Transition Metal Chemistry (2019) 44:229–236
https://doi.org/10.1007/s11243-018-0286-5

Mixed phosphine/*N*-heterocyclic carbene–palladium complexes: synthesis, characterization, crystal structure and application in the Sonogashira reaction in aqueous media

Aydın Aktaş[1] · Fatoş Erdemir[1] · Duygu Barut Celepci[2] · Yetkin Gök[1] · Muhittin Aygün[2]

Received: 18 August 2018 / Accepted: 29 October 2018 / Published online: 7 November 2018

Abstract
A series of 2-hydroxyethyl-substituted *N*-heterocyclic carbene–(NHC)PdX_2PPh_3 complexes have been synthesized by substitution of the pyridine or 3-chloropyridine ligand in (NHC)PdX_2(pyridine/3-chloropyridine) complexes with triphenylphosphine. The new complexes were characterized by ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$NMR, FTIR spectroscopy and elemental analysis. Also, the molecular and crystal structures of **1c** and **1d** have been obtained by single-crystal X-ray diffraction. The 2-hydroxyethyl-substituted (NHC)PdX_2PPh_3 complexes have been examined as catalysts for the Sonogashira cross-coupling reaction in water/DMF solvent mixtures.

Introduction

Pd-catalyzed C–C coupling reactions are of much current interest. An important contribution to this topic comes from the use of large, electron-rich phosphine ligands [1, 2], which are very effective for Pd-catalyzed C–C coupling. However, these ligands often cannot be synthesized easily due to their high-cost starting materials and difficult procedures. Triphenylphosphine is a cheap and easily accessible phosphine which is commonly used in Pd-catalyzed coupling reactions. Although PPh_3 complexes often show low activity in catalytic reactions, researchers are still interested in PPh_3 complexes thanks to their stability in air, low cost and commercial accessibility [3].

Over recent years, *N*-heterocyclic carbenes (NHCs) have become an important starting material, especially in organometallic chemistry [4], after it was discovered by Arduengo et al. [5] that NHCs are stable ligands. Their steric bulk, strong σ-donor and weak π-acceptor ability allow them to stabilize transition metal complexes which have wide potential as catalysts [6–9]. Thanks to these properties, NHCs can provide a useful alternative to phosphine ligands.

The Sonogashira coupling of terminal alkynes with aryl or vinyl halides is one of the most significant processes in C–C coupling reactions in synthetic chemistry and is widely used for the synthesis of many organic compounds [10–12]. In general, Cu(I) salts and palladium–phosphine complexes have been used as catalysts in the Sonogashira reaction under homogeneous conditions and the use of various ligands or additives can lead to higher yields [13]. In recent years, the Pd-based metal–NHC complexes have been used as catalysts in Sonogashira reactions and can show high catalytic activity. Hence, studies on the Sonogashira reaction catalyzed by (NHC)PdX_2PPh_3 complexes are of great interest. These complexes contain on NHC ligand that is easily adjustable electronically and sterically, plus a triphenylphosphine ligand that has different electronic properties.

In this paper, we report the synthesis, characterization and crystal structure determination of some 2-hydroxyethyl-substituted (NHC)PdX_2PPh_3 complexes. The structures of two of the complexes were confirmed by single-crystal X-ray diffraction. Also, we have examined the catalytic activity of the complexes for Sonogashira coupling reactions, finding excellent catalytic activity in this reaction.

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s11243-018-0286-5) contains supplementary material, which is available to authorized users.

✉ Aydın Aktaş
aydinaktash@hotmail.com

[1] Department of Chemistry, Faculty of Science, İnönü University, 44280 Malatya, Turkey

[2] Department of Physics, Faculty of Science, Dokuz Eylül University, 35160 Buca, İzmir, Turkey

Experimental

The complexes **1a**–**f** were all prepared under an inert atmosphere in flame-dried glassware using standard Schlenk techniques. The solvents were commercial products and were used without purification. All other reagents were purchased from Aldrich, Merck, VWR and abcr Chemical Co. and used without further purification. Melting points were recorded in glass capillaries under air with an Electrothermal-9200 melting point apparatus. FTIR spectra were recorded in the range 400–4000 cm^{-1} on a PerkinElmer Spectrum 100 FTIR spectrometer. The starting complexes were synthesized by the Schlenk technique at Inonu University Faculty of Science Catalysis Research Laboratory. ^{1}H, ^{31}P and ^{13}C NMR spectra were recorded using a Bruker AS 400 Merkur spectrometer operating at 400 MHz (^{1}H) or 100 MHz (^{13}C) in $CDCl_3$ with tetramethylsilane as an internal reference. Reaction products were analyzed 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 Technology Center (Malatya, TURKEY).

Single-crystal X-ray diffraction data for complexes **1c** and **1d** were collected at room temperature on a Rigaku-Oxford Xcalibur diffractometer with an Eos-CCD detector using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Data collection and reduction along with absorption corrections were performed using the CrysAlis^{Pro} software package [14]. Structure solutions were performed using SHELXT [15] embedded in Olex2 [16]. Refinement of coordinates and anisotropic thermal parameters of non-hydrogen atoms was carried out by the full-matrix least squares method in SHELXL [17]. For both complexes, hydrogen atoms were placed using standard geometric models with their thermal parameters riding on those of the parent atoms. The structure of the complex **1c** was a racemic twin with a twinning ratio of 0.51 (3):0.49 (3). To ensure satisfactory refinement of disordered groups in the structure, restraint instructions such as DFIX and RIGU were applied to refine some moieties. The details of the crystal data, data collection and structure refinement of both complexes are given in Table 1.

