Synthesis and reactivity of novel Schiff bases containing boronate esters

David W. Norman, Janet P. Edwards, Christopher M. Vogels, Andreas Decken, and Stephen A. Westcott

Abstract: Condensation of 2-aminophenol with boronate ester derivatives of benzaldehyde afforded the corresponding boron-containing Schiff bases, 2-$HOC_6H_4N{=}C(H)C_6H_4R$ (**1a**: R = 2-Bpin; **1b**: R = 3-Bpin; **1c**: R = 4-Bpin; pin = 1,2-$O_2C_2Me_4$). Crystals of **1b** were triclinic, space group $P\bar{1}$, a = 11.9420(6), b = 13.0871(7), and c = 13.2720(7) Å, α = 70.983(1), β = 67.793(1), and γ = 78.380(1)°, Z = 2. Reaction of 2-aminophenol with 2-$HC(O)C_6H_4B(OH)_2$ in EtOH, however, gave a macrocyclic dimer **2** with a OBOBO structural unit. The molecular structure of this dimer has been confirmed by an X-ray diffraction study. Crystals of **2** were monoclinic, space group $P2_1/c$, a = 10.0447(8), b = 21.0894(15), and c = 12.6214(9) Å, β = 105.301(2)°, Z = 4. Further reaction of these Schiff bases with manganese triacetate in toluene afforded 2-arylbenzoxazoles **3a**–**c** via an oxidative cyclization pathway. The molecular structure of the 4-Bpin derivative (**3c**) was characterized by an X-ray diffraction study. Crystals of **3c** were monoclinic, space group $P2_1/n$, a = 6.5392(3), b = 16.3330(8), and c = 16.1942(8) Å, β = 97.9620(10)°, Z = 4.

Key words: boron heterocycles, Schiff bases, arylbenzoxazoles.

Résumé : La condensation du 2-aminophénol avec des dérivés boronates de benzaldéhyde conduit à la formation des bases de Schiff correspondantes contenant du bore, 2-$HOC_6H_4N{=}C(H)C_6H_4R$ (**1a**: R = 2-Bpin; **1b**: R = 3-Bpin; **1c**: R = 4-Bpin; pin = 1,2-$O_2C_2Me_4$). Les cristaux du composé **1b** sont tricliniques, groupe d'espace $P\bar{1}$, avec a = 11,9420(6), b = 13,0871(7) et c = 13,2720(7) Å, α = 70,983(1), β = 67,793(1) et γ = 78,380(1)° et Z = 2. La réaction du 2-aminophénol avec le 2-$HC(O)C_6H_4B(OH)_2$ dans l'éthanol conduit toutefois à la formation du dimère macrocyclique **2** qui comporte une unité structurale OBOBO. La structure moléculaire de ce dimère a été confirmée par diffraction des rayons X. Les cristaux du composé **2** sont monocliniques, groupe d'espace $P2_1/c$, avec a = 10,0447(8), b = 21,0894(15) et c = 12,6214(9) Å, β = 105,301(2)° et Z = 4. Des réactions subséquentes de ces bases de Schiff avec du triacétate de manganèse dans le toluène conduisent à la formation des 2-arylbenzoxaoles (**3a**–**c**) par le biais d'une voie réactionnelle de cyclisation oxydante. La structure moléculaire du dérivé 4-Bpin (**3c**) a été caractérisée par diffraction des rayons X. Les cristaux du composé **3c** sont monocliniques, groupe d'espace $P2_1/n$, avec a = 6,5392(3), b = 16,3330(8) et c = 16,1942(8) Å, β = 97,9620(10)° et Z = 4.

Mots clés : hétérocycles du bore, bases de Schiff, arylbenzoxazoles.

[Traduit par la Rédaction]

Introduction

Compounds containing boronic acids [$RB(OH)_2$] or boronate esters [$RB(OR')_2$] have been used extensively as synthons in the Suzuki–Miyaura cross-coupling reaction for a variety of applications (1–11). Interest in these compounds also arises from their potent biological activities (12–21). For instance, aminoboronic acids are among the most potent inhibitors of serine proteases, a diverse group of proteolytic enzymes responsible for the generation of most disease processes (13–18). The synthesis of aminoboronic acid-containing compounds, however, is often a complicated procedure requiring several complex organic transformations (1, 7). As a result, the range of compounds containing boronic acids is surprisingly small. As part of our investigation into generating novel aminoboron compounds (22–24), we decided to examine the synthesis and reactivity of Schiff bases derived from 2-aminophenol and benzaldehydes containing boronate esters. Results of our study are presented herein.

