Synthesis, characterization, and reactivity of Pd(II) salicylaldimine complexes derived from aminophenols

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Abstract: Schiff bases, derived from the condensation of salicylaldehydes with 3- and 4-aminophenol, reacted with paladium(II) acetate to give the corresponding bis(*N*-arylsalicylaldiminato)palladium(II) complexes. These complexes have been found to be active catalysts for the Suzuki–Miyaura cross-coupling of aryl bromides and iodides with aryl boronic acids, using water as a solvent.

Key words: cross-coupling, green chemistry, palladium, salicylaldimines, Schiff base, Suzuki-Miyaura.

Résumé : Les bases de Schiff résultant de la condensation de salicylaldéhydes avec les 3- et 4-aminophénols réagissent avec l'acétate de palladium(II) pour conduire aux complexes correspondants bis(*N*-arylsalicylaldiminato)palladium(II). On a trouvé que ces complexes sont actifs dans les réactions de couplages croisés de Suzuki–Miyaura des bromures et des iodures d'aryles avec les acides arylboroniques, en présence d'eau comme solvant.

Mots-clés : couplage croisé, chimie verte, palladium, salicylaldimines, base de Schiff, Suzuki-Miyaura.

[Traduit par la Rédaction]

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 have been the subject of several excellent reviews (1). Indeed, the Suzuki–Miyaura cross-coupling reaction has become an attractive route to generating biaryls, compounds with vast applications ranging from pharmaceutical chemistry to materials science. The use of boronic acids in this cross-coupling process is especially advantageous, as these compounds are relatively nontoxic and thermally, air-, and moisture-stable (2).

Numerous advances have been made to this reaction since its discovery. For instance, the use of aryl chlorides as substrates and the ability to conduct the reaction at low temperature and at low catalyst loading have greatly increased the versatility of the Suzuki–Miyaura crosscoupling reaction. Catalyst development has also played a significant role in improving this reaction (3), as traditional palladium complexes used to catalyze this transformation contained air-sensitive phosphine ligands. Recently, catalysts, containing N-heterocyclic carbenes (4), and "ligandless" systems (5), as well as heterogeneous systems (6), 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 (4i, 7). 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 (8a). However, reactions were carried out in organic solvents (THF and toluene), and high yields were only achieved after long periods of time (days). Likewise, trinuclear triphenylphosphine Au(I) complexes with N,N,O-tridentate unsymmetrical Schiff base ligands catalyzed the Suzuki-Miyaura cross-coupling reaction to afford nonsymmetrical biaryls in good yields, whereas the Au(III) complexes gave only arylboronic homocoupling products (8b). As part of our ongoing investigation into designing new metal Schiff base complexes, we prepared several palladium complexes derived from salicylaldehydes and aminophenols and examined their ability to be used as catalysts for the green Suzuki-Miyaura cross-coupling reaction.

Received 28 February 2007. Accepted 10 April 2007. Published on the NRC Research Press Web site at canjchem.nrc.ca on 18 May 2007.

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Experimental

General

Reagents and solvents used were purchased from Aldrich Chemicals. Pd(OAc)₂ was purchased from Precious Metals Online Ltd. (Melbourne, AU). NMR spectra were recorded on a JEOL JNM-GSX270 FT spectrometer or a Varian Mercury Plus 200 NMR spectrometer. ¹H NMR chemical shifts are reported in ppm and are referenced to the residual solvent protons in the deuterated solvent at 270 and 200 MHz, respectively. ¹³C NMR chemical shifts are referenced to the solvent carbon resonances as internal standards at 68 and 50 MHz, respectively, and are reported in ppm. Multiplicities are reported as singlet (s), doublet (d), triplet (t), multiplet (m), broad (br), and overlapping (ov). Infrared spectra were obtained using a Mattson Genesis II FTIR spectrometer. 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 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 \times 0.25 mm i.d. \times 0.25 μ m) 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. Imines were prepared by established procedures (9).

