

Palladium(II) Schiff Base Complexes Derived from Allylamine and Vinylaniline

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Condensation of salicylaldehyde (2-HOC₆H₄C(O)H) with allylamine afforded the unsaturated salicylaldimine, 2-HOC₆H₄C(H)=NCH₂CH=CH₂. Similar reactivity was observed with substituted salicylaldehydes. Further reaction of these Schiff bases with palladium acetate or Na₂PdCl₄ afforded complexes of the type PdL₂, where L = deprotonated Schiff base. The molecular structure of the parent salicylaldimine palladium complex [*trans*-(2-OC₆H₄C(H)=NCH₂CH=CH₂)₂Pd] (**1**) was characterized by an X-ray diffraction study. Crystals of **1** were monoclinic, space group *P*2₁/*n*, *a* = 14.0005(9) Å, *b* = 7.2964(5) Å, *c* = 17.5103(12) Å, β = 100.189(1)°, *Z* = 4. Analogous chemistry with 4-vinylaniline also gave novel palladium complexes containing a pendant styryl group. Crystals of [*trans*-(2-HOC₆H₄C(H)=N-4-C₆H₄CH=CH₂)₂Pd] (**4**) were monoclinic, space group *P*2₁/*c*, *a* = 13.7710(14) Å, *b* = 11.0348(11) Å, *c* = 7.8192(8) Å, β = 98.817(2)°, *Z* = 2.

Key Words : Salicylaldimines, Allylamine, Palladium, Vinylaniline

Introduction

Compounds containing boronic acids [RB(OH)₂] or boronate esters [RB(OR)₂] have not only found extensive application in organic synthesis¹ but several of these molecules display significant biological activity.² For instance, boronic acid derivatives of amino acids are effective and reversible inhibitors of the serine proteases chymotrypsin and subtilisin.³⁻⁹ The mechanism of action for these compounds is believed to arise from the ability of the boron atom to coordinate *via* its empty p-orbital to the active hydroxyl groups of the enzyme. Boronic acid derivatives are also known to facilitate the transport of molecules across lipid bilayers,^{10,11} an important attribute in the area of drug delivery. Finally, a number of aminoboron compounds have shown remarkable potential in boron neutron capture therapy (BNCT) for the treatment of certain forms of cancer.¹² These properties, along with our interest in preparing biologically active boron compounds, prompted us to investigate the synthesis of metal complexes containing organic groups which could be readily functionalized into these boron containing compounds.

Palladium(II) complexes have been found to cleave proteins selectively in high yields.¹³ Unfortunately, the solubility, and hence the efficacy, of these metal complexes is sometimes dependent on the pH of the solution. Palladium amine complexes have also been investigated for their potential use as anticancer agents.¹⁴ With this in mind, we have prepared a number of palladium complexes containing salicylaldimine ligands derived from allylamine and vinylaniline and hypothesize that further hydroboration of the pendant C=C moieties in these complexes may prove to be a facile and gentle route to making novel boron-containing palladium compounds with improved physio-

logical solubilities, stabilities, and selectivities. The results of our initial investigations generating these palladium complexes are described herein.

Experimental Section

General. Reagents and solvents used were obtained from Aldrich Chemicals. PdCl₂ and Pd(OAc)₂ was purchased from Precious Metals Online Ltd. NMR spectra were recorded on a JEOL JNM-GSX270 FT NMR spectrometer. ¹H NMR chemical shifts are reported in ppm and are referenced to residual protons in deuterated solvent at 270 MHz. ¹³C NMR chemical shifts are referenced to solvent carbon resonances as internal standards at 68 MHz. Multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and overlapping (ov). Infrared spectra were obtained using a Mattson Genesis II FT-IR spectrometer and are reported in cm⁻¹. Melting points were measured uncorrected with a Mel-Temp apparatus. Microanalyses for C, H, and N were carried out at Guelph Chemical Laboratories Ltd. (Guelph, ON, Canada).

