Chemical Papers
https://doi.org/10.1007/s11696-019-00859-x

ORIGINAL PAPER

New (NHC)Pd(II)(PPh_3) complexes: synthesis, characterization, crystal structure and its application on Sonogashira and Mizoroki–Heck cross-coupling reactions

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Received: 22 April 2019 / Accepted: 22 June 2019

Abstract

In this study, new six Pd-based complexes containing mixture *N*-heterocyclic carbene (NHC) and triphenylphosphine (PPh_3) ligands were synthesized from the reaction of the (NHC)PdI_2(pyridine) with PPh_3. The new (NHC)PdI_2(PPh_3) complexes were characterized using FTIR, ^{1}H-NMR, ^{13}C-NMR, and ^{31}P-NMR spectroscopy and elemental analyses techniques. These spectra are consistent with the proposed formula. Molecular and crystal structure of two complexes was obtained using single-crystal X-ray diffraction method. Based on the crystal results, a *cis* geometry was assigned to all the complexes. These new complexes have been examined as the catalyst in the Sonogashira cross-coupling reaction. The catalytic conversions of the complexes were obtained between 71 and 99% from the reaction of phenylacetylene and aryl bromides. Also, these new complexes have been examined as the catalyst in the Mizoroki–Heck cross-coupling reaction. The catalytic conversions of the complexes were obtained between 80 and 100% from the reaction of styrene and aryl bromides.

Keywords Crystal structure · Mizoroki–Heck reactions · *N*-Heterocyclic carbenes · Palladium complex · Sonogashira reactions · Triphenylphosphine

Introduction

The activity of homogeneous catalysts is dependent on ancillary ligands, which are largely coordinated with the metal center (Cornils and Herrmann 1996; Beller and Bolm 1998). In recent years, the synthesis studies for the synthesis of palladium-based complexes containing both NHC and phosphine ligands have been increasing. In the beginning, the NHC ligands were selected as alternative ligands to the phosphine ligands (Glorius 2006; Diez-Gonzalez et al. 2009). Both that the metal-carbene bond is more resistant than the metal-phosphorus bond and that the property of the carbene ligand can be adjusted electronically and sterically are the most important reasons for this alternative. However, the catalysts containing both these ligands attracted the interest of organometallic chemists owing to their highly active and selective properties. Thus, various Pd(II)-based mixed NHC/phosphine complexes have been successfully designed for various cross-coupling reactions. Different methods are used for the synthesis of these complexes. One of these methods is the synthesis of Pd(II)-based mixed NHC/phosphine complexes by exchanging ligand from the pyridine-enhanced precatalyst preparation stabilization and initiation (PEPPSI) complexes containing the pyridine derivative ligands. These synthesized complexes have been widely used as the catalyst in cross-coupling reactions (Aktaş et al. 2018a, b, 2019; Boubakri et al. 2017; Dehimat et al. 2018; Touj et al. 2018; Herrmann et al. 2001, 2003; Liao et al. 2009; Chan et al. 2010; Diebolt et al. 2010; Schmid et al. 2013).

Pd(II)-based vinylic substitution of organometallic reagents was first reported by Heck (1982) who used stoichiometric amounts of Pd(II) salts. Palladium-catalyzed cross-coupling reactions gained the reputation they deserved by winning the Chemistry Nobel Prize in 2010. Heck and Nolley (1972) then independently reported the arylation of alkenes using aryl halides as electrophiles with a palladium complex as the catalyst in the presence of a base. In recent years, Mizoroki–Heck reactions have become an important

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tool for the formation of C–C bonds in organic syntheses (Mizoroki et al. 1971; Whitcombe et al. 2001; Dounay and Overman 2003; Beletskaya and Cheprakov 2000; Kondolff et al. 2003; Oestreich 2009; Watson 2016). Pd-based catalysts are used in the Mizoroki–Heck reactions because of their selectivity in the bonding of various electrophiles which are not toxic, and especially exhibiting high reactivity (Menezes da Silva et al. 2016).

The Pd catalyzed C(sp^2)–C(sp) cross-coupling reaction of terminal acetylenes with aryl halides are known as Sonogashira coupling (Sonogashira 2002). The triple bond (C≡C) in the alkynes that is found in material sciences and some important biochemicals is known as the ideal functional group for the synthesis of versatile and important organic molecules (Cosford et al. 2003; Bagley et al. 2005). This reaction is generally carried out using the copper (I) salts as the co-catalysts and amines as solvents (Alonso et al. 2003). Recently, in the Sonogashira cross-coupling reactions, we evaluated the potential reactivity and catalytic applications of Pd(II) complexes containing the mixed NHC/phosphine ligand (Aktaş et al. 2018a, b, 2019; Boubakri et al. 2017; Dehimat et al. 2018; Touj et al. 2018; Herrmann et al. 2001, 2003; Liao et al. 2009; Chan et al. 2010; Diebolt et al. 2010; Schmid et al. 2013).

As a continuation of our studies (Aktaş et al. 2018a, b, 2019) on the development of palladium-based mixed NHC/phosphine ligand catalysts, we describe here the synthesis of a series of Pd (II) based mixed NHC/phosphine complexes. In particular, these Pd (II) complexes containing mixed NHC/phosphine ligand can be used as effective catalysts in the Sonogashira and Mizoroki–Heck cross-coupling reactions with various aryl halides (aryl chlorides and aryl bromides). The structure of two of these complexes was confirmed by the single-crystal X-ray diffraction method. Also, we have researched the catalytic activity of all complexes in the Sonogashira and Mizoroki–Heck cross-coupling reactions and they demonstrated excellent activity in these cross-coupling reactions.

Experimental

All syntheses involving Pd(II) based mixed NHC/phosphine complexes **1a–f** were prepared under an inert atmosphere in flame-dried glassware using standard Schlenk techniques. The solvents used were commercially available and used without purification.

All other reagents were commercially available from Sigma-Aldrich, abcr and Merck 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), Phosphorous (^{31}P), and Carbon (^{13}C) NMR spectra were recorded using either a Bruker AS 400 Merkur spectrometer operating at 400 MHz (^1H), 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).

Single-crystal X-ray diffraction data of the complexes **1b** and **1f** were recorded at room temperature by ω-scan technique, on a Rigaku-Oxford Xcalibur diffractometer with an EOS-CCD area detector operated at 50 kV and 40 mA using graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å) from an enhance X-ray source with CrysAlis^{Pro} software (CrysAlis^{Pro} 2015). Data collections, reductions, and analytical absorption corrections were performed using CrysAlis^{Pro} software package (Clark and Reid 1995). Structure solutions were performed using SHELXT (Sheldrick 2015a) embedded in the Olex2 (Dolomanov 2009). Refinement of coordinates and anisotropic thermal parameters of non-hydrogen atoms were carried out by the full-matrix least-squares method in SHELXL (Sheldrick 2015b). For both complexes, hydrogen atoms were placed using standard geometric models and with their thermal parameters riding on those of their parent atoms. During the structure analysis, two disordered dichloromethane solvent molecules in the complex **1b** and two disordered chloroform solvent molecules in **1f** were observed. Total volumes of these solvent molecules are 293 Å^3 and 334 Å^3, respectively. Density identified in these solvent-accessible areas was calculated and corrected for using the solvent mask in Olex2. In **1b**, two carbon atoms are disordered with a 44:56 (C25:C25A; C26:C26A) population distribution in one of the benzene rings of PPh_3. The details of the crystal data, data collection and structure refinement of the complexes are given in Table 1.

