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Palladium salicylaldimine complexes derived from 2,3-dihydroxybenzaldehyde

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ABSTRACT

Schiff bases derived from condensation of 2,3-dihydroxybenzaldehyde with various primary amines, such as 1-adamantanamine hydrochloride, 2,6-dimethylaniline, 2,6-diethylaniline and 2,6-diisopropylaniline, react with palladium(II) acetate to give the corresponding bis(*N*-arylsalicylaldiminato)palladium(II) complexes. These complexes have been found to be active catalyst precursors for the Suzuki–Miyaura cross-coupling of aryl bromides and iodides with aryl boronic acids using water as a solvent.

1. Introduction

The use of palladium complexes to catalyze the coupling of organoboron compounds with aryl or vinyl halides has become one of the most widely used tools in organic synthesis. The scope and utility of the Suzuki–Miyaura reaction has been the subject of several excellent reviews [1–3]. Indeed, the Suzuki–Miyaura cross-coupling reaction has become an attractive route to generating biaryls, compounds with vast applications ranging from materials science to pharmaceutical chemistry. The use of boronic acids in this cross-coupling process is especially advantageous, compared to the analogous organotin species, as these boron compounds are relatively nontoxic and thermally, air- and moisture-stable [4].

The use of aryl chlorides as substrates and the ability to conduct this cross-coupling reaction at low temperatures and at low catalyst loading have greatly increased the versatility of the Suzuki–Miyaura cross-coupling reaction. Catalyst development has also played a significant role in improving this reaction [5–12] as traditional palladium complexes used to catalyze this transformation contain air-sensitive phosphine ligands. In recent years, however, the use of catalysts containing *N*-heterocyclic carbenes [13–15], oxazolines [16–18], and 'ligandless' systems [19–21], as well as heterogeneous systems [22–24], have also been employed. A considerable amount of research has also focused on designing water-soluble catalysts to provide a greener and more environmentally benign alternative to this reaction [25–30]. In a recent elegant study by Hong et al., it was found that (*N*-arylsalicylaldiminato)palladium(II) complexes are active catalysts for the Suzuki–Miyaura cross-coupling reaction of a wide array of aryl bromides [31]. However, reactions were carried out in organic solvents (THF and toluene) and high yields were only achieved after several days. Likewise, trinuclear triphenylphosphine Au(I) complexes with *N*,*N*,*O*-tridentate unsymmetrical Schiff base ligands catalyzed the Suzuki cross-coupling reaction to afford nonsymmetrical biaryls in good yields, whereas the Au(III) complexes gave only arylboronic homocoupling products [32]. As part of our ongoing investigation into designing new metal Schiff base complexes, we have prepared several palladium complexes derived from the condensation of 2,3-dihydroxybenzaldehyde with various primary amines, such as 1-adamantanamine hydrochloride, 2,6-dimethylaniline, 2,6-diethylaniline and 2,6-diisopropylaniline and examined their ability to be used as catalysts for the green Suzuki–Miyaura cross-coupling reaction.

2. Experimental

2.1. General procedures

Reagents and solvents used were purchased from Aldrich Chemicals. Palladium(II) acetate was purchased from Precious Metals Online Ltd. (Melbourne, AU). Schiff base **1c** was synthesized as previously reported [33]. NMR spectra were recorded on a JEOL

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JNM-GSX270 FT spectrometer. ^{1}H NMR chemical shifts are reported in ppm and referenced to residual solvent protons in deuterated solvent at 270 MHz. ^{13}C NMR chemical shifts are referenced to solvent carbon resonances as internal standards at 68 MHz and are reported in ppm. Multiplicities are reported as singlet (s), doublet (d), triplet (t), septet (sept), multiplet (m), broad (br), and overlapping (ov). The infrared spectra were obtained using a Mattson Genesis FT-IR spectrometer and are reported in cm^{-1}. Melting points were determined using a Mel-Temp apparatus and are uncorrected. Microanalyses for C, H, and N were carried out at Guelph Chemical Laboratories (Guelph, ON). GC/MS analyses were conducted using a Varian Saturn 2000 GC/MS/MS coupled to a CP-3800 GC. The GC was equipped with both the 1177 injection port with a CP-8410 liquid autoinjector connected to an SPB-1 (Supelco) fused silica column (30 m × 0.25 mm i.d. × 0.25 μm) and the 1079 solid injector chromatoprobe, attached to a 50 cm transfer line. The GC/MS spectrometer is controlled by the Saturn Workstation software, Version 5.51.

2.2. Synthesis of Schiff bases

2.2.1. Schiff base **1a**

2,3-Dihydroxybenzaldehyde (0.75 g, 5.46 mmol) dissolved in MeOH (15 mL) was added dropwise to a stirred MeOH (15 mL) solution of 1-adamantanamine hydrochoride (1.04 g, 5.56 mmol) and LiOH (0.14 g, 5.85 mmol). The reaction was allowed to proceed for 3 h at which point a precipitate was collected by suction filtration to afford **1a** as a yellow solid. Yield: 826 mg (56%); mp 218–220 °C. ^{1}H NMR ($CDCl_3$) δ: 8.15 (s, 1H, C(*H*)=N), 6.91 (d, *J* = 8.0 Hz, 1H, Ar), 6.70 (d, *J* = 8.0 Hz, 1H, Ar), 6.51 (t, *J* = 8.0 Hz, 1H, Ar), 1.97–1.93 (ov m, 15H, adamantyl). ^{13}C{^{1}H} ($CDCl_3$) δ: 162.6, 161.7, 147.9, 122.1, 115.3 (2C), 114.7, 68.7, 37.6, 37.1, 34.2, 31.9, 27.5, 27.0. IR (Nujol): 3163 (br, OH), 2924 (s), 2854 (s), 1644 (m, C=N), 1544 (m), 1513 (m), 1461 (m), 1394 (m), 1215 (m), 1025 (m), 741 (m).