Di-(2-allyliminomethylphenolato)palladium(II) (1). To a freshly prepared MeOH (10 mL) solution of Na₂PdCl₄ (0.43 g, 1.47 mmol) was added 2-allyliminomethylphenol (0.49 g, 3.04 mmol) and triethylamine (0.5 mL). The mixture was heated at reflux for 2 h and then allowed to cool to room temperature, at which point a green precipitate formed and was collected by suction filtration. The solid was then recrystallized from CHCl₃ (2 mL) to afford **1** (0.44 g, 70%) as a green solid. Mp 260 °C (decomposition). Spectroscopic NMR data (in CDCl₃): ¹H δ: 7.64 (s, 2H, N=CH), 7.24 (t of d, *J* = 8, 2 Hz, 2H, Ar), 7.18 (d of d, *J* = 8, 2 Hz, 2H, Ar), 6.87 (d, *J* = 8 Hz, 2H, Ar), 6.56 (t of d, *J* = 8, 2 Hz, 2H, Ar), 6.09 (d of d of t, *J* = 17, 10, 6 Hz, 2H, CH=CH₂), 5.27 (d of d, *J* = 17, 1 Hz, 2H, CH=CHH), 5.16 (d of d, *J* = 10, 1 Hz, 2H, CH=CHH), 4.38 (d, *J* = 6 Hz, 4H, CH₂CH=

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CH₂); ¹³C{¹H} δ: 164.6, 162.6, 136.2, 134.7, 134.2, 120.4, 120.3, 116.9, 115.1, 59.5. IR (nujol): 2922, 2856, 1595, 1537, 1466, 1450, 1433, 1398, 1350, 1319, 1200, 1147, 1024, 993, 976, 924, 901, 850, 806, 755, 688, 596. (Found: C, 51.40; H, 4.12; N, 6.04 C₂₀H₂₀N₂O₂Pd·0.5CHCl₃ requires C, 50.60; H, 4.21; N, 5.76%).

Di-(2-allyliminomethyl-4-diethylaminophenolato)palladium(II) (2). To a MeOH (10 mL) solution of Pd(OAc)₂ (0.20 g, 0.89 mmol) was added 2-allyliminomethyl-4-diethylaminophenol (0.45 g, 1.94 mmol). The mixture was stirred at room temperature for 5 h at which point a precipitate was collected by suction filtration to afford **2** (0.37 g, 73%) as a yellow-brown solid. Mp 178 °C (decomposition). Spectroscopic NMR data (in CDCl₃): ¹H δ: 7.35 (s, 2H, N=CH), 6.97 (d, *J* = 8 Hz, 2H, Ar), 6.15-6.01 (ov m, 6H, Ar & CH=CH₂), 5.23 (d of d, *J* = 17, 1 Hz, 2H, CH=CHH), 5.09 (d of d, *J* = 10, 1 Hz, 2H, CH=CHH), 4.26 (d, *J* = 6 Hz, 4H, CH₂CH=CH₂), 3.32 (q, *J* = 7 Hz, 8H, CH₂CH₃), 1.15 (t, *J* = 7 Hz, 12H, CH₂CH₃); ¹³C{¹H} δ: 165.9, 160.2, 152.9, 137.5, 135.4, 115.7, 111.4, 102.2, 98.9, 58.6, 44.4, 12.9. IR (nujol): 2931, 2908, 2854, 1594, 1506, 1458, 1421, 1377, 1311, 1247, 1226, 1132, 919, 813, 789, 715, 615. (Found: C, 56.35; H, 5.89; N, 9.43 C₂₈H₃₈N₄O₂Pd·C₂H₄O₂ requires C, 57.27; H, 6.74; N, 8.91%).

