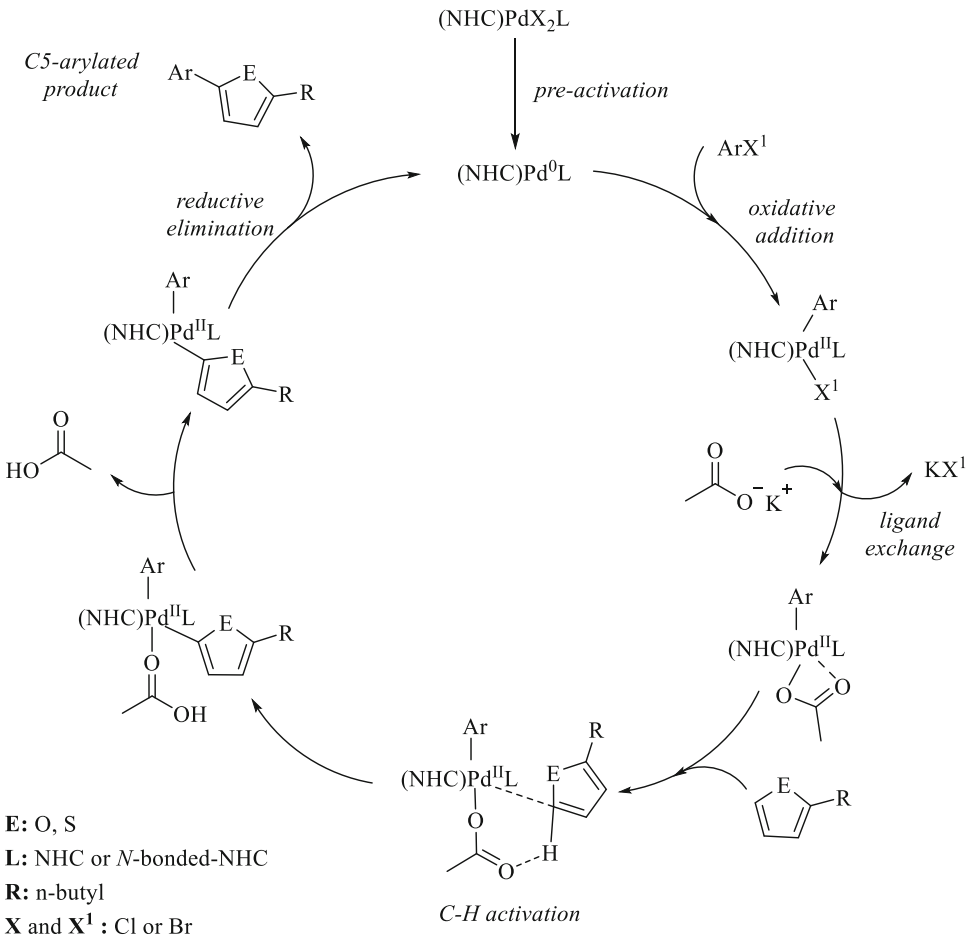


Figure 2. Graphical representation of the stacking molecules for *trans*-dibromoPd(II) complex **1b**. The environment of the metal center and the atoms, which play a role on the graph-set motifs are drawn as ball and stick style, while the rest are as wireframe drawing style. For the sake of clarity, hydrogen atoms not involved in bonding are omitted.



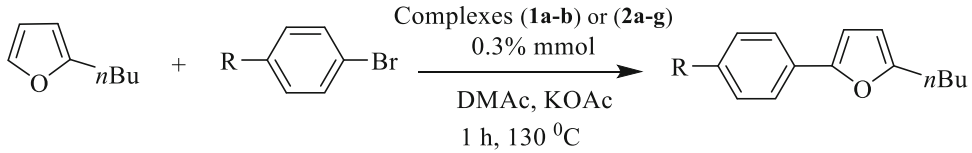
Scheme 3. Proposed catalytic cycle for the direct C–H bond arylation for N-coordinate-Pd(II)(NHC) and bis(NHC)Pd(II) Complexes.

