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Triphenylphosphinopalladium(II) complexes with ONO-donor ligands: syntheses, structures and catalytic applications in C–C cross-coupling reactions

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Reactions of 1-((2-hydroxy-5-R-phenylimino)methyl)naphthalen-2-ols (H_2L^n, n = 1–3 for R = H, Me, Cl, respectively) with [Pd(PPh_3)$_2$$Cl_2$] and Et_3N in toluene under reflux produced three new mononuclear square-planar palladium(II) complexes with the general formula [Pd(L^n)(PPh_3)] (1, R = H; 2, R = Me; 3, R = Cl). All the complexes were characterized using elemental analysis, solution conductivity and various spectroscopic (infrared, UV–visible and NMR) measurements. Molecular structures of 1–3 were confirmed using single-crystal X-ray diffraction analysis. In each complex, the fused 5,6-membered chelate rings forming phenolate-O, azomethine-N and naphtholate-O donor (L^n)$^{2-}$ and the PPh_3 form a square-planar ONOP coordination environment around the metal centre. Infrared and NMR spectroscopic features of 1–3 are consistent with their molecular structures. Electronic spectra of the three complexes display several strong primarily ligand-centred absorption bands in the range 322–476 nm. All the complexes were found to be effective catalysts for carbon–carbon cross-coupling reactions of arylboronic acids with aromatic and heteroaromatic aldehydes to form the corresponding diaryl ketones. Copyright © 2016 John Wiley & Sons, Ltd.

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Keywords: palladium(II) complexes; Schiff bases; crystal structures; catalysis; C-C coupling

Introduction

Diaryl ketone chromophores are encountered in various natural products, biologically active small molecules, pharmaceuticals, agrochemicals, fine chemicals and organic functional materials.[1–5] Quite a few methods are reported for the synthesis of diaryl ketone derivatives such as the Friedel–Crafts acylation of substituted aromatic rings,[6,7] the Fries rearrangement of aryl esters,[8] the reaction of Grignard reagents and acyl halides,[9] the Houben–Hoesch reaction of nitriles and arenes[10] and the palladium-catalysed carbonylative Suzuki reaction (using CO gas under pressure).[11,12] However, some drawbacks associated with these reactions are use of stoichiometric amounts of Lewis acids, highly acidic conditions, use of additives and poor compatibility with various functional groups. Alternative approaches to generate diaryl ketones involve the palladium-catalysed cross-coupling reactions of arylboronic acids with carboxylic acids, acid chlorides and acid anhydrides.[13–17] Examples for such palladium-catalysed coupling reactions of arylboronic acids with aromatic aldehydes for the synthesis of diaryl ketones are very few. To the best of our knowledge, there have been only three reports so far.[18–20] A one-pot palladium-catalysed coupling reaction of aryl aldehydes and organoboronic acids in the presence of P(1-nap)$_3$ and Cs_2CO_3 in toluene under aerobic conditions provided diaryl ketones in moderate to excellent yields.[18] A mild but efficient route for the preparation of 2-hydroxybenzophenone derivatives in high yields is reported to be the palladium-catalysed coupling of 2-hydroxyaryl aldehydes with arylboronic acids in O_2 atmosphere using $NaHCO_3$ as base and $CuCl_2$ as additive.[19] Preparation of diaryl ketones from aromatic aldehydes and organoboronic acids has been also achieved via palladium-catalysed 1,2-addition and oxidation by aryl iodides.[20] The advantages of the palladium-catalysed coupling reactions between aryl aldehydes and arylboronic acids include the easy availability of aldehydes and arylboronic acids, their stability in air and moisture and high functional group tolerance. Furthermore, palladium complexes are becoming increasingly popular as superior catalysts in bringing about carbon–carbon and carbon–heteroatom cross-coupling reactions of various types.[21–24] For all these reasons, the search for new and efficient catalysts for cross-coupling reactions is very appealing.

As a part of our ongoing investigations of the synthesis, characterization and catalytic applications of transition metal complexes,[25–27] herein we report the syntheses, X-ray structural characterization and physical properties of three new square-planar triphenylphosphinopalladium(II) complexes with ONO-donor 1-((2-hydroxy-5-R-phenylimino)methyl)naphthalen-2-ols (H_2L^n, where the two Hs stand for the two dissociable phenolic protons and n = 1–3 for R = H, Me, Cl, respectively) and their applications as ho-

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mogeneous catalysts for the formation of diaryl ketones from arylboronic acids and aryl aldehydes.

Experimental

Materials

2-Hydroxy-1-naphthaldehyde, 2-amino-4-R-phenols (R = H, Me and Cl) and the substrates (aldehydes and boronic acid derivatives) for the cross-coupling reactions were obtained from Sigma Aldrich and used as received. $PdCl_2$ was purchased from Arora Matthey Ltd., India, and used without further purification. All other chemicals and solvents used in this work were of reagent grade available commercially and used as supplied.

Physical Measurements

Microanalyses (CHN) were performed using a Thermo Finnigan Flash EA1112 series elemental analyser. Magnetic susceptibility measurements were performed with a Sherwood scientific balance. A Shimadzu LCMS 2010 liquid chromatograph–mass spectrometer (LC–MS) was used to verify the purity of the Schiff bases (H_2L^{1-3}). The solution electrical conductivities were measured using a Digisun DI-909 conductivity meter. The infrared (IR) spectra were recorded with a Jasco-5300 FT-IR spectrophotometer. A Shimadzu UV-3600 UV–VIS–NIR spectrophotometer was used to obtain the electronic spectra. The NMR spectra were recorded with a Bruker spectrometer.

General Procedure for Preparation of H_2L^{1-3}

The Schiff bases (H_2L^{1-3}) were prepared by condensation reactions of 2-hydroxy-1-napthaldehyde (10 mmol) with substituted 2-amino-4-R-phenols (R = H, Me and Cl) (10 mmol) in refluxing ethanol (20 ml) in the presence of glacial acetic acid (0.3 ml). The yellow solid that separated on cooling the reaction mixture was filtered, washed with cold ethanol and diethyl ether, and finally dried in vacuum.