Synthesis of dibromo[1-ethyl-3-(2-hydroxyethyl) benzimidazol-2-ylidene]triphenylphosphine palladium(II), 1a

Dibromo[1-ethyl-3-(2-hydroxyethyl)benzimidazol-2-ylidene]-3-chloropyridinepalladium(II) (114 mg, 0.2 mmol) and triphenylphosphine (52 mg, 0,2 mmol) were stirred in chloroform (10 mL) for 24 h at room temperature [18]. The solvent was then evaporated under vacuum to obtain the product as a yellow solid. The crude product was washed with *n*-pentane (or *n*-hexane) and recrystallized from chloroform/*n*-pentane (1:2) at room temperature. Yield: 87% (0.125 g); m.p.: 140–142 °C; $\nu_{(CN)}$: 1433 cm^{-1}; $\nu_{(O-H)}$: 3402 cm^{-1}. Anal. Calc. for $C_{29}H_{29}Br_2N_2OPPd$: C: 48.46; H: 4.07; N: 3.90. Found: C: 48.52; H: 4.12; N:

Table 1 Crystallographic data and structure refinement parameters for complexes **1c** and **1d**

	1c	**1d**
Formula	$C_{28}H_{27}I_2N_2OPPd$	$C_{29}H_{28}I_2N_2OPPd$
Formula weight (g/mol^{-1})	798.68	811.70
Crystal system	Orthorhombic	Monoclinic
Crystal size (mm^3)	0.211 × 0.197 × 0.167	0.558 × 0.474 × 0.296
Space group, *Z*	$Pca2_1$, 8	$P2_1/n$, 4
a(Å)	20.8434(9)	10.2247(4)
b (Å)	15.9965(7)	13.6487(5)
c (Å)	16.9539(8)	21.3273(8)
α, β, γ (°)	90, 90, 90	90, 96.871(3), 90
Volume (Å^3)	5652.8(4)	2954.93(19)
ρ_{calc} (mg m^{-3})	1.877	1.825
μ (mm^{-1})	2.921	2.796
F (000)	3072	1564
Reflections collected	22,528	12,665
Independent reflections/R_{int}	8669/0.061	5611/0.025
Parameters	636	327
GOF on F^2	0.772	1.028
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.039$ $wR_2 = 0.057$	$R_1 = 0.031$ $wR_2 = 0.068$
R indices (all data)	$R_1 = 0.086$ $wR_2 = 0.063$	$R_1 = 0.041$ $wR_2 = 0.072$

3.94. ^{1}HNMR (400 MHz, $CDCl_3$) δ (ppm) = 1.32 (t, 3H, *J:* 8 Hz –NCH_2CH_3); 1.64 (s, 1H, –NCH_2CH_2OH); 3.84 (m, 2H, –NCH_2CH_2OH); 4.40 (m, 2H, –NCH_2CH_2OH); 5.35 (m, 2H, –NCH_2CH_3); 6.77–8.05 (m, 19H, Ar–*H*). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 13.8 (–NCH_2CH_3); 29.7 (–NCH_2CH_3); 43.9 (–NCH_2CH_2OH); 60.3 (–NCH_2CH_2OH); 110.4–123.0–128.2–128.4–128.5–130.4–131.0–134.0–134.1–134.3 and 135.2. (Ar–*C*); 174.1 (2–*C*–Pd); ^{31}P {^{1}H}NMR ($CDCl_3$, 162 MHz, δ, ppm) = 26.5.

Synthesis of dibromo[1-(2-hydroxyethyl)-3-isopropylbenzimidazol-2-ylidene] triphenylphosphine palladium(II), 1b

Complex **1b** was prepared in the same way as described for **1a**, but using dichloro[1-(2-hydroxyethyl)-3-isopropylbenzimidazol-2-ylidene]-3-chloropyridinepalladium(II) (117 mg, 0.2 mmol) as the starting complex. Yield: 81% (0.119 g); m.p: 202–204 °C; $\nu_{(CN)}$: 1434 cm^{-1}; $\nu_{(O–H)}$: 3396 cm^{-1}. Anal. Calc. for $C_{30}H_{31}Br_2N_2OPPd$: C: 49.17; H: 4.26; N: 3.82. Found: C: 49.28; H: 4.34; N: 3.87. ^{1}HNMR (400 MHz, $CDCl_3$) δ (ppm) = 1.69 and 1.75 (d, 6H, *J:* 8 Hz –$NCH(CH_3)_2$); 2.21 (s, 1H, –NCH_2CH_2OH); 4.38 (m, 2H, –NCH_2CH_2OH); 4.68 (t, 2H, *J:* 6 Hz –NCH_2CH_2OH); 5.85 (m, 1H, –$NCH(CH_3)_2$); 7.26–7.81 (m, 19H, Ar–*H*). ^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) δ (ppm) = 20.1 and 20.4 (–$NCH(CH_3)_2$); 50.9 (–NCH_2CH_2OH); 54.7 (–$NCH(CH_3)_2$); 60.3 (–NCH_2CH_2OH); 111.3–111.6–111.9–112.0–112.2–112.3–112.4–127.9–128.0–128.3–128.4–128.5–130.3–131.1–133.7–135.2 and 135.3 (Ar–*C*); 174.9 (2–*C*–Pd); ^{31}P {^{1}H} NMR ($CDCl_3$, 162 MHz, δ, ppm) = 24.4.