Di-(2-allyliminomethyl-3,5-di-*tert*-butylphenolato)palladium(II) (3). To a MeOH (10 mL) solution of Pd(OAc)₂ (0.12 g, 0.53 mmol) was added 2-allyliminomethyl-3,5-di-*tert*-butylphenol (0.30 g, 1.10 mmol). The mixture was stirred at room temperature and after 5 h a precipitate was collected by suction filtration. The product was extracted with Et₂O (3 × 10 mL) and the solvent removed under vacuum to afford **3** (0.21 g, 62%) as a yellow-brown solid. Mp 166-168 °C (decomposition). Spectroscopic NMR data (in CDCl₃): ¹H δ: 7.51 (s, 2H, N=CH), 7.33 (d, *J* = 2 Hz, 2H, Ar), 6.95 (d, *J* = 2 Hz, 2H, Ar), 6.19 (d of d of t, *J* = 17, 10, 6 Hz, 2H, CH=CH₂), 5.43 (d of d, *J* = 17, 1 Hz, 2H, CH=CHH), 5.28 (d of d, *J* = 10, 1 Hz, 2H, CH=CHH), 4.54 (d, *J* = 6 Hz, 4H, CH₂CH=CH₂), 1.36 (s, 18H, ^tBu), 1.22 (s, 18H, ^tBu); ¹³C{¹H} δ: 163.6, 162.3, 138.8, 136.4, 136.0, 129.9, 128.1, 121.2, 117.6, 60.1, 35.4, 33.8, 31.4, 29.4. IR (nujol): 2922, 2858, 1595, 1533, 1460, 1412, 1377, 1321, 1257, 1200, 1165, 1039, 1001, 920, 837, 779, 723, 625, 552, 503. (Found: C, 65.93; H, 8.11; N, 4.15 C₃₆H₅₂N₂O₂Pd requires C, 66.38; H, 8.06; N, 4.30%).

Di-(2-[(4-vinylphenylimino)methyl]phenolato)palladium(II) (4). To a MeOH (10 mL) solution of Na₂PdCl₄ (0.41 g, 1.41 mmol) was added 2-[(4-vinylphenylimino)methyl]phenol (0.65 g, 2.91 mmol) and NEt₃ (1.0 mL) and the mixture was heated at reflux for 2 h. Upon cooling to room temperature, a yellow precipitate was collected by suction filtration and then recrystallized from toluene (5 mL) to afford **4** (0.60 g, 77%) as an orange-yellow solid. Mp 170 °C (decomposition). Spectroscopic NMR data (in CDCl₃): ¹H δ: 7.71 (s, 2H, N=CH), 7.45 (d, *J* = 8 Hz, 4H, Ar), 7.28 (d, *J* = 8 Hz, 4H, Ar), 7.16-7.09 (ov m, 4H, Ar), 6.78 (d of d, *J* = 18, 10 Hz, 2H, CH=CH₂), 6.50 (t, *J* = 8 Hz, 2H, Ar), 6.14 (d, *J* = 8 Hz, 2H, Ar), 5.80 (d, *J* = 18 Hz, 2H, CH=CHH), 5.30 (d, *J*

= 10 Hz, 2H, CH=CHH); ¹³C{¹H} δ: 165.2, 162.7, 149.1, 136.4, 136.0, 135.4, 134.5, 126.0, 124.9, 120.8, 120.3, 115.3, 114.0. IR (nujol): 2917, 2864, 2723, 1608, 1597, 1535, 1461, 1377, 1342, 1309, 1176, 1149, 1126, 1030, 979, 904, 847, 756, 615, 551. (Found: C, 64.98; H, 4.21; N, 4.84 C₃₀H₂₄N₂O₂Pd requires C, 65.39; H, 4.40; N, 5.09%).

Bis-(4-diethylamino-2-[(4-vinylphenylimino)methyl]phenolato)palladium(II) (5). To an EtOH (5 mL) solution of Pd(OAc)₂ (0.08 g, 0.36 mmol) was added 4-diethylamino-2-[(4-vinylphenylimino)methyl]phenol (0.23 g, 0.78 mmol). The mixture was allowed to stir at room temperature for 5 h, at which point a precipitate was collected by suction filtration to afford **5** (0.14 g, 56%) as a yellow-brown solid. Mp 246 °C (decomposition). Spectroscopic NMR data (in CDCl₃): ¹H δ: 7.43 (s, 2H, N=CH), 7.40 (d, *J* = 8 Hz, 4H, Ar), 7.28 (d, *J* = 8 Hz, 4H, Ar), 6.93 (d, *J* = 8 Hz, 2H, Ar), 6.73 (d of d, *J* = 18, 10 Hz, 2H, CH=CH₂), 5.96 (d of d, *J* = 8, 2 Hz, 2H, Ar), 5.73 (d, *J* = 18 Hz, 2H, CH=CHH), 5.25 (d, *J* = 2 Hz, 2H, Ar), 5.21 (d, *J* = 10 Hz, 2H, CH=CHH), 3.20 (q, *J* = 6 Hz, 8H, CH₂CH₃), 1.07 (t, *J* = 6 Hz, 12H, CH₂CH₃); ¹³C{¹H} δ: 166.3, 159.2, 153.2, 150.1, 136.7, 135.8, 134.8, 125.7, 125.5, 112.9, 111.8, 102.8, 99.0, 44.5, 12.8. IR (nujol): 2921, 2856, 1604, 1574, 1460, 1377, 1350, 1317, 1261, 1238, 1187, 1140, 1078, 1001, 954, 910, 850, 827, 775, 725, 698, 617, 511. (Found: C, 63.28; H, 5.66; N, 7.74 C₃₈H₄₂N₄O₂Pd·C₂H₄O₂ requires C, 63.77; H, 6.17; N, 8.08%).