X-ray crystallography

Crystals of **2b** were grown from a DMSO solution at 20 °C. 2e from a saturated THF solution at 5 °C, and 2f from a saturated CH₂Cl₂ solution at 5 °C. Single crystals were coated with Paratone-N oil, mounted using a glass fibre, and frozen in the cold stream of the goniometer. A hemisphere of data was collected on a Bruker AXS P4/SMART 1000 diffractometer using ω and θ scans with a scan width of 0.3° and exposure times of 10 s (2b), 30 s (2e), and 80 s (2f). The detector distances were 5 cm. The data were reduced (10a) and corrected for absorption (10b). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 (10c). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in Fourier difference maps and refined isotropically (2b) or included in calculated positions and refined using a riding model (2e and 2f).

Complex 2a

Palladium(II) acetate (100 mg, 0.45 mmol) was added to a solution of 2-((*E*)-(3-hydroxyphenylimino)methyl)phenol (200 mg, 0.94 mmol) in EtOH (15 mL). The solution was heated at reflux for 2 h, at which point the solvent was removed under vacuum, leaving a brown powder, which was washed with Et₂O (3 × 5 mL). Yield: 170 mg (71%); mp 284–286 °C dec. IR (Nujol): 3433 (br, OH), 2933 (s), 2910 (s), 2856 (s), 1608 (w), 1538 (w), 1457 (w), 1376 (w), 1272 (w), 1145 (w), 846 (w). Spectroscopic NMR data (in DMSO-*d*₆): ¹H δ : 9.61 (br s, OH, 2H), 8.02 (s, N=CH, 2H), 7.43 (d, *J* = 7.4 Hz, Ar, 2H), 7.23–7.13 (ov m, Ar, 4H), 6.78–6.73 (ov m, Ar, 6H), 6.50 (t, *J* = 7.4 Hz, Ar, 2H), 6.02

(d, J = 8.4 Hz, Ar, 2H). ¹³C{¹H} δ : 164.6, 163.7, 157.6, 150.6, 135.8, 135.6, 129.2, 120.7, 120.4, 115.8, 115.2, 113.8, 112.4. Anal. calcd. for C₂₆H₂₀N₂O₄Pd (%): C 58.82, H 3.80, N 5.28; found: C 58.43, H 3.49, N 5.12.

Complex 2b

Palladium(II) acetate (100 mg, 0.45 mmol) was added to a solution of 2-((*E*)-(4-hydroxyphenylimino)methyl)phenol (200 mg, 0.94 mmol) in EtOH (15 mL). The mixture was heated at reflux for 2 h, at which point the solvent was removed under vacuum. The resulting brown solid was washed with Et₂O (3 × 5 mL). Yield: 155 mg (65%); mp 306 °C dec. IR (Nujol): 2919 (s), 2854 (s), 1606 (w), 1542 (w), 1462 (m), 1376 (m), 1178 (w), 842 (w), 759 (w). Spectroscopic NMR data (in DMSO-*d*₆): ¹H δ : 9.49 (br s, O*H*, 2H), 7.99 (s, N=C*H*, 2H), 7.42 (d, *J* = 7.4 Hz, Ar, 2H), 7.23–7.14 (ov m, Ar, 6H), 6.83–6.76 (ov m, Ar, 4H), 6.48 (t, *J* = 7.2 Hz, Ar, 2H), 6.06 (d, *J* = 8.4 Hz, Ar, 2H). ¹³C{¹H} δ : 164.6, 163.7, 146.3, 141.3, 135.7, 135.3, 126.2, 120.8, 120.2, 115.1, 114.8. Anal. calcd. for C₂₆H₂₀N₂O₄Pd (%): C 58.82, H 3.80, N 5.28; found: C 58.46, H 3.47, N 5.27.