Synthesis of diiodo[1-(2-hydroxyethyl)-3-methylbenzimidazol-2-ylidene]triphenylphosphine palladium(II), 1c

Complex **1c** was prepared in the same way as described for **1a**, but using diiodo[1-(2-hydroxyethyl)-3-methylbenzimidazol-2-ylidene]pyridinepalladium(II) (160 mg, 0.2 mmol) as the starting complex. Yield: 86% (0.137 g); m.p: 118–120 °C; $\nu_{(CN)}$: 1435 cm^{-1}; $\nu_{(O–H)}$: 3443 cm^{-1}. Anal. Calc. for $C_{28}H_{27}I_2N_2OPPd$: C: 42.10; H: 3.41; N: 3.51. Found: C: 42.17; H: 3.37; N: 3.57. ^{1}HNMR (400 MHz, $CDCl_3$) δ (ppm) = 1.60 (s, 1H, –NCH_2CH_2OH); 3.84 (s, 3H, –NCH_3); 4.41 (t, 2H, *J*: 4 Hz –NCH_2CH_2OH); 4.70 (t, 2H, *J:* 4 Hz –NCH_2CH_2OH); 6.76–8.10 (m, 19H, Ar–*H*). ^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) δ (ppm) = 35.7 (–NCH_3); 51.0 (–NCH_2CH_2OH); 60.3 (–NCH_2CH_2OH); 109.6–109.9–110.8–111.1–123.0–123.2–127.9–128.0–128.2–128.3–128.5–130.4–130.7–131.1–132.1–132.1–132.3–134.3–134.4–135.2 and 135.3. (Ar–*C*); 177.3 (2–*C*–Pd); ^{31}P {^{1}H}NMR ($CDCl_3$, 162 MHz, δ, ppm) = 16.0 and 23.8.

Synthesis of diiodo[1-ethyl-3-(2-hydroxyethyl) benzimidazol-2-ylidene]triphenylphosphine palladium(II), 1d

Complex **1d** was prepared in the same way as described for **1a**, but using diiodo[1-ethyl-3-(2-hydroxyethyl) benzimidazol-2-ylidene]pyridinepalladium(II) (162 mg, 0.2 mmol) as the starting complex. Yield: 75% (0.122 g); m.p: 229–230 °C; $\nu_{(CN)}$: 1432 cm^{-1}; $\nu_{(O–H)}$: 3452 cm^{-1}. Anal. Calc. for $C_{29}H_{29}I_2N_2OPPd$: C: 42.86; H: 3.60; N: 3.45. Found: C: 42.80; H: 3.52; N: 3.53. ^{1}HNMR (400 MHz, $CDCl_3$) δ (ppm) = 1.42 (t, 3H, *J:* 8 Hz –NCH_2CH_3); 2.07 (s, 1H, –NCH_2CH_2OH); 3.94 (m, 2H, –NCH_2CH_2OH); 4.33 (m, 2H, –NCH_2CH_2OH); 4.63 (t, 2H, *J:* 8 Hz –NCH_2CH_3); 7.08–7.69 (m, 19H, Ar–*H*). ^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) δ (ppm) = 13.7 (–NCH_2CH_3); 44.3 (–NCH_2CH_3); 51.1 (–NCH_2CH_2OH); 60.3 (–NCH_2CH_2OH); 110.2–110.3–111.0–111.4–123.0–127.7–128.0–128.2–130.3–131.0–132.0–132.4–134.3–134.3–135.2 and 135.3. (Ar–*C*); 171.5 (2–*C*–Pd); ^{31}P {^{1}H}NMR ($CDCl_3$, 162 MHz, δ, ppm) = 26.7.

Synthesis of diiodo[1-(2-hydroxyethyl)-3-isopropylbenzimidazol-2-ylidene] triphenylphosphine palladium(II), 1e

Complex **1e** was prepared in the same way as described for **1a**, but using diiodo[1-(2-hydroxyethyl)-3-isopropylbenzimidazol-2-ylidene]pyridinepalladium(II) (175 mg, 0.2 mmol) as the starting complex. Yield: 80% (0.140 g); m.p: 202–204 °C; $\nu_{(CN)}$: 1434 cm^{-1}; $\nu_{(O–H)}$: 3340 cm^{-1}. Anal. Calc. for $C_{30}H_{31}I_2N_2OPPd$: C: 43.58; H: 3.78; N: 3.39. Found: C: 44.02; H: 3.84; N: 3.41. ^{1}HNMR (400 MHz, $CDCl_3$); δ 1.69 and 1.75 (d, 6H, *J:* 8 and 8 Hz –$NCH(CH_3)_2$); 2.21 (s, 1H, –NCH_2CH_2OH); 4.39 (m, 2H, –NCH_2CH_2OH); 4.68 and 4.74 (t, 2H, *J:* 6 and 6 Hz –NCH_2CH_2OH); 5.86 and 5.73 (m, 1H, –$NCH(CH_3)_2$); 7.19–7.76 (m, 19H, Ar–*H*). ^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$); δ 19.9 and 20.1 (–$NCH(CH_3)_2$); 50.9 (–NCH_2CH_2OH); 54.6 (–$NCH(CH_3)_2$); 60.3 (–NCH_2CH_2OH); 111.0–111.3–111.9–112.2–112.4–127.8–128.3–128.4–128.5–130.3–131.2–135.2 and 135.3 (Ar–*C*); 174.8 (2–*C*–Pd); ^{31}P {^{1}H}NMR ($CDCl_3$, 162 MHz, δ, ppm) = 24.3.

