Inorganica Chimica Acta 394 (2013) 391-400

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta



Palladium(II) complexes with salicylideneimine based tridentate ligand and triphenylphosphine: Synthesis, structure and catalytic activity in Suzuki–Miyaura cross coupling reactions

Manoharan Muthu Tamizh^a, Benjamin F.T. Cooper^b, Charles L.B. Macdonald^b, Ramasamy Karvembu^{a,*}

^a Department of Chemistry, National Institute of Technology, Tiruchirappalli 620 015, India
^b Department of Chemistry & Biochemistry, University of Windsor, Windsor, Ontario, Canada N9B 3P4

ARTICLE INFO

Article history: Received 1 May 2012 Received in revised form 16 August 2012 Accepted 18 August 2012 Available online 10 September 2012

Keywords: Salicylideneimine ligand Triphenylphosphine Palladium(II) Crystal structure Suzuki-Miyaura coupling

ABSTRACT

Square planar palladium(II) complexes of the type $[Pd(L)(PPh_3)]$ (**1–6**) (where L is the dianion of *N*-(2-mercaptophenyl)salicylideneimine or 5-substituted-*N*-(2-mercaptophenyl)salicylideneimine or *N*-(2-mercaptophenyl)naphthylideneimine) have been synthesised from the reactions between $[Pd(PPh_3)_4]$ and H₂L in dichloromethane-ethanol mixture. The new complexes have been characterized by analytical and spectral (electronic, IR, ¹H, ¹³C{¹H} and ³¹P{¹H} NMR spectroscopy) techniques. The structures of three complexes (**1**, **2** and **6**) have been solved by single-crystal X-ray diffraction experiments which indicate square planar coordination geometries around palladium(II) by O, N, S and P donor atoms. The palladium(II) complexes (**1–6**) exhibited good catalytic activity in Suzuki–Miyaura cross-coupling reaction between phenylboronic acid and 4-bromotoluene in *N*,*N*-dimethylacetamide at 100 °C. Complex **3** (1 mol%) was found to be the most active and hence was used for probing the scope of possible substrates. Heterocyclic boronic acid and heterocyclic aryl bromides have also been used as substrates to provide heterocyclic biaryls.

© 2012 Elsevier B.V. All rights reserved.

Inorganica Ihimica Acta

1. Introduction

Carbon-carbon coupling reactions particularly with aryl halides are some of the important processes in chemical industry that constitute a key step in the synthesis of more complex molecules from simple precursors. In the 1970's, several such coupling reactions between aryl halides and aryl magnesium/zinc in the presence of palladium/nickel complexes have been reported for the synthesis of biaryls [1–5]. In the later part of the same decade, Suzuki and Miyaura reported cross-coupling reactions between alkenylboranes and various organic halides [6-8], that are effectively catalyzed by a catalytic amount of [Pd(PPh₃)₄] in the presence of bases. In 1981, Suzuki and co-workers disclosed the palladium-catalyzed crosscoupling reaction of phenylboronic acid with aryl halides in the presence of bases to produce biaryls [9] and this has proven to be a quite general technique for carbon-carbon bond formation. The importance of these powerful cross-coupling synthetic methods was recognized by the 2010 Nobel Prize for Chemistry being awarded to Suzuki, Negishi and Heck [10,11]. Many organometallic reagents undergo similar cross-coupling reactions, but much attention has recently been focused on the use of organoboronic acids since they are thermally stable and inert to water and oxygen

[12]. Subsequently, many catalytic systems have been developed for Suzuki cross-coupling reactions using different palladium catalysts such as [Pd(PPh₃)₄] [13], [Pd(OAc)₂] [14], [PdCl₂(dppb)] [15], Pd(0) [16], [Pd(dba)₂] [17], [PdCl₂(PCy₃)₂] [18], [PdCl₂(PPh₃)₂] [19], [PdCl₂(dppf)] [20], Pd₂(dba)₃ [21], Pd nanoparticles [22], Pddoped KF/Al₂O₃ [23], Pd(OAc)₂/guanidine [24], Pd/imidazolium salt [25], etc. Most of these catalysts contain phosphine ligands. Palladium(II) complexes of salicylideneimine ligands have also been found to be useful as catalysts for Suzuki coupling reactions [26-30]. But palladium(II) complexes containing both salicylideneimine and phosphine ligands have rarely been used as catalysts in Suzuki coupling reactions. At the same time, phosphine-functionalized Schiff base complexes are known to be efficient catalysts for this reaction [31]. We disclose herein the synthesis of novel palladium(II) complexes containing both salicylideneimine based tridentate ligand and triphenylphosphine and its catalytic activity in Suzuki-Miyaura cross coupling reactions. Salicylideneimine based tridentate ligands employed in this study are shown in Fig. 1. The same ligands have already been used by us for the synthesis of Ni(II), Ru(II) and Cu(II) complexes [32-35]. The analogous ONS donor Schiff base ligands formed from 2-oxoquinoline-3-carbaldehyde were used for making Pd(II) complexes [36]. All these Schiff base complexes were found to be good catalysts for various organic transformations.



^{*} Corresponding author. Tel.: +91 431 2503636; fax: +91 431 2500133. *E-mail address:* kar@nitt.edu (R. Karvembu).

^{0020-1693/\$ -} see front matter @ 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.ica.2012.08.024



2. Experimental

2.1. Materials

Solvents were purified and dried by standard procedures [37]. PdCl₂ and salicylaldehyde were purchased from Loba Chemie, India and later was used after double distillation. 2-Hydroxy-5-methylbenzaldehyde, 2-hydroxy-5-methoxybenzaldehyde and 5-chloro-salicylaldehyde were purchased from Sigma–Aldrich and were used without further purification. 5-Bromo-2-hydroxybenzaldehyde and 2-hydroxy-1-naphthaldehyde were purchased from Merck and Alfa-Aesar, respectively. *o*-Aminothiophenol was purchased from S.D. Fine Chemicals, India. The metal precursor [Pd(PPh₃)₄] was prepared according to the literature method [38]. Schiff base ligands were prepared by the condensation between salicylaldehyde or its derivatives or 2-hydroxy-1-naphthaldehyde and *o*-aminothiophenol in ethanol [39,40].

2.2. Physical measurements

Elemental analyses for C, H, N and S were carried out on Thermoflash EA1112 series elemental analyzer. Electronic spectra were recorded on a PerkinElmer Lambda 25 UV-Vis double beam spectrophotometer in CH₂Cl₂ solvent in the 200–800 nm range. FT-IR spectra were obtained on a PerkinElmer Spectrum 100 FT-IR spectrophotometer as KBr pellet in the frequency range of 400-4000 cm⁻¹. The ¹H and ¹³C{¹H} NMR spectra were recorded in CDCl₃ or CD₂Cl₂ solution on Bruker Avance 500 spectrometer at 500.13 (¹H) and 125.76 (¹³C) MHz using TMS as internal standard. ³¹P{¹H} NMR spectra were recorded in CDCl₃ solution on Bruker Avance 500 spectrometer at 202.46 (³¹P) MHz using H₃PO₄ as external standard. The ¹H-¹H COSY 500.13 (¹H), ¹H-¹³C HSOC 500.13 (¹H) and ¹H-³¹P HMBC 400.13 (¹H) spectra were obtained by using the standard Bruker pulse programs. Gas chromatography was undertaken using a Shimadzu GC-2010 with a $60 \text{ m} \times 0.32 \text{ mm}$ Restek Rtx[®]-5 column.

2.3. X-ray crystallography

Slow crystallization from CH₂Cl₂/Et₂O yielded red crystals of **1**, **2** and **6**. Each subject crystal was covered in Nujol[®], mounted on a goniometer head and rapidly placed in the dry N₂ cold-stream of the low-temperature apparatus (Kryoflex) attached to the diffractometer. The data were collected using the sMART software [41] on a Bruker APEX CCD diffractometer using a graphite monochromator with Mo K α radiation (λ = 0.71073 Å). A hemisphere of data was collected using a counting time of 10 or 30 s per frame at -100 °C. Data reductions were performed using the sAINT-PLUS software [42] and the data were corrected for absorption using sADABS [43]. Each structure was solved by direct methods using sIR97 [44] and refined by full-matrix least-squares on F^2 with anisotropic

displacement parameters for the heavy atoms using SHELXL-97 [45] and the WINGX [46] software package, the solutions were assessed using tools in PLATON, and thermal ellipsoid plots were produced using SHELXTL [47]. All H atoms were placed in calculated positions with a C–H distance of 0.95 Å for the atoms attached to carbon atoms in the phenyl or imine groups or a C–H distance of 0.96 Å for the atoms attached to the methyl carbon atom. These atoms were included in the refinement using the riding model approximation with $U_{iso}(H) = 1.2U_{eq}(C)$ for the H atoms in the phenyl groups or $U_{iso}(H) = 1.5U_{eq}(C)$ for the H atoms in the methyl groups. For complex **2**, the squeeze [48] routine in PLATON was employed to remove a disordered and partial occupancy CH_2Cl_2 solvent molecule proximate to an inversion center; the process improved the $R_1(obs)$ value from *ca*. 0.067 to 0.046.

2.4. Synthesis of Pd(II) complexes of type [Pd(L)(PPh₃)]

Ligand (0.433 mmol) dissolved in CH_2Cl_2 (10 ml) was added to the suspension of $[Pd(PPh_3)_4]$ (0.433 mmol) in ethanol (10 ml), yielding a dark red solution after stirring at 27 °C for 30 min. The resulting solutions were evaporated to approximately 3 ml and cooled. Hexane (20 ml) was then added whereupon the product complex separated. The reddish brown colored complex was isolated by filtration in air, washed with small amounts of ethanol and hexane, and dried in *vacuo*.

2.4.1. [Pd(LS)(PPh₃)] (1)

 $[Pd(LS)(PPh_3)]$ (1) is prepared from $[Pd(PPh_3)_4]$ (0.5 g; 0.433 mmol) and H₂LS (0.099 g; 0.433 mmol). Yield: 170 mg (66%). M.p. 242 °C (dec.). Anal. Calc. for C₃₁H₂₄NPdOPS: C, 62.5; H, 4.1; N, 2.4; S, 5.4. Found: C, 62.1; H, 4.0; N, 2.5; S, 5.6%. UV-Vis (CH₂Cl₂), λ_{max}/nm ($\epsilon/dm^3 mol^{-1} cm^{-1}$): 231 (48225), 246 (54205), 299 (21060), 314 (16580), 328 (10195), 433 (11120). FT-IR (KBr disk), cm⁻¹: v(C=N) 1605, v(C-O) 1332, v(C-S) 750, v(Pd-O) 531, v(Pd-N) 464, bands due to PPh₃ 1434, 1098, 694. ¹H NMR (500 MHz, CDCl₃): δ = 6.64–6.71 (m, 2H, H2 and H4), 7.00–7.09 (m, 2H, H10 and H11), 7.30 (t, J = 8.5 Hz, 1H, H3), 7.42-7.53 (m, 11H, Hm, Hp and H5), 7.71-7.84 (m, 7H, Ho and H9), 8.95 (d, J = 15.5 Hz, 1H, H7) ppm. ¹³C{¹H} NMR (125.76 MHz, CDCl₃): *δ* = 114.91 (C4), 115.32 (C9), 119.44 (C6), 122.10 (C2), 122.29 (C10), 127.11 (C11), 128.28 (d, J = 11 Hz, Cm), 129.06 (d, J = 52 Hz, Cq), 129.26 (C12), 130.99 (d, J = 2.5 Hz, Cp), 134.90 (d, J = 11 Hz, Co), 135.14 (C5), 135.81 (C3), 143.95 (d, J = 8 Hz, C13), 148.40 (d, J = 2.5 Hz, C8), 153.65 (C7), 165.11 (C1) ppm. ¹P{¹H} NMR (202.46 MHz, CDCl₃): δ = 28.23 (s, 1P) ppm.