2.2.2. Schiff base **1b**

A MeOH (15 mL) solution of 2,3-dihydroxybenzaldehyde (0.96 g, 6.94 mmol) was added to a stirred solution of *p*-aminophenol (0.76 g, 6.93 mmol) in MeOH (10 mL). The reaction mixture was heated at reflux for 4 h at which point a precipitate formed and was collected by suction filtration to afford **1b** as a purple solid. Yield: 1.32 g (83%); mp 194–196 °C. ^{1}H NMR ($(CD_3)_2CO$) δ: 8.84 (s, 1H, C(*H*)=N), 7.35 (d, *J* = 8.8 Hz, 2H, Ar), 7.07–6.77 (ov m, 5H, Ar). ^{13}C{^{1}H} ($(CD_3)_2CO$) δ: 160.9, 157.2, 149.5, 145.9, 140.2, 123.0, 122.7, 119.6, 118.9, 118.0, 116.3. IR (Nujol): 2969 (br, OH), 2932 (br, OH), 2924 (s), 2907 (s), 2874 (s), 1623 (m, C=N), 1458 (m), 1376 (m), 1223 (m), 1169 (m), 831 (m), 733 (m).

2.2.3. Schiff base **1c**

^{1}H NMR ($CDCl_3$) δ: 8.58 (s, 1H, C(*H*)=N), 7.27 (d, *J* = 8.2 Hz, 2H, Ar), 7.05–6.77 (ov m, 5H, Ar), 3.85 (s, 3H, O*CH*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 160.3, 159.2, 149.9, 145.4, 140.6, 122.9, 122.4, 119.0, 118.7, 117.4, 114.9, 55.8. IR (Nujol): 2973 (br, OH), 2935 (br, OH), 2912 (s), 2869 (s), 1613 (m, C=N), 1462 (m), 1381 (m), 1218 (m), 1170 (m), 837 (m), 735 (m).

2.2.4. Schiff base **1d**

A MeOH (15 mL) solution of 2,3-dihydroxybenzaldehyde (1.16 g, 8.39 mmol) was added dropwise to a stirred MeOH (10 mL) solution of 2,6-dimethylaniline (1.01 g, 8.34 mmol). The reaction mixture was heated at reflux for 3 h. Upon cooling the solution to 5 °C, large red crystals precipitated and were collected by suction filtration to afford **1d**. Yield: 1.67 g (83%); mp 104–106 °C. ^{1}H NMR ($CDCl_3$) δ: 8.32 (s, 1H, C(*H*)=N), 7.14–7.03 (ov m, 4H, Ar), 6.95–6.81 (ov m, 2H, Ar), 2.22 (s, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 166.9, 149.7, 147.6, 145.4, 128.8, 128.7, 125.5, 123.1, 119.2, 118.3, 118.0, 18.7. IR (Nujol): 2952 (br, OH), 2871 (br, OH), 2868 (s), 1627 (m, C=N), 1520 (m), 1450 (m), 1376 (m), 1201 (m), 1023 (m), 766 (m).

2.2.5. Schiff base **1e**

A MeOH (15 mL) solution of 2,3-dihydroxybenzaldehyde (1.00 g, 7.23 mmol) was added dropwise to a stirred MeOH (10 mL) solution of 2,6-diethylaniline (1.07 g, 7.19 mmol). The solution was heated at reflux for 3 h at which point the volume was reduced to 5 mL under vacuum and hexane (20 mL) was added to the solution. After storing the solution at 5 °C a precipitate formed and was collected by suction filtration to afford **1e** as an orange solid. Yield: 1.56 g (81%); mp 115–118 °C. ^{1}H NMR ($CDCl_3$) δ: 8.32 (s, 1H, C(*H*)=N), 7.14–7.06 (ov m, 4H, Ar), 6.94–6.82 (ov m, 2H, Ar), 2.55 (q, *J* = 7.6 Hz, 4H, C*H*$_2$CH$_3$), 1.16 (t, *J* = 7.6 Hz, 6H, CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 166.9, 149.5, 146.9, 145.4, 134.7, 126.8, 125.8, 123.1, 119.2, 118.3, 118.0, 25.1, 15.0. IR (Nujol): 3444 (br, OH), 2972 (br, OH), 2953 (s), 2929 (s), 2918 (s), 2868 (s), 1623 (m, C=N), 1583 (m), 1462 (m), 1375 (m), 1103 (m), 1070 (m), 878 (m), 796 (m).