Synthesis of diiodo[bis-(2-hydroxyethyl)benzimidazol-2-ylidene]triphenylphosphine palladium(II), 1f

Complex **1f** was prepared in the same way as described for **1a**, but using diiodo[bis-(2-hydroxyethyl)benzimidazol-2-ylidene]pyridinepalladium(II) (129 mg, 0.2 mmol) as the starting complex. Yield: 77% (0.128 g); m.p: 299–301 °C; $\nu_{(CN)}$: 1434 cm^{-1}; $\nu_{(O–H)}$: 3419 cm^{-1}. Anal. Calc. for $C_{29}H_{29}I_2N_2O_2PPd$: C: 42.03; H: 3.53; N: 3.38. Found: C: 41.97; H: 3.58; N: 3.45. ^{1}HNMR (400 MHz, $CDCl_3$); δ 2.30

(s, 2H, –NCH_2CH_2OH); 4.52 (s, 4H, –NCH_2CH_2OH); 4.90 (t, 4H, *J:* 6 Hz –NCH_2CH_2OH); 7.22–7.84 (m, 19H, Ar–*H*). ^{13}C {^1H}NMR (100 MHz, $CDCl_3$); δ 51.5 and 51.6 (–NCH_2CH_2OH); 60.5 and 61.0 (–NCH_2CH_2OH); 110.8–110.9–123.8–124.7–127.9–128.1–128.2–134.8–134.9–135.0–135.1–135.2–135.8 and 138.0 (Ar–*C*); 169.7 (2–*C*–Pd); ^{31}P {^1H} NMR ($CDCl_3$, 162 MHz, δ, ppm) 26.9 and 27.3.

General method for the catalytic reactions

A mixture of phenylacetylene (1.5 mmol), the required aryl bromide (1 mmol), Cs_2CO_3 (2 mmol) and the complex **1a–f** (0.01 mmol) was dissolved in H_2O/DMF (2:1) (3 ml) in a small Schlenk tube. The mixture was stirred in an oil bath at 100 °C for 4 h as described in the literature [19] and then cooled to room temperature. The organic phase was then extracted with ethyl acetate. The organic phase was separated and dried over $MgSO_4$. The residue was passed through a 1-cm silica gel column using ethyl acetate/*n*-hexane (1/5) as the solvent mixture. After evaporating of the solvent, the products were assayed by gas chromatography. The conversions were calculated as the conversion of aryl bromide to diphenylacetylene.

Results and discussion

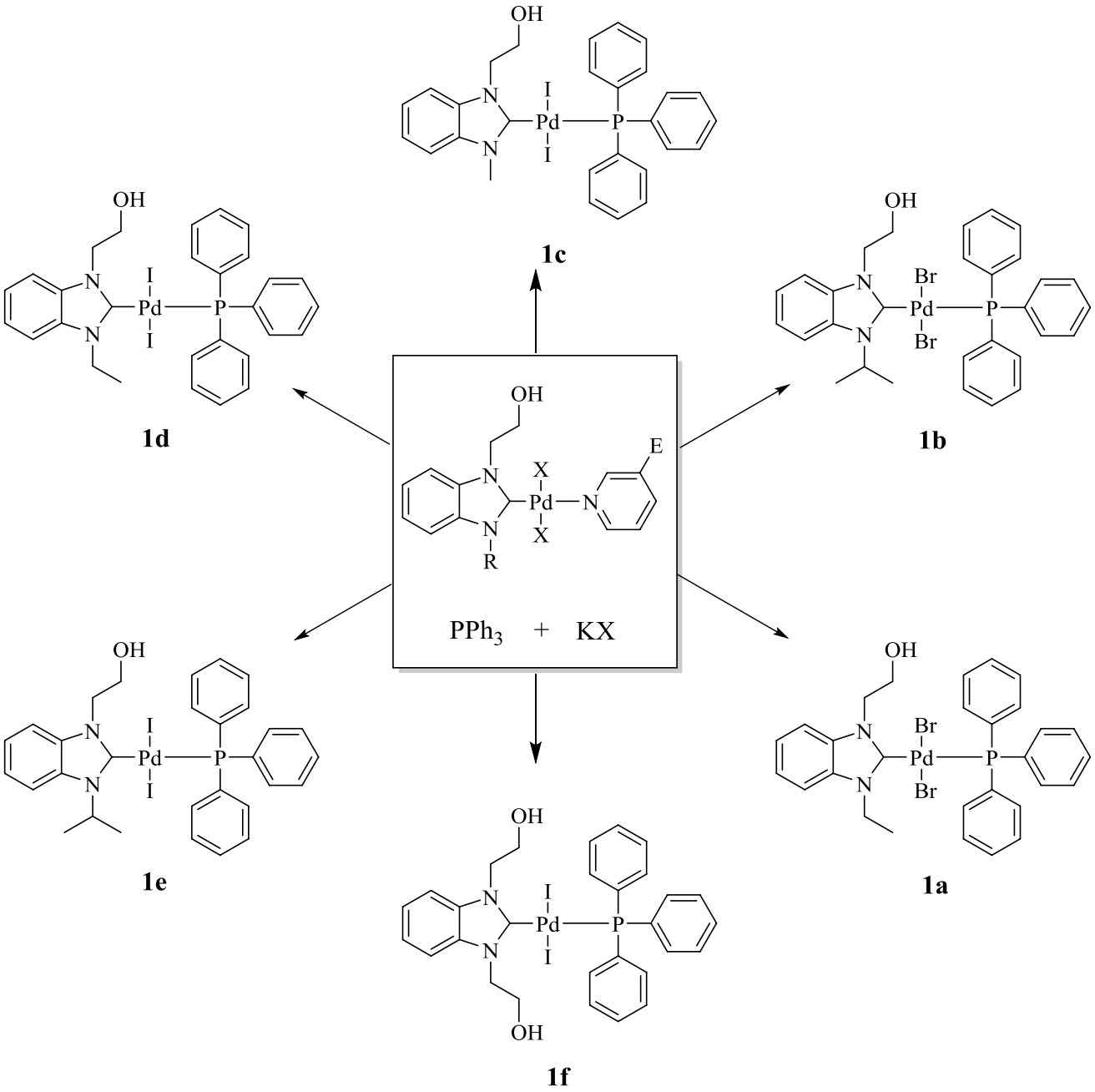
Synthesis of (NHC)PdX_2PPh_3 complexes (1a–f)