Results and discussion

Schiff bases are important intermediates in organic chemistry and have been used to prepare a number of pharmaco-

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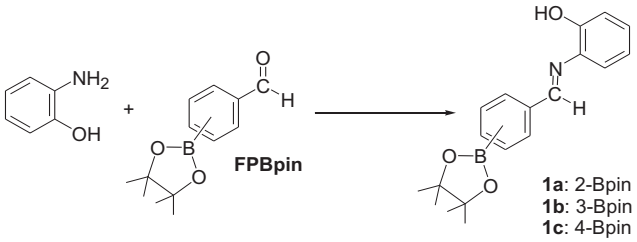
Table 1. Crystallographic data collection parameters for **1b**, **2**, and **3c**.

	1b	**2**	**3c**
Formula	$C_{38}H_{44}B_2N_2O_6$	$C_{26}H_{18}B_2N_2O_3 \cdot 1.5CH_2Cl_2$	$C_{19}H_{20}BNO_3$
FW	646.37	555.43	321.17
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a (Å)	11.9420(6)	10.0447(8)	6.5392(3)
b (Å)	13.0871(7)	21.0894(15)	16.3330(8)
c (Å)	13.2720(7)	12.6214(9)	16.1942(8)
α (°)	70.983(1)	90	90
β (°)	67.793(1)	105.301(2)	97.9620(10)
γ (°)	78.380(1)	90	90
V (Å^3)	1808.29(16)	2578.9(3)	1712.94(14)
Z	2	4	4
ρ_{calcd} (g cm^{-3})	1.187	1.431	1.245
Crystal size (mm^3)	0.40 × 0.35 × 0.20	0.30 × 0.30 × 0.35	0.18 × 0.23 × 0.55
T (K)	173(1)	173(1)	173(1)
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
μ (mm^{-1})	0.079	0.390	0.083
Total reflections[a]	19912	28199	18770
Total unique relections	12584	9224	6156
$I > 4\sigma(F)$	8560	7072	4173
No. of variables	521	432	302
R_{int}	0.0152	0.0211	0.0304
Theta range (°)	1.65–32.50	1.93–32.50	1.78–32.50
Largest difference peak/hole (e Å^{-3})	0.451/–0.281	0.715/–0.646	0.346/–0.137
S (GoF) on F^2 [a]	1.038	1.132	0.966
R_1 ($I > 2\sigma(I)$)[b]	0.0573	0.0.527	0.0488
wR_2 (all data)[c]	0.1736	0.1725	0.1379

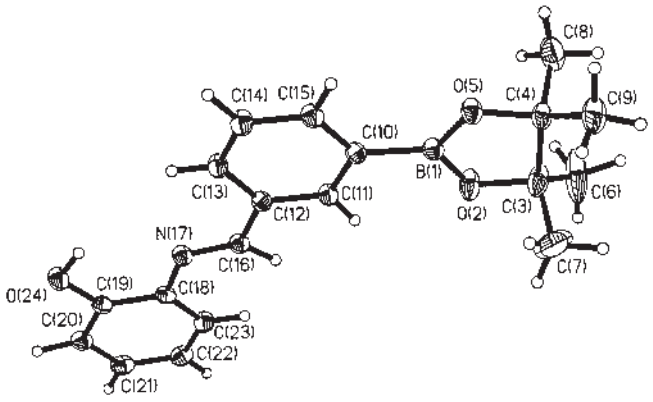
[a] $S = (\Sigma[w(F_o^2 - F_c^2)^2/(n-p))^{1/2}$.
[b] $R_1 = \Sigma||(F_o| - |F_c||/\Sigma|F_o|$.
[c] $wR_2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4)^{1/2}$, where $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = (\max(F_o^2, 0) + 2F_c^2)/3$. For **1b**, $a = 0.1068$, $b = 0$; for **2**, $a = 0.1088$, $b = 0.0676$; for **3c**, $a = 0.0859$, $b = 0$.