H_2L^1 (R = H). Yield 80%. LC–MS (*m/z*): calcd for $(M + H)^+$: 264.29. Found: 263.95. Anal. Calcd for $C_{17}H_{13}NO_2$ (263.28) (%): C, 77.55; H, 4.98; N, 5.32. Found (%): C, 77.42; H, 4.91; N, 5.38. Selected IR bands (KBr; cm^{-1}): 3483, 1633, 1622. ^1H NMR ($(CD_3)_2SO$; 400 MHz, δ, ppm): 15.74 (d, J = 10 Hz, 1H, NH), 10.36 (s, 1H, OH), 9.52 (d, J = 10 Hz, 1H, H^{11}), 8.40 (d, J = 8 Hz, 1H, H^8), 7.95 (d, J = 8 Hz, 1H, H^{17}), 7.81 (d, J = 9 Hz, 1H, H^4), 7.68 (d, J = 8 Hz, 1H, H^5), 7.49 (dd, J = 8, 8 Hz, 1H, H^7), 7.27 (dd, J = 8, 8 Hz, 1H, H^6), 7.12 (dd, J = 8, 8 Hz, 1H, H^{15}), 7.03 (d, J = 8 Hz, 1H, H^{14}), 6.96 (dd, J = 8, 8 Hz, 1H, H^{16}), 6.81 (d, J = 9 Hz, 1H, H^3). ^{13}C NMR ($(CD_3)_2SO$; 100 MHz, δ, ppm): 178.12 (C^2), 149.87 (C^{11}), 148.91 (C^{13}), 138.41 (C^4), 134.40 (C^{10}), 129.46 (C^5), 129.04 (C^9), 128.56 (C^7), 127.21 (C^{15}), 126.31 (C^{12}), 125.58 (C^3), 123.49 (C^6), 120.29 (C^{14}), 120.19 (C^8), 118.04 (C^{17}), 116.43 (C^{16}), 108.17 (C^1). UV–visible (Me_2NCHO; λ_{max}, nm (ε, 10^5 M^{-1} cm^{-1})): 470 (9.2), 448 (9.2), 422^{sh} (6.3), 355^{sh} (3.6), 325 (5.4).

H_2L^2 (R = Me). Yield 83%. LC–MS (*m/z*): calcd for $(M + H)^+$: 278.32. Found: 278.15. Anal. Calcd for $C_{18}H_{15}NO_2$ (277.31) (%): C, 77.96; H, 5.45; N, 5.05. Found (%): C, 78.12; H, 5.41; N, 5.13. Selected IR bands (KBr; cm^{-1}): 3486, 1633, 1614. ^1H NMR ($(CD_3)_2SO$; 400 MHz, δ, ppm): 15.71 (d, J = 10 Hz, 1H, NH), 10.10 (s, 1H, OH), 9.49 (d, J = 10 Hz, 1H, H^{11}), 8.40 (d, J = 8 Hz, 1H, H^8), 7.81 (s, 1H, H^{17}), 7.80 (d (partially merged with H^{17} singlet), J = 9 Hz, 1H, H^4), 7.67 (d, J = 8 Hz, 1H, H^5), 7.49 (dd, J = 8, 8 Hz, 1H, H^7), 7.27 (dd, J = 8, 8 Hz, 1H, H^6), 6.91 (br, s (AB → A_2) 2H, H^{14}, H^{15}), 6.79 (d, J = 9 Hz, 1H, H^3), 2.32 (s, 3H, Me). ^{13}C NMR ($(CD_3)_2SO$; 100 MHz, δ, ppm): 178.43 (C^2), 149.33 (C^{11}), 146.56 (C^{13}), 138.39 (C^4), 134.46 (C^{10}), 129.46 (C^9), 129.27 (C^{16}), 128.51 (C^3), 128.43 (C^7), 127.64 (C^6), 126.25 (C^1), 125.74 (C^{15}), 123.44 (C^{12}), 120.13 (C^5), 118.11 (C^8), 116.25 (C^{17}), 108.10 (C^{14}), 20.82 (Me). UV–visible (Me_2NCHO; λ_{max}, nm (ε, 10^5 M^{-1} cm^{-1})): 474 (8.8), 452 (8.9), 425^{sh} (6.1), 360^{sh} (3.1), 318 (4.7).

H_2L^3 (R = Cl). Yield 76%. LC–MS (*m/z*): calcd for $(M + H)^+$: 298.73. Found: 298.30. Anal. Calcd for $C_{17}H_{12}NO_2Cl$ (297.73) (%): C, 68.58; H, 4.06; N, 4.70. Found (%): C, 68.46; H, 4.12; N, 4.65. Selected IR bands (KBr; cm^{-1}): 3480, 1633, 1607. ^1H NMR ($(CD_3)_2SO$; 400 MHz, δ, ppm): 15.66 (d, J = 9 Hz, 1H, NH), 10.59 (s, 1H, OH), 9.54 (d, J = 9 Hz, 1H, H^{11}), 8.48 (d, J = 8 Hz, 1H, H^8), 8.14 (s, 1H, H^{17}), 7.84 (d, J = 9 Hz, 1H, H^4), 7.71 (d, J = 8 Hz, 1H, H^5), 7.51 (dd, J = 8, 8 Hz, 1H, H^7), 7.30 (dd, J = 8, 8 Hz, 1H, H^6), 7.14 (d, J = 8 Hz, 1H, H^{15}), 7.00 (d, J = 8 Hz, 1H, H^{14}), 6.82 (d, J = 9 Hz, 1H, H^3). ^{13}C NMR ($(CD_3)_2SO$; 100 MHz, δ, ppm): 177.55 (C^2), 150.68 (C^{11}), 147.96 (C^{13}), 138.65 (C^4), 134.27 (C^{10}), 130.74 (C^{12}), 129.45 (C^5), 128.57 (C^7), 126.52 (C^{16}), 126.46 (C^{15}), 125.14 (C^3), 124.11 (C^9), 123.78 (C^6), 120.68 (C^8), 117.76 (C^{17}), 117.56 (C^{14}), 108.66 (C^1). UV–visible (Me_2NCHO; λ_{max}, nm (ε, 10^5 M^{-1} cm^{-1})): 470 (10.0), 453 (9.6), 395^{sh} (4.1), 322 (5.3).