Bis-(3,5-di-*tert*-butyl-2-[(4-vinylphenylimino)methyl]phenolato)palladium(II) (6). To an EtOH (5 mL) solution of Pd(OAc)₂ (0.12 g, 0.53 mmol) was added 3,5-di-*tert*-butyl-2-[(4-vinylphenylimino)methyl]phenol (0.36 g, 1.07 mmol). The mixture was allowed to stir at room temperature for 6 h, at which point a precipitate was collected by suction filtration and the product was extracted with Et₂O (3 × 10 mL). Removal of the Et₂O under vacuum afforded **6** (0.24 g, 58%) as a red solid. Mp 186 °C (decomposition). Spectroscopic NMR data (in CDCl₃): ¹H δ: 7.93 (d, *J* = 8 Hz, 4H, Ar), 7.56 (s, 2H, N=CH), 7.44 (d, *J* = 8 Hz, 4H, Ar), 7.19 (d, *J* = 2 Hz, 2H, Ar), 6.91 (d, *J* = 2 Hz, 2H, Ar), 6.72 (d of d, *J* = 18, 10 Hz, 2H, CH=CH₂), 5.73 (d, *J* = 18 Hz, 2H, CH=CHH), 5.25 (d, *J* = 10 Hz, 2H, CH=CHH), 1.19 (s, 18H, ^tBu), 0.77 (s, 18H, ^tBu); ¹³C{¹H} δ: 163.8, 163.7, 150.8, 139.9, 137.0, 136.5, 136.2, 130.6, 128.0, 126.8, 125.0, 121.7, 114.0, 34.8, 33.8, 31.3, 28.8. IR (nujol): 2931, 2904, 2856, 1612, 1592, 1527, 1502, 1462, 1377, 1309, 1255, 1193, 1167, 1136, 987, 962, 906, 871, 843, 781, 740, 634, 526, 489. (Found: C, 70.76; H, 7.13; N, 3.51 C₄₆H₅₆N₂O₂Pd requires C, 71.24; H, 7.29; N, 3.61%).

X-ray Crystallography. Crystals of **1** and **4** were grown from saturated CH₂Cl₂ solutions 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 were collected on a Bruker AXS P4/SMART 1000 diffractometer using ω and θ scans with a scan width of 0.3° and 10 s exposure times. The detector distance was 5 cm. The data were reduced¹⁵ and corrected for absorption.¹⁶ The structure was solved by direct methods and refined by full-

matrix least squares on F^2 .¹⁷ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in Fourier difference maps and refined isotropically. A residual peak of $2.837 \text{ e}\text{\AA}^{-3}$ is observed in complex **4**, arising from the fact that the crystals were twinned and only the major component could be used for structure refinement. To minimize effects arising from the second component, the data was collected at 6 cm to maximize peak separation.