Scheme 1.



logically important compounds (29–34). For instance, Whiting and co-workers (29) have recently used imines containing boronate esters to make enantio-enriched γ-phenyl-γ-amino alcohols. In this study, we found that pinacol-protected derivatives of formylphenylboronic acid [(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (FPBpin)] add to 2-aminophenol in organic solvents to give crystalline compounds having spectroscopic data consistent with the Schiff bases **1a**–**c** (Scheme 1). As expected, a shift for the methine proton from 10 to 9 ppm is observed in the ^{1}H NMR spectra and a resonance at ca. 160 ppm in the ^{13}C NMR spectra corresponds to the N=CH carbon (25). Likewise, formation of these compounds can be monitored by the diagnostic C=N stretching band in the IR spectra at ca. 1620 cm^{-1} (31). Interestingly, a broad peak at around

Fig. 1. Molecular structure of **1b** with ellipsoids drawn at the 30% probability level. Hydrogen atoms were omitted for clarity.



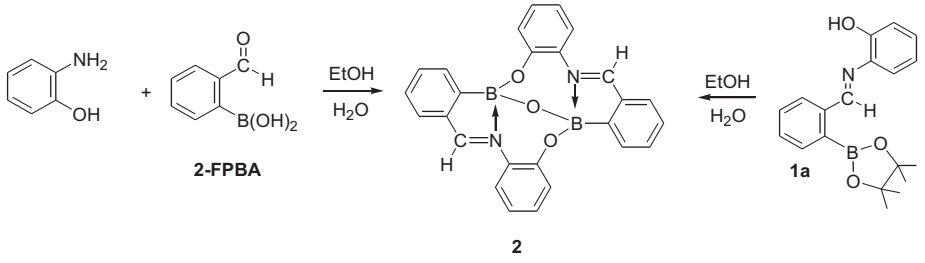
30 ppm in the ^{11}B NMR spectra indicates that the boron atom lies in a three-coordinate environment (35), even for the 2-Bpin derivative **1a**. This result is somewhat surprising in light of boron's propensity to form coordinative N→B bonds (36).

Although attempts to grow crystals of **1a** suitable for X-ray diffraction studies proved unsuccessful, the molecular structure of the 3-Bpin derivative **1b** (Fig. 1) confirms that no appreciable intermolecular interactions exist between the

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

Bond lengths (Å)		Bond angles (°)	
Compound 1b			
Molecule A		*Molecule A*	
B(1)—O(2)	1.3614(15)	O(2)-B(1)-O(5)	113.52(10)
B(1)—O(5)	1.3653(14)	O(2)-B(1)-C(10)	121.12(10)
B(1)—C(10)	1.5600(16)	O(5)-B(1)-C(10)	125.33(10)
C(12)—C(16)	1.4734(14)	N(17)-C(16)-C(12)	122.93(10)
C(16)—N(17)	1.2723(14)	C(16)-N(17)-C(18)	121.36(9)
N(17)—C(18)	1.4221(13)	O(24)-C(19)-C(20)	118.27(10)
C(19)—O(24)	1.3648(13)	O(24)-C(19)-C(18)	121.22(9)
Molecule B		C(21)-B(2)-N(8)	107.04(9)
B(31)—O(32)	1.3697(14)	B(2)-O(1)-B(1)	117.78(9)
B(31)—O(35)	1.3739(13)	C(10)-O(2)-B(2)	110.89(9)
B(31)—C(40)	1.5644(15)	C(30)-O(3)-B(1)	110.62(9)
C(42)—C(46)	1.4728(14)	C(9)-N(8)-B(2)	107.27(9)
C(46)—N(47)	1.2791(13)	C(29)-N(28)-B(1)	107.14(9)
N(47)—C(48)	1.4203(13)	*Molecule B*	
C(49)—O(54)	1.3675(14)	O(32)-B(31)-O(35)	113.35(9)
O(24)···H(39)	2.564	O(32)-B(31)-C(40)	120.54(9)
O(35)···H(24)	2.330	O(35)-B(31)-C(40)	126.10(9)
O(32)···H(21)	2.542	N(47)-C(46)-C(42)	123.45(10)
		C(46)-N(47)-C(48)	121.25(9)
Compound 2			
B(1)—O(1)	1.4194(16)	O(1)-B(1)-O(3)	110.67(9)
B(1)—O(3)	1.5075(15)	O(1)-B(1)-C(1)	120.21(10)
B(1)—C(1)	1.6493(18)	O(3)-B(1)-C(1)	108.79(10)
B(1)—N(28)	1.6544(15)	O(1)-B(1)-N(28)	108.44(9)
B(2)—O(1)	1.4154(16)	O(3)-B(1)-N(28)	99.42(8)
B(2)—O(2)	1.5162(15)	C(1)-B(1)-N(28)	107.24(9)
B(2)—C(21)	1.6476(17)	O(1)-B(2)-O(2)	111.14(9)
B(2)—N(8)	1.6581(16)	O(1)-B(2)-C(21)	119.63(10)
C(7)—N(8)	1.2958(15)	O(2)-B(2)-C(21)	109.36(9)
C(27)—N(28)	1.2976(15)	O(1)-B(2)-N(8)	108.67(9)
N(8)—C(9)	1.4196(15)	O(2)-B(2)-N(8)	98.89(8)
N(28)—C(29)	1.4226(15)		
C(7)—N(8)	1.2958(15)		