Synthesis

Synthesis of diiodo[1-benzyl-3-(2-hydroxyethyl)benzimidazol-2-ylidene]triphenylphosphinepalladium (II), 1a

For this synthesis of the $(NHC)PdI_2(PPh_3)$ complex, first, diiodo[1-benzyl-3-(2-hydroxyethyl)benzimidazol-2-ylidene]pyridinepalladium(II) (138 mg, 0.2 mmol) and triphenylphosphine PPh_3 (52 mg, 0,2 mmol) were added in chloroform (10 mL) at room temperature (Aktaş et al. 2018a, b, 2019). The reaction mixture was stirred for 24 h at room temperature. Then, solvents were evaporated under

Table 1 Crystallographic data and structure refinement parameters for **1b** and **1f**

	1b	**1f**
Formula	$C_{35}H_{33}I_2N_2OPPd$	$C_{38}H_{39}I_2N_2OPPd$
Formula weight (g/mol^{-1})	888.80	930.88
Crystal system	Monoclinic	Triclinic
Crystal size (mm^3)	0.454 × 0.251 × 0.244	0.475 × 0.363 × 0.275
Space group, *Z*	$P2_1/c$, 4	*P-1,* 2
a (Å)	15.8083(8)	10.8564(5)
b (Å)	11.8071(5)	12.0155(6)
c (Å)	19.1353(8)	16.0984(8)
α, β, γ (°)	90, 96.738(4), 90	84.738(4), 82.502(4), 85.119(4)
Volume (Å^3)	3546.9(3)	2067.53(18)
ρ_{calc} (mg m^{-3})	1.664	1.495
μ (mm^{-1})	2.337	2.008
F (000)	1728	912
Reflections collected	11,151	10,081
Independent reflections	6208 [$R_{int}=0.0231$, $R_{sigma}=0.0411$]	7250 [$R_{int}=0.0211$, $R_{sigma}=0.0494$]
Parameters	399	411
GOF on F^2	1.036	1.032
Final *R* indices [$I>2\sigma(I)$]	$R_1=0.0379$ $wR_2=0.0927$	$R_1=0.0398$ $wR_2=0.0790$
R indices (all data)	$R_1=0.0539$ $wR_2=0.1002$	$R_1=0.0563$ $wR_2=0.0870$

vacuum to get the product as a yellow solid. The crude product was washed with *n*-pentane and recrystallized from chloroform/*n*-pentane (1:2) at room temperature. Yield: 73% (0.128 g); m.p: 88–90 °C; $\nu_{(CN)}$: 1434 cm^{-1}; $\nu_{(O-H)}$: 3453 cm^{-1}. Anal. Calc. for $C_{34}H_{31}I_2N_2OPPd$: C: 46.68; H: 3.57; N: 3.20. Found: C: 46.73; H: 3.50; N: 3.23. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 2.17 (s, 1H, –NCH_2CH_2OH); 3.96 (s, 2H, NCH_2CH_2OH); 4.10 (s, 2H, –NCH_2CH_2OH); 5.81 (s, 2H, –$NCH_2(C_6H_5)$; 6.27–7.63 (m, 23H, Ar–*H*). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 51.3 (–NCH_2CH_2OH); 54.5 (–$NCH_2(C_6H_5)$); 59.9 (–NCH_2CH_2OH); 110.9–111.8–127.9–128.0–128.1–128.2–128.4–128.6–128.9–130.3–131.1–131.9–132.3–134.5 and 135.3 (Ar–*C*); 171.7 (2-*C*). ^{31}P {^{1}H} NMR ($CDCl_3$, 162 MHz, δ, ppm) = 27.0.

Synthesis of diiodo[1-(2-hydroxyethyl)-3-(2-methylbenzyl)benzimidazol-2-ylidene] triphenylphosphinepalladium(II), 1b

The synthesis of **1b** was prepared in the same way as that described for **1a**, but diiodo[1-(2-hydroxyethyl)-3-(2-methylbenzyl)benzimidazol-2-ylidene]palladium(II) (141 mg, 0.2 mmol) was used instead of diiodo[1-(2-hydroxyethyl)-3-benzylbenzimidazol-2-ylidene]pyridine palladium(II). Yield: 77% (0.137 g); m.p: 149–151 °C; $\nu_{(CN)}$: 1433 cm^{-1}; $\nu_{(O-H)}$: 3446 cm^{-1}. Anal. Calc. for $C_{35}H_{33}I_2N_2OPPd$: C: 47.29; H: 3.74; N: 3.15. Found: C: 47.32; H: 3.72; N: 3.12. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.62 (s, 1H, –NCH_2CH_2OH); 2.33 and 2.49 (s, 3H, –$NCH_2C_6H_4(CH_3)$); 2.94 and 3.01 (s, 2H, –NCH_2CH_2OH); 4.42 and 4.75 (s, m, 2H, –NCH_2CH_2OH); 5.29 and 5.85 (s, 2H, –$NCH_2C_6H_4(CH_3)$); 6.99–7.89 (m, 23H, Ar–*H*). ^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) δ (ppm) = 19.7 (–$NCH_2C_6H_4(CH_3)$); 50.3 and 50.4 (–NCH_2CH_2OH); 51.4 and 53.4 (–$NCH_2C_6H_4(CH_3)$); 59.8 and 60.3 (–NCH_2CH_2OH); 111.0–111.3–111.5–123.1–127.7–127.8–127.9–128.3–128.4–130.3–135.1–135.2–135.3 and 149.8 (Ar–*C*); 178.3 (2-*C*) ^{31}P {^{1}H}NMR ($CDCl_3$, 162 MHz, δ, ppm) = 16.1 and 24.3.

Synthesis of diiodo[1-(2-hydroxyethyl)-3-(3-methylbenzyl)benzimidazol-2-ylidene] triphenylphosphinepalladium(II), 1c

The synthesis of **1c** was prepared in the same way as that described for **1a**, but diiodo[1-(2-hydroxyethyl)-3-(3-methylbenzyl)benzimidazol-2-ylidene]pyridinepalladium(II) (141 mg, 0.2 mmol) was used instead of dichloro[1-(2-hydroxyethyl)-3-benzylbenzimidazol-2-ylidene] pyridinepalladium(II). Yield: 72% (0.128 g); m.p: 138–140 °C; $\nu_{(CN)}$: 1433 cm^{-1}; $\nu_{(O-H)}$: 3738 cm^{-1}. Anal. Calc. for $C_{35}H_{33}I_2N_2OPPd$: C: 47.29; H: 3.74; N: 3.15. Found: C: 47.33; H: 3.78; N: 3.09. ^{1}HNMR (400 MHz, $CDCl_3$) δ (ppm) = 5.35 (s, 1H, –NCH_2CH_2OH); 2.53 (s, 3H, –$NCH_2C_6H_4(CH_3)$); 4.48 (s, 2H, –NCH_2CH_2OH); 4.99 (t, 2H, $J=6$ Hz –NCH_2CH_2OH); 6.01 (s, 2H, –$NCH_2C_6H_4$–); 6.55-7.49 (m, 23H, Ar–*H*). ^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) δ (ppm) = 20.0 (–$NCH_2C_6H_4(CH_3)$); 51.8 (–NCH_2CH_2OH); 52.4 (–$NCH_2C_6H_4(CH_3)$); 61.1 (–NCH_2CH_2OH);

110.6–111.2–111.4–114.1–123.4–123.4–126.5–128.2–128.7–130.6–132.2–135.0–138.4–148.3–149.3–157.4 and 158.0. (Ar–*C*); 167.0 (2-*C*). ^{31}P {^{1}H}NMR (CDCI$_3$, 162 MHz, δ, ppm) = 29.5.