2.4.2. $[Pd(LM)(PPh_3)](2)$

 $[Pd(LM)(PPh_3)]$ (2) is prepared from $[Pd(PPh_3)_4]$ (0.25 g; 0.216 mmol) and H₂LM (0.0526 g; 0. 0.216 mmol). Yield: 60 mg (46%). M.p. 239 °C (dec.). Anal. Calc. for C₃₂H₂₆NPdOPS: C, 63.0; H, 4.3; N, 2.3; S, 5.3. Found: C, 62.9; H, 4.4; N, 2.3; S, 5.3%. UV-Vis (CH₂Cl₂) λ_{max}/nm ($\epsilon/dm^3 mol^{-1} cm^{-1}$): 231 (43925), 247 (48855), 300 (18605), 317 (14025), 332 (8265), 442 (8950). FT-IR (KBr disk), cm⁻¹: v(C=N) 1589, v(C-O) 1324, v(C-S) 750, v(Pd-O) 531, v(Pd-N) 467, bands due to PPh₃ 1433, 1096, 694. ¹H NMR $(500 \text{ MHz}, \text{CDCl}_3)$: $\delta = 2.28$ (s, 3H, H4'), 6.61 (d, I = 9 Hz, 1H, H2), 6.99–7.08 (m, 2H, H10 and H11), 7.14 (dd, J = 8.7, 2.4 Hz, 1H, H3), 7.25 (d, J = 1.6 Hz, 1H, H5), 7.39-7.47 (m, 7H, Hm and H12), 7.47-7.53 (m, 3H, Hp), 7.71 (dd, / = 7.8, 1.9 Hz, 1H, H9), 7.73-7.80 (m, 6H, Ho), 8.90 (d, J = 15.5 Hz, 1H, H7) ppm. ¹³C{¹H} NMR $(125.76 \text{ MHz}, \text{ CDCl}_3): \delta = 20.14 (C4'), 115.23 (C9), 118.91 (C6),$ 121.84 (C2), 122.24 (C10), 123.62 (C4), 126.94 (C11), 128.26 (d, *J* = 12 Hz, Cm), 129.19 (d, *J* = 51 Hz, Cq), 129.30 (C12), 130.95 (d, *J* = 2 Hz, Cp), 134.52 (C5), 134.91 (d, *J* = 11 Hz, Co), 137.06 (C3), 143.84 (d, J = 7.5 Hz, C13), 148.57 (d, J = 2 Hz, C8), 153.42 (C7), 163.61 (C1) ppm. ${}^{31}P{}^{1}H$ NMR (202.46 MHz, CDCl₃): δ = 28.14 (s, 1P) ppm.

2.4.3. [Pd(LO)(PPh₃)] (3)

 $[Pd(LO)(PPh_3)]$ (3) is prepared from $[Pd(PPh_3)_4]$ (0.25 g; 0.216 mmol) and H₂LO (0.0561 g; 0. 0.216 mmol). Yield: 65 mg (48%). M.p. 242 °C (dec.). Anal. Calc. for C₃₁H₂₄NPd₂OPS: C, 61.4; H, 4.2; N, 2.2; S, 5.1. Found: C, 61.4; H, 4.2; N, 2.3; S, 5.2%. UV-Vis (CH₂Cl₂) λ_{max}/nm ($\epsilon/dm^3 mol^{-1} cm^{-1}$): 229 (44380), 247 (47085), 302 (18110), 321 (11950), 338 (6420), 465 (8350). FT-IR (KBr disk), cm⁻¹: v(C=N) 1591, v(C-O) 1315, v(C-S) 746, v(Pd-O) 530, v(Pd-N) 457, bands due to PPh₃ 1433, 1098, 693. ¹H NMR $(500 \text{ MHz}, \text{ CDCl}_3)$: $\delta = 3.79$ (s, 3H, H4'), 6.63 (d, J = 9.5 Hz, 1 H,H2), 6.87 (d, J = 3.2 Hz, 1H, H5), 6.99-7.08 (m, 3H, H3, H10 and H11), 7.40-7.47 (m, 7H, Hm and H12), 7.47-7.53 (m, 3H, Hp), 7.71–7.80 (m, 7H, Ho and H9), 8.92 (d, J = 15.5 Hz, 1H, H7) ppm. ¹³C{¹H} NMR (125.76 MHz, CDCl₃): δ = 56.07 (C4'), 114.17 (C5), 115.23 (C9), 117.73 (C6), 122.23 (C10), 123.12 (C2), 126.49 (C3), 128.25 (d, J = 11 Hz, Cm), 129.14 (d, J = 51 Hz, Cq), 129.35 (C12), 130.97 (d, J = 2 Hz, Cp), 134.91 (d, J = 11 Hz, Co), 143.90 (d, *J* = 8 Hz, C13), 148.48 (d, *J* = 2 Hz, C8), 149.14 (C4), 152.77 (C7), 161.24 (C1) ppm. ³¹P{¹H} NMR (202.46 MHz, CDCl₃): δ = 29.50 (s, 1P) ppm.

2.4.4. [Pd(LC)(PPh₃)] (4)

 $[Pd(LC)(PPh_3)]$ (4) is prepared from $[Pd(PPh_3)_4]$ (0.5 g; 0.433 mmol) and H₂LC (0.114 g; 0.433 mmol). Yield: 145 mg (53%). M.p. 246 °C (dec.). Anal. Calc. for C₃₁H₂₃ClNPdOPS: C, 59.1; H, 3.7; N, 2.2; S, 5.1. Found: C, 59.0; H, 3.7; N, 2.3; S, 5.1%. UV-Vis (CH₂Cl₂) λ_{max}/nm ($\epsilon/dm^3 mol^{-1} cm^{-1}$): 230 (50590), 248 (56675), 299 (21775), 317 (16595), 331 (11580), 442 (11875). FT-IR (KBr disk), cm⁻¹: v(C=N) 1602, v(C-O) 1320, v(C-S) 741, v(Pd-O) 530, v(Pd-N) 468, bands due to PPh₃ 1434, 1096, 693. ¹H NMR (500 MHz, CDCl₃, 25 °C): δ = 6.60 (d, J = 9.1 Hz, 1H, H2), 6.99-7.09 (m, 2H, H10 and H11), 7.19 (dd, J = 9.1, 2.8 Hz, 1H, H3), 7.40-7.47 (m, 8H, Hm, H5 and H12), 7.48-7.54 (m, 3H, Hp), 7.69 (d, *I* = 8.2 Hz, 1H, H9), 7.71–7.79 (m, 6H, Ho), 8.85 (d, *I* = 15.1 Hz, 1H, H7) ppm, ${}^{13}C{}^{1}H$ NMR (125.76 MHz, CDCl₃); δ = 115.41 (C9), 118.79 (C6), 119.96 (C4), 122.43 (C10), 123.64 (C2), 127.44 (C11), 128.32 (d, J = 12 Hz, Cm), 128.90 (d, J = 52 Hz, Cq), 129.30 (C12), 131.09 (d, J = 2 Hz, Cp), 133.49 (C5), 134.86 (d, J = 12 Hz, Co), 134.98 (C3), 144.38 (d, J = 7.5 Hz, C13), 148.04 (d, J = 2.5 Hz, C8), 152.59 (C7), 163.67 (C1) ppm. 13C-DEPT 135 NMR (125.76 MHz, $CDCl_3$): $\delta = 115.41$ (C9), 122.43 (C10), 123.62 (C2), 127.44 (C11), 128.33 (d, J = 12 Hz, Cm), 129.30 (C12), 131.09 (d, J = 2 Hz, Cp), 133.49 (C5), 134.85 (d, J = 12 Hz, Co), 152.59 (C7) ppm. ¹P{¹H} NMR (202.46 MHz, CDCl₃, 25 °C): *δ* = 29.48 (s, 1P) ppm.

2.4.5. [Pd(LB)(PPh₃)] (5)

 $[Pd(LB)(PPh_3)]$ (5) is prepared from $[Pd(PPh_3)_4]$ (0.5 g; 0.433 mmol) and H₂LB (0.133 g; 0.433 mmol). Yield: 143 mg (49%). M.p. 252 °C (dec.). Anal. Calc. for C₃₁H₂₃BrNPdOPS: C, 55.2; H, 3.4; N, 2.1; S, 4.8. Found: C, 55.1; H, 3.5; N, 2.1; S, 4.6%. UV-Vis (CH₂Cl₂) λ_{max}/nm ($\epsilon/dm^3 mol^{-1} cm^{-1}$): 230 (41880), 248 (49930), 300 (17900), 316 (12885), 332 (6885), 443 (9555). FT-IR (KBr disk), cm⁻¹: v(C=N) 1597, v(C-O) 1317, v(C-S) 747, v(Pd-O) 531, v(Pd–N) 467, bands due to PPh₃ 1434, 1098, 694. ¹H NMR $(500 \text{ MHz}, \text{ CDCl}_3)$: $\delta = 6.55 \text{ (d, } J = 9.1 \text{ Hz}, 1 \text{ H}, \text{ H2}), 6.99 - 7.10 \text{ (m,}$ 2H, H10 and H11), 7.30 (dd, J = 9.1, 2.5 Hz, 1H, H3), 7.41-7.48 (m, 7H, Hm and H12), 7.49–7.55 (m, 3H, Hp), 7.58 (d, J = 2.8 Hz, 1H, H5), 7.70 (d, J = 7.9 Hz, 1H, H9), 7.72-7.78 (m, 6H, Ho), 8.85 (d, J = 15.1 Hz, 1H, H7) ppm. ¹³C{¹H} NMR (125.76 MHz, CDCl₃): δ = 105.43 (C4), 115.41 (C9), 120.88 (C6), 122.44 (C10), 124.04 (C2), 127.47 (C11), 128.33 (d, *J* = 11 Hz, Cm), 128.83 (d, *J* = 52 Hz, Cq), 129.29 (C12), 131.10 (d, *J* = 2 Hz, Cp), 134.85 (d, *J* = 12 Hz, Co), 136.71 (C5), 137.51 (C3), 144.34 (d, J = 7.5 Hz, C13), 147.99