Results and Discussion

As part of our ongoing research into making novel metal complexes containing aminoboron ligands,¹⁸ we decided to prepare a number of metal complexes containing pendant unsaturated allyl and vinyl fragments. Our initial investigations have been directed at making diamagnetic palladium (II) complexes owing to their ease of synthesis¹⁹ and known biological activities. For instance, related Pd(II) benzoyl-benzylideneamine derivatives display high antitumor activity towards certain forms of cancer.²⁰

Addition of allylamine to salicylaldehydes gives compounds having NMR and FT-IR spectroscopic data consistent with the corresponding salicylaldimines. For example, for the parent salicylaldehyde compound a singlet at δ 8.33 ppm is observed in the ^1H NMR spectra for the imine methine peak and the diagnostic C=N stretching band is found in the FT-IR spectra at 1620 cm^{-1} .²¹⁻²³ Subsequent reaction of these salicylaldimines with $\text{Pd}(\text{OAc})_2$ or Na_2PdCl_4 afforded square planar bis(*N*-allylsalicylaldiminato)palladium(II) complexes **1-3** (Figure 1) in moderate yields (62-73%). Complexes **1-3** 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 upon coordination of the ligand to the metal centre. For instance, the singlet at δ 8.33 ppm for the free ligand derived from salicylaldehyde and allylamine shifts to 7.64 ppm in complex **1**. Most notable, however, is the absence of the broad OH stretch in the FT-IR spectra when the ligands are coordinated to palladium. The C=N stretch is still observed but is now found at 1595 cm^{-1} in the metal complexes.

Complex **1** has also been characterized by an X-ray diffraction study (Figure 2). Crystallographic data are pre-

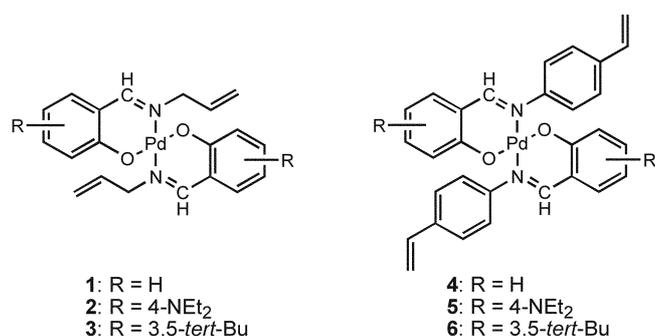


Figure 1. Palladium Schiff base complexes derived from allylamine and vinylaniline.

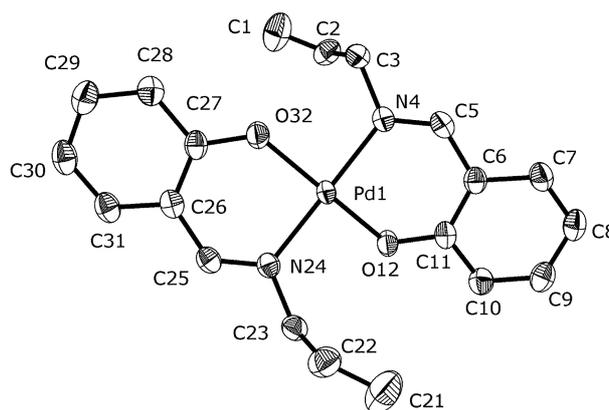


Figure 2. A view of complex **1**, with displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted.