The synthetic route for the new 2-hydroxyethyl-substituted (NHC)PdX_2PPh_3 complexes described in this study is shown in Scheme 1. These complexes **1a–f** have been synthesized by substituting the pyridine or 3-chloropyridine ligand in (NHC)PdX_2(pyridine/3-chloropyridine) complexes [20] with triphenylphosphine. The new complexes are air and moisture stable and soluble in solvents such as toluene, dichloromethane and chloroform. The (NHC)PdX_2PPh_3 complexes were obtained as yellow solids in 82 to 88% yield and characterized by FTIR, ^1H and ^{13}C NMR spectroscopic methods and elemental analysis. The spectra are consistent with the proposed formulae. Thus, the ^1H NMR spectra showed no signs of the pyridine/3-chloropyridine peaks between 8.00 and 9.00 of the starting PEPPSI (pyridine-enhanced precatalyst preparation stabilization and initiation) complexes. Instead, an increase in aromatic peaks between 7.00 and 8.00, attributed to the triphenylphosphine ligands, was observed. Similarly the ^{13}C NMR spectra showed no signs of the pyridine/3-chloropyridine peaks observed between 149.0 and 150.0 for the corresponding PEPPSI complexes. Instead, an increase in aromatic peaks between 120.0 and 130.0 from the triphenylphosphine ligands was observed. Also, the Pd–$C_{carbene}$ resonances that are observed between 160.0 and 162.0 in the ^{13}C spectra of the PEEPSI complexes were highly downfield shifted at δ 174.1, 174.9, 177.3, 171.5, 174.8 and 169.7 ppm for complexes **1a–f**, respectively. The FTIR data clearly indicated the presence of ν(CN) at 1433, 1434, 1435, 1432, 1434, 1434 cm^{-1} plus ν(OH) at 3402, 3396, 3443, 3452, 3340 and 3419 for the (NHC)PdX_2PPh_3 complexes **1a–f**, respectively. All spectroscopic data are consistent with the literature [19, 21–23]. Also, we have obtained X-ray crystal structures of complexes **1c** and **1d**.

The catalytic activities of (NHC)PdX_2PPh_3 complexes **1a–f** were examined for the Sonogashira reaction. Under the optimum conditions, phenylacetylene (1.5 mmol), 4-aryl bromide (1 mmol), (NHC)Pd(II)PPh_3 complex (0.01 mmol) and Cs_2CO_3 (2 mmol) were added to H_2O/DMF (2 ml/1 ml) in open air. The mixture was stirred at 100 °C for 4 h and the product isolated as described in the Experimental section, and then analyzed by GC. The results were calculated on the basis of conversion of the aryl bromide to diphenylacetylene product, as listed in Table 2. Also, the dimerization product of phenylacetylene was observed in the product mixture, but not taken into account in the conversion calculations.

The electronic and structural properties of a complex are important considerations that determine its catalytic activity [24]. Consideration of the results in Table 2 reveals that the different substituents on the NHC ligands have moderate effects on the yields, while the choice of halide ligand (bromide or iodide) does not seen to have much effect.

In general, substrates containing electron withdrawing groups (–$COCH_3$) showed higher conversions than those containing the electron donating groups (–OCH_3 and –CH_3). Comparing the aryl bromides, 4-bromoacetophenone with an electron withdrawing group on the aromatic ring showed higher conversions than 4-bromoanisole with its electron donating group (Table 2). The conversion of the 4-bromotoluene with its substituent is higher than 4-bromoanisole containing the methoxy group. This can be related to the strength of the C–Br bond; when this bond is less polarized due to electron donating groups (–CH_3, –OCH_3) in the para position on the aromatic ring, the strength of the bond is increased. Previous studies have utilized bulky substituents on benzimidazole, whereas in our study, smaller aliphatic substituents have been used [19, 21–23]. Therefore, in similar studies, the catalytic conversions tended to be slightly higher than those observed in the present study. Considering the proposed catalytic mechanism for the Sonogashira cross-linking reaction [19], the presence of bulky groups facilitates the elimination step, thereby increasing the catalytic conversions. However, unlike the previous studies, we have used an environmentally friendly water-based solvent system in our study. Overall, we can conclude that (NHC)PdX_2PPh_3 complexes **1a–f** with different electronic and structural properties are highly efficient catalysts in Sonogashira coupling reactions (Table 2).