2.2.6. Schiff base **1f**

A MeOH (15 mL) solution of 2,3-dihydroxybenzaldehyde (0.79 g, 5.68 mmol) was added dropwise to a stirred MeOH (10 mL) solution of 2,6-diisopropylaniline (1.01 g, 5.70 mmol). The reaction mixture was heated at reflux for 4 h at which point the reaction volume was reduced to 5 mL under vacuum and the solution stored at 5 °C. A solid precipitated and was collected by suction filtration to afford **1f** as an orange solid. Yield: 1.59 g (94%); mp 138–141 °C. ^{1}H NMR ($CDCl_3$) δ: 8.28 (s, 1H, C(*H*)=N), 7.20–7.07 (ov m, 4H, Ar), 6.96–6.82 (ov m, 2H, Ar), 2.99 (sept, *J* = 7.0 Hz, 2H, C*H*$(CH_3)_2$), 1.19 (d, *J* = 7.0 Hz, 12H, CH$(CH_3)_2$). ^{13}C{^{1}H} δ: 167.0, 149.6, 145.7, 145.5, 139.2, 126.1, 123.6, 123.2, 119.3, 118.3, 118.2, 28.4, 23.8, 22.7. IR (Nujol): 3462 (br, OH), 2948 (br, OH), 2917 (s), 2911 (s), 2865 (s), 1622 (m, C=N), 1584 (m), 1469 (m), 1272 (m), 1205 (m), 1101 (m), 1059 (m), 933 (m), 869 (m).

2.3. Synthesis of palladium complexes

2.3.1. Complex **2a**

Palladium(II) acetate (200 mg, 0.90 mmol) was added to a solution of (*E*)-3-((adamantylimino)methyl)benzene-1,2-diol (502 mg, 1.85 mmol) in EtOH (50 mL). The solution was heated at reflux for 2 h, at which point a brick-red solid was collected by suction filtration and washed with EtOH (3 × 10 mL) and Et_2O (3 × 10 mL) to afford **2a**. Yield: 478 mg (82%); mp 240–243 °C (decomposition). *Anal.* Calc. for $C_{34}H_{40}N_2O_4Pd$ (647.18): C, 63.10; H, 6.24; N, 4.33. Found: C, 63.55; H, 6.38; N, 4.44%. ^{1}H NMR ($CDCl_3$) δ: 13.02 (br s, O*H*, 2H), 12.98 (br s, 2H, O*H*), 7.99 (s, 2H, N=C*H*), 7.94 (s, 2H, N=C*H*), 6.83 (d, *J* = 7.4 Hz, 2H, Ar), 6.74 (d, *J* = 7.4 Hz, 2H, Ar), 6.63 (d, *J* = 7.4 Hz, 2H, Ar), 6.49–6.39 (ov m, 4H, Ar), 6.29 (d, *J* = 7.4 Hz, 2H, Ar), 2.24–2.17 (br ov m, 24H, adamantyl), 1.97–1.94 (br ov m, 12H, adamantyl), 1.81–1.65 (br ov m, 24H, adamantyl). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 173.1, 166.3, 160.8, 157.5, 151.5, 146.9, 124.2, 121.3, 119.7, 118.1, 117.0, 115.1, 114.9, 112.2, 65.0, 56.5, 43.0, 42.7, 36.2, 35.6, 30.4, 29.1. IR (Nujol): 3426 (br, OH), 2949 (s), 2926 (s), 1590 (m, C=N), 1458 (m), 1256 (m), 1111 (m), 1026 (m), 881 (m), 740 (m).

2.3.2. Complex **2b**

Palladium(II) acetate (250 mg, 1.12 mmol) was added to a solution of (*E*)-3-((4-hydroxyphenylimino)methyl)benzene-1,2-diol (529 mg, 2.31 mmol) in EtOH (50 mL). The mixture was heated at reflux for 2 h, at which point a brown solid was collected by

suction filtration and washed with EtOH (3 × 10 mL) and Et_2O (3 × 5 mL) to afford **2b**. Yield: 509 mg (81%); mp 290–294 °C (decomposition). *Anal.* Calc. for $C_{26}H_{20}N_2O_6Pd$ (562.90): C, 55.47; H, 3.59; N, 4.98. Found: C, 55.65; H, 3.68; N, 5.12%. ^{1}H NMR ($CDCl_3$) δ: 9.74 (s, 2H, O*H*), 8.06 (s, 2H, N=C*H*), 7.24 (d, *J* = 8.6 Hz, 4H, Ar), 6.96 (d, *J* = 7.6 Hz, 2H, Ar), 6.84 (d, *J* = 8.6 Hz, 4H, Ar), 6.68 (d, *J* = 7.6 Hz, 2H, Ar), 6.42 (t, *J* = 7.6 Hz, 2H, Ar), 4.97 (s, 2H, O*H*). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 164.3, 156.7, 152.1, 147.0, 140.8, 125.8, 125.4, 119.1, 115.9, 115.8, 115.5. IR (Nujol): 3369 (br, OH), 3316 (br, OH), 2930 (s), 2895 (s), 1595 (m, C=N), 1452 (m), 1377 (m), 1210 (m), 1097 (m), 898 (m), 739 (m).