Complex 2c

Palladium(II) acetate (100 mg, 0.45 mmol) was added to a solution of 2-((*E*)-(3-hydroxyphenylimino)methyl)-4bromophenol (264 mg, 0.90 mmol) in EtOH (15 mL). The mixture was heated at reflux for 2 h, at which point the solvent was removed under vacuum. The resulting dark-brown powder was washed with Et₂O (3 × 5 mL). Yield: 199 mg (64%); mp 223 °C dec. IR (Nujol): 3164 (br, OH), 2950 (s), 2900 (s), 1591 (m), 1459 (s), 1376 (m), 1294 (w), 1145 (w), 960 (w), 827 (w). Spectroscopic NMR data (in DMSO-*d*₆): ¹H δ: 9.63 (br s, OH, 2H), 8.03 (s, N=CH, 2H), 7.65 (d, *J* = 7.4 Hz, Ar, 2H), 7.26–7.15 (ov m, Ar, 4H), 6.72–6.65 (ov m, Ar, 6H), 5.94 (d, *J* = 8.4 Hz, Ar, 2H). ¹³C{¹H} δ: 163.5, 163.2, 157.6, 150.3, 137.8, 136.9, 129.3, 122.6, 122.5, 115.7, 114.1, 112.2, 105.3. Anal. calcd. for C₂₆H₁₈Br₂N₂O₄Pd (%): C 45.34, H 2.64, N 4.07; found: C 44.93, H 2.80, N 4.16.

Complex 2d

Palladium(II) acetate (120 mg, 0.53 mmol) was added to a solution of 2-((*E*)-(4-hydroxyphenylimino)methyl)-4-bromophenol (312 mg, 1.07 mmol) in EtOH (15 mL), and the solution was heated at reflux for 2 h. Following the removal of the solvent under vacuum, the resulting orange powder was washed with Et₂O (3 × 5 mL). Yield: 150 mg (41%); mp 246–247 °C dec. IR (Nujol): 3242 (br, OH), 3220 (br, OH), 2923 (s), 2854 (s), 1612 (w), 1504 (w), 1462 (m), 1375 (w), 1288 (w), 1213 (w), 1166 (w). Spectroscopic NMR data (in DMSO-*d*₆): ¹H δ : 9.62 (br s, O*H*, 2H), 8.02 (s, N=C*H*, 2H), 7.65 (d, *J* = 1.7 Hz, Ar, 2H), 7.26 (d of d, *J* = 8.7, 1.7 Hz, Ar, 2H), 7.13 (d, *J* = 8.4 Hz, Ar, 4H), 6.78 (d, *J* = 8.4 Hz, Ar, 4H), 5.97 (d, *J* = 8.7 Hz, Ar, 2H). Anal. calcd. for C₂₆H₁₈Br₂N₂O₄Pd (%): C 45.34, H 2.64, N 4.07; found: C 45.10, H 2.45, N 4.01.

Complex 2e

Palladium(II) acetate (100 mg, 0.45 mmol) was added to a solution of 1-((E)-(3-hydroxyphenylimino)methyl)napht-halen-2-ol (237 mg, 0.90 mmol) in EtOH (10 mL). The mix-





ture was heated at reflux for 2 h, at which point an orangebrown solid was collected by suction filtration. The solid was dissolved in hot THF (10 mL), filtered, hexane (5 mL) was added, and the solution was stored at 5 °C for 2 d. The resulting orange precipitate was collected by suction filtration. Yield: 200 mg (70%); mp 310 °C dec. IR (Nujol): 3183 (br, OH), 2956 (w, ov), 2917 (s), 2852 (m), 1594 (m), 1538 (w), 1462 (m), 1376 (w), 1288 (w), 1149 (w). Spectroscopic NMR data (in DMSO- d_6): ¹H δ : 9.66 (br s, OH, 2H), 8.60 (s, N=CH, 2H), 8.05 (d, J = 8.4 Hz, Ar, 2H), 7.68 (d, J =8.4 Hz, Ar, 4H), 7.43 (t, J = 6.9 Hz, Ar, 2H), 7.30–7.21 (ov m, Ar, 4H), 6.92–6.90 (ov m, Ar, 4H), 6.82 (d, J =7.7 Hz, Ar, 2H),), 6.27 (d, J = 9.2 Hz, Ar, 2H). ¹³C{¹H} δ : 165.8, 157.8, 157.4, 151.5, 136.2, 134.6, 129.6, 129.4, 128.6, 126.9, 123.5, 123.2, 120.9, 116.3, 114.0, 112.9, 111.0. Anal. calcd. for C34H24N2O4Pd (%): C 64.71, H 3.84, N 4.44; found: C 64.93, H 3.63, N 4.45.