General Procedure for Synthesis of $[Pd(L^n)(PPh_3)]$ (1–3)

To a solution of H_2L^n (0.2 mmol) and Et_3N (0.3 ml) in toluene (20 ml), solid $[Pd(PPh_3)_2Cl_2]$ (0.2 mmol) was added. The reaction mixture was stirred under reflux for 1 h and the progress of the reaction was monitored using TLC. At the end of the reaction, the reaction mixture was cooled to room temperature and filtered to remove the precipitate of Et_3NHCl. The filtrate containing the complex was evaporated under reduced pressure and the solid obtained was washed thoroughly with *n*-hexane, cold ethanol and diethyl ether, and finally dried in air. The complexes were thus obtained as orange solids in 69–73% yields.

$[Pd(L^1)(PPh_3)]$ (**1**). Yield 70%. Anal. Calcd for $C_{35}H_{26}NO_2PPd$ (629.94) (%): C, 66.73; H, 4.16; N, 2.22. Found (%): C, 66.53; H, 4.09; N, 2.28. Selected IR bands (KBr; cm^{-1}): 1600 (C=N); 744, 695, 515 (PPh_3). ^1H NMR ($(CD_3)_2SO$; 400 MHz, δ, ppm): 9.79 (d, J = 17 Hz, 1H, H^{11}), 8.70 (d, J = 8 Hz, 1H, H^5), 8.36 (d, J = 8 Hz, 1H, H^{17}), 7.78–7.72 (m, 8H, PPh_3 *ortho* Hs, H^4, H^8), 7.65–7.58 (m, 10H, PPh_3 *meta/para* Hs, H^7), 7.34 (dd, J = 8, 8 Hz, 1H, H^6), 7.04 (dd, J = 8, 8 Hz, 1H, H^{15}), 6.78 (d, J = 8 Hz, 1H, H^3), 6.70 (dd, J = 8, 8 Hz, 1H, H^{16}), 6.63 (d, J = 8 Hz, 1H, H^{14}). ^{13}C NMR ($(CD_3)_2SO$; 100 MHz, δ, ppm): 167.59 (C^{13}), 167.56 (C^2), 163.60 (C^{11}), 142.60 (C^{12}), 139.38 (C^9), 134.63 (d, $^2J_{C,P}$ = 9 Hz, C_o of PPh_3), 131.82 (d, $^4J_{C,P}$ = 2 Hz, C_p of PPh_3), 129.31 (d, $^3J_{C,P}$ = 9 Hz, C_m of PPh_3), 129.11 (C^{15}), 128.94 (d, $^1J_{C,P}$ = 23 Hz, C_i of PPh_3), 128.66 (C^{10}), 128.03 (C^5), 127.19 (C^{17}), 124.47 (C^7), 123.21 (C^8), 121.59 (C^6), 119.07 (C^{16}), 116.90 (C^3), 115.55 (C^{14}), 111.41 (C^1). ^{31}P NMR ($(CD_3)_2SO$; 160 MHz, δ, ppm): 22.30. UV–visible (Me_2NCHO; λ_{max}, nm (ε, 10^4 M^{-1} cm^{-1})): 473 (10.8), 449 (10.7), 425^{sh} (7.0), 355^{sh} (3.6), 326 (5.6).

$[Pd(L^2)(PPh_3)]$ (**2**). Yield 73%. Anal. Calcd for $C_{36}H_{28}NO_2PPd$ (644.01) (%): C, 67.14; H, 4.38; N, 2.17. Found (%): C, 67.28; H, 4.41; N, 2.14. Selected IR bands (KBr; cm^{-1}): 1609 (C=N); 747, 695, 516 (PPh_3). ^1H NMR ($(CD_3)_2SO$; 400 MHz, δ, ppm): 9.75 (d, J = 18 Hz, 1H, H^{11}), 8.79 (d, J = 8 Hz, 1H, H^5), 8.52 (s, 1H, H^{17}), 7.75–7.70 (m, 8H, PPh_3 *ortho* Hs, H^4, H^8), 7.64–7.56 (m, 10H, PPh_3 *meta/para* Hs, H^7), 7.34 (dd, J = 8, 8 Hz, 1H, H^6), 7.04 (d, J = 9 Hz, 1H, H^{15}), 6.74 (d, J = 9 Hz, 1H, H^3), 6.60 (d, J = 9 Hz, 1H, H^{14}), 2.29 (s, 3H, Me). ^{13}C NMR ($(CD_3)_2SO$; 100 MHz, δ, ppm): 167.58 (C^{13}), 167.55 (C^2), 163.53 (C^{11}), 142.62 (C^{12}), 139.36 (C^9), 134.54 (d, $^2J_{C,P}$ = 14 Hz, C_o of PPh_3), 131.97 (C^{16}), 131.84 (d, $^4J_{C,P}$ = 6 Hz, C_p of PPh_3), 129.29 (d, $^3J_{C,P}$ = 6 Hz, C_m of PPh_3), 129.14 (C^{17}), 128.95 (d, $^1J_{C,P}$ = 27 Hz, C_i

of PPh_3), 128.69 (C^{15}), 128.01 (C^4), 127.17 (C^{10}), 124.40 (C^5), 123.23 (C^7), 121.62 (C^8), 119.09 (C^6), 116.94 (C^3), 115.15 (C^{14}), 111.44 (C^1), 21.09 (Me). ^{31}P NMR ($(CD_3)_2SO$; 160 MHz, δ, ppm): 22.25. UV–visible (Me_2NCHO; λ_{max}, nm (ε, 10^4 M^{-1} cm^{-1})): 476 (9.5), 452 (9.6), 427^{sh} (6.8), 360^{sh} (3.3), 322 (4.8).