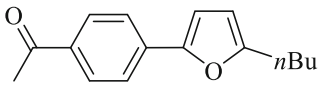
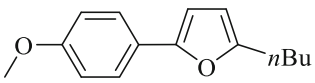
stability of the intermediate formed by the ligand exchange in the catalytic cycle (Scheme 3). Thus, we can think that both properties increase the catalytic activity of complexes.

We have examined the direct arylation reactions of para-substituted aryl halides (chloride/bromide) with 2-*n*-butylfuran and 2-*n*-butylthiophene in the presence of the *N*-coordinate-Pd(II)(NHC) complexes **1a–b** and the bis(NHC)Pd(II) complexes **2a–g** as catalysts. Firstly, we examined the reaction of 2-*n*-butylfuran with 4-bromoacetophenone and 4-bromoanisole by using complexes **1a–b** and **2a–g** as the catalysts. When the effects of **1a–b** in the formation of the products **3** and **4** were analyzed, the conversions were observed at 91–97% and 62–63% respectively (Table 3). When the effects of **2a–g** in the formation of the products **3** and **4** were analyzed, the conversions were observed at 95–99% and 75–98% respectively (Table 3). The bis(NHC)Pd(II) complexes **2a–g** demonstrated higher conversions than the *N*-coordinate-Pd(II)(NHC) complexes **1a–b**. When the bis(NHC)Pd(II) complexes **2a–g** are used as the catalyst, the desired product **3** was obtained in the excellent conversion in the arylation reaction of 2-*n*-butyl furan with 4-bromoacetophenone. But, the conversions obtained from the reaction of 4-bromoanisole with 2-*n*-butylfuran are lower for the arylation product **4** (Table 3). When the *N*-coordinate-Pd(II)(NHC) complexes **1a–b** were compared with them, the conversions for the product **3** were higher while the conversions for the products **4** were obtained lower (Table 3). These results show the electron-withdrawing group (-$COCH_3$) exhibits higher conversions than the electron-donating group (-OCH_3) in the para position (Table 3).

Secondly, the arylation reaction of 2-*n*-butylthiophene with 4-bromoacetophenone and 4-bromoanisole were examined by using all complexes **1a–b** and **2a–g** as the catalyst. When the effects of **1a–c** in the formation of the products **5** and **6** were analyzed, the conversions were observed at 89–91% and 63–69% respectively (Table 4). When the effects of **2a–g** in the formation of the products **5** and **6** were analyzed, the conversions were observed at 87–99% and 66–93% respectively (Table 4). When the *N*-coordinate-

Table 3. *N*-coordinate-Pd(II)(NHC) complexes (**1a–b**) and bis(NHC)Pd(II) complexes (**2a–g**) catalyzed direct arylation of 2-*n*-butylfuran by using aryl bromides.

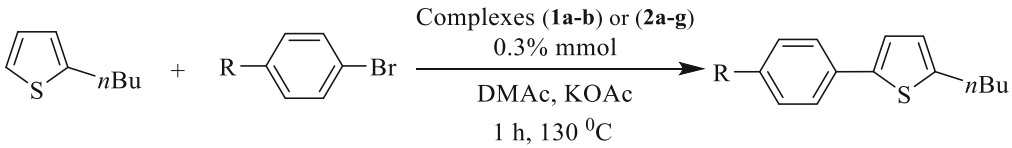


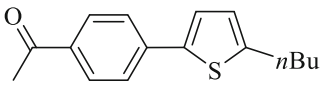
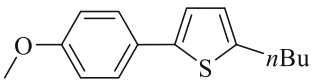
Entry	R	Product	Cat.	% Conv.
1			**1a**	91
2			**1b**	97
3			**2a**	95
4	-$COCH_3$	 **3**	**2b**	>99
5			**2c**	>99
6			**2d**	>99
7			**2e**	>99
8			**2f**	>99
9			**2g**	>99
10			**1a**	63
11			**1b**	62
12			**2a**	75
13	-OCH_3	 **4**	**2b**	94
14			**2c**	79
15			**2d**	82
16			**2e**	98
17			**2f**	78
18			**2g**	77

Reaction conditions: 2-*n*-butylfuran (2 mmol), aryl bromide (1 mmol), *N*-coordinate-Pd(II)(NHC) complexes (**1a–b**) or bis(NHC)Pd(II) complexes (**2a–g**) (0.3% 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.