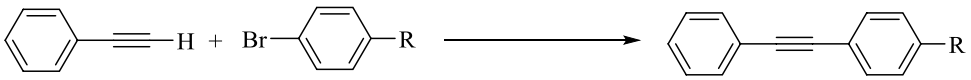
Scheme 1 Synthesis of the (NHC)Pd$X_2$$PPh_3$ complexes **1a**–**f**. **E** = H or Cl; **X** = Br or I

Structural description of complexes 1c and 1d

The molecular structure of complex **1c** is depicted in Fig. 1. The complex crystallizes in the orthorhombic space group $Pca2_1$ and contains two crystallographically independent molecules [labeled **1** (Pd1) and **2** (Pd2)] in the asymmetric unit. In each case, the palladium(II) centers display a distorted square planar geometry, being coordinated by the carbon atom of the *N*-benzylbenzimidazole ligand, phosphorus from the PPh_3 and two iodide ligands in a *cis* configuration. The trans angles indicate distortions of the geometry [C1–Pd1–I1 = 174.8(4)°, P1–Pd1–I2 = 171.81(10)°, C29–Pd2–I3 = 178.1(3)°, P2–Pd2–I4 = 172.81(10)°]. The bond angles around the coordination spheres are in the range of 83.0(3)°–94.37(10)° for complex **1** and 84.2(3)°–93.97(5)° for complex **2**. The *N*-benzylbenzimidazole ligands are oriented almost perpendicular, at 89.4(4)° and 88.1(3)° to the Pd/C/P/I/I planes.

Molecules **1** and **2** are interconnected by two hydrogen bonds: O1–H1···$I3^{i}$ [H1···$I3^{i}$ = 2.90 Å, O1–$I3^{i}$ = 3.559(16)

Table 2 Catalytic activity of phenyl acetylene with aryl bromides in Sonogashira coupling reactions catalyzed by complexes **1a–f**



Entry	*R*	Product	Cat.	Conversion (%)
1	$-CH_3$	**2**	**1a**	99
2			**1b**	81
3			**1c**	98
4			**1d**	65
5			**1e**	73
6			**1f**	98
7	$-OCH_3$	**3**	**1a**	87
8			**1b**	68
9			**1c**	67
10			**1d**	56
11			**1e**	51
12			**1f**	58
13	$-COCH_3$	**4**	**1a**	97
14			**1b**	99
15			**1c**	99
16			**1d**	94
17			**1e**	82
18			**1f**	96

Reaction conditions phenylacetylene (1.5 mmol), 4-bromotoluene (1 mmol), (NHC)PdX_2PPh_3 complex **1a–f** (0.01 mmol) and Cs_2CO_3 (2 mmol) in H_2O/DMF (2:1) (3 ml) stirred at 100 °C for 4 h

Å, O1–H1···I1^{i} = 139°] and C6–H6···I4^{i} [H6···I4^{i} = 3.00 Å, C6–I4^{i} = 3.827(18) Å, C6–H6···I4^{i} = 148°], symmetry code: (1) $1-x, 2-y, ½+z$. (see Supporting Information)

Complex **1d** crystallizes in the monoclinic space group $P2_1/n$. X-ray structural analysis reveals that the central Pd(II) atom again has a distorted square planar environment, defined by a carbon atom from the *N*-benzylbenzimidazole ligand, a phosphorus atom from PPh_3 and two iodide ligands in a *cis* arrangement (Fig. 2). The bond angles around the metal center all deviate slightly from 90° [I1–Pd1–I2 = 91.878(13)°, I1–Pd1–P1 = 91.27(3)°, I2–Pd1–C1 = 86.53(10)°, P1–Pd1–C1 = 90.43(10)°] and 180° [I1–Pd1–C1 = 176.56(10)°, I2–Pd1–P1 = 176.33(3)°]. The PdI_2PC moiety is almost coplanar, with an RMS deviation of 0.045 Å. The *N*-benzylbenzimidazole ligand is oriented almost perpendicular (86.23(10)°) to the Pd1/C1/P1/I1/I2 plane. The Pd–C(carbene) bond length [1.995(4) Å] is comparable with that of a very similar complex reported by Hahn et al. [1.962(5) Å] [25], but slightly smaller than those observed in *trans* diiodo Pd(II) complexes [26–28]. This indicates that the carbene ligands are more strongly bound to the Pd center in the *cis* form. The phosphorus atom has a distorted tetrahedral environment, with bond angles C12–P1–C18, C12–P1–C24, C18–P1–C24 of 104.72(17)°, 104.13(18)° and 105.70(18)°, respectively.

The crystal structure of **1d** shows an intermolecular O–H···I hydrogen bond, intramolecular C–H···I and C–H···O weak interactions and π···π stacking interactions [Cg1 = C1/N1/N2/C6/C11 and Cg2 = C12/17, Cg1–Cg2 = 3.476(2) Å]. The complex molecules form an infinite zigzag chain along the *b* axis via the O1–H1···I1^{2i} hydrogen bonds. (see Supporting Information)

Conclusions

In this paper, we have reported the synthesis of a series of 2-hydroxyethyl-substituted (NHC)PdX_2PPh_3 complexes. The complexes were examined as catalysts for the Sonogashira cross-coupling reaction in water/DMF solvent mixture and showed excellent activities. X-ray studies of complexes **1c** and **1d** showed that both have distorted square planar geometries.