$[Pd(L^3)(PPh_3)]$ (**3**). Yield 69%. Anal. Calcd for $C_{35}H_{25}ClNO_2PPd$ (664.42) (%): C, 63.27; H, 3.79; N, 2.11. Found (%): C, 63.15; H, 3.71; N, 2.07. Selected IR bands (KBr; cm^{-1}): 1610 (C=N); 751, 690 and 537 (PPh_3). ^1H NMR ($(CD_3)_2SO$; 400 MHz, δ, ppm): 9.76 (d, J = 17 Hz, 1H, H^{11}), 8.80 (d, J = 8 Hz, 1H, H^5), 8.54 (s, 1H, H^{17}), 7.79–7.71 (m, 8H, PPh_3 *ortho* Hs, H^4, H^8), 7.66–7.58 (m, 10H, PPh_3 *meta/para* Hs, H^7), 7.36 (dd, J = 8, 8 Hz, 1H, H^6), 7.05 (d, J = 9 Hz, 1H, H^{15}), 6.76 (d, J = 9 Hz, 1H, H^3), 6.61 (d, J = 9 Hz, 1H, H^{14}). ^{13}C NMR ($(CD_3)_2SO$; 100 MHz, δ, ppm): 167.59 (C^{13}), 167.55 (C^2), 163.57 (C^{11}), 142.64 (C^{12}), 139.36 (C^9), 134.51 (d, $^2J_{C,P}$ = 7 Hz, C_o of PPh_3), 131.94 (C^{15}), 131.86 (d, $^4J_{C,P}$ = 6 Hz, C_p of PPh_3), 129.31 (d, $^3J_{C,P}$ = 5 Hz, C_m of PPh_3), 129.12 (C^{17}), 128.94 (d, $^1J_{C,P}$ = 16 Hz, C_i of PPh_3), 128.79 (C^4), 128.01 (C^{10}), 127.18 (C^5), 124.48 (C^{16}), 123.27 (C^7), 121.67 (C^8), 119.11 (C^6) 116.90 (C^3), 115.64 (C^{14}), 111.41 (C^1). ^{31}P NMR ($(CD_3)_2SO$; 160 MHz, δ, ppm): 22.25. UV–visible (Me_2NCHO; λ_{max}, nm (ε, 10^4 M^{-1} cm^{-1})): 473 (11.9), 449 (11.7), 423^{sh} (7.5), 355^{sh} (3.9), 326 (6.1).

General Procedure for Coupling of Arylboronic Acids with Aromatic Aldehydes

Arylboronic acid (1 mmol), aldehyde (1.5 mmol), Cs_2CO_3 (3 mmol), catalyst (5 mol%) and toluene (3 ml) were taken in a round-bottom flask. The mixture was then heated under reflux for 18 h under aerobic conditions and monitored by TLC. At the end of the specified time, the reaction mixture was cooled to room temperature, quenched with 1 N HCl (5 ml) and finally extracted with ethyl acetate (2 × 5 ml). The combined extracts were dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue obtained was subjected to flash chromatography on a silica gel column to purify the desired ketone. All the ketones synthesized by this method are known compounds and they were characterized using ^1H NMR and ^{13}C NMR analysis.

X-ray Crystallography

Single crystals of **1** and **3** were grown by slow diffusion of *n*-hexane into dimethylformamide solutions of the corresponding complexes at room temperature. Complex **1** crystallizes without any solvent molecule, whereas **3** crystallizes in the solvated form **3**·Me_2NCHO. On the other hand, X-ray-quality crystals of **2** were obtained as **2**·Me_2SO·$0.5H_2O$ by slow diffusion of diethyl ether into its dimethylsulfoxide solution. Determination of the unit cell parameters and the intensity data collections at 298 K for **1** were carried out using monochromated Mo K_α radiation (λ = 0.71073 Å) with a Bruker-Nonius SMART APEX CCD single-crystal X-ray diffractometer. The SMART and the SAINT-Plus packages[28] were used for data acquisition and data extraction, respectively, and the SADABS program[29] was used for absorption correction. Unit cell parameters and intensity data at 298 K for each of **2**·Me_2SO·$0.5H_2O$ and **3**·Me_2NCHO were obtained using monochromated Cu K_α radiation (λ = 1.54184 Å) with an Oxford Diffraction Xcalibur Gemini single-crystal X-ray diffractometer. In each case, the data collection, reduction and absorption correction were performed using CrysAlisPro software.[30] Some residual absorption effect observed for **2**·Me_2SO·$0.5H_2O$ was treated with an additional correction using the program XABS2.[31] All three structures were solved by direct methods and refined by full-matrix least-squares procedures using SHELX-97 programs[32] accessible through the WinGX package.[33] For **2**·Me_2SO·$0.5H_2O$, the oxygen atom of the half occupancy water molecule was refined isotropically and its hydrogen atoms located in a difference map were refined with geometric and thermal restraints. The remaining non-hydrogen atoms in **2**·Me_2SO·$0.5H_2O$ and all the non-hydrogen atoms in both **1** and **3**·Me_2NCHO were refined anisotropically. The hydrogen atoms in all three structures (except for the water hydrogen atoms in **2**·Me_2SO·$0.5H_2O$) were placed at idealized positions and refined by using a riding model. Molecular graphics were obtained with the Platon[34] and the Mercury[35] packages. Selected crystal data and the refinement summary for all three structures are listed in Table 1.