Complex 2f

Complex 2f was prepared by the modification of a known procedure (11). Palladium(II) acetate (100 mg, 0.45 mmol) was added to a solution of 1-((E)-(4-hydroxyphenylimino)methyl)naphthalen-2-ol (237 mg, 0.90 mmol) in EtOH (10 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 THF (50 mL), filtered, hexane (20 mL) was added, and the solution stored at 5 °C for 5 d. The resulting orange precipitate was collected by suction filtration. Yield: 125 mg (44%); mp 300 °C dec. IR (Nujol): 2917 (s), 2854 (m), 1612 (w), 1592 (w), 1454 (m), 1376 (w), 1000 (w). Spectroscopic NMR data (in DMSO-d₆): ¹H δ: 9.58 (br s, OH, 2H), 8.57 (s, N=CH, 2H), 8.05 (d, J = 8.6 Hz, Ar, 2H), 7.68 (d, J = 8.6 Hz, Ar, 4H), 7.41 (t, J = 7.7 Hz, Ar, 2H), 7.32 (d, J = 8.4 Hz, Ar, 4H), 7.23 (t, J = 7.2 Hz, Ar, 2H), 6.83 (d, J = 8.4 Hz, Ar, 4H), 6.29 (d, J = 9.4 Hz, Ar, 2H). Anal. calcd. for $C_{34}H_{24}N_2O_4Pd$ (%): C 64.71, H 3.84, N 4.44; found: C 64.48, H 3.52, N 4.32.

Suzuki-Miyaura cross-coupling reactions

An aryl halide (1 mmol) and a boronic acid (1 mmol) were added to a solution of H_2O (10 mL), K_2CO_3 (276 mg, 2 mmol), and palladium complex (0.5 mol %). The solution was heated at reflux for 2 h. An organic extraction was performed using dichloromethane (2 × 10 mL), whereupon the solution was diluted by a factor of 100 and analyzed in duplicate using GC–MS spectroscopy.

Results and discussion

Salicylaldimines

Schiff bases are remarkable compounds that have been utilized extensively in organic syntheses (12). For instance, a recent report describes a highly diastereo- and enantioselective asymmetric aldol reaction of glycinate Schiff bases with aldehydes (12a). In this study, we have found that salicylaldehydes add to 3- and 4-aminophenol to give compounds having spectroscopic data consistent with the Schiff bases 1a-1f. As expected, the proton, initially assigned to the aldehyde group, shifts from 10 to 9 ppm in the ¹H NMR spectra upon conversion to the imine functionality, and a resonance at ~160 ppm in the ¹³C NMR spectra corresponds to the N=CH methine carbon. Likewise, formation of these compounds can be monitored by the diagnostic C=N stretching band in the IR spectra at ~1620 cm⁻¹ (12b). Attempts to make the corresponding Schiff bases from 2-aminophenol led to products arising from a competing oxidative cyclization reaction (13).

Metal complexes

We have found that addition of 1a-1f to $Pd(OAc)_2$ afforded bis(*N*-arylsalicylaldiminato)palladium(II) complexes (Scheme 1) in moderate yields (41%-71%). Complexes 2a-2f have been characterized by a number of physical methods, including multinuclear NMR spectroscopy. A significant upfield shift in the ¹H NMR spectra is observed for the imine methine proton, from ~9 ppm to ~8 ppm, upon coordination of the ligand to the d⁸ metal centre. The diagnostic

Fig. 1. Inert-atmosphere MALDI-MS spectra (pyrene matrix) showing simulated (top) and observed (bottom) isotope patterns for **2a**.