Scheme 2.



Lewis acidic boron atom and the imine nitrogen. Crystallographic data are given in Table 1[3], selected bond distances and angles shown in Table 2, and atomic coordinates are provided in Table 3. The imine C(16)—N(17) bond distances of 1.272(1) (molecule A) and 1.279(1) Å (molecule B) are comparable to azomethine compounds derived from salicylaldehyde and phenylboronic acid (31, 36). The B—O bond distances (av = 1.368(1) Å) are also typical for three-coordinate Bpin groups (25) and significantly shorter than those observed in chelate complexes with diphenylborinic

[3] Supplementary material may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada. For information on obtaining material electronically go to http://www.nrc.ca/cisti/irm/unpub_e.shtml. Crystallographic information has also been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge via 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 3. Atomic coordinates (1×10^4) and equivalent isotropic displacement parameters (Å^2, 1×10^3) for **1b**.

	x	*y*	*z*	U_{eq}
B(1)	7513(1)	8388(1)	1906(1)	33(1)
O(2)	6389(1)	8904(1)	1967(1)	54(1)
C(3)	6550(1)	10035(1)	1315(2)	59(1)
C(4)	7814(1)	10186(1)	1285(1)	38(1)
O(5)	8412(1)	9075(1)	1419(1)	38(1)
C(6)	5508(2)	10737(1)	1944(3)	121(1)
C(7)	6545(3)	10104(2)	142(2)	128(1)
C(8)	7787(2)	10526(1)	2297(2)	68(1)
C(9)	8574(1)	10934(1)	204(1)	58(1)
C(10)	7705(1)	7127(1)	2332(1)	31(1)
C(11)	6690(1)	6527(1)	2767(1)	32(1)
C(12)	6794(1)	5395(1)	3145(1)	30(1)
C(13)	7940(1)	4841(1)	3092(1)	38(1)
C(14)	8955(1)	5420(1)	2673(1)	43(1)
C(15)	8842(1)	6552(1)	2296(1)	36(1)
C(16)	5695(1)	4819(1)	3570(1)	32(1)
N(17)	5721(1)	3790(1)	3847(1)	33(1)
C(18)	4645(1)	3262(1)	4232(1)	30(1)
C(19)	4829(1)	2127(1)	4464(1)	31(1)
C(20)	3846(1)	1505(1)	4844(1)	37(1)
C(21)	2680(1)	2019(1)	5001(1)	40(1)
C(22)	2486(1)	3141(1)	4774(1)	41(1)
C(23)	3460(1)	3764(1)	4387(1)	38(1)
O(24)	5964(1)	1599(1)	4323(1)	41(1)
B(31)	–536(1)	2119(1)	4135(1)	30(1)
O(32)	–66(1)	1931(1)	4981(1)	46(1)
C(33)	–1100(1)	1903(2)	6028(1)	58(1)
C(34)	–2127(1)	1576(1)	5771(1)	38(1)
O(35)	–1764(1)	2027(1)	4528(1)	31(1)
C(36)	–748(2)	1077(3)	7001(1)	120(1)
C(37)	–1337(2)	3050(2)	6157(2)	97(1)
C(38)	–2138(1)	355(1)	6003(1)	61(1)
C(39)	–3395(1)	2074(1)	6330(1)	49(1)
C(40)	299(1)	2426(1)	2865(1)	29(1)
C(41)	1498(1)	2642(1)	2605(1)	31(1)
C(42)	2304(1)	2928(1)	1492(1)	30(1)
C(43)	1900(1)	2997(1)	605(1)	41(1)
C(44)	718(1)	2790(1)	842(1)	48(1)
C(45)	–82(1)	2512(1)	1960(1)	38(1)
C(46)	3528(1)	3174(1)	1310(1)	32(1)
N(47)	4348(1)	3417(1)	333(1)	32(1)
C(48)	5509(1)	3665(1)	201(1)	29(1)
C(49)	6313(1)	3879(1)	–927(1)	34(1)
C(50)	7492(1)	4142(1)	–1203(1)	40(1)
C(51)	7872(1)	4189(1)	–351(1)	41(1)
C(52)	7085(1)	3992(1)	763(1)	41(1)
C(53)	5909(1)	3732(1)	1039(1)	36(1)
O(54)	5925(1)	3833(1)	–1756(1)	51(1)