2.4.6. [Pd(LN)(PPh₃)] (6)

 $[Pd(LN)(PPh_3)]$ (6) is prepared from $[Pd(PPh_3)_4]$ (0.5 g; 0.433 mmol) and H₂LN (0.121 g; 0.433 mmol). Yield: 173 mg (62%). M.p. 247 °C. Anal. Calc. for C35H26NPdOPS: C, 65.1; H, 4.1; N, 2.2; S, 5.0. Found: C, 65.0; H, 4.1; N, 2.2; S, 5.0%. UV-Vis (CH₂Cl₂) $\lambda_{\rm max}/{\rm nm}$ ($\varepsilon/{\rm dm^3 \ mol^{-1} \ cm^{-1}}$): 232 (54300), 248 (56085), 271 (36630), 324 (14370), 340 (10455), 451 (12065), 472 (9900). FT-IR (KBr disk), cm^{-1} : v(C=N) 1614, v(C-O) 1339, v(C-S) 742, v(Pd–O) 532. v(Pd–N) 457, bands due to PPh₃ 1435, 1095, 692. ¹H NMR (500 MHz, CDCl₃): δ = 6.80 (d, *J* = 9.1 Hz, 1H, H2), 7.06– 7.13 (m, 2H, H10 and H11), 7. 30 (t, / = 6.9 Hz, 1H, H3'), 7.42-7.60 (m, 11H, Hm, Hp, H6' and H12), 7.62-7.73 (m, 2H, H3, H4'), 7.75-7.89 (m, 7H, Ho and H9), 8.23 (d, J = 8.5 Hz, 1H, H5'), 9.95 (d, I = 15.7 Hz, 1H, H7) ppm. ¹³C{¹H} NMR (125.76 MHz, CDCl₃): $\delta = 109.74$ (C6), 115.38 (C9), 119.56 (C5'), 122.42 (C10), 122.48 (C3'), 125.15 (C2), 126.46 (C11), 127.14 (C4'), 127.67 (C6'), 128.34 (d, J = 11 Hz, Cm), 129.12 (C12), 129.17 (d, J = 51 Hz, Cq), 129.21 (C4'), 131.01 (d, J = 2.5 Hz, Cp), 134.86 (d, J = 11 Hz, Co), 135.35 (C5), 135.77 (C3), 143.06 (d, J = 7.5 Hz, C13), 147.26 (C7), 149.86 (d, J = 2 Hz, C8), 165.87 (C1) ppm. ¹P{¹H} NMR $(202.46 \text{ MHz}, \text{CDCl}_3): \delta = 28.06 \text{ (s, 1P) ppm.}$

2.5. General procedure for the Suzuki-Miyaura cross coupling reaction

To the catalyst (1.0 mol%) dissolved in 1 ml DMAc, aryl bromide (1.0 mmol), phenyl boronic acid (1.5 mmol) in 1 ml ethanol, K_2CO_3 (2.0 mmol) in 1 ml water and DMAc (5 ml) were all added. The mixture was heated at 100 °C for 12 h. Then, the mixture was cooled, water was added and the product was extracted with ethylacetate. The organic layer was washed with brine, dried over Na₂SO₄, filtered, passed through celite, and analyzed by GC. Yields were based on corresponding aryl bromides.

3. Results and discussion

3.1. Synthesis

The syntheses of palladium(II) complexes are summarized in Scheme 1. The desired complexes of the type $[Pd(L)(PPh_3)]$ (1-6) (L = dianion of tridentate ONS donor Schiff base ligand) have been prepared from the reactions between $[Pd(PPh_3)_4]$ and the respective ligand (H₂LS, H₂LM, H₂LO, H₂LC, H₂LB or H₂LN) in ethanol–dichloromethane mixture at 25–27 °C. The palladium(II) complexes were characterized by elemental analysis and spectroscopic methods (FT-IR, UV–Vis and ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR). Structures of representative complexes **1**, **2** and **6** were examined by X-ray crystallography. The data show that a single Schiff base ligand displaces three triphenylphosphine ligands in the precursor. The coordination behavior of Schiff base ligands towards palladium(II) is very similar to that observed in nickel(II), copper(II) and ruthenium(II) complexes [32–35]. All the palladium(II) complexes are red in color and soluble in common organic solvents.

3.2. FT-IR spectra

A strong band around 1615 cm^{-1} due to v(C=N) of the ligands shifts to $1589-1614 \text{ cm}^{-1}$ in the complexes, indicating the azomethine coordination to palladium through nitrogen [49]. The coordination of azomethine nitrogen atom is further supported by the presence of a new band in the range $457-468 \text{ cm}^{-1}$, assignable to v(Pd-N) [50]. All the ligands exhibited a medium intensity band in the region $1304-1320 \text{ cm}^{-1}$ due to phenolic v(C-O). This band



Scheme 1. Synthesis of the palladium(II) complexes [R = H (1), CH₃ (2), OCH₃ (3), Cl (4) or Br (5)].

became shifted to higher wave number and appeared in the region $1315-1339 \text{ cm}^{-1}$ in palladium complexes, suggesting the coordination of phenolic oxygen atom to palladium. Further evidence for oxygen coordination arises from the appearance of a new band around 530 cm^{-1} in all the palladium complexes, which are assignable to v(Pd-O) [51]. A weak band observed in the region 750–757 cm⁻¹ corresponding to v(C-S) in the ligands, shifts to lower wave number (741–750 cm⁻¹) which supports coordination of thiolato sulfur atom with the palladium center [52]. Three bands are observed around 1434, 1096 and 693 cm⁻¹ for the coordinated triphenylphosphine molecule [53].

229–472 nm and the spectra are given in Fig. S1 (Online Supplementary material). The bands appeared in the region 229–302 nm have been assigned to intra-ligand transitions [32]. Moreover, a set of less intense bands in the region 314–340 nm have been ascribed to metal-to-ligand charge transfer (MLCT) transitions [54,55]. The electronic spectra of palladium complexes also showed bands attributable to d–d spin allowed transitions in the region 442–465 nm [56].

3.4. NMR spectra

3.3. Electronic spectra

Electronic spectra of each of the palladium complexes recorded in dichloromethane solution showed six bands in the region In their ¹H NMR spectra, each of the palladium(II) complexes (**1–6**) exhibited multiplets in the region 6.61–7.89 ppm for the aromatic protons of the coordinated Schiff base and for those of triphenylphosphine. An assignment to individual aromatic protons has been made based on ¹H–¹H COSY spectrum of **4** and is given



Fig. 2. Molecular structure of [Pd(LS)(PPh₃)] (1) showing 50% displacement ellipsoids.



Fig. 3. Molecular structure of [Pd(LM)(PPh₃)] (2) showing 50% displacement ellipsoids.

in Online Supplementary material (Fig. S2). The absence of resonances due to phenolic and thiolato hydrogen atoms indicates the deprotonation of these groups and the Schiff base behaves as dianionic ligands. A doublet (${}^{4}J$ = 15.13–15.78 Hz) observed in the ¹H NMR spectra of all the complexes in the region 8.85-9.95 ppm has been assigned to the HC=N resonance. ¹H-³¹P HMBC spectrum of 1 (Fig. S3) revealed that this doublet is due to the four bond coupling of phosphorus in triphenylphosphine with the azomethine proton [57]. The coupling between the phosphorus atom and the aromatic protons of the phenyl rings attached to it is also identified by the ¹H-³¹P HMBC spectrum. Complexes **2** and **3** each exhibit a singlet at 2.28 and 3.79 ppm that corresponds to methyl and methoxy protons respectively. In the ¹³C NMR spectra of all the complexes, azomethine carbon resonances are observed in the 148.08–149.08 ppm range [58]. The resonances for the C–S, C–N, C-O and C-P carbon atoms are observed in the regions 143.03-144.41, 147.99-149.86, 161.24-165.87 and 128.20-134.95 ppm. respectively [59,60]. The methyl and methoxy carbon atoms present in complexes 2 and 3 exhibited signals at 20.14 and 56.07 ppm, respectively. The assignment of all the aromatic carbon resonances is made with the help of ¹H-¹³C HSQC. ³¹P NMR spectra of all the complexes exhibited a singlet around 28 ppm suggesting the presence of one coordinated triphenylphosphine in each of these palladium(II) complexes [61].

3.5. X-ray crystallography

The structures of **1**, **2** and **6** were determined by single crystal X-ray diffraction method. Thermal ellipsoid plots of complexes **1**, **2** and **6** are shown in Figs. 2–4 respectively. The crystallographic and measurement data are shown in Table 1. Selected bond lengths and bond angles are listed in Table 2. Compounds **1** and **2** are triclinic and crystallize in the space group $P\bar{1}$ with Z = 2, whereas **6** is

monoclinic and crystallizes in the space group $P2_1/c$ with Z = 4. The palladium ion in each complex is coordinated by one Schiff base anion via the O, N and S atoms, producing a six membered chelate ring with the O and N atoms and a five membered ring with the S and N atoms. The fourth coordination site of the palladium in the complexes is occupied by the P atom of the triphenylphosphine ligand. The angles between adjacent atoms in the coordination sphere of palladium in 1, 2 and 6 are close to the ideal value of 90°, with most notable deviation being the O(1)-Pd(1)-P(1) angle of 83.67(8)° in complex 1. The structures of 1, 2 and 6 adopt a near square planar geometry with O(1)-Pd(1)-S(1) and N(1)-Pd(1)-P(1) bond angles in the ranges $175.72(4)-179.03(9)^{\circ}$ and 176.44(8)-177.57(5)°, respectively. The Pd(1)-O(1), Pd(1)-N(1), Pd(1)-S(1) and Pd(1)-P(1) bond lengths in **1**, **2** and **6** are in the ranges 2.019(2)-2.046(3), 2.0359(17)-2.078(3), 2.2502(10)-2.2771(10) and 2.2794(9)-2.3056(9) Å, respectively, which are in agreement with the reported values for such distances [31,57]. It should be noted, however, that the Pd(1)-N(1) bond length in each of the complexes is longer than the value of 2.01 Å predicted on the basis of the covalent radii of N (sp^2) and palladium (0.70 and 1.30 Å, respectively) [62], reflecting the strong trans influence of the phosphine ligand [63]. Conversely, the Pd(1)-P(1) bond length in each of these complexes is shorter than the sum of the single bond radii for palladium and phosphorus (2.41 Å), suggesting some partial multiple bond character between the palladium and phosphorus atom [64]. The sum of the bond angles around N(1) (ca. 359°) in these complexes is in accordance with sp^2 hybridization [65].