Synthesis of diiodo[1-(2-hydroxyethyl)-3-(4-methylbenzyl)benzimidazol-2-ylidene] triphenylphosphinepalladium(II), 1d

The synthesis of **1d** was prepared in the same way as that described for **1a**, but diiodo[1-(2-hydroxyethyl)-3-(4-methylbenzyl)benzimidazol-2-ylidene]pyridinepalladium(II) (141 mg, 0.2 mmol) was used instead of diiodo[1-(2-hydroxyethyl)-3-benzylbenzimidazol-2-ylidene] pyridinepalladium(II). Yield: 73% (0.130 g); m.p: 88–90 °C; $\nu_{(CN)}$: 1433 cm^{-1}; $\nu_{(O-H)}$: 3442 cm^{-1}. Anal. Calc. for $C_{35}H_{33}I_2N_2OPPd$: C: 47.29; H: 3.74; N: 3.15. Found: C: 47.33; H: 3.76; N: 3.12. ^{1}HNMR (400 MHz, CDCI$_3$) δ (ppm) = 1.60 (s, 1H, –NCH$_2$CH$_2$O*H*); 2.29 and 2.34 (s, 3H, –NCH$_2$C$_6$H$_4$(C*H$_3$*)); 4.41 (s, 2H, –NC*H$_2$*CH$_2$OH); 5.29 (s, 2H, –NCH$_2$C*H$_2$*OH); 5.84 (s, 2H, –NC*H$_2$*C$_6$H$_4$–); 6.94-7.72 (m, 23H, Ar–*H*). ^{13}C {^{1}H}NMR (100 MHz, CDCI$_3$) δ (ppm) = 21.2 (–NCH$_2$C$_6$H$_4$(*C*H$_3$)); 50.3 and 51.2 (–N*C*H$_2$CH$_2$OH); 53.2 and 54.2 (–N*C*H$_2$H$_4$(CH$_3$));110.8–111.8–122.9–123.0–127.9–128.0–128.1–128.2–128.4–129.4–130.3–131.1–131.7–132.0–132.4–134.4–134.5–134.6–135.1–135.3 and 137.8. (Ar–*C*); 171.5 (2-*C*). ^{31}P {^{1}H}NMR (CDCI$_3$, 162 MHz, δ, ppm) = 16.0 and 23.9.

Synthesis of diiodo[1-(2-hydroxyethyl)-3-(2,4,6-trimethylbenzyl)benzimidazol-2-ylidene]triphenylphosphinepalladium(II), 1e

The synthesis of **1e** was prepared in the same way as that described for **1a**, but diiodo[1-(2-hydroxyethyl)-3-(2,4,6-trimethylbenzyl)benzimidazol-2-ylidene] pyridinepalladium(II) (146 mg, 0.2 mmol) was used instead of diiodo[1-(2-hydroxyethyl)-3-benzyl benzimidazol-2-ylidene] pyridinepalladium(II). Yield: 70% (0.128 g); m.p: 283–285 °C; $\nu_{(CN)}$: 1434 cm^{-1}; $\nu_{(O-H)}$: 3359 cm^{-1}. Anal. Calc. for $C_{37}H_{37}I_2N_2OPPd$: C: 48.47; H: 4.07; N: 3.06. Found: C: 48.51; H: 4.10; N: 3.09. ^{1}HNMR (400 MHz, CDCI$_3$) δ (ppm) = 1.57 (s, 1H, –NCH$_2$CH$_2$O*H*); 1.91 and 2.25 (s, 9H, –NCH$_2$C$_6$H$_2$(C*H$_3$*)$_3$); 4.33 (m, 2H, –NC*H$_2$*CH$_2$OH); 4.69 (m, 2H, –NCH$_2$C*H$_2$*OH); 5.77 (s, 2H, –NC*H$_2$*C$_6$H$_2$–); 6.81–7.66 (m, 21H, Ar–*H*). ^{13}C {^{1}H}NMR (100 MHz, CDCI$_3$) δ (ppm) = 14.7 and 18.6 (–NCH$_2$C$_6$H$_2$(*C*H$_3$)$_3$); 42.5 (–N*C*H$_2$CH$_2$OH); 56.2 (–N*C*H$_2$C$_6$H$_2$(CH$_3$)$_3$); 62.6 (–NCH$_2$*C*H$_2$OH); 111.3–125.0–128.2–128.3–129.0–129.5–131.4–132.7–134.9–135.1–138.2 and 149.6. (Ar–*C*); 174.2 (2-*C*). ^{31}P {^{1}H}NMR (CDCI$_3$, 162 MHz, δ, ppm) = 27.0 and 29.7.

Synthesis of diiodo[1-(2-hydroxyethyl)-3-(2,3,5,6-tetramethylbenzyl)benzimidazol-2-ylidene]triphenylphosphinepalladium(II), 1f

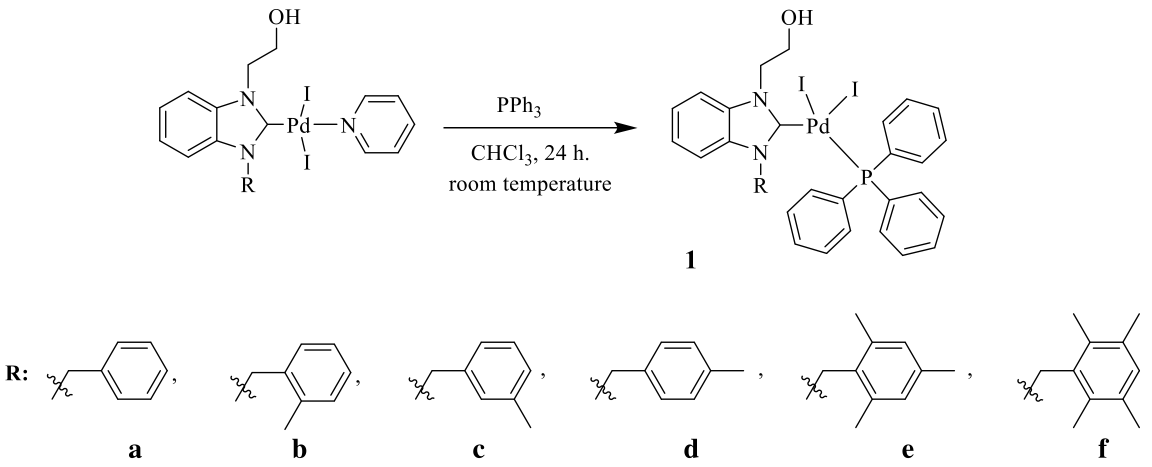
The synthesis of **1e** was prepared in the same way as that described for **1a**, but diiodo[1-(2-hydroxyethyl)-3-(2,3,5,6-tetramethylbenzyl)benzimidazol-2-ylidene] pyridinepalladium(II) (149 mg, 0.2 mmol) was used instead of diiodo[1-(2-hydroxyethyl)-3-benzyl benzimidazol-2-ylidene] pyridinepalladium(II). Yield: 65% (0.121 g); m.p: 168–169 °C; $\nu_{(CN)}$: 1434 cm^{-1}; $\nu_{(O-H)}$: 3556 cm^{-1}. Anal. Calc. for: $C_{38}H_{39}I_2N_2OPPd$: C: 49.03; H: 4.22; N: 3.01. Found: C: 49.01; H: 4.26; N: 3.05. ^{1}HNMR (400 MHz, CDCI$_3$) δ (ppm) = 1.57 (s, 1H, –NCH$_2$CH$_2$O*H*); 1.93, 2.13 and 2.23 (s, 15H, –NCH$_2$C$_6$(C*H$_3$*)$_5$); 4.42 (m, 2H, –NC*H$_2$*CH$_2$OH); 4.77 (t, 2H, *J:* 4 Hz –NCH$_2$C*H$_2$*OH); 5.93 (s, 2H, –NC*H$_2$*C$_6$(CH$_3$)$_5$); 7.00–7.76 (m, 19H, Ar–*H*). ^{13}C {^{1}H} NMR (100 MHz, CDCI$_3$) δ (ppm) = 15.4 and 19.8 (–NCH$_2$C$_6$H$_4$(*C*H$_3$)); 44.3 (–N*C*H$_2$CH$_2$OH); 54.6 (–N*C*H$_2$C$_6$H$_4$(CH$_3$)); 65.8 (–NCH$_2$*C*H$_2$OH); 110.5–111.1–111.6–122.4–122.9–123.2–127.7–127.9–128.0–128.3–128.4–129.4–130.3–130.4–132.0–132.5–132.7–133.1–134.3–135.2–135.3–135.6 and 136.3. (Ar–*C*); 173.4 (2-*C*). ^{31}P {^{1}H} NMR (CDCI$_3$, 162 MHz, δ, ppm) = 12.8–15.9 and 23.7.