2.3.3. Complex **2c**

Palladium(II) acetate (250 mg, 1.12 mmol) was added to a solution of (*E*)-3-((4-methoxyphenylimino)methyl)benzene-1,2-diol (550 mg, 2.26 mmol) in EtOH (50 mL). The mixture was heated at reflux for 2 h, at which point an orange solid was collected by suction filtration and washed with EtOH (3 × 5 mL) and Et_2O (3 × 5 mL) to afford **2c**. Yield: 525 mg (79%); mp 276–278 °C (decomposition). *Anal.* Calc. for $C_{28}H_{24}N_2O_6Pd$ (590.96): C, 56.90; H, 4.10; N, 4.74. Found: C, 57.11; H, 4.25; N, 5.03%. ^{1}H NMR ($CDCl_3$) δ: 7.72 (s, 2H, N=C*H*), 7.29 (d, *J* = 8.4 Hz, 4H, Ar), 6.99 (d, *J* = 8.4 Hz, 4H, Ar), 6.76–6.70 (ov m, 4H, Ar), 6.45 (t, *J* = 7.4 Hz, 2H, Ar), 4.92 (s, 2H, O*H*), 3.87 (s, 6H, OCH_3). IR (Nujol): 3393 (br, OH), 2970 (s), 2881 (s), 1602 (m, C=N), 1547 (m), 1457 (m), 1377 (m), 1246 (m), 1181 (m), 864 (m), 744 (m).

2.3.4. Complex **2d**

Palladium(II) acetate (250 mg, 1.12 mmol) was added to a solution of (*E*)-3-((2,6-dimethylphenylimino)methyl)benzene-1,2-diol (557 mg, 2.31 mmol) in EtOH (50 mL) and the solution was heated at reflux for 2 h. An orange solid was collected by suction filtration and washed with EtOH (3 × 5 mL). The resulting orange powder was dissolved in hot CH_2Cl_2 (10 mL) and stored at 5 °C. The resulting red-orange precipitate was collected by suction filtration to afford **2d**. Yield: 550 mg (84%); mp 316 °C (decomposition). *Anal.* Calc. for $C_{30}H_{28}N_2O_4Pd$ (587.02): C, 61.38; H, 4.82; N, 4.77. Found: C, 61.56; H, 4.71; N, 4.89%. ^{1}H NMR ($CDCl_3$) δ: 7.57 (s, 2H, N=C*H*), 7.33–7.21 (ov m, 6H, Ar), 6.76 (dd, *J* = 7.4, 1.5 Hz, 2H, Ar), 6.72 (dd, *J* = 8.2, 1.5 Hz, 2H, Ar), 6.46 (t, *J* = 8.0 Hz, 2H, Ar), 4.69 (s, 2H, O*H*), 2.40 (s, 12H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 163.4, 153.2, 147.5, 146.9, 132.1, 128.4, 127.0, 124.4, 118.7, 116.2, 115.7, 19.0. IR (Nujol): 3427 (br, OH), 2959 (s), 2901 (s), 1605 (m, C=N), 1550 (m), 1451 (m), 1310 (m), 1235 (m), 1172 (m), 1084 (m), 890 (m), 738 (m).

2.3.5. Complex **2e**

Palladium(II) acetate (250 mg, 1.12 mmol) was added to a solution of (*E*)-3-((2,6-diethylphenylimino)methyl)benzene-1,2-diol (606 mg, 2.25 mmol) in EtOH (50 mL). The mixture was heated at reflux for 2 h, at which point an orange-brown solid was collected by suction filtration. The solid was dissolved in hot CH_2Cl_2 (10 mL) and stored at 5 °C for 2 days. The resulting orange precipitate was collected by suction filtration to afford **2e**. Yield: 585 mg (81%); mp 322–325 °C (decomposition). *Anal.* Calc. for $C_{34}H_{36}N_2O_4Pd$ (643.12): C, 63.49; H, 5.65; N, 4.36. Found: C, 63.58; H, 5.78; N, 4.55%. ^{1}H NMR ($CDCl_3$) δ: 7.59 (s, 2H, N=C*H*), 7.41 (dd, *J* = 7.9, 7.1 Hz, 2H, Ar), 7.26 (d, *J* = 8.0 Hz, 4H, Ar), 6.76 (dd, *J* = 7.1, 1.5 Hz, 2H, Ar), 6.71 (dd, *J* = 7.9, 1.5 Hz, 2H, Ar), 6.45 (t, *J* = 8.0 Hz, 2H, Ar), 4.67 (s, 2H, O*H*), 2.82 (m, 8H, CH_2CH$_3$), 1.28 (t, *J* = 7.7 Hz, 12H, CH$_2$CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 163.6, 153.1, 147.5, 145.7, 137.7, 127.4, 126.4, 124.3, 118.3, 116.1, 115.6, 24.9, 14.4. IR (Nujol): 3447 (br, OH), 2969 (s), 2870 (s), 1605 (m, C=N), 1548 (m), 1377 (m), 1227 (m), 1087 (m), 861 (m).