3.6. Catalytic activity

All the palladium complexes (1-6) can be stored for prolonged periods and are air, light and moisture stable. Given these



Fig. 4. Molecular structure of [Pd(LN)(PPh₃)] (6) showing 50% displacement ellipsoids.

Table 1

Crystal data, data collection and structure refinement parameters for [Pd(LS)(PPh₃)] (1), [Pd(LM)(PPh₃)] (2) and [Pd(LN)(PPh₃)] (6).

Pempirical formulaC ₃₁ H ₂₄ NPdOPSC ₃₃ H ₂₄ NPdOPSC ₃₃ H ₂₄ NPdOPSFormula veight595.98610.01646.06Colordark reddark redHabitblockblock0.60 × 0.40 × 0.30Cystal dimension (m)0.20 × 0.0 × 0.01 × 0.10 × 0.100.60 × 0.40 × 0.30Cystal systemriclinc0.60 × 0.40 × 0.30A (A)0.911(15)0.9028(7)0.7331(12)b (A)0.9141(17)12.1482(9)0.9339(10)c (A)0.9247(2)10.7331(2)c (A)0.9247(2)9.039(10)c (A)0.9247(2)9.039(10)c (A)0.9247(2)9.039(10)c (A)0.9247(2)9.039(10)c (A)0.1249(2)7.37480(10)9.039(10)c (A)10.1249(2)7.37480(10)9.039(10)c (A)9.357(2)84.5460(10)9.040(10)c (A)1317.04)1397.57.456.5c (A)1317.04)1397.5137.2c (M)1317.04)1397.5131.2c (M)1.5031.450.11.421.4Absorption coefficient (m) ⁻¹ 1.6890.040.017.3c (M)0.1161.11.51.41.51.41.51.4c (M)0.134.11.550/61910.316.4c (M)0.134.11.550/61910.31.4c (M)0.14.11.550/61910.31.4c (M)0.14.11.550/61910.31.4c (M)0.14.10.14.40.14.4c (M)0.14.1 <th>Parameters</th> <th>$[Pd(LS)(PPh_3)] (1)$</th> <th>[Pd(LM)(PPh₃)] (2)</th> <th>[Pd(LN)(PPh₃)] (6)</th>	Parameters	$[Pd(LS)(PPh_3)] (1)$	[Pd(LM)(PPh ₃)] (2)	[Pd(LN)(PPh ₃)] (6)
Formula weight595.58610.01646.06Colordark reddark redHabitblockblockblockCrystal systemtriclinicmonocilinicSpace group P^{1} P^{1} P_{2}/c a (Å)0.01247(17)12.1482(9)29.070(3) c (Å)10.1247(17)12.1482(9)9.0339(10) c (Å)10.1247(2)3.7480(10)90 c (Å)10.1247(2)3.7480(10)90 c ($^{\circ}$)1317.0(4)1397.52745.0(5) Z ($^{\circ}$)56.48(2)20.200(3)104.2240(10) γ ($^{\circ}$)56.48(2)1372.210(10)90 γ ($^{\circ}$)56.48(2)2.210(10)90 γ ($^{\circ}$)50.38(1)1397.52745.0(5) Z (χ)2.00031.4501.421 ρ_{00} 60.48(2)0.2111341 ρ_{00} 1.5031.4501.421 ρ_{00} 6.496201312 λ (Ms ($x)$) (Å)0.710730.710730.71073 λ (Ms ($x)$) (Å)0.710730.710730.71073 λ (Ms (x_2) (Å)0.351/54970.414-27.50 ω , ϕ α_{ab} 0.0310.0458/01110.0257/00721 $Absorptic norefricterIs54/54970.045180.0257/00721Absorptic norefricterIs54/54970.0458/01110.0257/00721Absorptic norefricterIs54/54970.0458/01110.0257/00721Absorptic norefricterIs54/54970.0458/011$	Empirical formula	C ₃₁ H ₂₄ NPdOPS	C ₃₂ H ₂₆ NPdOPS	C ₃₅ H ₂₆ NPdOPS
Color dark red dark red block block block Habit block block block block Crystal dimension (mm) $2.0 \times 0.20 \times 0.20 \times 0.20$ $2.0 \times 0.10 \times 0.10 \times 0.10$ $0.60 \times 0.40 \times 0.30$ Crystal system triclinic triclinic monoclinic monoclinic Space group \vec{p} P_i P_2 /c monoclinic a (Å) 0.01247(17) 12.1482(9) $2.907(3)$ $2.907(3)$ x (Å) 10.1249(2) $7.37480(10)$ $9.038(10)$ $9.04220(10)$ x (Å) 9.537(2) 8.4560(10) $9.4220(10)$ $9.028(7)$ x (Å) 1317.0(4) 1397.5 2745.0(5) $7.450(5)$ Z 2 2 7.073 7.1073 7.1073 Absorption coefficient (mm ⁻¹) 0.869 0.821 $1.40 - 27.50$ $3.57(2) - 3.54 \times 37.711 \le 4.54 V(Mo (Å) 0.71073 0.71073 7.1073 7.1073 7.1073 V(Mo (Å) 0.41 - 27.43 + 2.7 - 18 \le 4.54 - 5.1 - 18 < 4.54 - 5.1 - 18 < 4.5$	Formula weight	595.98	610.01	646.06
HabitblockblockblockblockCrystal dimensin (mm)0.20 × 0.20 × 0.20 × 0.200.20 × 0.10 × 0.100.60 × 0.40 × 0.30Crystal gystemtriclinicmonoclinicmonoclinicSpace grouppipiPiP2,/ca (Å)9.0411(15)9.0028(7)10.7831(12)b (Å)10.1247(17)12.1482(9)0.3039(10)c (Å)14.7840(2)14.1443(11)9.0339(10)a (*)9.2357(2)84.5460(10)04.2240(10)g (*)9.5357(2)84.5460(10)04.2240(10)g (*)9.5448(2)7.0221(01)90g (*)9.5148(2)7.0221(01)90g (*)9.5148(2)7.0221(01)90g (*)13.10.(4)1397.52745.0(5)Z (K) (Mg/m ³)15.031.4501.421Absorption coefficient (mm ⁻¹)0.8990.8210.821f (Mo Kx) (Å)0.710730.710730.71073g Amge (*)1.41-27.431.50-27.490.40-27.50g Amge (*)1.41-27.431.50-27.490.40-27.50g Ange (*)1.41-27.431.51-57.57(61910.51 + 6.13, -37 ≤ k ≤ 37, -11 ≤ l ≤ 1g Ange (*)0.310.0180.010Referent methodIssue status1.1 ≤ h ≤ 11, -15 ≤ k ≤ 15, -18 ≤ l ≤ 1Referent methodIssue status1.1 ≤ h ≤ 11, -15 ≤ k ≤ 15, -18 ≤ l ≤ 1Pinare f (Harment methodIssue status0.0210Pinare f (Harment method0.359/0.09280.0458(101)0.0207/0.0	Color	dark red	dark red	dark red
C rystal dimension (mm) 0.20 × 0.20 × 0.20 0.20 × 0.10 × 0.10 0.60 × 0.40 × 0.30 Crystal system triclinic monoclinic Space group \bar{P} P P_2 /c a (A) 9.0411(15) 9.0028(7) 10.7831(12) b (Å) 10.1247(17) 12.1482(9) 9.0339(10) c (Å) 10.7870(2) 9.0339(10) 9.0339(10) c (Å) 10.1249(2) 7.37480(10) 9.0339(10) g (°) 9.2357(2) 84.5460(10) 104.2240(10) g (°) 9.0517(2) 137.04 1397.5 274.50(5) Z 2 2 4 4 V (Å) 1317.0(4) 1397.5 274.50(5) Z 2 2 4 4 Absorption coefficient (mm ⁻¹) 0.869 8.21 1332 Absorption coefficient (mm ⁻¹) 0.869 0.7073 0.71073 Absorption coefficient (mm ⁻¹) 0.361 0.7073 0.71073 Acting (M kaz) (Å) 0.71073 0.71073 0.5	Habit	block	block	block
Cysal system riclinic triclinic monoclinic Space group \bar{p} \bar{p} \bar{p} \bar{p}_1/c \bar{p}_2/c a (Å) 0.0411(15) $\bar{p}_0028(7)$ $10.7831(12)$ \bar{p}_2/c b (Å) 10.1247(17) 12.1482(9) $20.070(3)$ $\bar{p}_0039(10)$ c (Å) 10.1249(2) 14.1443(11) $90.0339(10)$ $\bar{p}_0039(10)$ c (Å) 10.1249(2) 84.5460(10) $104.2240(10)$ $\bar{p}_000000000000000000000000000000000000$	Crystal dimension (mm)	$0.20\times0.20\times0.20$	$0.20\times0.10\times0.10$	$0.60 \times 0.40 \times 0.30$
Space group $p\bar{1}$ $p\bar{1}$ P_2_1/c a (Å)9.0411(5)9.0028(7)10.7831(12) b (Å)10.1247(17)12.1482(9)9.073(3) c (Å)10.1249(2)7.37480(10)9.0339(10) x (°)101.249(2)7.37480(10)90 γ (°)9.0339(10)0.042240(10) γ (°)9.0357(2)84.5460(10)104.2240(10) γ (°)9.048(2)7.2210(10)90 γ (Å)1317.0(4)1397.52745.0(5) Z 24 T (K)173(2)1.4501.421 D_{calc} (Mg/m ³)1.5031.4501.421 $Absorption coefficient (mm-1)0.8690.8210.71073Absorption coefficient (mm-1)0.8690.8210.71073A (Mo Kx) (Å)0.710730.710730.71073A (Mo Kx) (Å)0.412-7.431.50-27.491.40-27.50A (Mo Kx) (Å)0.0310.04180.0210A (Mo Kx) (Å)0.0310.04180.0210A (Mo Carretterterterterterterterterterterterter$	Crystal system	triclinic	triclinic	monoclinic
a (Å)9.0411(15)9.0028(7)10.7831(12)b (Å)10.1247(17)12.1482(9)29.070(3)c (Å)14.7840(2)14.1443(11)9.339(10) α (°)101.249(2)7.37480(10)90 α (°)92.357(2)84.60(10)104.2240(10) γ (°)96.148(2)7.02210(10)90 γ (°)96.148(2)1397.52745.0(5) Z 247.3(2) Z 24 T (K)15031.4501.421 D_{calc} (Mg/m ³)1.5031.4508.21 D_{calc} (Mg/m ³)1.5030.8210.841 $F(000)$ 6046.201.312 A (MoxQ) (Å)0.710730.710730.71073 I (MoxQ) (Å)0.710730.710730.71073 I (Marge (°)1.41-27.431.50-27.49 $.40-27.50$ $Scan type$ ω, ϕ $.0, \phi h = 0$ $.0, \phi h = 0$ $Indx$ ranges $-1 \leqslant i \preccurlyeq 11, -12 \leqslant i \leqslant 12, -18 \leqslant i $ $11 \leqslant i \leqslant 11, -15 \leqslant i \leqslant 15, -18 \leqslant i $ $13 \leqslant i \leqslant 3, -37 \leqslant i \leqslant 3, -11 \leqslant i \leqslant 11$ $Refinemt method$ IIII-Artix least-squares on P^2 IIII (Same SMART APEX CCD $Init R init cest N/wR [1> 207(1)]0.0359(.00280.0458(.01101)0.0257(.00721Rink (ald ata)0.0459(.00280.0458(.01101)0.0257(.00721Rink (ald Arban (e^{A^3}))0.0459(.00280.0458(.01101)0.0388.00.8076Rink (ald Arban (e^{A^3}))0.0543(.0110)0.0257(.00721Rink (ald Arban (e^{A^3}))0.0543($	Space group	PĪ	ΡĪ	P2 ₁ /c
b (Å)10.1247(17)12.142(9)29.070(3)c (Å)14.7840(2)14.143(11)9.0339(10)c (°)101.249(2)73.7480(10)90 β (°)92.357(2)84.5460(10)104.2240(10) γ (°)96.148(2)70.2210(10)90 γ (Å)1317.0(4)1397.52745.0(5)Z24T (K)173(2)173(2)173(2) ρ_{alc} (Mg/m ³)1.5031.4501.421Absorption coefficient (mm ⁻¹)0.8690.8210.841 $r(000)$ 6046201312 i (Mo Ka) (Å)0.710730.710730.71073 θ Range (°)1.41-27.431.50-27.49.40-27.50 i (Mo Kay) (Å)0.3310.0480.0210Reficentions collected/unique13594/549715750(61910.13 < h < 13, -37 < k < 37, -11 < l < 1 < 1	a (Å)	9.0411(15)	9.0028(7)	10.7831(12)