General procedure for the catalytic activity of (NHC)PdI$_2$PPh$_3$ complexes in Sonogashira cross-coupling reaction

For the catalytic activity of (NHC)PdI$_2$PPh$_3$ complexes in Sonogashira cross-coupling reaction, first, phenylacetylene (1.5 mmol), aryl halides (1 mmol), Cs$_2$CO$_3$ (2 mmol) and (NHC)PdI$_2$PPh$_3$ complexes **1a–f** (0.01 mmol) were dissolved in DMF (2 ml) in a small Schlenk tube as described in the literature (Aktaş et al. 2018a, b, 2019). The reaction mixture was stirred in an oil bath at 80 °C for 4 h. Then, the reaction mixture was cooled to room temperature. The solvent was evaporated under vacuum. The mixture was passed through (1 cm thick) silica gel column using an ethyl acetate/*n*-hexane (1/5) solvent mixture. After the excess of the solvent was evaporated, the products were checked by gas chromatography (GC). The conversions were calculated as the conversion of aryl halides to diphenylacetylene products.

General procedure for the catalytic activity of (NHC)PdI$_2$PPh$_3$ complexes in Mizoroki–Heck cross-coupling reaction

For the catalytic activity of (NHC)PdI$_2$PPh$_3$ complexes in Mizoroki–Heck cross-coupling reaction, first, styrene (1.5 mmol), aryl halides (1 mmol), KOAc (2 mmol) and (NHC)PdI$_2$PPh$_3$ complexes **1a–f** (0.01 mmol) were dissolved in DMF/(CH$_3$)$_2$CHOH (1:1) (2 ml) in a small Schlenk



Scheme 1 Synthesis (NHC)PdI_2PPh_3 complexes **1a**–**f**

tube. The reaction mixture was stirred in an oil bath at 80 °C for 4 h. Then, the reaction mixture was cooled to room temperature. The solvent was evaporated under vacuum. The mixture was passed through (1 cm thick) silica gel column using an ethyl acetate/*n*-hexane (1/5) solvent mixture. After the excess of the solvent was evaporated, the products were checked by gas chromatography (GC). The conversions were calculated as the conversion of aryl halides to diphenylethene products.

Results and discussion

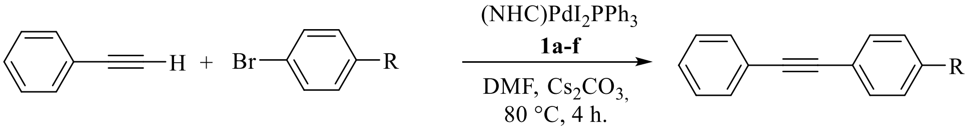
Synthesis of (NHC)PdI_2PPh_3 complexes (1a–f)

In here we have defined the new 2-hydroxyethyl-substituted (NHC)PdI_2PPh_3 complexes illustrated in Scheme 1. These complexes **1a**–**f** have been prepared from the (NHC) PdI_2(pyridine) complexes (PEPPSI) with the PPh_3. The air and moisture-stable complexes **1a**–**f** are soluble in halogenated solvents such as dichloromethane and chloroform. The new (NHC)PdI_2PPh_3 complexes were obtained as a yellow solid in between 65 and 77% yields. The isolated products were identified and characterized on the basis of elemental and spectroscopic analysis (FTIR, ^1H, ^{13}C, ^{31}P NMR and elemental analyses data) techniques. The ^1H-NMR spectra of (NHC)PdI_2PPh_3 complexes, when compared with the starting PEPPSI complexes (Erdemir et al. 2019), the pyridine peaks between 7.50 and 9.00 were not observed. Instead, an increase in aromatic peaks between 7.00 and 8.00, attributed to the PPh_3, was observed. Similarly, no signs of the pyridine peaks on ^{13}C-NMR spectra were observed between 153.0 and 155.0 for the corresponding PEPPSI complexes. Instead, an increase in aromatic peaks between 120.0 and 130.0 from the PPh_3 was observed. Also, the Pd–Carbene resonances that are observed between 160.0 and 162.0 in the ^{13}C NMR spectra of the starting PEEPSI complexes were highly downfield shifted at δ 171.7, 178.3, 167.0, 171.5, 174.2 and 173.4 ppm for complexes **1a–f**, respectively. The Pd–P resonances of the (NHC)PdI_2PPh_3 complexes in the ^{31}P NMR spectra appeared highly downfield shifted at δ 27.0, 16.1–24.3, 25.9, 16.0–23.9, 25.3 and 12.8–15.9–23.7 ppm for **1a–f**, respectively. The FT-IR data clearly indicated the presence of ν(CN) at 1434, 1433, 1433, 1433, 1434, 1434 cm^{-1} for the (NHC)PdI_2PPh_3 complexes **1a–f**, respectively. The FT-IR data clearly indicated the presence of ν(OH) at 3453, 3446, 3738, 3442, 3359 and 3556 cm^{-1} for the (NHC)PdI_2PPh_3 complexes **1a–f**, respectively. The results of all data are consistent with similar studies (Aktaş et al. 2018a, b, 2019; Boubakri et al. 2017; Dehimat et al. 2018; Touj et al. 2018). When we evaluated which is one of the analytical techniques used to prove the synthesis of compounds, it was observed that the calculated values were very close to the found values. Also, we have obtained an appropriate single-crystal for complexes **1b** and **1f** by using X-ray diffraction method.

The catalytic activity of (NHC)PdI_2PPh_3 complexes in Sonogashira cross-coupling reaction

In this work, we performed the Sonogashira coupling reaction in DMF using (NHC)PdI_2PPh_3 complexes **1a–f** as catalyst. Thanks to the unique electronic properties of NHC and PPh_3 ligands, all complexes exhibited high catalytic activity in the Sonogashira cross-coupling reaction. In the literature, when the DMF was used as the solvent, the catalytic activities of (NHC)Pd(II)PPh_3 complexes in Sonogashira cross-coupling reaction obtained higher conversions (Aktaş et al. 2018a, b). Thus, we used DMF as the solvent. The catalytic activities of (NHC)PdI_2PPh_3 complexes **1a–f** were

Table 2 The catalytic activity of phenylacetylene with aryl bromides in Sonogashira cross-coupling reactions catalyzed by (NHC)PdI_2PPh_3 complexes **1a–f**



2-4

Entry	R	Product	Cat.	Conversion (%)
1	$–COCH_3$	2	**1a**	92
2			**1b**	89
3			**1c**	> 99
4			**1d**	> 99
5			**1e**	99
6			**1f**	94
7	$–CH_3$	3	**1a**	82
8			**1b**	78
9			**1c**	79
10			**1d**	96
11			**1e**	97
12			**1f**	94
13	$–OCH_3$	4	**1a**	79
14			**1b**	75
15			**1c**	71
16			**1d**	83
17			**1e**	90
18			**1f**	89