C=N stretching band in the FTIR spectra has also shifted from ~1620 cm⁻¹ to ~1595 cm⁻¹ upon coordination to the metal centre (14). Elemental analyses are also consistent with bis Schiff base formulation, and complex **2a** has also been characterized by a mass spectrometry IA-MALDI-TOF study (15), which showed an excellent match between simulated and observed isotope patterns (Fig. 1).

Complex **2b** has been characterized by a single-crystal Xray diffraction study (Fig. 2). Crystallographic data are provided in Table 1.³ The environment about Pd is squareplanar, supplemented by hydrogen bonds of 2.679(2) Å, resulting in an octahedral environment and a twodimensional network. DMSO molecules hydrogen bond at a distance of 1.93(3) Å and long S…O bonds of 3.2437(15) Å complete the formation of the two-dimensional sheets. The Pd—O and Pd—N distances of 1.9843(13) Å and 2.0257(14) Å, respectively, are similar to those seen in related complexes (8*a*, 9). Similar copper complexes have recently been reported to be active catalysts in the polymerization of norbornene (16).

Interestingly, the molecular structure of **2e** (Fig. 3) has also been characterized by a single-crystal X-ray diffraction study, and in this case, the metal lies in a distorted squareplanar geometry with a cis- N_2O_2 donor set. The naphthyl groups are distorted from the Pd(N,O)₂ plane and result in a parallel alignment of the phenol groups. The C(6)—C(25)

Fig. 2. The molecular structure of **2b** with ellipsoids drawn at the 50% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°) for **2b**: Pd— O(16) No. 1, 1.9842(13); Pd—O(16), 1.9843(13); Pd—N(8) No. 1, 2.0256(14); Pd—N(8), 2.0257(14); O(1)—C(2), 1.367(2); C(5)—N(8), 1.439(2); N(8)—C(9), 1.292(2); C(15)—O(16), 1.311(2); O(16) No. 1–Pd–O(16), 180.00(6); O(16) No. 1–Pd– N(8) No. 1, 90.89(5); O(16)–Pd–N(8) No. 1, 89.11(5); O(16) No. 1–Pd–N(8), 89.11(5); O(16)–Pd–N(8), 90.89(5); N(8) No. 1–Pd– N(8), 180.00(7); C(2)–O(1)–H(1), 111.8(19); O(1)–C(2)–C(3), 121.90(17); O(1)–C(2)–C(7), 118.57(17).



distance of 3.349(8) Å suggests that intramolecular arenearene stacking may be important (17). While it is unclear at this time why these ligands lie in a cis configuration, this unusual arrangement has been observed recently in bulky bis(N-3,5-Bu^t-2-phenyl-(R)-salicylaldiminato)copper(II) complexes, where small changes in the substituents resulted in drastic changes in the molecular structure and in the corresponding redox properties (18). Attempts to obtain single crystals of the corresponding 4-hydroxyl derivative 2f were complicated by crystal twinning and the deposition of very thin plates from solutions of 2f. However, the preliminary structure of 2f clearly shows the trans-arrangement of the ligands (Fig. 4). As these conformers are indistinguishable by NMR spectroscopy, further structural studies are therefore needed to understand the nature of these discrepancies.

Catalytic activity

As mentioned previously, Hong et al. found that crosscoupling reactions of aryl bromides and phenyl boronic acids could be catalyzed by $Pd(OAc)_2$ and 2-[1-(2,4,6-trimethylphenylimino)ethyl]phenol (HL) (8*a*). Reactions were carried out in organic solvents (THF and toluene) at

³ Supplementary data for this article are available on the journal Web site (canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada. DUD 5163. For more information on obtaining material, refer to http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml. CCDC 637015, 637101, and 637199 contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Table 1. Crystallographic data collection parameters for 2b, 2e, and 2f.