2.3.6. Complex **2f**

Palladium(II) acetate (250 mg, 1.12 mmol) was added to a solution of (*E*)-3-((2,6-diisopropylphenylimino)methyl)benzene-1,2-diol (687 mg, 2.31 mmol) in EtOH (50 mL). The mixture was heated at reflux for 2 h, at which point an orange–brown precipitate was collected by suction filtration. The solid was dissolved in hot CH_2Cl_2 (10 mL) and stored at 5 °C for 3 days. The resulting orange precipitate was collected by suction filtration to afford **2f**. Yield: 666 mg (85%); mp 325–328 °C (decomposition). *Anal.* Calc. for $C_{38}H_{44}N_2O_4Pd$ (699.26): C, 65.27; H, 6.36; N, 4.01. Found: C, 65.41; H, 6.49; N, 4.28%. ^{1}H NMR ($CDCl_3$) δ: 7.59 (s, 2H, N=C*H*), 7.46 (dd, *J* = 7.9, 7.4 Hz, 2H, Ar), 7.30 (d, *J* = 7.7 Hz, 4H, Ar), 6.76 (dd, *J* = 7.4, 1.5 Hz, 2H, Ar), 6.71 (dd, *J* = 7.9, 1.5 Hz, 2H, Ar), 6.45 (t, *J* = 7.7 Hz, 2H, Ar), 4.62 (s, 2H, O*H*), 3.50 (sept, *J* = 6.9 Hz, 4H, C*H*(CH$_3$)$_2$), 1.30 (d, *J* = 6.9 Hz, 12H, CH(CH_3)$_2$), 1.18 (d, *J* = 6.9 Hz, 12H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 163.1, 153.1, 147.5, 144.0, 142.4, 127.7, 124.3, 123.8, 118.2, 116.1, 115.6, 28.6, 24.3, 23.3. IR (Nujol): 3432 (br, OH), 2939 (s), 2882 (s), 1600 (m, C=N), 1457 (m), 1377 (m), 1230 (m), 1081 (m), 778 (m), 725 (m).

2.4. Suzuki–Miyaura cross-coupling reactions

The appropriate palladium complex (2 mol%) was added to a mixture of an aryl halide (1 mmol), a boronic acid (1 mmol), and K_2CO_3 (2 mmol) in H_2O (10 mL). The reaction mixture was heated at reflux for 4 hrs. The organic phase was extracted with CH_2Cl_2 (2 × 10 mL), dried over $MgSO_4$, and the solution concentrated under vacuum. The coupling products were characterized by ^{1}H and ^{13}C NMR spectroscopy and GC–MS.

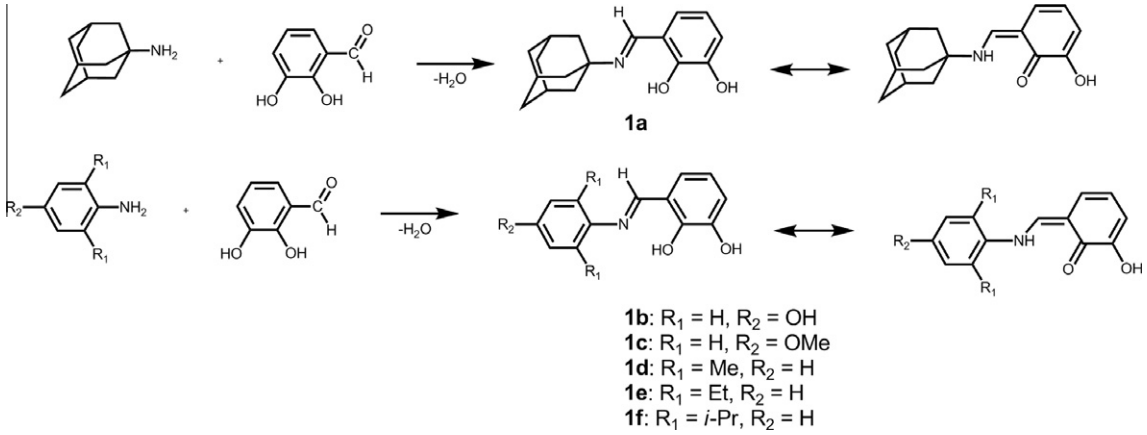
2.5. X-ray crystallography

Crystals of **1a** were grown from a 1:1 mixture of THF and CH_2Cl_2 at 5 °C, **1b** from a saturated acetone solution at 5 °C, **1d** from a saturated hexane solution at 5 °C, and **2d** from a 1:1 solution of CH_2Cl_2 and hexane at 5 °C. Single crystals were coated with Paratone-N oil, mounted using a polyimide MicroMount and frozen in the cold stream of the goniometer. A hemisphere of data were collected on a Bruker AXS P4/SMART 1000 diffractometer using ω and θ scans with a scan width of 0.3° and an exposure times of 10 (**1b**, **1d**) and 20 (**1a**, **2d**) s. The detector distances were 5 cm. The data were reduced [34] and corrected for absorption [35]. The structures were solved by direct methods and refined by full-matrix least squares on F^2 [36]. Data collection for **1d** was carried out at 223 K as lower temperatures resulted in the loss of crystallinity. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in Fourier difference maps and refined isotropically.

3. Results and discussion

3.1. Salicylaldimines

Schiff bases are remarkable compounds that have been utilized extensively in organic syntheses. In this present study, we have found that condensation of 2,3-dihydroxybenzaldehyde with various primary amines, such as 1-adamantanamine hydrochloride, 2,6-dimethylaniline, 2,6-diethylaniline and 2,6-diisopropylaniline gave the corresponding salicylaldimines in high yields (Scheme 1). Schiff bases have been characterized by multinuclear NMR spectroscopy, FT-IR spectroscopy, melting point, and by X-ray diffraction. Adamantanamine was chosen as a representative alkyl derivative that would be stable to air and water. The crystal structure of (*E*)-3-((4-methoxyphenylimino)methyl)benzene-1,2-diol, **1c**, has recently been studied by single-crystal X-ray diffraction