Note: U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

acid (ca. 1.5 Å), where the boron atom is four coordinate (37).

Compounds **1b** and **1c** could also be prepared in ethanol using a catalytic amount of formic acid. However, we found that reactions of 2-FPBpin with 2-aminophenol in ethanol containing adventitious water gave the novel Schiff base dimer **2** as the only new boron-containing product. It is possible that the formation of **2** proceeds via initial cleavage of the pinacol groups in 2-FBpin to give 2-formylphenylboronic acid. We found that the reaction of this aldehyde with 2-aminophenol in wet ethanol does indeed give condensation product **2** (Scheme 2). Another possible route to this

Table 4. Atomic coordinates (1×10^4) and equivalent isotropic displacement parameters (Å^2, 1×10^3) for **2**.

	x	*y*	*z*	U_{eq}
B(1)	9593(1)	1517(1)	9052(1)	19(1)
B(2)	7404(1)	1500(1)	9527(1)	19(1)
O(1)	8796(1)	1702(1)	9776(1)	20(1)
O(2)	6647(1)	1812(1)	10282(1)	22(1)
O(3)	11096(1)	1669(1)	9538(1)	24(1)
C(1)	9466(1)	790(1)	8550(1)	20(1)
C(2)	10229(2)	666(1)	7778(1)	27(1)
C(3)	10353(2)	61(1)	7355(1)	32(1)
C(4)	9737(2)	–461(1)	7723(1)	31(1)
C(5)	8986(1)	–364(1)	8486(1)	25(1)
C(6)	8809(1)	255(1)	8879(1)	20(1)
C(7)	7956(1)	263(1)	9655(1)	21(1)
N(8)	7362(1)	756(1)	9939(1)	19(1)
C(9)	6546(1)	744(1)	10702(1)	20(1)
C(10)	6152(1)	1370(1)	10859(1)	21(1)
C(11)	5304(1)	1491(1)	11555(1)	25(1)
C(12)	4868(2)	975(1)	12076(1)	30(1)
C(13)	5265(2)	351(1)	11916(1)	31(1)
C(14)	6122(1)	229(1)	11230(1)	26(1)
C(21)	6440(1)	1536(1)	8251(1)	19(1)
C(22)	5095(1)	1294(1)	8075(1)	24(1)
C(23)	4121(1)	1301(1)	7049(1)	29(1)
C(24)	4456(1)	1570(1)	6145(1)	29(1)
C(25)	5761(1)	1835(1)	6284(1)	25(1)
C(26)	6761(1)	1818(1)	7318(1)	20(1)
C(27)	8068(1)	2119(1)	7308(1)	20(1)
N(28)	9256(1)	2010(1)	7995(1)	19(1)
C(29)	10526(1)	2302(1)	7973(1)	20(1)
C(30)	11552(1)	2078(1)	8887(1)	21(1)
C(31)	12920(1)	2278(1)	9048(1)	25(1)
C(32)	13221(1)	2692(1)	8273(1)	28(1)
C(33)	12192(1)	2907(1)	7359(1)	27(1)
C(34)	10815(1)	2717(1)	7200(1)	23(1)
C(35)	9221(2)	1628(1)	5013(2)	53(1)
Cl(1)	7883(1)	1469(1)	3830(1)	59(1)
Cl(2)	10769(1)	1232(1)	4970(1)	70(1)
C(36)	5563(7)	236(3)	4741(4)	68(1)
Cl(3)	6687(2)	6(1)	5931(1)	86(1)
Cl(4)	3872(2)	–2(1)	4638(2)	112(1)

Note: U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Fig. 2. Molecular structure of **2** with ellipsoids drawn at the 30% probability level. Hydrogen atoms were omitted for clarity.