Table 1. Crystallographic data collection parameters for **1** and **4**

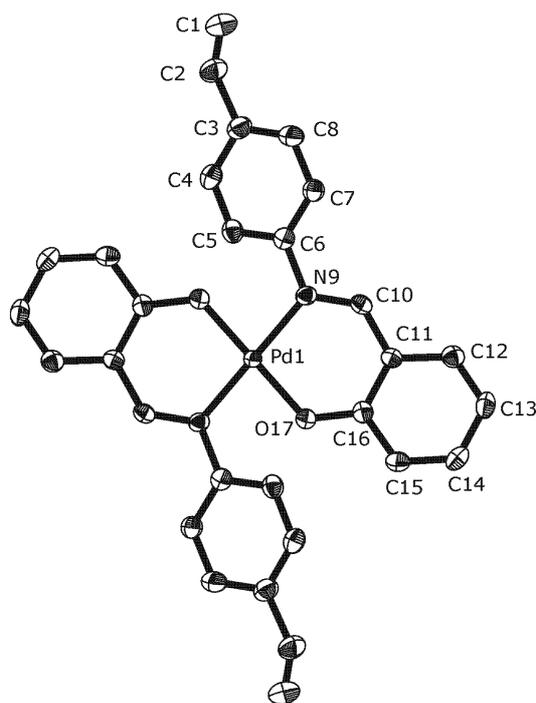
Complex	1	4
Formula	$\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_2\text{Pd}$	$\text{C}_{30}\text{H}_{24}\text{N}_2\text{O}_2\text{Pd}$
fw	426.78	550.91
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
<i>a</i> , Å	14.0005(9)	13.7710(14)
<i>b</i> , Å	7.2964(5)	11.0348(11)
<i>c</i> , Å	17.5103(12)	7.8192(8)
<i>b</i> , deg	100.189(1)	98.817(2)
<i>V</i> , Å ³	1760.5(2)	1174.2(2)
<i>Z</i>	4	2
ρ_{calcd} , mg m ⁻³	1.610	1.558
Crystal size, mm ³	0.125 × 0.275 × 0.4	0.025 × 0.125 × 0.35
Temperature, K	198(1)	198(1)
Radiation	MoK α ($\lambda = 0.71073$)	MoK α ($\lambda = 0.71073$)
μ , mm ⁻¹	1.069	0.822
Total reflections	8769	5736
Total unique reflections	3017	1978
No. of variables	306	208
R_{int}	0.0192	0.0279
Theta range, deg	1.72 to 25.00	2.38 to 24.99
Largest difference peak/hole, e Å ⁻³	0.536/-0.251	2.837/-0.584
<i>S</i> (GoF) on F^2	1.035	1.080
$R1^a$ ($I > 2\sigma(I)$)	0.0191	0.0367
$wR2^b$ (all data)	0.0547	0.1108

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR2 = (\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^4)])^{1/2}$, where $w = 1 / [\sigma^2(F_o^2) + (0.0352 * P)^2 + (0.3338 * P)]$ (**1**) and $w = 1 / [\sigma^2(F_o^2) + (0.0757 * P)^2 + (1.0088 * P)]$ (**4**), where $P = (\max(F_o^2, 0) + 2 * F_c^2) / 3$.

sented in Table 1 and selected bond distances and angles are given in Table 2. The palladium atom assumes a slightly distorted square planar configuration with *trans* bis(salicylaldiminato) groups. The Pd-O distances of 1.979(1) and 1.982(1) Å and the Pd-N bond lengths of 2.013(1) and 2.015(1) Å are similar to those seen in related complexes.²⁴⁻²⁷ For instance, distances of 1.966(8) and 2.067(10) Å for the Pd-O and Pd-N bonds, respectively, are found in a related bis-salicylideneaminato palladium complex derived from 2-hydroxy-4-(*n*-hexyloxy)benzaldehyde and 4-*n*-hexylani-

Table 2. Selected bond distances (Å) and angles (°) for **1**

Pd(1)-O(12)	1.979(1)
Pd(1)-O(32)	1.982(1)
Pd(1)-N(24)	2.013(1)
Pd(1)-N(4)	2.015(1)
C(1)-C(2)	1.288(3)
C(21)-C(22)	1.284(3)
N(4)-C(5)	1.285(2)
N(24)-C(25)	1.283(2)
O(12)-Pd(1)-O(32)	179.77(4)
O(12)-Pd(1)-N(24)	88.60(5)
O(32)-Pd(1)-N(24)	91.49(5)
O(12)-Pd(1)-N(4)	91.41(5)
O(32)-Pd(1)-N(4)	88.50(5)
N(24)-Pd(1)-N(4)	179.46(5)
C(1)-C(2)-C(3)	124.4(2)
C(21)-C(22)-C(23)	124.9(2)
N(4)-C(3)-C(2)	111.66(15)
N(24)-C(23)-C(22)	112.15(15)
C(5)-N(4)-C(3)	117.59(15)
C(25)-N(24)-C(23)	117.55(15)
C(5)-N(4)-Pd(1)	122.73(12)
C(25)-N(24)-Pd(1)	122.71(12)
C(3)-N(4)-Pd(1)	119.69(10)
C(23)-N(24)-Pd(1)	119.73(11)
N(4)-C(5)-C(6)	127.05(17)
N(24)-C(25)-C(26)	127.09(16)

**Figure 3.** A view of complex **4**, with displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted.

line.²⁶ The C=C distances in **1** are ave = 1.286(3) Å, are well within the range expected for double bonds found in allyl derivatives. The C=N bond distances are ave = 1.284(2) Å, which are consistent with a slight elongation of the C-N double bond when coordinated to a late metal center.²⁵ The allyl groups are approximately centrosymmetric to one another but no significant interaction with a metal center is observed, thereby allowing access for further functionalization to the corresponding boronate esters *via* a subsequent hydroboration reaction.