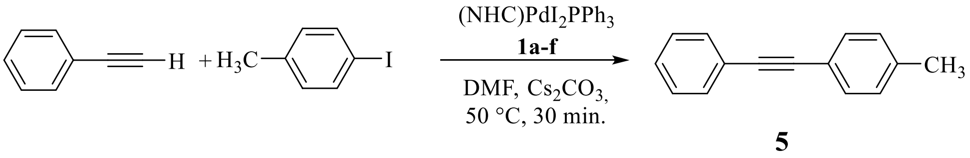
Reaction conditions Phenylacetylene (1.5 mmol), 4-bromoaryl (1 mmol), (NHC)PdI_2PPh_3 complexes **1a–f** (0.01 mmol) and Cs_2CO_3 (2 mmol) were added in DMF (3 ml) to the Schlenk tube in open air. It was stirred at 80 °C for 4 h

examined in Sonogashira cross-coupling reactions under optimum conditions (Aktaş et al. 2018a, b). Phenylacetylene (1.5 mmol), 4-arylhalides (1 mmol), (NHC)PdI_2PPh_3 complexes **1a–f** (0.01 mmol) and Cs_2CO_3 (2 mmol) were added in DMF (2 ml) to the Schlenk tube in open air. It was stirred at 80 °C for 4 h. Then, the solvent (DMF) was evaporated under vacuum. The residue was passed through a silica gel column (1 cm thick) by using ethyl acetate/*n*-hexane (1/5) solvent mixture. After the redundancy of the solvent was evaporated, the products were checked using GC. The results were calculated as the conversion of the aryl halides to diphenylacetylene products. Conversions were illustrated in Tables 2, 3 and 4. Also, the dimerization product of phenylacetylene was observed at the end of the catalysis experiments (Nishihara et al. 2000; Aktaş et al. 2018a, b). But this dimerization product was not taken into account in the conversion calculations.

Here, we examined the catalytic effects of (NHC)PdI_2PPh_3 complexes **1a–f** in the coupling reactions of aryl halides and phenyl acetylene. The (NHC)PdI_2PPh_3 complexes **1a–f** exhibited high catalytic activity as the catalyst in the Sonogashira cross-coupling reactions. As mentioned in our recently published study, the electronic properties of aryl halides are effective in catalytic conversions (Aktaş et al. 2018a, b). In the catalytic experiments performed with the aryl halides (containing chloride, bromide, and iodide) different results were obtained (Tables 2, 3, 4).

In the result of the experiments with iodinated aryl halides, very high conversions were obtained in a shorter time (Table 3), while in the result of experiments with chlorinated aryl halides, very low conversions were obtained over a longer time (Table 4). This is related to the durability or weakness of the bond between carbon ($C_{benzene}$) and halogen atoms (C–X). First, when the orbitals forming the $C_{benzene}$–X bond in the aryl halide are examined [$C_{benzene}$ ($2sp^2$), Cl (3p), Br (4p) and I (5p) orbital], the overlap rates of the orbitals are $2sp^2–3p > 2sp^2–4p > 2sp^2–5p$, respectively. The durability of the $C_{benzene}$–X bond happens due to the fact that the orbital overlap decreases in the following order: $C_{benzene}–Cl > C_{benzene}–Br > C_{benzene}–I$. Second, the anion stability of the leaving group (halides) decreases in the following order: $I^- > Br^- > Cl^-$. The more stable the anion (halides)

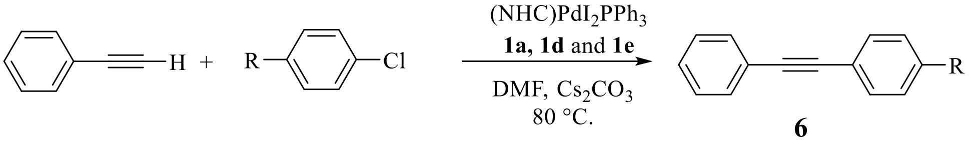
Table 3 The catalytic activity of phenylacetylene with iodotoluene in Sonogashira cross-coupling reactions catalyzed by (NHC)PdI_2PPh_3 complexes **1a–f**



Entry	Product	Cat.	Conversion (%)
1	5	1a	97
2		1b	94
3		1c	98
4		1d	99
5		1e	99
6		**1f**	>99

Reaction conditions Phenylacetylene (1.5 mmol), 4-iodotoluene (1 mmol), (NHC)PdI_2PPh_3 complexes **1a–f** (0.01 mmol) and Cs_2CO_3 (2 mmol) were added in DMF (3 ml) to the Schlenk tube in open air. It was stirred at 50 °C for 30 min

Table 4 The catalytic activity of phenyl acetylene with 4-chloroacetophenone in Sonogashira cross-coupling reactions catalyzed by (NHC)PdI_2PPh_3 complexes **1a, 1d** and **1e**



Entry	R	Product	Cat.	Conversion (%)
1	$-COCH_3$	6	1a	18
2			1d	21
3			**1e**	32

Reaction conditions Phenylacetylene (1.5 mmol), 4-chloroacetophenone (1 mmol), (NHC)PdI_2PPh_3 complex **1a, 1d** and **1e** (0.01 mmol) and Cs_2CO_3 (2 mmol) were added in DMF (3 ml) to the Schlenk tube in open air. It was stirred at 80 °C for 16 h

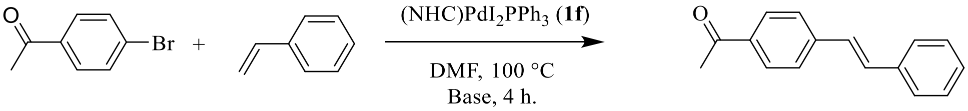
is, the weaker the C–X bond is. Thus, the conversions of substrates in catalytic reactions decrease, respectively, as follows: aryl iodide > aryl bromide > aryl chloride (Tables 2, 3, 4).

The groups of $-OCH_3$, $-CH_3$ and $-COCH_3$ in the para position of the aryl halides used as substrates affect the aromatic ring electronically (Aktaş et al. 2013, 2018a, b, 2019; Aktas and Gök 2014, 2015; Sarı et al. 2017; Erdoğan et al. 2018; Gök et al. 2018; Gök et al. 2019). The electron withdrawing group ($-COCH_3$) weakens the $C_{benzene}$–X bond in the para position while the electron donating groups ($-CH_3$ and $-OCH_3$) strengthen the $C_{benzene}$–X bond. Thus, when electron withdrawing groups ($-COCH_3$) are used in substrates, the conversions of catalytic reactions are higher (Table 2). But, when electron donating groups ($-CH_3$, $-OCH_3$) are used, the conversions of catalytic reactions are less (Tables 3, 4).

Finally, in our study, the substitution groups that were different in the (NHC)PdI_2PPh_3 complexes **1a–f** had little effect on catalytic conversions. The conversions were obtained slightly higher in the catalytic reactions containing bulky substituents. Also, the (NHC)PdI_2PPh_3 complexes **1a–f** were observed to be active catalysts compared to the similar studies previously published (Aktaş et al. 2018a, b, 2019; Boubakri et al. 2017; Dehimat et al. 2018; Touj et al. 2018).

In a similar study that we have published recently, (NHC)Pd(II)PPh_3 complexes containing chloride and bromide ligand were used for the same catalytic reaction (Aktaş et al. 2018a, b, 2019). We observed that the halide ligands in the complexes had little effect on catalytic activity.