Results and Discussion

Synthesis and Some Properties

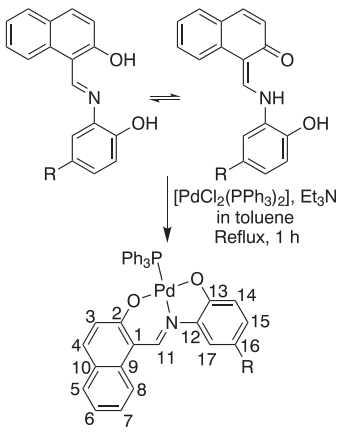
$[Pd(PPh_3)_2Cl_2]$ was prepared using one mole equivalent of $PdCl_2$ and two mole equivalents of PPh_3 by following a reported procedure.[36] The Schiff bases (H_2L^{1-3}) were synthesized in yields of *ca* 80% via condensation reactions of one mole equivalent each of 2-hydroxy-1-naphthaldehyde and the corresponding 2-amino-4-R-phenols (R = H, Me and Cl) using a procedure very similar to that reported in the literature.[37] The identities of all the Schiff bases were authenticated by elemental analysis, LC–MS and spectroscopic (IR, UV–visible and ^1H NMR) measurements. Reactions of equimolar amounts of $[Pd(PPh_3)_2Cl_2]$ with the corresponding H_2L^{1-3} in toluene under reflux in basic conditions resulted in the formation of the three new mononuclear palladium(II) complexes of general formula $[Pd(L^n)(PPh_3)]$ (**1**–**3**) in reasonably good (69–73%) yields (Scheme 1). The elemental analysis data of the complexes are in satisfactory agreement with their formulation and it appears that the Schiff base coordinates to the metal centre as a dibasic tridentate ligand in each of the three complexes. All three complexes are orange in colour and found to be non-hygroscopic and air stable at room temperature. The diamagnetic nature of **1**–**3** is consistent with the +2 oxidation state and square-planar coordination environment around the metal centre in them. They have moderate to high solubility in toluene, chloroform, dichloromethane, acetonitrile, methanol, dimethylformamide and dimethylsulfoxide, producing orange solutions. In solution, each of the three complexes is electrically non-conducting. This non-electrolytic behaviour of **1**–**3** is consistent with their corresponding molecular formulas as neutral species.

Description of Molecular Structures

In order to confirm the coordination mode of $(L^n)^{2-}$ towards the metal centre and the overall coordination geometry by X-ray crystallography, single crystals of all three complexes were grown. They crystallize as **1**, **2**·Me_2SO·$5H_2O$ and **3**·Me_2NCHO. The ORTEP views of **1**–**3** are shown in Fig. 1 and the bond lengths and bond angles associated with their corresponding metal centres are listed in Table 2 . The gross molecular structures of all three complexes are very similar. In each complex molecule, the deprotonated dianionic Schiff base ligand $(L^n)^{2-}$ coordinates to the metal centre via the phenolate-O, the azomethine-N and the naphtholate-O atoms and forms fused 5,6-membered chelate rings. The P-atom of the PPh_3 ligand satisfies the fourth coordination site of the metal centre. The geometry about the palladium in each complex is distorted square-planar as is evidenced from the bond parameters around

Table 1. Selected crystal data and refinement summary

	1	**2**·Me_2SO·0.5H_2O	**3**·Me_2NCHO
Chemical formula	$C_{35}H_{26}NO_2PPd$	$C_{38}H_{35}NO_{3.5}PSPd$	$C_{38}H_{32}ClN_2O_3PPd$
Formula weight	629.94	731.10	737.48
λ (Å)	0.71073	1.54184	1.54184
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	11.0301(10)	8.9935(7)	9.0012(2)
b (Å)	29.444(3)	10.6700(11)	10.8248(5)
c (Å)	8.7819(8)	17.1125(11)	16.9146(8)
α (°)	90	81.639(7)	79.223(4)
β (°)	105.645(1)	89.585(6)	87.848(3)
γ (°)	90	88.984(7)	87.294(3)
V (Å^3)	2746.5(4)	1624.4(2)	1616.53(11)
Z	4	2	2
ρ (g cm^{-3})	1.523	1.495	1.515
μ (mm^{-1})	0.768	5.999	6.188
Reflections collected	28 404	10 619	10 132
Reflections unique	5405	5970	6058
Reflections [$I \geq 2\sigma(I)$]	4865	4339	5605
Parameters	361	419	417
$R1$, $wR2$ [$I \geq 2\sigma(I)$]	0.0303, 0.0730	0.0994, 0.2643	0.0372, 0.0944
$R1$, $wR2$ [all data]	0.0343, 0.0751	0.1228, 0.2919	0.0404, 0.0983
GOF on F^2	1.056	1.038	1.064
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.475, −0.272	1.465, −1.389	1.101, −0.571



Scheme 1. Synthesis of [Pd(L^n)(PPh_3)] (**1**–**3** for n = 1–3, respectively) from 1-((2-hydroxy-5-R-phenylimino)methyl)naphthalen-2-ols (H_2L^n, n = 1–3 for R = H, Me and Cl, respectively).

the metal centre (Table 2). There is essentially no deviation (0.002 (1)–0.005(3) Å) of the metal centre from the plane (rmsd 0.008–0.035 Å) constituted by the four coordinating atoms. In general, the metal to coordinating atom bond lengths are unexceptional and comparable with the corresponding bond lengths observed in mononuclear palladium(II) complexes containing similar coordinating atoms.[38,39]

Spectroscopic Characterization

IR spectroscopy was used to further ascertain the mode of coordination of $(L^n)^{2-}$ to the palladium(II) centre in [Pd(L^n)(PPh_3)]. The free H_2L^n show the characteristic broad band centred at *ca* 3483 cm^{-1} for the phenolic-OH group. All of the three Schiff bases display a pair of sharp and strong closely spaced bands at *ca* 1633 and *ca* 1614 cm^{-1}. It is known that Schiff bases having the 2-hydroxy-1-arylidene moiety are known to exhibit tautomerism between the keto-amine and phenol-imine forms (Scheme 1).[40–42] It is very likely that these two bands are associated with the C=O and the C=N stretching frequencies of the equilibrium mixture of the two tautomers of H_2L^n.[41,42] However, no band assignable to the N–H group of the keto-amine form is observed in any of the spectra. The absence of the bands associated with the phenolic-OH and the keto group in the spectra of **1**–**3** indicates complete deprotonation of the Schiff base and its coordination via the phenolate-O and the naphtholate-O atoms to the palladium(II) centre in each complex. Coordination of the azomethine-N to the metal centre is confirmed by the shift of the C=N stretching frequency to slightly lower wavenumbers for the complexes (*ca* 1607 cm^{-1}) when compared to that for the free Schiff bases (*ca* 1614 cm^{-1}). In addition, **1**–**3** display the characteristic three strong bands at *ca* 747, *ca* 693 and *ca* 523 cm^{-1} for the coordinated PPh_3.[43,44]