c (Å)147840(2)14.143(11)9.0339(10) α (°)101.249(2)7.37480(10)90 β (°)92.357(2)84.5460(10)104.2240(10) γ (°)96.148(2)7.0210(10)90 V (Å)1317.0(4)1397.52745.0(5) Z 227.173(2)173(2) D_{ac} (Mg/m ³)1.5031.4501.421 h_{acor} (Mg/m ³)1.5031.4500.841 $h(b \propto)$ (Å)0.710730.710730.71073 $Absorption coefficient (mm-1)0.8690.710730.71073\delta (Mo K\alpha) (Å)0.710730.710730.71073\beta (Nage (°)1.41-27.431.50-27.491.40-27.50Scant type\phi, \phi\phi\phi\phiIndex ranges-11 \le h \le 11, -12 \le k \le 12, -18 \le l \le 18-11 \le h \le 15, -18 \le l \le 18-13 \le h \le 13, -37 \le k \le 37, -11 \le l \le 11Refinement methodIsopartic kast-squares or P^2Isopartic kast-squares or P^2Isopartic kast-squares or P^2Final R indices R1/mg/2 [l \ge cot()]0.0359(0.09280.0458(0.1101)0.0257(0.0721Ap_{max} and \Delta p_{min} (A^{-3})0.654 and -0.8370.781 and -0.5830.898 and -0.515AcoreIsopartic kast-squares or P^2Isopartic kast-squares or P^2Isopartic kast-squares or P^2Pinal R indices R1/mg/2 [l \ge 2cot()]0.0359(0.09280.0458(0.1101)0.0257(0.0721AcoreIsopartic kast-squares or P^2Isopartic kast-squares or P^2Isopartic kast-squares or P^2$	b (Å)	10.1247(17)	12.1482(9)	29.070(3)
α (°)101.249(2)73.7480(10)90 β (°)92.357(2)84.5460(10)104.2240(10) γ (°)96.148(2)70.2210(10)90 γ (%)96.148(2)70.2210(10)90 V (Å ³)1317.0(4)1397.52745.0(5) Z 244 T (K)173(2)173(2)173(2) D_{calc} (Mg/m ³)1.5031.4501.421Absorption coefficient (mm ⁻¹)0.8690.8210.841 f (000)604620312312 λ (Mo K α) (Å)0.710730.710730.71073 δ (Mag (°)1.41-27.431.50-27.491.40-27.50Scan type ω, ϕ ω, ϕ $-13 \le h \le 13, -37 \le k \le 37, -11 \le l < 11$ h (Act ranges $-11 \le h \le 11, -12 \le k \le 12, -18 \le l \le 18$ $-11 \le h \le 11, -15 \le k \le 15, -18 \le l \le 18$ $Reflections collected/unique3594/54970.004180.0210R_{ht}0.03310.04180.2170Outsmulti-scan sabassmulti-scan sabassFinal R indices R1/wR_2 [l > 2\sigma(l)]0.0359/0.09280.0458/0.11010.0257/0.0721R/wR_2 (all data)0.0490/0.12000.0591/0.11600.0380/0.0876Godoness-of-fitt on P^21.0850.781 and -0.5830.898 and -0.515A f_{max} and A p_{min} (h^2^{-3})0.654 and -0.8370.781 and -0.5830.898 and -0.515A f_{Max} (all data)0.654 and -0.8370.781 and -0.5830.898 and -0.515A f_{Max}0.591/0.325<$	<i>c</i> (Å)	14.7840(2)	14.1443(11)	9.0339(10)
β (°)92.357(2)84.5460(10)104.2240(10)γ (°)96.148(2)70.2210(10)90V (Å)1317.0(4)1397.52745.0(5)Z224T (K)173(2)173(2)173(2) D_{calc} (Mg/m³)1.5031.4500.821Absorption coefficient (mm ⁻¹)0.8690.8210.841F(000)6046203112 δ (Mo Kα) (Å)0.110730.710730.71073Scan type $α, φ$ $α, φ$ $α, φ$ Index ranges-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -18 ≤ l ≤ 18-11 ≤ h ≤ 11, -15 ≤ k ≤ 15, -18 ≤ l ≤ 18-13 ≤ h ≤ 13, -37 ≤ k ≤ 37, -11 ≤ l ≤ 11Reflections collected/unique13594/54970.04180.02100.0210Rint0.03310.04180.0257/00721IDiffractometermulti-scan saAbasFinal R indices R1/wR2 [I > 2σ(J)]0.0359/0.09280.0458/0.11010.0257/0.0721Rink0.0490/0.12000.0591/0.11600.3038/0.0876Godness-of from P ² 1.0851.0351.240Ap _{max} and Ap _{min} (e Å ⁻³)0.654 and -0.8370.781 and -0.5830.898 and -0.515Dat/restraints/parameters5497/03256191/03340.898 and -0.515	α (°)	101.249(2)	73.7480(10)	90
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	β(°)	92.357(2)	84.5460(10)	104.2240(10)
V (Å3)1317.0(4)1397.52745.0(5)Z24Z24T (K)173(2)173(2)173(2) D_{calc} (Mg/m3)1.5031.4501.421Absorption coefficient (mm^-1)0.8690.8210.841F(000)6046201312 $\dot{\alpha}$ (Ms (α) (Å)0.710730.710730.71073 θ Range (°)1.41-27.431.50-27.491.40-27.50Scan type ϕ, ϕ ϕ, ϕ $-11 \leq h \leq 11, -15 \leq k \leq 15, -18 \leq 16$ $-13 \leq h \in 13, -37 \leq k \leq 37, -11 \leq l \leq 11$ Reflections collected/unique13594/54970.0418 -0.0210 $-0.0517/6209$ Refnement methodIIIIIIDiffractometermulti-scan sabaseFinal R indices $R1/wR_2$ [$l > 2\sigma(l)$]0.0359/0.09280.0458/0.11010.0257/0.0721Absorption correctionmulti-scan sabaseFinal R indices $R1/wR_2$ [$l > 2\sigma(l)$]0.0359/0.09280.0458/0.11010.02308/0.0876Adpmax and Δp_{min} (e^{Λ^{-3})0.654 and -0.8370.781 and -0.5830.898 and -0.515Data/restraints/parameters5497/0/3256191/0/3346209/0/365	γ (°)	96.148(2)	70.2210(10)	90
Z224T (K)173(2)173(2)173(2) D_{calc} (Mg/m³)1.5031.4501.421Absorption coefficient (mm ⁻¹)0.8690.8210.841F(000)6046201312 λ (Mo Ka) (Å)0.710730.710730.71073 θ Range (°)1.41-27.430.70730.71073Index ranges $-11 \leqslant h \leqslant 11, -12 \leqslant k \le 12, -18 \leqslant l \leqslant 1$ $-11 \leqslant h \leqslant 11, -15 \leqslant k \le 15, -18 \leqslant l \leqslant 1$ $-13 \leqslant h \leqslant 13, -37 \leqslant k \leqslant 37, -11 \leqslant l \leqslant 11$ Reflections collected/unique13594/54970.04180.0210Rint0.03310.04180.0210Diffractometermulti-scan sabasesFinal R indices R1/wR2 [l > 2cr(l)]0.0359/0.09280.0458/0.11010.0257/0.0721R1/wR2 (all data)0.0490/0.12000.0591/0.11600.0308/0.0876Goodness-of-fit on F^2 1.0851.0351.240 $A c_{pmax}$ and $A c_{pmin}$ (e Å ⁻³)0.654 and -0.8370.781 and -0.5830.898 and -0.515Data/restraints/parameters5497/0/3256191/0/3346209/0/365	V (Å ³)	1317.0(4)	1397.5	2745.0(5)
T (K)173(2)173(2)173(2) D_{calc} (Mg/m ³)1.5031.4501.421 D_{calc} (Mg/m ³)0.8690.8210.841 $Absorption coefficient (mm-1)0.8690.8210.8410,006046201312\lambda (Mo \alpha) (Å)0.710730.710730.71073\theta Range (°)1.41–27.431.50–27.491.40–27.50Scan type\omega, \phi\omega, \phi\omega, \phiIndex ranges-11 \le h \le 11, -12 \le k \le 12, -18 \le l \le 18-11 \le h \le 15, -18 \le l \le 18-13 \le h \le 37, -11 \le l \le 11Reflections collected/unique1359/549715750/619130517/6209R_{int}0.03310.04180.0210Refinement methodmulti-scan sADABSDiffractometermulti-scan sADABSAbsorption correctionmulti-scan sADABSFinal R indices R1/wR2 [I > 2σ(I)]0.0359/0.09280.0458/0.11010.0257/0.0721R1/wR2 (all data)0.0490/0.12000.0591/0.11600.3088/0.0876Goodness-of-fit on F21.0851.0351.240\Delta \rho_{max} and \Delta \rho_{min} (e Å-3)0.654 and -0.8370.781 and -0.5830.898 and -0.515Data/restraints/parameters5497/0/3256191/0/3346209/0/365$	Ζ	2	2	4
$ \begin{array}{cccc} D_{calc} (Mg/m^3) & 1.503 & 1.450 & 1.421 \\ Absorption coefficient (mm^{-1}) & 0.869 & 0.821 & 0.841 \\ P(000) & 604 & 620 & 1312 \\ \lambda (Mo K\alpha) (Å) & 0.71073 & 0.71073 & 0.71073 \\ \theta Range (°) & 1.41-27.43 & 1.50-27.49 & 1.40-27.50 \\ Scan type & \omega, \phi & \omega, \phi & \omega, \phi \\ Index ranges & -11 \leqslant h \leqslant 11, -12 \leqslant k \leqslant 12, -18 \leqslant l \leqslant 18 \\ Index ranges & -11 \leqslant h \leqslant 11, -12 \leqslant k \leqslant 12, -18 \leqslant l \leqslant 18 \\ P(lettions collected/unique & 13594/5497 & 15750/6191 & 30517/6209 \\ Refinement method & 0.0331 & 0.0418 & 0.0210 \\ Refinement method & full-matrix least-squares on F^2 \\ Bruker SMART APEX CCD \\ Mabor prior correction & multi-scan sabaBS \\ Final R indices R1/wR_2 [I 2 2 \sigma(I)] & 0.0359/0.0928 & 0.0458/0.1101 & 0.0257/0.0721 \\ R1/wR_2 (all data) & 0.0490/0.1200 & 0.0591/0.1160 & 0.3038/0.0876 \\ Goodness-of-fit on F^2 & 1.085 & 1.035 & 1.240 \\ \Delta \rho_{max} and \Delta \rho_{min} (e Å^{-3}) & 0.654 and -0.837 & 0.781 and -0.583 & 0.898 and -0.515 \\ Data/restraints/parameters & 5497/0/325 & 6191/0/334 & 6209/0/365 \\ \end{array}$	T (K)	173(2)	173(2)	173(2)
Absorption coefficient (mm^-1)0.8690.8210.841 $F(000)$ 604 620 1312 $i (M0 K\alpha) (\dot{A})$ 0.71073 0.71073 0.71073 $\theta Range (°)$ $1.41-27.43$ $1.50-27.49$ $1.40-27.50$ Scan type ω, ϕ ω, ϕ $-11 \leq h \leq 11, -12 \leq k \leq 12, -18 \leq l \leq 18$ $-11 \leq h \leq 15, -18 \leq l \leq 18$ $-13 \leq h \leq 33, -37 \leq k \leq 37, -11 \leq l \leq 11$ Reflections collected/unique $13594/5497$ $15750/6191$ $30517/6209$ R_{int} 0.0331 0.0418 0.0210 Refinement method $III = III = III = IIII = IIII = IIII = IIII = IIII = IIII = IIIII = IIIII = IIIII = IIIII = IIIII = IIIIII$	D_{calc} (Mg/m ³)	1.503	1.450	1.421