Table 5 The catalytic activities of $(NHC)PdI_2PPh_3$ complex **1f** using different bases in the Mizoroki–Heck cross-coupling reactions



Entry	Solvent	Base	Temperature (°C)	Time (h)	Conversion (%)
1	DMF	$KOBu^t$	100	4	99
2	DMF	K_2CO_3	100	4	58
3	DMF	NaOH	100	4	70
4	DMF	KOH	100	4	99
5	DMF	Na_2CO_3	100	4	54
6	DMF	Cs_2CO_3	100	4	94
7	DMF	$KACO_3$	100	4	99
8	DMF	KOAc	100	4	100

Reaction conditions Styrene (1.5 mmol), 4-bromoacetophenone (1 mmol), $(NHC)PdI_2PPh_3$ complex **1f** (0.01 mmol) and base (2 mmol) were added in DMF (3 ml) to the Schlenk tube in open air. Was stirred at 100 °C for 4 h

The catalytic activity of $(NHC)PdI_2PPh_3$ complexes in Mizoroki–Heck Cross-coupling reaction

We performed the Mizoroki–Heck cross-coupling reaction using $(NHC)PdI_2PPh_3$ complexes **1a–f** as the catalyst. To determine the optimum conditions, suitable base was selected first. The $(NHC)PdI_2PPh_3$ complex **1f** was mixed with styrene and 4-bromoacetophenone in DMF (3 ml), at 100 °C for 4 h using $KOBu^t$, K_2CO_3, NaOH, KOH, Na_2CO_3, K_2CO_3, Cs_2CO_3, and KOAc bases. Then, DMF was removed under vacuum and the reaction mixture was purified by passing it through a silica gel column (1 cm thick) in a mixture of ethyl acetate/*n*-hexane (1/5). After the redundant solvent was evaporated, the remaining reaction mixture was injected into the GC. The conversion was calculated as the conversion of 4-bromoacetophenone to the products. The conversions are illustrated in Table 5. When KOAc was used as the base, the highest conversion was obtained. Thus KOAc was used as a base in the next experiments.

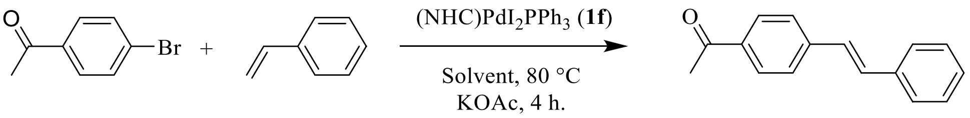
The selection of the solvent is important for catalytic reactions. The solvent must dissolve the base, substrates and especially the Pd complex in the solvent. Another important issue is the coordination of the solvent (such as water and pyridine) to the metal center. This condition can affect the catalytic activity of Pd complexes because of its altering the structure of the Pd complex (Li et al. 2019).

The solvents were determined after selecting the base for optimum conditions. The styrene (1.5 mmol), 4-bromoacetophenone (1 mmol), $(NHC)PdI_2PPh_3$ complex **1f** (0.01 mmol) and KOAc (2 mmol) were added in the solvent (3 ml) to the Schlenk tube in open air. It was stirred at 80 °C for 4 h. Three different solvents (DMF, $(CH_3)_2CHOH$, and EtOH) and three solvent mixtures [DMF/$(CH_3)_2$CHOHv(1/2), DMF/H_2O (2/1), and EtOH/H_2O (1/2)] were used. The results of the experiment were checked using GC. The conversion of the products was calculated by taking 4-bromoacetophenone into consideration. The conversions were illustrated in Table 6. The high conversion was obtained when DMF and DMF/$(CH_3)_2CHOH$ (1/2) solvent mixture was used as the solvent. The DMF/$(CH_3)_2CHOH$ (1/2) solvent system was used since it is cheaper. Thus DMF/$(CH_3)_2CHOH$ (1/2) mixture was used as the solvent in the following experiments.

The palladium-catalyzed Mizoroki–Heck cross-coupling reaction is the most effective way to bind aryl/vinyl halides. After Heck's pioneering work, Mizoroki et al. published preliminary results for the purification of the alkenes catalyzed by iodobenzene in the presence of potassium acetate. Then, Mizoroki et al. (Mori et al. 1973) extended their preliminary study to aryl bromides. However, they were discovered to be much less reactive than aryl iodides. The reactivity of the aryl halides decreases in the following order: PhI > PhBr ≫ PhCl. Then, Mizoroki et al. reported that the use of the phosphine ligand (PPh_3) was somewhat advantageous (Mori et al. 1973). Dieck and Heck (1974) developed the use of PPh_3 with palladium acetate. After this study, a mechanism for reactions catalyzed by palladium acetate was proposed by Dieck and Heck (1974) against monophosphine ligands. The mechanism (Heck 1978, 1979) was presented as a catalytic cycle for successive reactions by Heck.

In our study, we used the $(NHC)PdI_2PPh_3$ complexes **1a–f** for the Palladium-catalyzed Mizoroki–Heck cross-coupling reaction. In this reaction, we examined the coupling of styrene and aryl halides. In general, we observed

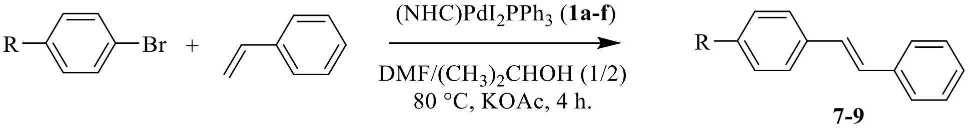
Table 6 The catalytic activities of (NHC)PdI_2PPh_3 complex **1f** using different solvents in the Mizoroki–Heck cross-coupling reactions



Entry	Solvent	Base	Temperature (°C)	Time (h)	Conversion (%)
1	DMF/H_2O	KOAc	80	4	35
2	EtOH/H_2O	KOAc	80	4	24
3	EtOH	KOAc	80	4	12
4	$(CH_3)_2CHOH$	KOAc	80	4	73
5	DMF	KOAc	80	4	100
6	DMF/**$(CH_3)_2$CHOH**	KOAc	80	4	100

Reaction conditions Styrene (1.5 mmol), 4-bromoacetophenone (1 mmol), (NHC)PdI_2PPh_3 complex **1f** (0.01 mmol) and KOAc (2 mmol) were added in the solvent (1/2) (3 ml) to the Schlenk tube in open air. Was stirred at 80 °C for 4 h

Table 7 The catalytic activity of styrene with arylbromide in the Mizoroki–Heck cross-coupling reactions catalyzed by (NHC)PdI_2PPh_3 complexes **1a–f**



7-9

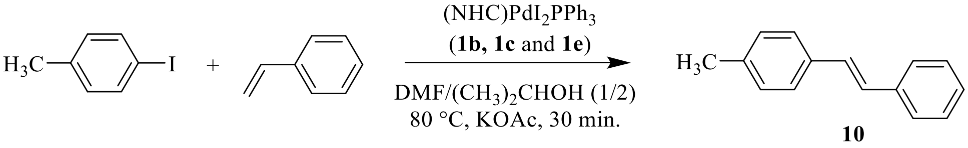
Entry	R	Product	Cat.	Conversion (%)
1	$–COCH_3$	7	**1a**	100
2			**1b**	100
3			**1c**	100
4			1d	88
5			**1e**	100
6			**1f**	100
7	$–OCH_3$	8	1a	85
8			**1b**	98
9			**1c**	97
10			1d	95
11			1e	82
12			1f	80
13	$–CH_3$	9	1a	88
14			1b	85
15			**1c**	95
16			1d	83
17			1e	85
18			1f	80

Reaction conditions Styrene (1.5 mmol), arylbromide (1 mmol), (NHC)PdI_2PPh_3 complexes **1a–f** (0.01 mmol) and KOAc (2 mmol) were added in DMF/$(CH_3)_2CHOH$ (1/2) (3 ml) to the Schlenk tube in open air. Was stirred at 80 °C for 4 h

that all the (NHC)PdI_2PPh_3 complexes **1a–f** were active. The reactivity of the aryl halides was obtained in accordance with the literature as PhI > PhBr ≫ PhCl, respectively (Oestreich 2009).