Scheme 1. Synthesis of salicylaldmines derived from condensation of 2,3-dihydroxybenzaldehyde with various primary amines.

and solid state NMR experiments, where the detailed structural analysis reveals the presence of four tautomeric structures [33,37]. Indeed, a recent paper by Woźniak and co-workers has shown that in solution the predominant form of these salicylaldimines is the imine-enol tautomer form. However, in the solid state the tautomeric equilibrium is shifted and the NH is present as the major species [38]. As expected, Schiff base derivatives **1a**–**f** have a shift for the aldehyde proton from 10 to *ca.* 8.3 ppm in the ^{1}H NMR spectra and a resonance at *ca.* 160 ppm in the ^{13}C NMR spectra for the N=CH methine carbon, consistent with a traditional imine form in solution. Compound **1a** has also been characterized by a single crystal X-ray diffraction study, the molecular structure of which is shown in Fig. 1, along with pertinent bond distances and angles. Crystallographic data for **1a** and other structures are found in Table 1. The asymmetric unit contains two independent molecules that differ in the orientation of the adamantyl group. Not surprisingly, the crystal packing shows extensive intermolecular hydrogen bonding. The 'imine' bond, C(1)–N(1), distance is 1.300(2) Å, which is significantly shorter than the adjacent C(8)–N(1) bond of 1.467(2) Å, still retains a significant amount of double bond character, indicative of a true Schiff base and is similar to the data reported for **1c** [33]. However, the two 'hydroxy' groups have noticeably different bond distances of C(3)–O(1) 1.299(2) and C(4)–O(2) 1.364(2) Å, where the former shows significant C=O double bond contribution. Also, the relatively short C(1)–C(2) bond

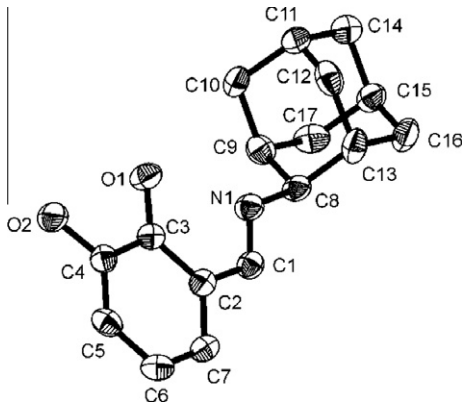


Fig. 1. The molecular structure of one of the independent molecules of **1a** with ellipsoids drawn at the 50% probability level. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–N(1) 1.300(2), C(1)–C(2) 1.414(3), C(2)–C(3) 1.427(3), C(3)–O(1) 1.299(2), C(3)–C(4) 1.424(3), C(4)–O(2) 1.364(2), C(8)–N(1) 1.467(2), C(8)–C(9) 1.528(3); N(1)–C(1)–C(2) 122.60(19), C(1)–N(1)–C(8) 123.77(18), O(1)–C(3)–C(4) 120.22(17), O(2)–C(4)–C(5) 119.44(18).

distance of 1.414(3) Å implies a significant contribution from the enamine (NHCH=C) form in the solid state.

The aryl derivatives **1b**–**f** all give similar spectroscopic solution data to that found for **1a**, suggesting the imine form is predominant under these conditions. We have also characterized **1b** and **1d** by single X-ray diffraction studies and their structures are shown in Fig. 2. For compound **1d**, there are four independent molecules in the asymmetric unit that differ in the orientation of the arene rings. An extensive network of hydrogen bonding is also present in the crystal lattice, as is frequently observed in these compounds [38]. Bond distances and angles are similar to those observed in **1a** and are consistent with a mixture of the imine and the enamine tautomers. As expected, considerable hydrogen bonding is observed in these species.

3.2. Metal complexes

We have found that addition of **1a**–**f** to $Pd(OAc)_2$ afforded bis (*N*-arylsalicylaldiminato)palladium(II) complexes (Scheme 2) in high yields (~80%). Complexes **2a**–**f** have been characterized by a number of physical methods, including multinuclear NMR spectroscopy. A significant upfield shift in the ^{1}H NMR spectra is observed for the imine methine proton, from *ca.* 8.3 ppm to *ca.* 7.7 ppm, upon coordination of the ligand to the d^8 metal centre. The diagnostic C=N stretching band in the FT-IR spectra has also shifted from *ca.* 1620 cm^{-1} to *ca.* 1595 cm^{-1} upon coordination to the metal centre [39]. Elemental analyses are also consistent with bis-Schiff base formulation. Complex **2a** appears to be a mixture of two isomers, as observed by multinuclear NMR spectroscopy.

Although we were unable to get single crystals of **2a**–**c**, complex **2d** has been characterized by a single crystal X-ray diffraction study (Fig. 3). The environment about Pd is roughly square planar. The Pd–O and Pd–N distances of 1.985(2) Å and 2.016(2) Å, respectively, are similar to those seen in related complexes [40–42] and are expected for a typical Schiff base ligand (containing a short C=N bond distance of 1.295(3) Å) coordinated to a metal centre, where the imine form is predominant.

3.3. Catalytic activity

As mentioned previously, Hong et al. found that cross-coupling reactions of arylbromides and phenyl boronic acids could be catalyzed by $Pd(OAc)_2$ and 2-[1-(2,4,6-trimethylphenylimino)ethyl]phenol (HL). Reactions were carried out in organic solvents (THF and toluene) at room temperature and high yields of the desired products were only achieved after long periods

Table 1
Crystallographic data collection parameters for **1a**, **1b**, **1d** and **2d**.