Pd(II)(NHC) complexes **1a–b** are used as the catalysts, better conversions were obtained in the arylation reaction of 4-bromoacetophenone and 2-*n*-butylthiophene. When the bis(NHC)Pd(II) complexes **2a–g** are used as the catalysts, excellent conversions were obtained in the arylation reaction of 4-bromoacetophenone and 2-n-butylthiophene (Table 4). But, the conversions obtained from the reaction of 4-bromoanisole with 2-*n*-butylthiophene for all complexes **1a–b** and **2a–g** are lower in the arylation products (Table 4). These results show that the electron-withdrawing group (-$COCH_3$) exhibits higher conversions than the electron-donating group (-OCH_3) in the para position (Table 4). The bis(NHC)Pd(II) complexes **2a–g** showed higher conversions than the *N*-coordinate-Pd(II)(NHC) complexes **1a–b**. In general, 2-*n*-butylfuran exhibited higher conversions than 2-*n*-butylthiophene with the same aryl bromide (Table 3, 4).

Table 4. *N*-coordinate-Pd(II)(NHC) complexes (**1a–b**) and bis(NHC)Pd(II) complexes (**2a–g**) catalyzed direct arylation of 2-*n*-butylthiophene by using aryl bromides.

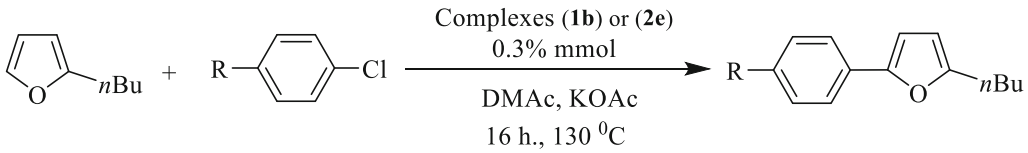


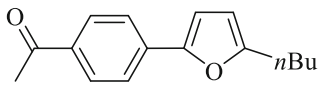
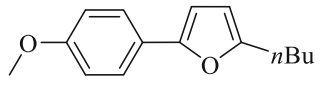
Entry	R	Product	Cat.	% Conv.
1			**1a**	89
2			**1b**	91
3			**2a**	87
4			**2b**	>99
5	-$COCH_3$	 **5**	**2c**	>99
6			**2d**	>99
7			**2e**	98
8			**2f**	>99
9			**2g**	>99
10			**1a**	63
11			**1b**	69
12			**2a**	66
13			**2b**	74
14	-OCH_3	 **6**	**2c**	86
15			**2d**	83
16			**2e**	76
17			**2f**	93
18			**2g**	78

Reaction conditions: 2-*n*-butylthiophene (2 mmol), aryl bromide (1 mmol), *N*-coordinate-Pd(II)(NHC) complexes (**1a–b**) or bis(NHC)Pd(II) complexes (**2a–g**) (0.3% 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.

Finally, when alkyl/aryl chloride used, the conversion of arylation product was obtained less than alkyl/aryl bromide (Table 5, 6). The experiments were carried out with the *N*-coordinate-Pd(II)(NHC) complex **1b** and the bis(NHC)Pd(II) complex **1e** at 16 h. We examined the arylation reaction of 2-*n*-butylfuran with 4-chloroacetophenone and 4-chloroanisole by using the complexes **1b** and **2e** as the catalyst. When the effect of the *N*-coordinate-Pd(II)(NHC) complex **1b** was analyzed in the formation of the product **3** and **4**, the conversions were observed at 89% and 63%, respectively (Table 5). When the effect of the bis(NHC)Pd(II) complex **2e** was analyzed in the formation of the product **3** and **4**, the conversions were observed at 99% and 68%, respectively (Table 5). When the effect of the *N*-coordinate-Pd(II)(NHC)

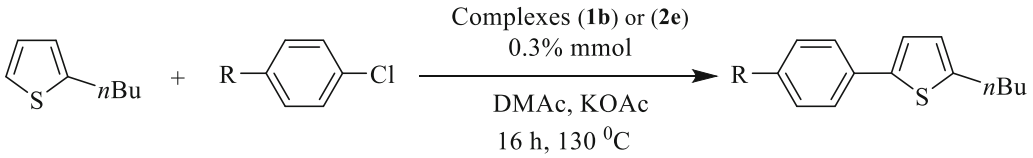
Table 5. *N*-coordinate-Pd(II)(NHC) complex **1b** and bis(NHC)Pd(II) complex **2e** catalyzed direct arylation of 2-*n*-butylfuran by using aryl chlorides.