Here, the coupling reactions of the aryl bromides with styrene were examined as catalysts for all (NHC)PdI_2PPh_3 complexes **1a–f**. The results we obtained from the Mizoroki–Heck cross-coupling were in parallel with the results

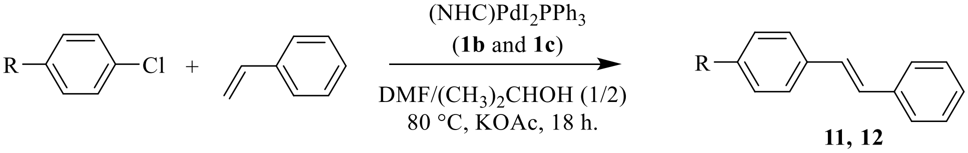
Table 8 The catalytic activity of styrene with 4-iodotoluene in the Mizoroki–Heck cross-coupling reactions catalyzed by (NHC)PdI_2PPh_3 complexes (**1b**, **1c** and **1e**)



Entry	Product	Cat.	Conversion (%)
1	10	**1b**	98
2		1c	96
3		1e	89

Reaction conditions Styrene (1.5 mmol), 4-iodotoluene (1 mmol), (NHC)PdI_2PPh_3 complex **1b**, **1c** and **1e** (0.01 mmol) and KOAc (2 mmol) were added in DMF/$(CH_3)_2CHOH$ (1/2) (3 ml) to the Schlenk tube in open air. Was stirred at 80 °C for 30 min

Table 9 The catalytic activity of styrene with arylchloride in the Mizoroki–Heck cross-coupling reactions catalyzed by (NHC)PdI_2PPh_3 complexes (**1b** and **1c**)



Entry	R	Product	Cat.	Conversion (%)
1	$–COCH_3$	11	**1a**	17
2			1b	11
7	$–OCH_3$	12	1a	3
8			1b	4

Reaction conditions Styrene (1.5 mmol), arylchloride (1 mmol), (NHC)PdI_2PPh_3 complexes (**1b** and **1c**) (0.01 mmol) and KOAc (2 mmol) were added in DMF/$(CH_3)_2CHOH$ (1/2) (3 ml) to the Schlenk tube in open air. Was stirred at 80 °C for 18 h

we obtained from Sonogashira coupling reactions (above). The experimental results show that the electronic effects of the aryl bromides are effective on the conversions of catalytic reactions (Tables 7, 8, 9). When electron withdrawing groups ($–COCH_3$) were used in substrates, the conversions of catalytic reactions are higher (Table 7). But, when electron donating groups ($–CH_3$, $–OCH_3$) were used, the conversions of catalytic reactions are less (Tables 8, 9). When the (NHC)PdI_2PPh_3 complexes **1a–f** were compared among themselves, there are very few differences between the conversions of catalytic reactions (Tables 7, 8, 9). We observed that the conversion in catalytic experiments increased slightly while using generally bulky (NHC)PdI_2PPh_3 complexes. The reason for this difference in catalytic conversion may be the ease of the reductive elimination in the catalytic cycle.

Second, we performed coupling reactions using styrene with aryl chloride and aryl iodide substrates for the Mizoroki–Heck cross-coupling reaction. In these experiments, we used the (NHC)PdI_2PPh_3 complexes **1a** and **1b** for chloride substrate (Table 8) and the (NHC)PdI_2PPh_3 complexes **1b, 1c** and **1e** for iodide substrate (Table 9). As a result of these experiments, in the conversions of the catalytic reactions that were used aryl iodides, very high conversions were obtained in 30 min as we expected (Table 8). In contrast, when aryl chlorides were used in the catalytic reactions, very low conversions were obtained at 18 h (Table 9). These results are consistent with the literature (Siemeling et al. 2012).

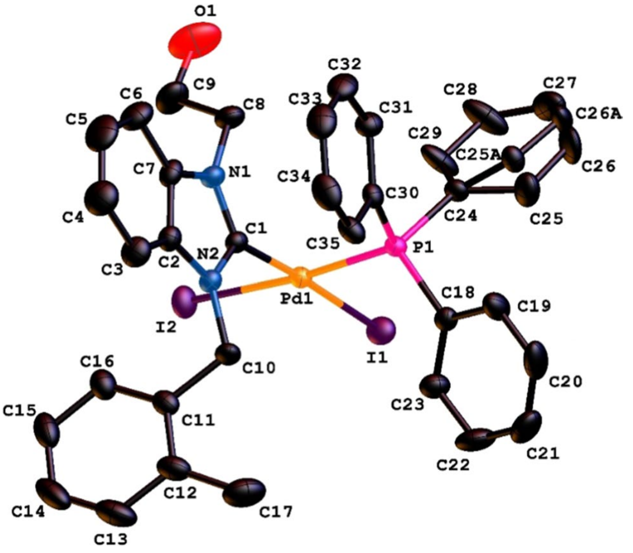


Fig. 1 Molecular structure of **1b** showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 25% probability level. Selected bond parameters (Å, °): Pd1–I1 2.6465(5), Pd1–I2 2.6681(5), Pd1–P1 2.2963(13), Pd1–C1 1.990(5), C1–N1 1.345(6), C1–N2 1.358(6), N1–C8 1.472(7), N2–C10 1.464(6), C9–O1 1.422(9); I1–Pd1–I2 92.474(17), I1–Pd1–P1 92.03(3), I1–Pd1–C1 176.63(14), I2–Pd1–P1 174.42(4), I2–Pd1–C1 85.25(13), P1–Pd1–C1 90.40(14), C1–N1–C8 124.9(5), N1–C8–C9 114.0(5), C8–C9–O1 108.5(6), C1–N2–C10 125.8(4), N2–C10–C11 114.4(5), Pd1–P1–C18 115.69(17), Pd1–P1–C24 113.02(18), Pd1–P1–C30 113.60(16)

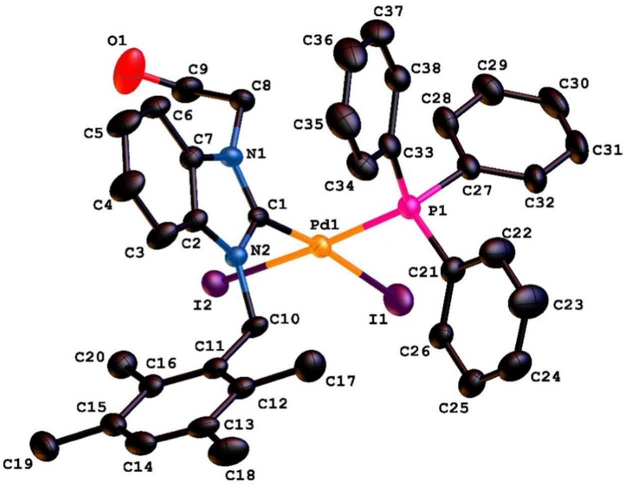


Fig. 2 Molecular structure of **1f** showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 25% probability level. Selected bond parameters (Å, °): Pd1–I1 2.6283(5), Pd1–I2 2.6433(5), Pd1–P1 2.2804(12), Pd1–C1 1.987(4), C1–N1 1.357(5), C1–N2 1.353(5), N1–C8 1.457(6), N2–C10 1.477(5), C9–O1 1.398(6); I1–Pd1–I2 90.765(16), I1–Pd1–P1 91.57(3), I1–Pd1–C1 172.91(13), I2–Pd1–P1 176.22(4), I2–Pd1–C1 87.21(11), P1–Pd1–C1 91.87(12), C1–N1–C8 123.6(4), N1–C8–C9 113.0(4), C8–C9–O1 111.0(5), C1–N2–C10 121.1(4), N2–C10–C11 115.3(4), Pd1–P1–C21 114.10(17), Pd1–P1–C27 112.18(17), Pd1–P1–C33 114.81(15)