Complex	2b·2DMSO	2e·THF	$2f \cdot CH_2Cl_2$
Chemical formula	$C_{30}H_{32}N_2O_6PdS_2$	$C_{38}H_{32}N_2O_5Pd$	$C_{35}H_{26}Cl_2N_2O_4Pd$
Formula mass	687.10	703.06	715.88
Crystal dimensions (mm ³)	$0.30 \times 0.25 \times 0.075$	$0.20 \times 0.15 \times 0.05$	$0.23 \times 0.10 \times 0.03$
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	P1
Z	2	4	2
a (Å)	13.8014(6)	12.015(6)	10.697(11)
<i>b</i> (Å)	10.7869(5)	19.479(10)	12.002(12)
<i>c</i> (Å)	9.9018(5)	14.427(7)	12.527(12)
α (°)	90	90	86.302(16)
β(°)	97.226(1)	108.093(7)	80.518(15)
γ (°)	90	90	72.555(16)
Volume (Å ³)	1462.42(12)	3210(3)	1513(3)
$D_{\text{calcd.}} \text{ (mg m}^{-3}\text{)}$	1.560	1.455	1.571
<i>T</i> (K)	173(1)	173(1)	198(1)
Radiation	Mo K α ($\lambda = 0.71073$ Å)	Mo K α ($\lambda = 0.71073$ Å)	Mo K α ($\lambda = 0.71073$ Å)
$\mu (mm^{-1})$	0.824	0.625	0.833
Total reflections collected	9941	8823	9729
Total unique reflections	3278	8823	6352
No. of variables	251	418	402
θ (°)	1.49-27.50	1.78–27.49	1.65-27.49
Goodness-of-fit on F^2	1.089	1.135	1.052
$R_1^a [I > 2\sigma(I)]$	0.0232	0.0667	0.0893
$wR_2^{\ b}$ (all data)	0.0660	0.2025	0.2922
Largest diff. Peak and hole (e $Å^{-3}$)	0.598 and -0.415	1.216 and -0.903	3.542 and -2.704

 ${}^{a}R_{1} = \Sigma |(|F_{o}| - |F_{c}|)| / \Sigma |F_{o}|.$

 ${}^{b}wR_{2} = [\Sigma w(F_{0}^{2} - F_{c}^{2})^{2}/\Sigma(F_{0}^{4})]^{1/2}$ where $w = 1/[\sigma^{2}(F_{0}^{2}) + (0.0359 \times P)^{2} + (0.485 \times P)]$ for **2b**, $w = 1/[\sigma^{2}(F_{0}^{2}) + (0.0868 \times P)^{2}]$ for **2e**, and $w = 1/[\sigma^{2}(F_{0}^{2}) + (0.1616 \times P)^{2}]$ for **2f** where $P = [\max(F_{0}^{2}, 0) + 2 \times F_{c}^{2}]/3$.

room temperature, and high yields of the desired products were only achieved after long periods 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 PdL₂. 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 the decomposition of the catalyst precursor during the reaction, are responsible for the observed catalytic activity in these systems (7o).

In this preliminary study, preformed complexes 2a-2fwere examined for their ability to catalyze the coupling of 4iodotoluene and phenyl boronic acid in water. Reactions were conducted in air using 0.5 mol% catalyst loading and potassium carbonate at reflux. Remarkably, all reactions with these bis Schiff base complexes gave near-quantitative yield of the unsymmetrical biaryl cross-coupling product after only 2 h (Table 2, entry 1). Complex **2f** gave the most consistent results with minimal amount of catalyst decomposition; therefore, it was used in all the catalytic studies. While reactions with bromotoluene also gave high yields of the desired biaryl product (Table 2, entry 2), these catalysts failed to couple reactions with chlorotoluene (Table 2, entry 3). The electronic nature of the aryl group had little effect on activity, as both the methoxy- (Table 2, entry 4) and fluorosubstituted iodobenzene (Table 2, entry 5) derivatives gave excellent yields of the desired product. Reactions of 4iodotoluene and naphthalboronic acid using 0.5 mol% of **2f** also gave near-quantitative yields of the corresponding cross-coupling product.