$F(00)$ 6046201312 λ (Mo Kα) (Å)0.710730.710730.71073 θ Range (°)1.41–27.431.50–27.491.40–27.50Scan type ω, ϕ ω, ϕ ω, ϕ Index ranges $-11 \le h \le 11, -12 \le k \le 12, -18 \le l \le 18$ $-11 \le h \le 15, -18 \le l \le 18$ $-13 \le h \le 13, -37 \le k \le 37, -11 \le l \le 11$ Reflections collected/unique13594/549715750/619130517/6209 R_{int} 0.03310.04180.0210Refinement methodfull-matrix least-squares on F^2 Bruker SMART APEX CCDDiffractometermulti-scan sADABS1.559/0.0721Final R indices $R1/wR_2$ [$I \ge 2\sigma(I)$]0.0359/0.09280.0458/0.11010.0257/0.0721R1/wR_2 (all data)0.0490/0.12000.0591/0.11600.0308/0.0876Goodness-of-fit on F^2 1.0851.0351.240 $\Delta \rho_{max}$ and $\Delta \rho_{min}$ (e \tilde{A}^{-3})0.654 and -0.8370.781 and -0.5830.898 and -0.515Data/restraints/parameters5497/0/3256191/0/3346209/0/365	Absorption coefficient (mm ⁻¹)	0.869	0.821	0.841
$\begin{array}{cccc} \lambda \ (Mo \ K\alpha) \ (\mathring{A}) & 0.71073 & 0.71073 & 0.71073 & 0.71073 \\ \theta \ Range \ (\circ) & 1.41-27.43 & 1.50-27.49 & 1.40-27.50 \\ & & & & & & & & & & & & & & & & & & $	F(000)	604	620	1312
θ Range (°)1.41–27.431.50–27.491.40–27.50Scan type $ω, \phi$ $ω, \phi$ $ω, \phi$ $ω, \phi$ Index ranges $-11 \leqslant h \leqslant 11, -12 \leqslant k \leqslant 12, -18 \leqslant l \leqslant 18$ $-11 \leqslant h \leqslant 11, -15 \leqslant k \leqslant 15, -18 \leqslant l \leqslant 18$ $-13 \leqslant h \leqslant 13, -37 \leqslant k \leqslant 37, -11 \leqslant l \leqslant 11$ Reflections collected/unique13594/549715750/619130517/6209Rint0.03310.04180.0210Refinement methodfull-matrix least-squares on F^2 Bruker SMART APEX CCDDiffractometermulti-scan sADABS-Final R indices R1/wR2 [l > 2σ(l)]0.0359/0.09280.0458/0.11010.0257/0.0721R1/wR2 (all data)0.0490/0.12000.0591/0.11600.0308/0.0876Goodness-of-fit on F^2 1.0851.0351.240 $\Delta \rho_{max}$ and $\Delta \rho_{min}$ (e $Å^{-3}$)0.654 and -0.8370.781 and -0.5830.898 and -0.515Data/restraints/parameters5497/0/3256191/0/3346209/0/365	λ (Mo Kα) (Å)	0.71073	0.71073	0.71073
$\begin{array}{llllllllllllllllllllllllllllllllllll$	θ Range (°)	1.41-27.43	1.50–27.49	1.40-27.50
$ \begin{array}{cccc} Index \ ranges & -11 \leqslant h \leqslant 11, -12 \leqslant k \leqslant 12, -18 \leqslant l \leqslant 18 & -11 \leqslant h \leqslant 11, -15 \leqslant k \leqslant 15, -18 \leqslant l \leqslant 18 & -13 \leqslant h \leqslant 13, -37 \leqslant k \leqslant 37, -11 \leqslant l \leqslant 11 \\ Reflections \ collected/unique & 13594/5497 & 15750/6191 & 30517/6209 \\ \hline R_{int} & 0.031 & 0.0418 & 0.0210 \\ \hline Refinement \ method & full-matrix \ least-squares \ on \ F^2 & \\ Bruker \ SMART \ APEX \ CCD & \\ Multi-scan \ sADABS & \\ \hline Final \ R \ indices \ R1/wR_2 \ [l > 2\sigma(l)] & 0.0359/0.0928 & 0.0458/0.1101 & 0.0257/0.0721 \\ \hline R1/wR_2 \ (all \ data) & 0.0490/0.1200 & 0.0591/0.1160 & 0.0308/0.0876 \\ \hline Goodness-of-fit \ on \ F^2 & 1.085 & 1.035 & 1.240 \\ \hline \Delta \rho_{max} \ and \ \Delta \rho_{min} \ (e \ A^{-3}) & 0.654 \ and \ -0.837 & 0.781 \ and \ -0.583 & 0.898 \ and \ -0.515 \\ \hline Data/restraints/parameters & 5497/0/325 & 6191/0/334 & 6209/0/365 \\ \hline \end{array}$	Scan type	ω , ϕ	ω, ϕ	ω , ϕ
Reflections collected/unique 13594/5497 15750/6191 30517/6209 R_{int} 0.0331 0.0418 0.0210 Refinement method full-matrix least-squares on F^2 Full-matrix least-squares on F^2 Full-matrix least-squares on F^2 Diffractometer Bruker SMART APEX CCD multi-scan sADABS TOTO Absorption correction multi-scan sADABS 0.0257/0.0721 R1/wR ₂ (all dat) 0.0490/0.1200 0.0591/0.1160 0.0308/0.0876 Goodness-of-fit on F^2 1.085 1.035 1.240 $\Delta \rho_{max}$ and $\Delta \rho_{min}$ (e Å ⁻³) 0.654 and -0.837 0.781 and -0.583 0.898 and -0.515 Data/restraints/parameters 5497/0/325 6191/0/334 6209/0/365	Index ranges	$-11 \leqslant h \leqslant 11, -12 \leqslant k \leqslant 12, -18 \leqslant l \leqslant 18$	$-11 \leqslant h \leqslant 11, -15 \leqslant k \leqslant 15, -18 \leqslant l \leqslant 18$	$-13 \leqslant h \leqslant 13, -37 \leqslant k \leqslant 37, -11 \leqslant l \leqslant 11$
R_{int} 0.031 0.0418 0.0210 Refinement method full-matrix least-squares on F^2 full-matrix least-squares on F^2 Fruiter SMART APEX CCD Diffractometer Bruker SMART APEX CCD multi-scan sADABS 0.0257/0.0721 Absorption correction 0.0490/0.1200 0.0591/0.1160 0.0308/0.0876 R1/wR ₂ (all data) 0.0490/0.1200 0.0591/0.1160 0.0308/0.0876 Goodness-of-fit on F^2 1.085 1.035 1.240 Δρ _{max} and Δρ _{min} (e Å ⁻³) 0.654 and -0.837 0.781 and -0.583 0.898 and -0.515 Data/restraints/parameters 5497/0/325 6191/0/334 6209/0/365	Reflections collected/unique	13594/5497	15750/6191	30517/6209
Refinement method full-matrix least-squares on F^2 Diffractometer Bruker SMART APEX CCD Absorption correction multi-scan sADABS Final R indices $R1/wR_2$ [$I > 2\sigma(I)$] 0.0359/0.0928 0.0458/0.1101 0.0257/0.0721 R1/wR_2 (all data) 0.0400/0.1200 0.0591/0.1160 0.0308/0.0876 Godness-of-fit on F^2 1.085 1.035 1.240 $\Delta \rho_{max}$ and $\Delta \rho_{min}$ (e Å ⁻³) 0.654 and -0.837 0.781 and -0.583 0.898 and -0.515 Data/restraints/parameters 5497/0/325 6191/0/334 6209/0/365	R _{int}	0.0331	0.0418	0.0210
Diffractometer Bruker SMART APEX CCD multi-scan sADABS Absorption correction multi-scan sADABS Final R indices R1/wR2 [I > 2 σ (I)] 0.0359/0.0928 0.0458/0.1101 0.0257/0.0721 R1/wR2 (all data) 0.0490/0.1200 0.0591/0.1160 0.0308/0.0876 Godness-of-fit on F^2 1.085 1.035 1.240 $\Delta \rho_{max}$ and $\Delta \rho_{min}$ (e Å ⁻³) 0.654 and -0.837 0.781 and -0.583 0.898 and -0.515 Data/restraints/parameters 5497/0/325 6191/0/334 6209/0/365	Refinement method		full-matrix least-squares on F^2	
Absorption correction multi-scan saDabs Final R indices R1/wR2 [I > 2σ(I)] 0.0359/0.0928 0.0458/0.1101 0.0257/0.0721 R1/wR2 (all data) 0.0490/0.1200 0.0591/0.1160 0.0308/0.0876 Goodness-of-fit on F^2 1.085 1.035 1.240 Δρ _{max} and Δρ _{min} (e Å ⁻³) 0.654 and -0.837 0.781 and -0.583 0.898 and -0.515 Data/restraints/parameters 5497/0/325 6191/0/334 6209/0/365	Diffractometer		Bruker SMART APEX CCD	
Final R indices $R1/wR_2 [I > 2\sigma(I)]$ 0.0359/0.09280.0458/0.11010.0257/0.0721 $R1/wR_2$ (all data)0.0490/0.12000.0591/0.11600.0308/0.0876Goodness-of-fit on F^2 1.0851.0351.240 $\Delta \rho_{max}$ and $\Delta \rho_{min}$ (e Å ⁻³)0.654 and -0.8370.781 and -0.5830.898 and -0.515Data/restraints/parameters5497/0/3256191/0/3346209/0/365	Absorption correction		multi-scan sadabs	
R1/wR2 (all data)0.0490/0.12000.0591/0.11600.0308/0.0876Goodness-of-fit on F^2 1.0851.0351.240 $\Delta \rho_{max}$ and $\Delta \rho_{min}$ (e Å ⁻³)0.654 and -0.8370.781 and -0.5830.898 and -0.515Data/restraints/parameters5497/0/3256191/0/3346209/0/365	Final R indices $R1/wR_2$ [I > $2\sigma(I)$]	0.0359/0.0928	0.0458/0.1101	0.0257/0.0721
Goodness-of-fit on F^2 1.0851.0351.240 $\Delta \rho_{max}$ and $\Delta \rho_{min}$ (e Å ⁻³)0.654 and -0.8370.781 and -0.5830.898 and -0.515Data/restraints/parameters5497/0/3256191/0/3346209/0/365	$R1/wR_2$ (all data)	0.0490/0.1200	0.0591/0.1160	0.0308/0.0876
$\Delta \rho_{max}$ and $\Delta \rho_{min}$ (e Å ⁻³)0.654 and -0.8370.781 and -0.5830.898 and -0.515Data/restraints/parameters5497/0/3256191/0/3346209/0/365	Goodness-of-fit on F^2	1.085	1.035	1.240
Data/restraints/parameters 5497/0/325 6191/0/334 6209/0/365	$\Delta ho_{ m max}$ and $\Delta ho_{ m min}$ (e Å $^{-3}$)	0.654 and -0.837	0.781 and -0.583	0.898 and -0.515
	Data/restraints/parameters	5497/0/325	6191/0/334	6209/0/365