Structural description of the complex 1b and 1f

Molecular structures of two *cis*-(NHC)PdI$_2$PPh$_3$ complexes **1b** and **1f** are shown in Figs. 1 and 2. The Pd-metal ions are coordinated by NHC and PPh$_3$ ligands, and two iodide atoms in *cis* disposition. In the complex **1b**, NHC ligand connects to a methylbenzyl on the *ortho*-position, and a hydroxyethyl via methylene bridges, while in **1f**, NHC ligand connects to a tetramethylbenzyl and a hydroxyethyl, similarly through the methylene bridges. Coordination spheres around the Pd(II) atoms adopt slightly *distorted square-planar* geometry. PPdI$_2$C planes are almost planar with the r.m.s deviations of 0.054 and 0.093 Å for **1b** and **1f**, respectively. Pd–C$_{\text{carbene}}$ bond lengths are 1.990(5) Å in **1b**, 1.992(6) Å in **1f**, are comparable with similar *cis*-(NHC)PdI$_2$PPh$_3$ complexes in our previous study and the study of Hahn et al. (Aktaş et al. 2019; Hahn et al. 2004). Considering bond angles around the phosphorus atoms, both complexes have *distorted* tetrahedral environments. The NHC ligands are oriented almost perpendicular to Pd/C/P/I/I planes with the values of 89.21(10)° for **1b**, 87.06(10)° for **1f**. The palladium–iodide bond lengths *trans* to the carbenes are very slightly shorter than that trans to the phosphines. In the literature, it is suggested that the reason for the longer Pd–I bond distance, which *trans* to the phosphine ligand is due to the fact that the strong trans effect of phosphine (Zamora et al. 2012; Modak et al. 2015). Thus, palladium(II) complexes bearing both NHC and phosphine ligands usually adopt a square planar *cis*-configuration due to this transphobia. Hydroxethyl groups are almost perpendicular to the NHC ring systems of **1b** and **1f**, with the C1–N1–C8–C9 torsion angles to be 103.33(2)° and 99.30(4)°, respectively. On the other hand, in **1b**, the torsion angle [C1–N2–C10–C11] between the NHC and methylbenzyl is − 121.25(2)°, while this value, in **1f**, is − 166.18(9)° between the NHC and tetramethylbenzyl fragment.

The crystal structure of complex **1b** is stabilized by C–H···N type intra-molecular interactions and Van der Waals forces. Stacking of the molecules, viewing along the *c*-axis, are shown in Fig. 3. In **1f**, molecules connect to each other via the O1–H1···I2^{i} inter-molecular hydrogen bonds, to form a dimeric $R_2^2(16)$ graph-set motif (Fig. 4) (Etter and MacDonald 1990). In addition, intra-molecular C–H···N type interactions and C–H···π stacking interactions are responsible for the stabilization of the crystal structure [C3–H3···Cg1, C3···Cg1 = 3.467(5) Å, C3–H3···Cg1 = 145°, Cg1: C11/16; C31–H31···Cg2, C31···Cg2 = 3.525(7) Å, C31–H31···Cg2 = 137°, Cg2: C2/7].

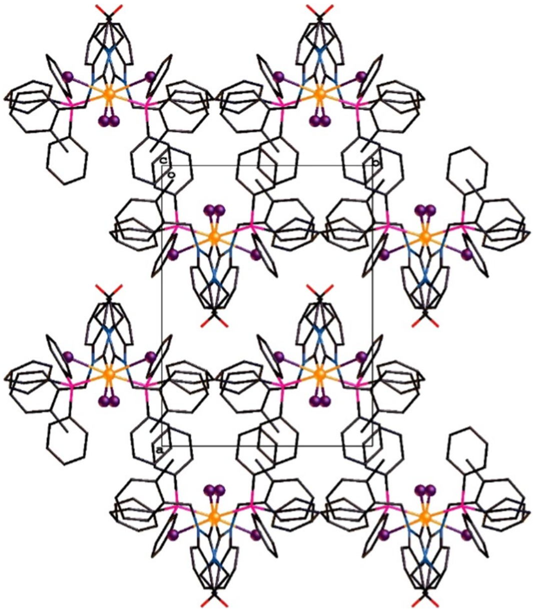


Fig. 3 Stacking of the molecules of complex **1b**, viewed along the *c*-axis. The Pd metals and iodide anions are shown as balls, while the other atoms are shown as stick drawing style. For the sake of clarity, hydrogen atoms are omitted

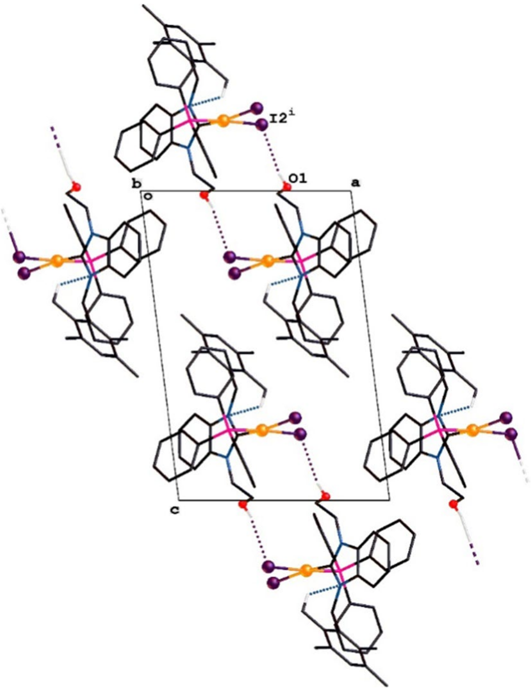


Fig. 4 Graphical representation of molecular packing within the unit cell for the complex **1f**, viewed along the *b*-axis. Molecules connect to each other via the O1–H1•••I2^{i} hydrogen bonds [H1•••I2^{i} = 2.74 Å, O1–I2^{i} = 3.511(5) Å, O1–H1•••I2^{i} = 158°, symmetry code ^{i}1–x, 1–y, –z]. Oxygen atoms, iodide anions and palladium atoms, are shown as ball and stick drawing style, the other atoms shown as only stick drawing style. For the clarity, hydrogen atoms not to play role in bonding are omitted

Conclusion

In conclusion, we reported the synthesis of new 2-hydroxyethyl substituted (NHC)PdI$_2$PPh$_3$ **1a–f** using PPh$_3$ and starting PEPPSI complexes. The catalytic activities of these complexes were examined in the Sonogashira cross-coupling and Mizoroki–Heck cross-coupling reaction. All complexes showed excellent activity when the aryl iodide and aryl bromide were used in these reactions. But, all complexes showed less activity when the aryl chloride was used in these reactions. The crystal structures of the complexes **1b** and **1f** were performed using single-crystal X-ray diffraction technique. The results of the analysis indicate that both (NHC)PdI$_2$PPh$_3$ complexes adopt distorted square-planar environments around the Pd(II) centers.

Acknowledgements The authors acknowledge Dokuz Eylul University for the use of the Rigaku Oxford Xcalibur Eos Diffractometer (purchased under University Research Grant no.: 2010.KB.FEN.13). The authors thank the Inonu University Faculty of Science Department of Chemistry for the spectroscopy and elemental analysis characterization of compounds.

Compliance with ethical standards

Conflicts of interests The authors declare that there are no conflicts of interests.

Appendix A: Supplementary data

CCDC 1897240 for **1b** and 1897153 for **1f** contain the supplementary crystallographic data. 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, e-mail: deposit@ccdc.cam.ac.uk.

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