Complex	**1a**	**1b**	**1d**	**2d**
Chemical formula	$C_{17}H_{21}NO_2$	$C_{13}H_{11}NO_3$	$C_{15}H_{15}NO_2$	$C_{30}H_{28}N_2O_4Pd$
Formula mass	271.35	229.23	241.28	586.94
Crystal dimensions (mm^3)	0.30 × 0.30 × 0.15	0.60 × 0.20 × 0.05	0.50 × 0.45 × 0.20	0.25 × 0.15 × 0.12
Crystal system	orthorhombic	monoclinic	monoclinic	monclinic
Space group	*Pbca*	*P*2(1)/*c*	*C*2/*c*	*P*2(1)/*n*
Z	16	8	32	2
a (Å)	10.5400(15)	12.495(4)	21.462(5)	9.7635(18)
b (Å)	12.4581(18)	8.356(3)	21.379(5)	9.8597(18)
c (Å)	42.926(6)	20.097(6)	23.168(6)	13.427(3)
α (°)	90	90	90	90
β (°)	90	97.627(4)	112.370(5)	94.067(2)
γ (°)	90	90	90	90
V ($Å^3$)	5636.5(14)	2079.9(11)	9830(4)	1289.3(4)
ρ_{calcd} ($mg\ m^{-3}$)	1.279	1.464	1.304	1.512
T (K)	198(1)	173(1)	223(1)	173(1)
Radiation	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
μ (mm^{-1})	0.083	0.105	0.087	0.759
Total reflections	36 870	13 836	32 380	8623
Unique reflections	6418	4591	11 004	2876
No. of variables	529	395	889	172
θ (°)	0.95–27.50	2.04–27.50	1.46–27.50	2.50–27.50
Goodness-of-fit (GOF) on F^2	1.101	1.111	1.019	1.152
R_1[a] ($I > 2\sigma(I)$)	0.0464	0.0412	0.0456	0.0342
wR_2[b] (all data)	0.1183	0.1101	0.1396	0.1020
Largest diff. Peak and hole (e $Å^{-3}$)	0.256 and −0.192	0.273 and −0.193	0.274 and −0.201	1.721 and −1.182

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.
[b] $wR_2 = (\sum[w(F_o^2 - F_c^2)^2]/\sum[F_o^4])^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0301*P)^2 + (3.7324*P)]$ (**1a**), $= 1/[\sigma^2(F_o^2) + (0.0268*P)^2 + (1.3172*P)]$ (**1b**), $= 1/[\sigma^2(F_o^2) + (0.0661*P)^2 + (0.9072*P)]$ (**1d**), and $= 1/[\sigma^2(F_o^2) + (0.0499*P)^2 + (0.3022*P)]$ (**2d**), where $P = (\max(F_o^2, 0) + 2*F_c^2)/3$.

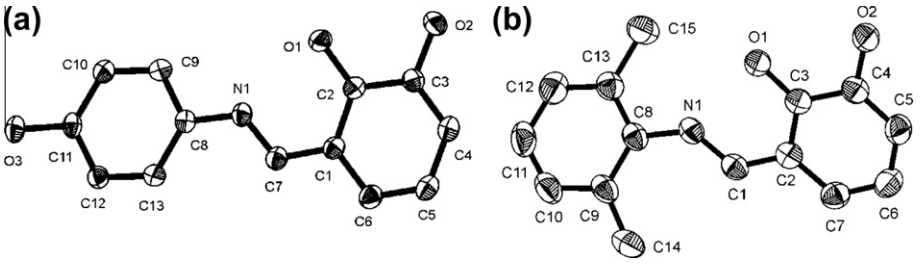
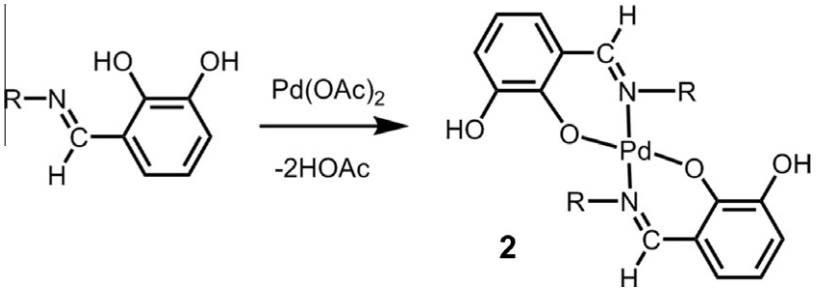


Fig. 2. (a) The molecular structure of one of the independent molecules of **1b** with ellipsoids drawn at the 50% probability level. Hydrogen atoms omitted for clarity. (b) The molecular structure of one of the independent molecules of **1d** with ellipsoids drawn at the 50% probability level. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°) for **1b**, C(1)–C(7) 1.428(3), C(2)–O(1) 1.321(2), C(2)–C(3) 1.425(3), C(3)–C(4) 1.369(3), C(3)–O(2) 1.372(2), C(7)–N(1) 1.300(2), C(8)–N(1) 1.422(2); C(2)–C(1)–C(7) 120.27(17), O(1)–C(2)–C(1) 122.45(17), O(1)–C(2)–C(3) 120.24(18), N(1)–C(7)–C(1) 122.01(19), C(7)–N(1)–C(8) 125.60(17). Selected bond lengths (Å) and angles (°) for **1d**, C(1)–N(1) 1.307(2), C(1)–C(2) 1.410(2), N(1)–C(8) 1.425(2), C(3)–O(1) 1.3028(18), C(4)–O(2) 1.3678(18); N(1)–C(1)–C(2) 122.00(15), C(1)–N(1)–C(8) 127.80(14), O(1)–C(3)–C(4) 120.19(14), O(1)–C(3)–C(2) 122.40(14).