favorable properties, the catalytic activity of each of these complexes in the Suzuki–Miyaura coupling reaction of 4-bromotoluene with phenylboronic acid was investigated in DMAc–H₂O mixture at 100 °C with 1 mol% of catalyst and results are summarized in

Table 3. It was found that the use of complex **3** as a catalyst provided good yield of biaryl (92%) after 12 h without requiring the use of an inert atmosphere. Hence, complex **3** was selected as the catalyst in order to assess the scope of substrates that may

Table 2						
Selected	bond	lengths	(Å)	and	angles	(°).

	$[Pd(LS)(PPh_3)] (1)$	$[Pd(LM)(PPh_3)]$ (2)	$[Pd(LN)(PPh_3)]$ (6)
Pd(1) - O(1)	2.046(3)	2.019(2)	2.0193(14)
Pd(1) - N(1)	2.078(3)	2.053(3)	2.0359(17)
Pd(1)-S(1)	2.2771(10)	2.2502(10)	2.2530(6)
Pd(1)-P(1)	2.3056(9)	2.2794(9)	2.2815(6)
O(1) - C(1)	1.326(4)	1.301(4)	1.293(2)
N(1)-C(7)	1.317(5)	1.302(4)	1.306(3)
N(1)-C(8)	1.447(5)	1.429(5)	1.430(3)
S(1)-C(13)	1.789(4)	1.754(4)	1.755(2)
P(1)-C(14)	1.845(3)	1.817(4)	1.820(2)
P(1)-C(20)	1.848(4)	1.826(4)	1.828(2)
P(1)-C(26)	1.853(4)	1.836(4)	1.820(2)
C(1)-C(6)	1.431(5)	1.415(5)	1.419(3)
C(6)-C(7)	1.448(5)	1.422(5)	1.418(3)
C(8)-C(13)	1.424(5)	1.394(5)	1.398(3)
C(4)-X	0.95 (X = H)	1.517(5) (X = C(4')	1.409(3) (X = C(4'))
O(1) - Pd(1) - S(1)	179.03(9)	177.98(8)	175.72(4)
N(1)-Pd(1)-P(1)	176.44(8)	176.84(8)	177.57(5)
O(1)-Pd(1)-N(1)	93.55(11)	92.87(11)	91.33(6)
N(1)-Pd(1)-S(1)	86.47(8)	86.37(8)	86.15(5)
O(1) - Pd(1) - P(1)	83.67(8)	90.07(7)	91.08(4)
S(1)-Pd(1)-P(1)	96.35(4)	90.72(4)	91.43(2)
Pd(1)-O(1)-C(1)	125.5(2)	126.1(2)	125.73(13)
Pd(1)-N(1)-C(7)	121.3(2)	122.0(2)	122.39(14)
Pd(1)-N(1)-C(8)	117.9(2)	117.4(2)	117.24(13)
Pd(1)-S(1)-C(13)	98.73(13)	98.48(13)	98.46(7)
Pd(1)-P(1)-C(14)	120.46(12)	114.47(12)	111.67(7)
Pd(1)-P(1)-C(20)	106.57(11)	113.93(12)	113.96(7)
Pd(1)-P(1)-C(26)	112.77(11)	115.07(12)	114.51(7)
C(14)-P(1)-C(20)	105.78(16)	103.42(16)	105.57(10)
C(20)-P(1)-C(26)	104.83(16)	103.92(17)	104.66(9)
C(20)-P(1)-C26)	105.31(16)	104.70(16)	105.63(9)
C(1)-C(6)-C(7)	125.5(3)	125.4(3)	122.86(18)
C(6)-C(7)-N(1)	129.0(3)	128.6(3)	128.72(19)
C(7)-N(1)-C(8)	120.8(3)	120.6(3)	119.84(18)
C(8)-C(9)-S(1)	120.5(3)	121.2(3)	120.27(16)

Table 3

Evaluation of complexes 1-6 as catalysts for the Suzuki-Miyaura cross-coupling of 4-bromotoluene with phenylboronic acid.^a



^a Reaction conditions: 4-bromotoluene (1 mmol), phenylboronic acid (1.5 mmol) in 1 ml of ethanol, K₂CO₃ (2 mmol) in 1 ml of H₂O, catalyst (1 mol%) in 1 ml of DMAc, additional DMAc (5 ml), stirring for 12 h, 100 °C.

^b Yield is determined by GC with area normalization.

be coupled using this system and the cross-coupling reactions between various aryl bromides and arylboronic acids were investigated. Interestingly, the new palladium(II) complexes exhibited better catalytic activity compared to its precursor, [Pd(PPh₃)₄] (Table 3). The reaction between 4-bromobenzene and phenylboronic acid proceeded smoothly to yield 96% of biphenyl (Table 4, entry 1). Of course, other reported palladium complexes for this reaction are more efficient or comparable with the complexes presented in this paper [31,66,67]. The coupling reaction of aryl bromides bearing an electron donating group, such as CH₃ and OCH₃, with phenylboronic acid produced biaryls in good yields (92% and 87%) (Table 4, entries 2 and 3). But, 3,5-dimethyl-1-bromobenzene generated the substituted biphenyl in only 65% yield (Table 4, entry 4). Electron deficient aryl bromides, such as 4-bromoacetophenone, 4bromobenzaldehyde, 4-bromobenzoinc acid, 4-trifluoromethyl-1bromobenzene, 4-nitro-1-bromobenzene and 2-bromonaphthalene, reacted with phenylboronic acid to produce biaryls in high yield, ranging from 84% to 98% (Table 4, entries 5–10) under the same reaction conditions. Using this methodology, the coupling between aryl bromides and phenylboronic acid that contain electron-donating as well as electron-withdrawing groups, proceeded efficiently to afford the corresponding products. However there are some systems in which the electronic effect of substituents had a great influence on the efficacy of the coupling reaction [28,68], which hinders synthetic applicability of those approaches. When heterocyclic aryl halides were used for cross coupling with phenyl boronic acid using catalyst **3**, a decrease in the yield of product (to between 69% and 84%) was observed; although these

Table 4

Yields from Suzuki-Miyaura cross-coupling reactions catalyzed by complex **3**.^a

Entry	ArB(OH) ₂	Ar-X	Product	Yield ^b (%)
1	OH OH	Br		96
2	OH OH	Br		92 (86) ^c
3		Br	────────────────────────────────────	87 (78)
4		Br		65 (55)
5	OH OH	Br		97 (95)
6	OH OH	Br - O OH	✓ → → → → → → → → → → → → → → → → → → →	98 (90)
7	OH OH	Br - O OH	ОН	93 (92)
8		Br CF3	CF3	84 (68)
9		Br - NO ₂		98 (95)
10		Br		94 (89)
11	OH OH	Br		80
		ОН	ОН	
12	OH OH	Br-		84 (75)
13	OH OH			72 ^d
14		$Br \longrightarrow N$		69 ^d
15		Br-		58

Table 4 (continued)



^a Reaction conditions: 4-bromoarene (1 mmol), arylboronic acid (1.5 mmol), catalyst 3 (1 mol%), additional DMAc (5 ml), stirring for 12 h, 100 °C.

^b Yield is determined by GC with area normalization.

^c Isolated yields are given in parenthesis.

^d Yield is determined by GC-MS.

yields are lower than those presented above, they are still reasonably good (Table 4, entries 12–14). In fact, the lowest yield was found in the reaction of 2-bromopyridine with pyridine-3-boronic acid to produce isonicoteine in 58% yield (Table 4, entry 15); we postulate that the low yield may be due to chelating ability of isonicoteine with the metal which has the capacity to alter the nature of catalyst. Reaction of 2-bromo naphthalene with pyridine-3boronic acid gave product in 78% yield (Table 4, entry 16). Palladium black was observed in all the present coupling reactions. Hence, the catalysis may not be true homogeneous [69].