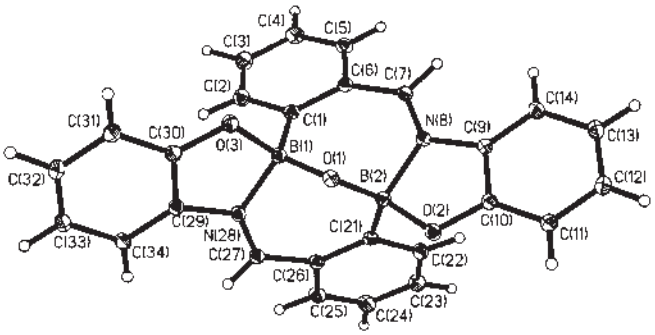
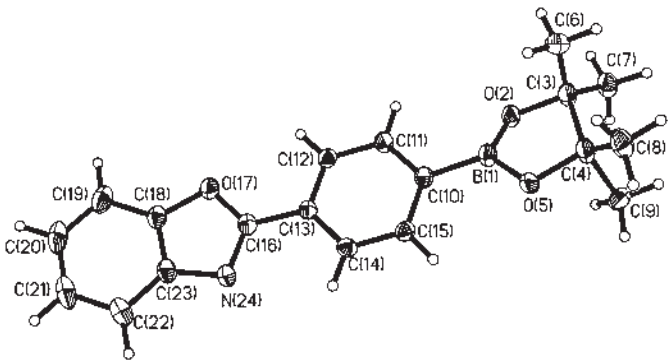
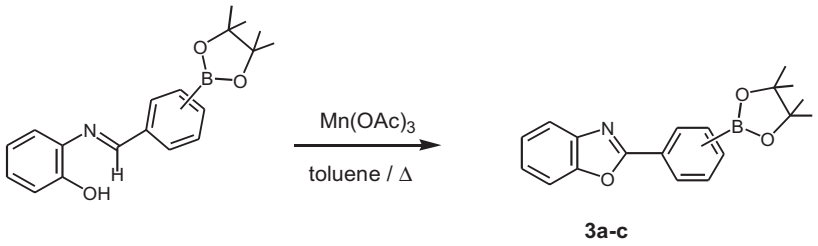


Fig. 3. Molecular structure of **3c** with ellipsoids drawn at the 30% probability level. Hydrogen atoms were omitted for clarity.



Scheme 3.



Scheme 4.

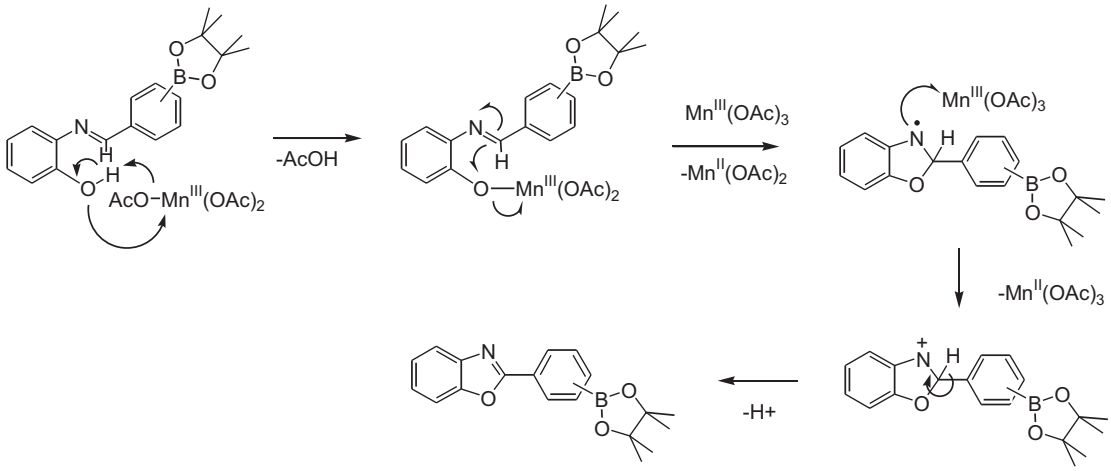


Table 5. Selected bond lengths (Å) and angles (°) for **3c**.