The coordination of $(L^n)^{2-}$ to the metal centre in the complexes is further probed by ^{1}H NMR and ^{13}C NMR studies. The spectra of the free Schiff bases (H_2L^{1-3}) and the corresponding complexes (**1**–**3**) were recorded using their $(CD_3)_2SO$ solutions and the spectroscopic data are listed in the experimental section under the respective compounds. The resonances in H_2L^1 and H_2L^3 are assigned as reported earlier,[40] while those in H_2L^2 and **1**–**3** are tentatively assigned. The ^{1}H NMR spectra of H_2L^{1-3} display a doublet and a singlet in the ranges 15.66–15.74 (J ~ 10 Hz) and 10.10–10.59 ppm, respectively. The keto-amine tautomer of H_2L^n is anticipated to show a downfield-shifted doublet due to the resonance of the –NH– proton that is coupled with the adjacent methine (=CH–) proton (Scheme 1). The appearance of the doublet

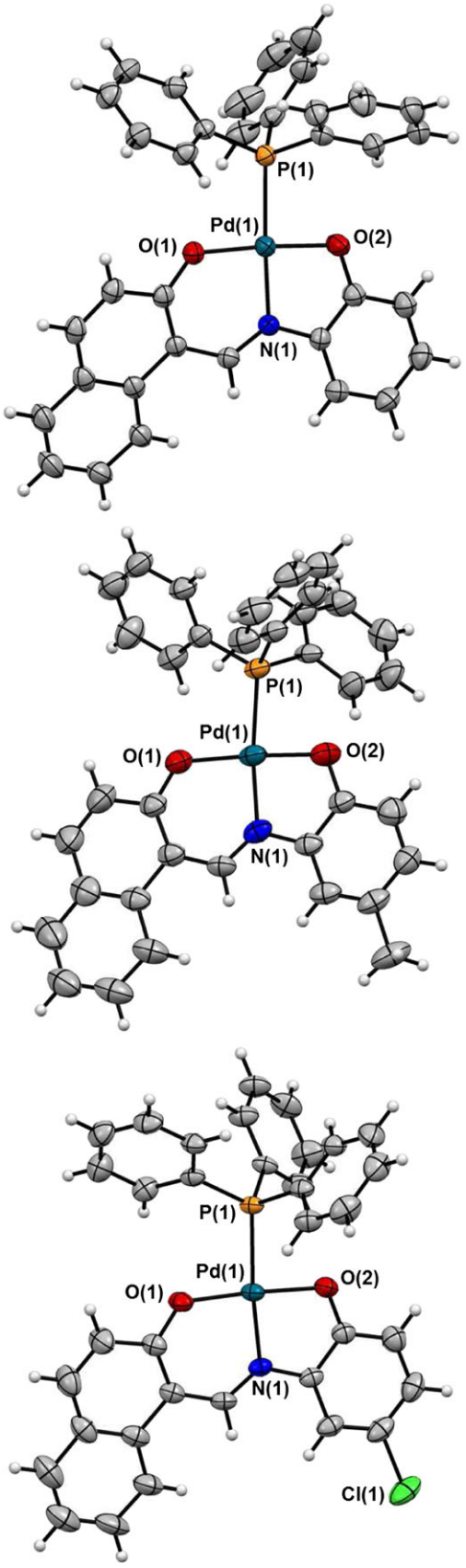


Figure 1. ORTEP representations of $[Pd(L^1)(PPh_3)]$ (**1**) (top), $[Pd(L^2)(PPh_3)]$ (**2**) (middle) and $[Pd(L^3)(PPh_3)]$ (**3**) (bottom). In each of the three plots, thermal ellipsoids for all the non-hydrogen atoms are shown at the 40% probability level and only the hetero atoms are labelled for clarity.

Table 2. Metal-centred bond lengths (Å) and angles (°)

	1	**2**·Me_2SO·0.5H_2O	**3**·Me_2NCHO
Pd(1)–O(1)	1.9710(16)	1.995(7)	1.973(2)
Pd(1)–N(1)	1.9946(18)	1.995(7)	2.002(2)
Pd(1)–O(2)	1.9968(17)	1.980(8)	1.993(2)
Pd(1)–P(1)	2.2806(6)	2.285(2)	2.2832(7)
O(1)–Pd(1)–N(1)	92.45(7)	92.3(3)	92.93(9)
O(1)–Pd(1)–O(2)	176.04(7)	175.5(3)	176.26(8)
O(1)–Pd(1)–P(1)	90.80(5)	93.8(2)	92.85(6)
N(1)–Pd(1)–O(2)	83.60(7)	83.7(3)	83.76(9)
N(1)–Pd(1)–P(1)	176.68(6)	173.6(2)	174.08(7)
O(2)–Pd(1)–P(1)	93.16(5)	90.3(2)	90.50(7)

at *ca* 15.7 ppm clearly indicates that the 2-hydroxy-1-naphthaylidene moiety of H_2L^n in $(CD_3)_2SO$ exists predominantly in the keto-amine form.[40] The singlet at *ca* 10.35 ppm is attributed to the OH proton of the amino phenol fragment of H_2L^n. Absence of both these signals in the spectra of the complexes supports the dianionic form of the ligand and hence its coordination to the palladium(II) centre via the phenolate-O and the naphtholate-O atoms. The =CH– proton of H_2L^n resonates as a doublet within 9.49–9.54 ppm (J ~ 10 Hz) due to coupling with the adjacent NH proton. In contrast, the azomethine (CH=N) proton in **1**–**3** appears as a doublet at slightly downfield (9.75–9.79 ppm) with a larger coupling constant (J ~ 17 Hz). The downfield shift suggests deshielding of the azomethine proton due to the coordination of its N-atom to the palladium(II) centre, while the doublet splitting is attributed to coupling with the metal-coordinated ^{31}P. The protons of the methyl group of the coordinated $(L^2)^{2-}$ in **2** are observed as a singlet at 2.29 ppm. The aromatic protons of $(L^n)^{2-}$ and PPh_3 appear in the expected regions with the expected coupling patterns.