4. Conclusions

In conclusion, we have reported convenient syntheses and comprehensive characterization of six new palladium(II) complexes (1-6) containing salicylideneimine based tridentate ligand and triphenylphosphine. The solid state structures of complexes 1, 2 and 6 were determined by X-ray crystallography. The complexes showed the expected square planar geometry about the metal center. The complexes were applied to the Suzuki-Miyaura cross-coupling reaction between 4-bromobenzene and phenylboronic acid and found that **3** was the most active and was suitable for use without an inert atmosphere. Complex 3 was further used to assess the efficacy of cross-coupling reactions between various aryl halides and boronic acids. The coupling reactions were effective with electron-donating as well as electron-withdrawing substituents on the aryl halide. Heterocyclic boronic acid and aryl halides were also used successfully in Suzuki-Miyaura cross-coupling reactions with this catalyst. The palladium(II) complexes reported in this paper are air and light stable compared to its precursor, $[Pd(PPh_3)_4]$.

Acknowledgements

R.K. and M.M. gratefully acknowledge CSIR [01(2137)/07/EMR-II] for financial support. We thank SAIF, IIT-Madras, Chennai and NRC, SIF, IISC, Bangalore for NMR measurements. Funding from DST through FIST Programme is acknowledged. C.L.B.M. acknowledges NSERC for financial support. We also thank the reviewers for useful suggestions.

Appendix A. Supplementary material

CCDC 853722, 853723 and 727007 contain the supplementary crystallographic data for complexes **1**, **2** and **6**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2012.08.024.

References

- [1] R.J.P. Corriu, J.P. Masse, Chem. Commun. (1972) 144a.
- [2] K. Tamao, K. Sumitani, M. Kumada, J. Am. Chem. Soc. 94 (1972) 4374.

- [3] K.M. Tamao, A.N. Miyake, T. Matsuda, Y. Kiso, M. Kumada, Chem. Lett. 4 (1975) 133.
- [4] A. Sekiya, N. Ishikawa, J. Organomet. Chem. 118 (1976) 349.
- [5] E. Negishi, A.O. King, N. Okukado, J. Org. Chem. 42 (1977) 1821.
- [6] N. Miyaura, K. Yamada, A. Suzuki, Tetrahedron Lett. 20 (1979) 3437.
- [7] N. Miyaura, A. Suzuki, Chem. Commun. (1979) 866.
- [8] N. Miyaura, T. Yano, A. Suzuki, Tetrahedron Lett. 21 (1980) 2865.
- [9] N. Miyaura, T. Yanagi, A. Suzuki, Synth. Commun. 11 (1981) 513.
- [10] A. Suzuki, Angew. Chem., Int. Ed. Engl. 50 (2011) 6722.
- [11] T.J. Colacot, Platinum Met. Rev. 55 (2011) 84.
- [12] N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457.
- [13] A. Bahl, W. Grahn, S. Stadler, F. Feiner, G. Bourhill, C. Bräuchle, A. Reisner, P.G. Jones, Angew. Chem., Int. Ed. Engl. 34 (1995) 1485.
- [14] M. Beller, J.G.E. Krauter, A. Zapf, Angew. Chem., Int. Ed. Engl. 36 (1997) 772.
- [15] K. Jones, M. Keenan, F. Hibbert, Synlett 1996 (1996) 509.
- [16] R. Dalessio, A. Rossi, Synlett 1996 (1996) 513.
- [17] M.B. Goldfinger, K.B. Crawford, T.M. Swager, J. Org. Chem. 63 (1998) 1676.
- [18] F. Firooznia, C. Gude, K. Chan, Y. Satoh, Tetrahedron Lett. 39 (1998) 3985.
- [19] M.B. Goldfinger, K.B. Crawford, T.M. Swager, J. Am. Chem. Soc. 119 (1997) 4578.
- [20] T. Ishiyama, Y. Itoh, T. Kitano, N. Miyaura, Tetrahedron Lett. 38 (1997) 3447.
- [21] C. Zhang, J. Huang, M.L. Trudell, S.P. Nolan, J. Org. Chem. 64 (1999) 3804.
- [22] M. Perez-Lorenzo, J. Phys. Chem. Lett. 3 (2012) 167.
- [23] G.W. Kabalka, R.M. Pagni, C.M. Hair, Org. Lett. 1 (1999) 1423.
- [24] S. Li, Y. Lin, J. Cao, S. Zhang, J. Org. Chem. 72 (2007) 4067.
- [25] G.A. Grasa, M.S. Viciu, J. Huang, C. Zhang, M.L. Trudell, S.P. Nolan, Organometallics 21 (2002) 2866.
- [26] E. Tas, A. Kilic, M. Durgun, I. Yilmaz, I. Ozdemir, N. Gurbuz, J. Organomet. Chem. 694 (2009) 446.
- [27] I.D. Kostas, B.R. Steele, A. Terzis, S.V. Amosova, A.V. Martynov, N.A. Makhaeva, Eur. J. Inorg. Chem. 2006 (2006) 2642.
- [28] J. Cui, M. Zhang, Y. Zhang, Inorg. Chem. Commun. 13 (2010) 81.
- [29] E.G. Bowes, G.M. Lee, C.M. Vogels, A. Decken, S.A. Westcott, Inorg. Chim. Acta 377 (2011) 84.
- [30] B.J. Tardiff, J.C. Smith, S.J. Duffy, C.M. Vogels, A. Decken, S.A. Westcott, Can. J. Chem. 85 (2007) 392.
- [31] P.R. Kumar, S. Upreti, A.K. Singh, Polyhedron 27 (2008) 1610.
- [32] M. Muthu Tamizh, K. Mereiter, K. Kirchner, B.R. Bhat, R. Karvembu, Polyhedron 28 (2009) 2157.
- [33] M. Muthu Tamizh, B. Varghese, A. Endo, R. Karvembu, Spectrochim. Acta 77A (2010) 411.
- [34] M. Muthu Tamizh, K. Mereiter, K. Kirchner, R. Karvembu, J. Organomet. Chem. 700 (2012) 194.
- [35] S. Priyarega, M. Muthu Tamizh, S. Ganesh Babu, R. Karvembu, K. Natarajan, Indian J. Chem. 51A (2012) 453.
- [36] S. Priyarega, D. Senthil Raja, S. Ganesh Babu, R. Karvembu, T. Hashimoto, A. Endo, K. Natarajan, Polyhedron 34 (2012) 143.
- [37] D.D. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals, Fourth ed., Buttrewort-Heinemann, Oxford, 1996.
- [38] J.J. Levison, S.D. Robinson, Inorg. Synth. 13 (1972) 121.
- [39] F. Tisato, F. Refosco, U. Mazzi, G. Bandoli, M. Nicolini, J. Chem. Soc., Dalton Trans. (1987) 1693.
- [40] L.D. Albin, M. Jacobson, D.B. Olson, US Patent 5,426,085, 1995.
- [41] SMART, Bruker AXS Inc., Madison, WI, 2001
- [42] SAINT PLUS, Bruker AXS Inc., Madison, WI, 2001.
- [43] SADABS, Bruker AXS Inc., Madison, WI, 2001.
- [44] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, J. Appl. Crystallogr. 32 (1999) 115.
- [45] G. Sheldrick, Acta Crystallogr. 64A (2008) 112.
- [46] L. Farrugia, J. Appl. Crystallogr. 32 (1999) 837
- [47] G.M. Sheldrick, Bruker AXS Inc., Madison, WI, 2001.
- [48] P. van der Sluis, A.L. Spek, Acta Crystallogr. 46A (1990) 194.
- [49] J.E. Kovic, Spectrochim. Acta 23 (1967) 183.
- [50] B.J. Hathaway, A.E. Underhill, J. Chem. Soc. (1961) 3091.
- [51] R. Karvembu, K. Natarajan, Polyhedron 21 (2002) 219.[52] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination
- Compounds, Fourth ed., Wiley, New York, 1986.
- [53] V. Philip, V. Suni, M.R.P. Kurup, M. Nethaji, Polyhedron 23 (2004) 1225.
- [54] J. Fornies, S. Fuertes, J.A. Lopez, A. Martin, V. Sicilia, Inorg. Chem. 47 (2008) 7166.

- [55] S. Fernandez, J. Fornies, B. Gil, J. Gomez, E. Lalinde, Dalton Trans. (2003) 822.
- [62] L. Pauling, The Nature of Chemical Bond, Third ed., Cornell University Press, [56] I.P. Romm, A.A. Malkov, S.A. Lebedev, V.V. Levashova, T.M. Buslaeva, Russ. J. New York, 1960.
- Phys. Chem. A 85 (2011) 248. [57] M. López-Torres, A. Fernández, J.J. Fernández, A. Suárez, S. Castro-Juiz, M.T. Pereira, J.M. Vila, J. Organomet. Chem. 655 (2002) 127.
- [58] R. Karvembu, S. Hemalatha, R. Prabhakaran, K. Natarajan, Inorg. Chem. Commun. 6 (2003) 486.
- [59] J. Gradinaru, A. Forni, V. Druta, S. Quici, A. Britchi, C. Deleanu, N. Gerbeleu, Inorg. Chim. Acta 338 (2002) 169.
- [60] S.K. Gupta, P.B. Hitchcock, Y.S. Kushwah, G.S. Argal, Inorg. Chim. Acta 360 (2007) 2145.
- [61] P. Chellan, N. Shunmoogam-Gounden, D.T. Hendricks, J. Gut, P.J. Rosenthal, C. Lategan, P.J. Smith, K. Chibale, G.S. Smith, Eur. J. Inorg. Chem. 2010 (2010) 3520.
- [63] J. Vila, M. Gayoso, M. López Torres, J.J. Fernandez, A. Fernández, J.M. Ortigueira, N.A. Bailey, H. Adams, J. Organomet. Chem. 511 (1996) 129.
- [64] R. Bosque, C. López, X. Solans, M. Font-Bardia, Organometallics 18 (1999) 1267. [65] R.L. Beddoes, L. Dalton, J.A. Joule, O.S. Mills, J.D. Street, C.I.F. Watt, J. Chem. Soc.,
- Perkin Trans. 2 (1986) 787. [66] Z.-Z. Zhou, F.-S. Liu, D.-S. Shen, C. Tan, L.-Y. Luo, Inorg. Chem. Commun. 14 (2011) 659.
- [67] Y. He, C. Cai, Catal. Commun. 12 (2011) 678.
- [68] P. Paul, S. Datta, S. Halder, R. Acharyya, F. Basuli, R.J. Butcher, S.-M. Peng, G.-H. Lee, A. Castineiras, M.G.B. Drew, S. Bhattacharya, J. Mol. Catal. A: Chem. 344 (2011) 62.
- [69] J.A. Widegren, R.G. Finke, J. Mol. Catal. A: Chem. 198 (2003) 317.