Scheme 2. Synthesis of Schiff base palladium complexes **2a**–**f**.

of time (days). Interestingly, only one molar equivalent of the *N*,*O*-bidentate Schiff base ligand was used in this study, although the catalyst resting state appears to be the corresponding bis Schiff base compound PdL_2. Reduced catalytic activity was observed for reactions using this bis Schiff base compound as the active catalyst precursor was believed to be the mono Schiff base compound PdL(OAc)(solvent). It is also possible that palladium nanoparticles, formed by decomposition of the catalyst precursor during the reac-

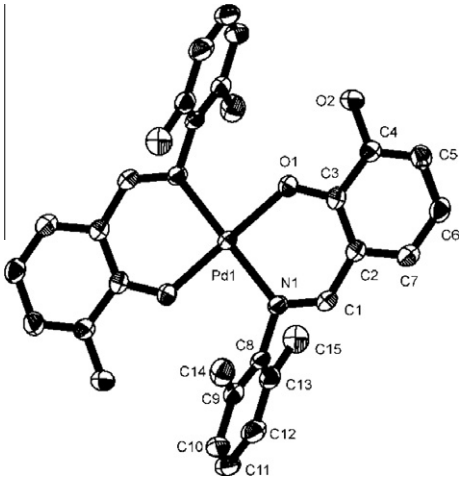
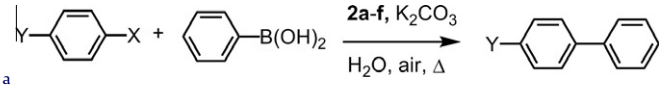


Fig. 3. The molecular structure of **2d** with ellipsoids drawn at the 50% probability level. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–O(1) 1.985(2), Pd(1)–N(1) 2.016(2), N(1)–C(1) 1.295(3), N(1)–C(8) 1.441(4), O(1)–C(3) 1.320(3), C(4)–O(2) 1.366(4); O(1)–Pd(1)–N(1) 92.11(9), C(1)–N(1)–C(8) 116.4(2), C(1)–N(1)–Pd(1) 124.30(19), C(8)–N(1)–Pd(1) 119.24(17), C(3)–O(1)–Pd(1) 124.4(2).

Table 2
Suzuki–Miyaura cross-coupling reactions catalyzed by complexes **2a**–**f**.



[a]

Entry	X	Y	Yield (%)[b]
1	I	CH_3	60
2	Br	CH_3	60
3	Cl	CH_3	0
4	I	OMe	75
5	I	F	10

[a] Reaction conditions: 1 mmol of 4-halotoluene; 1 mmol of phenyl boronic acid; 0.5 mol% of catalyst; 10 mL H_2O.

[b] Yields determined by GC–MS with respect to an internal standard from an average of at least two runs and product formation confirmed by multinuclear NMR spectroscopy.

tion are responsible for the observed catalytic activity in these systems [43].

In this study, preformed complexes **2a**–**f** were examined for their ability to catalyze the coupling of 4-iodotoluene and phenyl boronic acid in water. Reactions were conducted in the air using 0.5 mol% catalyst loading and potassium carbonate at reflux. Reactions with these bis Schiff base complexes all gave moderate yields of the unsymmetrical biaryl cross-coupling product after 2 h (Table 2, entry 1) along with significant amounts of homo-coupled products. Complex **2b** gave the most consistent results with minimal amount of catalyst decomposition and it was therefore used in all of the additional catalytic studies. While reactions with 4-bromotoluene also gave only moderate yields of the desired biaryl product (entry 2), these catalysts failed to couple reactions with 4-chlorotoluene (entry 3). The electronic nature of the aryl group had a significant effect on activity as the methoxy derivative (entry 4) gave slightly more of the desired product while the fluoro-substituted iodobenzene derivative (entry 5) shut down the reaction and gave only minor amounts (*ca.* 10%) of the corresponding product.

4. Conclusion

In summary, we have prepared a series of (*N*-arylsalicylaldiminato)palladium(II) complexes derived from condensation with 2,3-dihydroxybenzaldehyde and various primary amines, such as 1-adamantanamine hydrochloride, 2,6-dimethylaniline, 2,6-diethylaniline and 2,6-diisopropylaniline and examined their ability to catalyze the Suzuki–Miyaura cross-coupling reaction. While no significant activity is observed with aryl chlorides, these complexes catalyze the coupling of both aryl bromides and aryl iodides with phenylboronic acid in water in moderate yield. Although these results are promising, further work is needed to make other water soluble catalyst precursors that will prove to be more durable and effective in these catalyzed cross-coupling reactions.

Acknowledgements

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Appendix A. Supplementary material

CCDC 807117, 807118, 807119, and 807120 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.07.051.

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