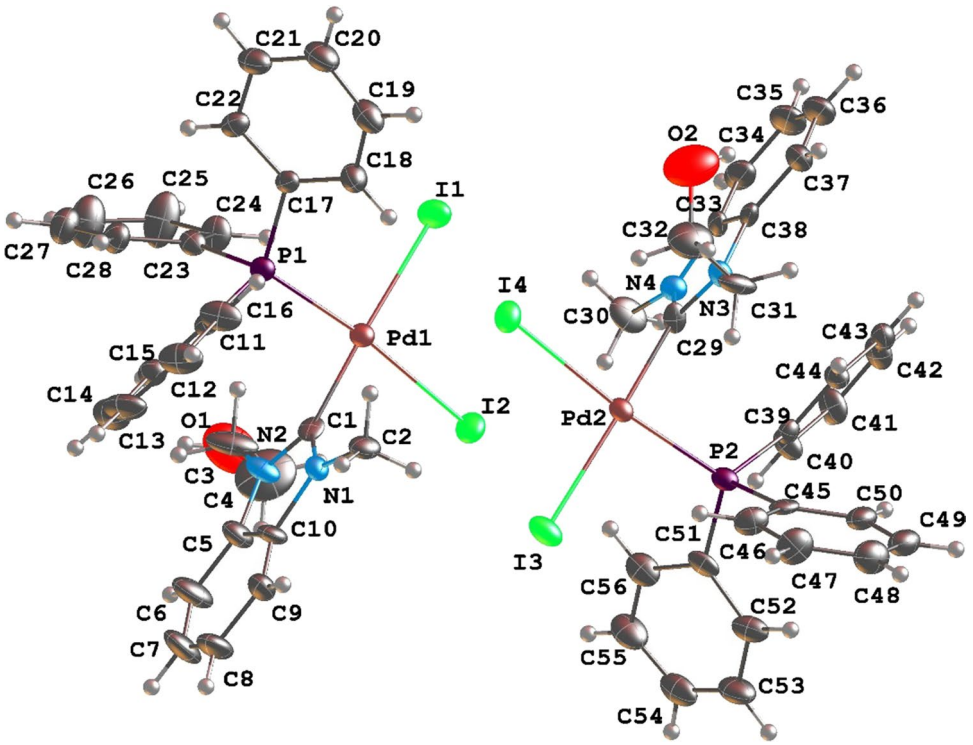


Fig. 1 Molecular structure of complex 1c showing the atom labeling scheme. Displacement ellipsoids are drawn at the 25% probability level. Selected bond parameters (Å) molecule 1: Pd1–I1 2.6398(14), Pd1–I2 2.6501(12), Pd1–P1 2.290(3), Pd1–C1 1.946(13), C4–O1 1.386(11); I1–Pd1–I2 93.40(4), I1–Pd1–P1 94.33(10), I1–Pd1–C1 174.8(4), I2–Pd1–P1 171.83(10), I2–Pd1–C1 82.9(3), P1–Pd1–C1 89.5(3), C11–P1–Pd1 113.2(4), C17–P1–Pd1 115.6(4), C23–P1–Pd1 113.2(4), C3–C4–O1 110.5(16); molecule 2: Pd2–I3 2.6524(13), Pd2–I4 2.6473(12), Pd2–P2 2.287(3), Pd2–C29 1.968(12), C32–O2 1.342(17); I3–Pd2–I4 93.99(4), I3–Pd2–P2 92.71(10), I3–Pd2–C29 178.1(4), I4–Pd2–P2 172.87(10), I4–Pd2–C29 84.1(3), P2–Pd2–C29 89.2(4), C39–P2–Pd2 114.3(4), C45–P2–Pd2 114.6(4), C51–P2–Pd2 114.0(5), C31–C32–O2 114.9(17)