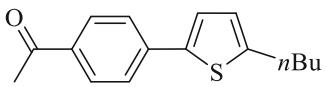
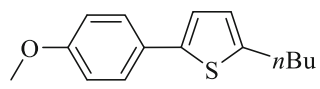


Entry	R	Product	Cat.	% Conv.
1	-$COCH_3$		**1b**	89
2	-$COCH_3$	 **3**	**2e**	99
3	-OCH_3		**1b**	63
4	-OCH_3	 **4**	**2e**	68

Reaction conditions: 2-*n*- butylfuran (2 mmol), aryl bromide (1 mmol), *N*-coordinate-Pd(II)(NHC) complex (**1b**) or bis(NHC)Pd(II) complex (**2e**) (0.3% mmol), KOAc (1 mmol), DMAc (2 mL), 130 °C, 16 h, product purity was checked by GC and NMR, conversions were calculated according to aryl chloride.

Table 6. *N*-coordinate-Pd(II)(NHC) complex **1b** and bis(NHC)Pd(II) complex **2e** catalyzed direct arylation of 2-*n*-butylthiophene by using aryl chlorides.



Entry	R	Product	Cat.	%Conv.
1	-$COCH_3$		**1b**	54
2	-$COCH_3$	 **5**	**2e**	67
3	-OCH_3		**1b**	41
4	-OCH_3	 **6**	**2e**	51

Reaction conditions: 2-*n*-butylthiophene (2 mmol), aryl bromide (1 mmol), *N*-coordinate-Pd(II)(NHC) complex (**1b**) or bis(NHC)Pd(II) complex (**2e**) (0.3% mmol), KOAc (1 mmol), DMAc (2 mL), 130 °C, 16 h, product purity was checked by GC and NMR, conversions were calculated according to aryl chloride.

complex **1b** was analyzed in the formation of the product **5** and **6**, the conversions were observed at 54% and 41%, respectively (Table 5). When the effect of the bis(NHC)Pd(II) complex **2e** was analyzed in the formation of the product **5** and **6**, the conversions were observed at 67% and 51%, respectively (Table 6). When chlorinated substrates are used, it has become even more pronounced difference between the arylation reaction involving 2-*n*-butylfuran and 2-*n*-butylthiophene compounds. The synthesized complexes have been highly active catalysts in our study when compared to the similar studies related to bis(NHC)Pd(II) complexes published.[43, 55–62]

4. Conclusions

As a result, we reported the synthesis of the two *N*-coordinate-Pd(II)(NHC) complexes **1a–b** and the seven 2-hydroxyethyl substituted bis(NHC)Pd(II) complexes **2a–g**. All complexes (**1a–b** and **2a–g)** were prepared from the 2-hydroxyethyl substituted NHC precursors and palladium acetate. The catalytic activity of these complexes (**1a–b** and **2a–g)** have been investigated that they are more efficient and stable catalysts for the direct arylation reactions of 2-*n*-butylfuran and 2-*n*-butylthiophene with aryl chloride/bromide. The molecular and crystal structure of the complex 1b is determined by single-crystal X-ray diffraction method. X-ray structural analysis shows that the metal coordination environment of the complex features slightly distorted square planar geometry, in which the C- and N-bounded NHC ligands, and the bromide atoms are trans to each other.

Supplementary Information (SI)

Crystallographic data as .cif files for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Center with CCDC 1888300 for **1b**. Copies of the data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK. Fax: (+44) 1223-336-033, email: deposit@ccdc.cam.ac.uk.

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Compliance with ethical standards

Conflicts of interest There are no conflicts of interest to declare.

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