The ^{13}C NMR spectra of H_2L^{1-3} and **1**–**3** are consistent with their corresponding different types of magnetically non-equivalent carbons (Scheme 1). The spectra of **1**–**3** show a downfield shift (*ca* 163 ppm) of the azomethine carbon (C^{11}) resonance relative to that of the free Schiff bases (*ca* 150 ppm) indicating coordination of the azomethine nitrogen to the metal centre. In the spectra of H_2L^{1-3}, the C=O carbon (C^2) of the naphthalen-2-one fragment and the C–OH carbon (C^{13}) of the phenol fragment appear at *ca* 178 and *ca* 148 ppm, respectively. All three complexes display two very closely spaced signals at *ca* 168 ppm. These are attributed to the C^2 and the C^{13} atoms of $(L^n)^{2-}$. The upfield shift of C^2 and the downfield shift of C^{13} are consistent with the coordination of the naphtholate-O and the phenolate-O of $(L^n)^{2-}$ to the palladium(II) centre in **1**–**3**. Resonances due to other aromatic carbons of the coordinated $(L^n)^{2-}$ and PPh_3 in all three complexes are unexceptional. The ^{31}P NMR spectra of **1**–**3** display a singlet resonance in the region *ca* 22.3 ppm indicating the presence of one PPh_3 group in each of the three complexes.[25]

Electronic spectra of the free Schiff bases (H_2L^{1-3}) and the corresponding complexes (**1**–**3**) were recorded in dimethylformamide. All the spectroscopic profiles are very similar. Several strong absorptions in two groups are observed. Similarity of the spectra of the Schiff bases to those of the complexes indicates that the absorptions displayed by the complexes are due to ligand-centred transitions rather than charge transfer transitions. Further, when the solvent was varied from toluene to dimethylformamide, it is observed that the absorption maxima of the lowest energy bands of

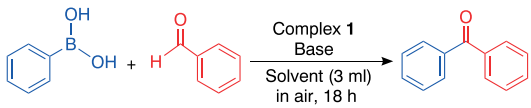
the complexes remain unchanged with the change of solvent polarity. This insensitivity to the solvent polarity indicates that these are primarily due to the π–π^* transitions associated with the aromatic fragment of the ligand.

Catalysis Studies

A review of the literature on metal-mediated reactions of arylboronic acids with carbonyl compounds indicates that there is no set rule that a definite solvent or a certain base can be used to enhance the efficiency of these cross-coupling reactions. Thus, various reaction conditions such as solvent, base, temperature and catalyst loading need to be optimized first. The reaction between phenylboronic acid and benzaldehyde to furnish benzophenone mediated by complex **1** in air was selected as a model coupling reaction, and solvent, base, temperature and catalyst loading were varied to ascertain the optimum conditions (Table 3). The extent of ketone formation is solvent dependent and, among the various solvents screened (entries 1–5), toluene is found to be the most effective. Among the various bases screened, Cs_2CO_3 in toluene results in good yield (entry 5). Other bases such as K_2CO_3, KOH, Et_3N or NaOAc show very poor activities in toluene (entries 6–9). In refluxing toluene, the reaction proceeds very well (entry 5); while a decrease in temperature (entries 10–12) results in reduced yield and no ketone is formed at room temperature. Also as expected, controlled experiments show that in the absence of catalyst, base and air (as oxidant), no ketone is obtained. Thus under aerobic conditions in refluxing toluene, 10 mol% of **1** in the presence of Cs_2CO_3 as base (entry 5) in 18 h is able to facilitate most effectively the reaction of phenylboronic acid with benzaldehyde affording the diphenyl ketone in 93% yield. Under the above conditions, the reaction was then performed with various catalyst loadings (entries 13–15) in order to find the effectiveness of **1**. Reducing the amount of **1** from 10 to 5 mol% (entries 5 and 13) does not significantly reduce the yield of the ketone formed. However, when either 2 or 1 mol% (entries 14 and 15) of **1** is used, there is a significant decrease in the yield of the ketone. Henceforth for further reactions using various substrates, 5 mol% of **1** in toluene under reflux and aerobic conditions, Cs_2CO_3 as base (entry 13) and 18 h reaction time were used as optimal conditions.

After establishing the optimal reaction conditions as described above, the coupling reactions of a variety of aromatic and heteroaromatic aldehydes with phenylboronic acid (as a representative arylboronic acid derivative) were then carried out to scrutinize the electronic and steric effects of aldehydes on the efficiency of the catalytic reaction (Table 4). The reactions were also performed using each of **1**–**3** as catalyst. All three complexes provide comparable yields for a given substrate and hence the substituents on the ligands do not affect the catalytic efficiencies. Benzaldehydes with various electron-withdrawing and electron-donating substituents at *para* position react with phenylboronic acid facilely to afford the corresponding diaryl ketones in excellent yields (≥90%; entries 1–5). Thus the reactions progress efficiently in each case and the results indicate that the *para* substituent on the benzaldehydes has little or no influence on the catalytic coupling of the aldehydes with phenylboronic acid. On the other hand, *meta*-substituted benzaldehydes (entries 6 and 7) couple slightly less effectively (85–91% yields) than the corresponding *para*-substituted derivatives (entries 2 and 4). Notably, sterically hindered *ortho*-substituted benzaldehydes also participate in the cross-coupling and the desired products are obtained in 70–79% yields (entries 8 and 9). The same protocol was also applied to the coupling of heteroaromatic aldehydes with phenylboronic acid (entries 10–12). Relatively low yields (60–69%) of the corresponding heteroarylphenyl ketones indicate that heteroaromatic aldehydes are somewhat less effective substrates.