Similar reactivity is observed in reactions of salicylaldehydes with 4-vinylaniline and the corresponding palladium(II) complexes **4-6** (Figure 1) have been prepared, using the methodology described above, in moderate yields (56-77%). The vinyl peaks for **4** are at 6.78, 5.80, and 5.30 ppm in the ¹H NMR spectra, and at *ca.* 136.4 and 115.3 in the ¹³C NMR spectra, both of which indicate that the vinyl group is not coordinated to a palladium atom.²⁸ Indeed, this observation has been confirmed by carrying out an X-ray diffraction study on **4** (Figure 3). Crystallographic data are presented in Table 1 and selected bond distances and angles are given in Table 3. The molecule is centrosymmetric with the palladium atom assuming a slightly distorted square planar configuration with *trans* bis(salicylaldiminato) groups. The Pd-O distance of 1.987(2) Å and the Pd-N bond length of 2.033(3) Å are similar to those for the allyl complex **1**. The vinyl groups have a C-C bond length of 1.304(6) Å, once again consistent with a double bond. The aromatic ring of the vinylaniline moiety is not coplanar with the O-Pd-N plane and forms a tetrahedral angle of 27.1°. Styryl compounds **4-6** are the first examples, to the best of our knowledge, of Schiff base metal complexes derived from 4-vinylaniline. Similar vanadyl salen complexes containing vinylbiphenyl groups have recently been prepared and anchored to single-wall carbon nanotubes for the hetero-

Table 3. Selected bond distances (Å) and angles (°) for **4**

Pd(1)-O(17)	1.987(2)
Pd(1)-N(9)	2.033(3)
C(1)-C(2)	1.304(6)
C(2)-C(3)	1.475(5)
C(6)-N(9)	1.435(4)
N(9)-C(10)	1.292(4)
C(16)-O(17)	1.315(5)
O(17)-Pd(1)-N(9)	90.74(10)
C(1)-C(2)-C(3)	126.5(4)
C(7)-C(6)-C(5)	119.6(3)
C(7)-C(6)-N(9)	120.9(3)
C(5)-C(6)-N(9)	119.5(3)
C(8)-C(7)-C(6)	119.6(3)
C(10)-N(9)-C(6)	118.1(3)
C(10)-N(9)-Pd(1)	121.7(2)
C(6)-N(9)-Pd(1)	120.1(2)
N(9)-C(10)-C(11)	126.7(3)
C(16)-O(17)-Pd(1)	120.5(2)

geneous catalytic cyanosilylation of aldehydes.²⁹ As no appreciable intramolecular or intermolecular interaction is observed with the vinyl groups and the palladium atom in **4**, or with the allyl group in **1**, hydroboration of these unsaturated fragments will be examined in an effort to generate novel boron-containing metal complexes. Unfortunately, initial attempts to affect the hydroboration of these palladium complexes containing pendent C=C double bonds with catecholborane (1,3,2-benzodioxaborole) proved unsuccessful and resulted in degradation of the starting metal complex. We are in the process of examining this reaction in more detail with other hydroborating agents, in an effort to make the corresponding palladium boronate ester complexes, and will report our results in due course.

Conclusions

In summary, we have prepared a number of *trans* Schiff base palladium(II) complexes derived from allylamine and vinylaniline. The resulting complexes assume a square planar configuration where the unsaturated groups do not show any appreciable interaction with a metal center. We are examining the hydroboration of **1-6** in an attempt to make metal complexes containing air stable boronic acids and boronate esters.

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Supplementary material. Crystallographic data for the structural analysis of **1** and **4** have been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 233296 and 233297. Copies of this information may be obtained free of charge from: The director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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