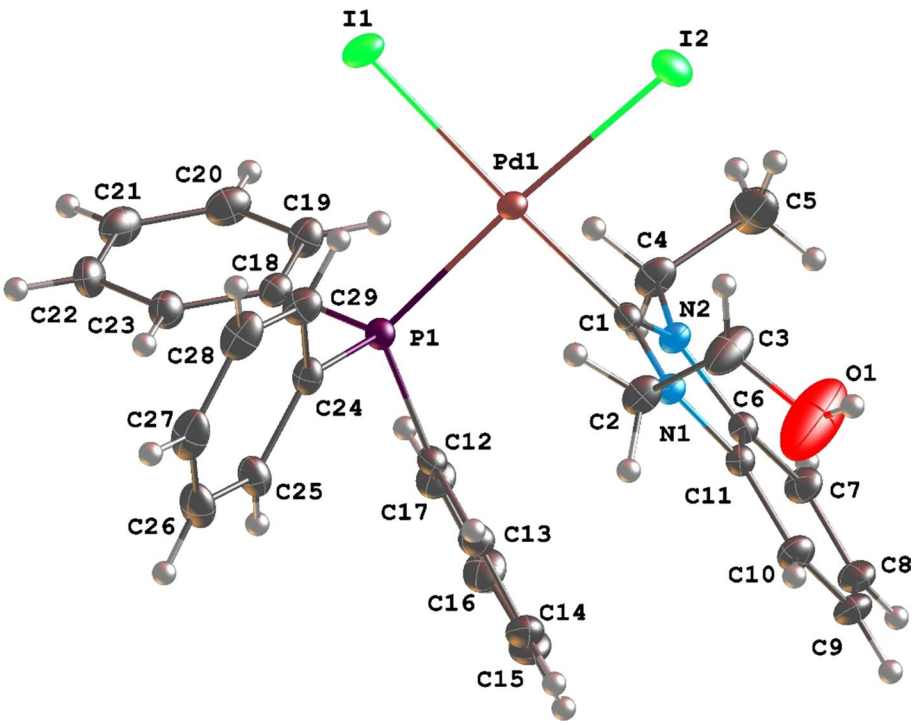


Fig. 2 Molecular structure of 1d showing the atom labeling scheme. Displacement ellipsoids are drawn at the 25% probability level. Selected bond parameters (Å): Pd1–I1 2.6554(4), Pd1–I2 2.6381(4), Pd1–P1 2.2917(10), Pd1–C1 1.995(4), C3–O1 1.343(7); I1–Pd1–I2 91.878(13), I1–Pd1–P1 91.27(3), I1–Pd1–C1 176.56(10), I2–Pd1–P1 176.33(3), I2–Pd1–C1 86.53(10), P1–Pd1–C1 90.43(10), N1–C2–C3 113.9(4), C2–C3–O1 109.2(4), N2–C4–C5 112.5(4), Pd1–P1–C12 113.88(12), Pd1–P1–C18 114.18(13), Pd1–P1–C24 113.25(13); N1–C2–C3–O1 -71.7(7), C1–N2–C4–C5 110.7(5), C6–N2–C4–C5 -70.9(5), C1– N1–C2–C3 -105.2(4), C11–N1–C2–C3 78.0(5)

Supplementary

Crystallographic data as.cif files for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Center with CCDC 1856309 for **1c** and 1856310 for **1d**. 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.

Acknowledgements The authors acknowledge Dokuz Eylül University for the use of the Oxford Rigaku Xcalibur Eos Diffractometer (purchased under University Research Grant No: 2010.KB.FEN.13). The authors thank the İnönü University Faculty of Science Department of Chemistry for the spectroscopy data and İnönü University Scientific and Technology Center for the elemental analyses of the compounds.

References

1. Lundgren RJ, Peters BD, Alsabeh PG, Stradiotto M (2010) Angew Chem Int Ed 49:4071
2. Surry DS, Buchwald SL (2008) Angew Chem Int Ed 47:6338
3. Guram AS, Buchwald SL (1994) J Am Chem Soc 116:7901
4. Lin JCY, Huang RTW, Lee CS, Bhattacharyya A, Hwang WS, Lin IJB (2009) Chem Rev 109:3561
5. Ardueng AJ III, Harlow RL, Kline M (1991) J Am Chem Soc 113:361
6. Dragutan V, Dragutan I, Delaude L, Demonceau A (2007) Coord Chem Rev 251:765
7. Nirmala M, Viswanathamurthi P (2016) J Chem Sci 128:9
8. Roymahapatra G, Samanta T, Seth SK, Mahapatra A, Chattopadhyay SK, Dinda J (2015) J Chem Sci 127:1057
9. Velazquez HD, Verpoort F (2012) Chem Soc Rev 41:7032
10. Molnár Á (2011) Chem Rev 111:2251
11. Yin LX, Liebscher J (2007) Chem Rev 107:133
12. Sisodiya S, Wallenberg LR, Lewin E, Wendt OF (2015) Appl Catal A Gen 503:69
13. Jin GY, Zhang XX, Cao S (2013) Org Lett 15:3114
14. CrysAlis^{Pro} Software System, Version 1.171.38.43 Rigaku Corporation (2015) Oxford UK
15. Sheldrick GM (2015) Acta Crystallogr A 71:3
16. Dolomanov OV, Bourhis LJ, Gildea RJ, Howard JAK, Puschmann H (2009) J Appl Cryst 42:339
17. Sheldrick GM (2015) Acta Crystallogr C 71:3
18. Kumar A, Katari M, Ghosh P (2013) Polyhedron 52:524
19. Aktaş A, Barut Celepci D, Gök Y, Aygün M (2018) ChemistrySelect 3:10932
20. Aktaş A, Barut Celepci D, Gök Y, Aygün M (2018) ChemistrySelect 3:9974
21. Dehimat ZI, Yaşar S, Tebbani D, Özdemir İ (2018) Inor Chim Acta 469:325
22. Touj N, Yaşar S, Özdemir N, Hamdi N, Özdemir İ (2018) J Organomet Chem 860:59
23. Boubakri L, Yaşar S, Dorcet V, Roisnel T, Bruneau C, Hamdi N, Özdemir İ (2017) New J Chem 41:5105
24. Flanigan DM, Romanov-Michailidis F, White NA, Rovis T (2015) Chem Rev 115:9307
25. Hahn FE, Lügger T, Beinhoff M (2004) Z Naturforsch 59b:196
26. Huynh HV, Ho JHH, Neo TC, Koh LL (2005) J Organomet Chem 690:3854
27. Calo´ V, Sole RD, Nacci A, Schingaro E, Scordari F (2000) Eur J Org Chem 2000:869
28. Kernbach U, Lügger T, Hahn FE, Fehlhammer WP (1997) J Organomet Chem 541:51