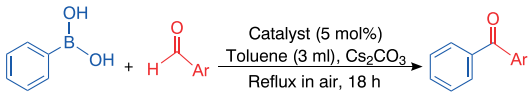
Table 3. Optimization of conditions for the model reaction[a]



Entry	Solvent	Base	*T* (°C)	**1** (mol%)	Yield (%)[b]
1	MeCN	Cs_2CO_3	80	10	30
2	DMF	Cs_2CO_3	110	10	32
3	EtOH	Cs_2CO_3	80	10	35
4	1,4-Dioxane	Cs_2CO_3	100	10	46
5	Toluene	Cs_2CO_3	110	10	93
6	Toluene	K_2CO_3	110	10	36
7	Toluene	KOH	110	10	48
8	Toluene	Et_3N	110	10	28
9	Toluene	NaOAc	110	10	21
10	Toluene	Cs_2CO_3	85	10	81
11	Toluene	Cs_2CO_3	60	10	42
12	Toluene	Cs_2CO_3	25[c]	10	NR[d]
13	Toluene	Cs_2CO_3	110	5	90
14	Toluene	Cs_2CO_3	110	2	76
15	Toluene	Cs_2CO_3	110	1	42

[a]Phenylboronic acid: 1 mmol; benzaldehyde: 1.5 mmol; base: 3 mmol.
[b]Isolated yield (average of two independent runs).
[c]Room temperature.
[d]No reaction.

Table 4. Reaction of phenylboronic acid with various aldehydes[a]



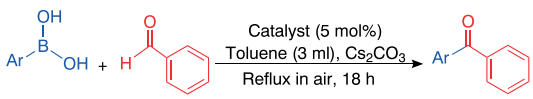
Entry	Ar	Yield (%)[b]		
		Catalyst **1**	Catalyst **2**	Catalyst **3**
1	Ph	90	92	94
2	4-ClPh	97	95	96
3	4-NCPh	93	90	95
4	4-MePh	94	96	93
5	4-MeOPh	96	94	92
6	3-ClPh	90	91	89
7	3-MePh	86	87	85
8	2-ClPh	76	79	77
9	2-MePh	72	70	74
10	2-Thiophenyl	68	66	69
11	2-Furanyl	63	61	65
12	2-Pyridinyl	63	60	61

[a]Phenylboronic acid: 1 mmol; aldehyde: 1.5 mmol; Cs_2CO_3: 3 mmol.
[b]Isolated yield (average of two independent runs).

Under the above optimum reaction conditions, the cross-coupling reactions of benzaldehyde with various arylboronic acids were conducted to determine the generality of this catalytic method towards aromatic boronic acids (Table 5). Except for the reaction with 4-cyanoboronic acid (entry 3), all other reactions provide the desired ketones in moderate to excellent isolated yields. The low solubility of 4-cyanoboronic acid in toluene limits its accessible amount for the reaction and therefore a relatively low yield of the ketone is obtained. In general, the coupling appears to be invariant to the electronic nature of the *para*-substituted phenylboronic acids as the reactions with both electron-rich and electron-poor phenylboronic acid derivatives proceed smoothly (entries 1–5). As observed in the preceding reaction, here also the catalytic abilities of **1**–**3** are comparable.

A detailed investigation needs to be carried out to establish the mechanism of the observed catalytic activities of **1**–**3**. However, based on a literature report[45] of similar carbon–carbon cross-coupling reactions catalysed by palladium(0) complexes, a possible sequence of reactions involving the present catalyst system is as follows: generation of an active organopalladium species in the reaction of the complex with arylboronic acid ($ArB(OH)_2$), insertion of aryl aldehyde (Ar'CHO) to the Pd–Ar bond to form a Pd–OArAr' species, elimination of a secondary alcohol and addition of arylboronic acid to regenerate the organopalladium species and finally oxidation of the secondary alcohol to the desired ketone under the aerobic reaction conditions.

Table 5. Reaction of benzaldehyde with various boronic acids[a]



Entry	Ar	Yield (%)[b]		
		Catalyst **1**	Catalyst **2**	Catalyst **3**
1	Ph	90	95	92
2	4-ClPh	96	91	93
3	4-NCPh	60	66	63
4	4-MePh	88	91	87
5	4-MeOPh	83	85	80

[a]Arylboronic acid: 1 mmol; benzaldehyde: 1.5 mmol; Cs_2CO_3: 3 mmol.
[b]Isolated yield (average of two independent runs).

Though some palladium-catalysed coupling reactions of arylboronic acids with aromatic aldehydes for the synthesis of diaryl ketones have been reported,[18–20] a direct comparison of **1**–**3** with the catalyst systems reported earlier is difficult due to the differences in the reaction conditions such as solvent, base, temperature, reaction time and catalyst loading. However, in terms of the obtained yields, the efficiencies of the present palladium(II) complexes are comparable or slightly superior to those reported in the literature.

Conclusions

Palladium(II) complexes with the general formula $[Pd(L^n)(PPh_3)]$ (**1**–**3**) were produced in reactions of the Schiff bases 1-((2-hydroxy-5-R-phenylimino)methyl)naphthalen-2-ols (H_2L^n, R = H, Me, Cl) with $[Pd(PPh_3)_2Cl_2]$. Elemental analysis and other physical properties are consistent with the general formula of the complexes. Single-crystal X-ray diffraction studies reveal the fused 5,6-membered chelate rings forming phenolate-O, azomethine-N and naphtholate-O coordination mode of the ligand $(L^n)^{2-}$ and a square-planar ONOP environment around the metal centre in each of **1**–**3**. The spectroscopic (IR, UV–visible and NMR) features complement the molecular structures very well. All three complexes have been successfully applied as homogeneous catalysts in the reactions of arylboronic acids with aryl halides. We believe that this is the first report of the one-pot synthesis of diaryl ketones via carbon–carbon cross-coupling reactions of arylboronic acids with aryl aldehydes catalysed by palladium(II) Schiff base complexes.

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Supporting information

CCDC 1470949–1470951 contain the supplementary crystallographic data for **1**,**2**·Me_2SO·0.5H_2O and **3**·Me_2NCHO, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.