Conclusion

In summary, we have prepared a series of (*N*-arylsalicylaldiminato)palladium(II) complexes, derived from aminophenols, and examined their ability to catalyze the Suzuki–Miyaura cross-coupling reaction. Although no significant activity is observed with aryl chlorides, these complexes effectively catalyze the coupling of both aryl bromides and aryl iodides. Further work is needed to expand the scope of this reaction, the results of which will be published in due course.

Acknowledgements

Thanks are gratefully extended to the American Chemical Society-Petroleum Research Fund (Grant No. 37824-B1), Canada Research Chairs Program, Canadian Foundation for Innovation (CFI)-Atlantic Innovation Fund, Natural Science and Engineering Research Council of Canada (NSERC), and **Fig. 3.** (*a*) The molecular structure of **2e** with ellipsoids drawn at the 30% probability level. Hydrogen atoms and a molecule of THF were omitted for clarity. (*b*) An alternate side-on view of **2e** showing the distortion of the Pd(N,O)₂ backbone and the parallel arrangement of the phenol groups. Selected bond lengths (Å) and angles (°) for **2e**: Pd—O(40), 1.997(5); Pd—O(20), 2.012(4); Pd—N(8), 2.015(5); Pd—N(28), 2.029(5); O(1)—C(7), 1.378(8); N(8)—C(9), 1.318(8); C(19)—O(20), 1.331(7); N(28)—C(29), 1.312(8); C(39)—O(40), 1.320(8); O(40)–Pd–O(20), 83.92(18); O(40)–Pd–N(8), 173.1(2); O(20)–Pd–N(8), 89.9(2); O(40)–Pd–N(28), 89.2(2); O(20)–Pd–N(28), 173.1(2); N(8)–Pd–N(28), 97.0(2); C(5)–N(8)–Pd, 120.9(4); C(9)–N(8)–Pd, 122.7(5); C(29)–N(28)–Pd, 120.0(5); C(25)–N(28)–Pd, 122.1(4).





YX +	B(OH) ₂	H_2O , air, Δ	
Entry	Х	Y	Yield $(\%)^a$
1	Ι	CH ₃	>95
2	Br	CH ₃	>95
3	C1	CH ₃	5
4	Ι	OMe	>95
5	Ι	F	>95

2f, K₂CO₃

Table 2. Suzuki–Miyaura cross-coupling reactions catalyzed by complex 2f.

Note: Reaction conditions: 1 mmol of 4-halotoluene, 1 mmol of phenyl boronic acid, and 10 mL H₂O.

"Yields were determined by GC-MS, with respect to an internal standard, from an average of at least two runs and product formation was confirmed by multinuclear NMR spectroscopy.

Fig. 4. The molecular structure of one of the independent molecules of 2f with ellipsoids drawn at the 30% probability level. Selected bond lengths (Å) and angles (°) for 2f: Pd(1)-O(20), 1.990(6); Pd(1)—N(8), 2.015(8); Pd(2)—N(28), 1.943(10); Pd(2)—O(40), 1.980(7); O(20)–Pd(1)–O(20) No. 1, 180.000(1); O(20)-Pd(1)-N(8), 89.3(3); O(20) No. 1-Pd(1)-N(8), 90.7(3); O(20)-Pd(1)-N(8) No. 1, 90.7(3); O(20) No. 1-Pd(1)-N(8) No. 1, 89.3(3); N(8)-Pd(1)-N(8) No. 1, 180.0(4); N(28)-Pd(2)-N(28) No. 2, 180.000(1); N(28)-Pd(2)-O(40) No. 2, 90.7(3); N(28) No. 2-Pd(2)-O(40) No. 2, 89.3(3); N(28)-Pd(2)-O(40), 89.3(3); N(28) No. 2-Pd(2)-O(40), 90.7(3); O(40) No. 2-Pd(2)-O(40), 180.0(4).



Mount Allison University for financial support. JCS thanks NSERC for an Undergraduate Student Research Award (USRA). We also thank Dan Durant and Roger Smith for their expert technical assistance, Johanna M. Blacquiere and Dr. Deryn E. Fogg (University of Ottawa) for the MALDI-TOF spectra, and anonymous reviewers for helpful suggestions.

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