Bond lengths (Å)	
B(1)—O(2)	1.3366(15)
B(1)—O(5)	1.3430(12)
B(1)—O(2A)	1.4681(19)
B(1)—C(10)	1.5635(13)
C(16)—O(17)	1.3229(12)
C(16)—N(24)	1.3407(12)
O(17)—C(18)	1.4015(12)
C(23)—N(24)	1.3927(11)
Bond angles (°)	
O(2)-B(1)-O(5)	112.08(9)
O(2)-B(1)-O(2A)	33.74(8)
O(5)-B(1)-O(2A)	111.56(10)
O(2)-B(1)-C(10)	122.89(10)
O(5)-B(1)-C(10)	123.52(8)
O(2A)-B(1)-C(10)	120.81(10)
O(17)-C(16)-N(24)	115.88(8)
O(17)-C(16)-C(13)	122.50(8)
N(24)-C(16)-C(13)	121.45(8)

dimer involves initial formation of **1a** with subsequent cleavage of the pinacol group to give a boronic acid Schiff base. This transient imine could rapidly dehydrate to form **2**. Indeed, we observed that addition of ethanol to preformed **1a** gave bright yellow crystals of dimer **2**.

The molecular structure of **2** is shown in Fig. 2 and crystallographic data are given in Table 1. Selected bond distances and angles shown in Table 2, and atomic coordinates are provided in Table 4. The two fragments form seven-membered rings and are connected via a BOB bridge (B(1)-O(1)-B(2) = 117.8°) with average B—O bond distances of 1.417(2) Å. Interestingly, the two phenolic B—O distances are slightly longer (1.508(2) and 1.516(2) Å) than the bridged BOB bonds. Similar distances and angles have been reported for other BOB ring systems (38–47). The aldimine functionality in **2** is stabilized by N→B interactions with average B—N bonds of 1.651(2) Å. Similar bond distances have been reported in related oxime (48) and salen derivatives (49–51). The ^{11}B NMR spectra of **2** show a peak at 7 ppm, which also suggests that the boron atom remains four coordinate in solution (52). Although blue electroluminescence has been observed in similar organoboron compounds (40–42), this behavior is not observed for **2**.

As Schiff bases are ubiquitous in transition metal chemistry, we decided to investigate the use of these compounds as ligands for biologically active metals (such as Fe, Mo, Cu). Although initial attempts failed in this regard, we found that reaction of these Schiff bases gave the corresponding boron-containing benzoxazoles in varying yields (Scheme 3). Benzoxazoles are an important family of compounds that are found in a variety of natural products with potent biological activities (53–62). As a result, these compounds have attracted a considerable amount of attention for their medicinal and agrochemical uses.

Although the synthesis of benzoxazoles can be accomplished via a number of different methods, oxidative intramolecular cyclization of readily prepared phenolic Schiff bases provides a general route to these important organic compounds (62–67). Indeed, recent work by Varma et al. (61, 62) has shown that manganese triacetate can be used as a relatively benign oxidizing agent for reactions involving

Table 6. Atomic coordinates (1×10^4) and equivalent isotropic displacement parameters (Å^2, 1×10^3) for **3c**.

	x	*y*	*z*	U_{eq}
B(1)	4684(2)	7560(1)	5615(1)	39(1)
O(2)	2796(2)	7448(1)	5823(1)	41(1)
O(2A)	2680(2)	7151(1)	5408(1)	42(1)
C(3)	2719(2)	6560(1)	6103(1)	45(1)
C(4)	5067(2)	6415(1)	6430(1)	48(1)
O(5)	6087(1)	7064(1)	6043(1)	48(1)
C(6)	1977(4)	6059(2)	5430(2)	59(1)
C(6A)	1449(5)	5775(2)	5614(2)	55(1)
C(7)	1355(8)	6587(2)	6820(3)	51(1)
C(7A)	1484(10)	6850(3)	6717(4)	50(1)
C(8)	5904(4)	5605(1)	6373(2)	56(1)
C(8A)	5905(5)	5666(2)	5859(3)	64(1)
C(9)	5722(3)	6742(2)	7397(1)	52(1)
C(9A)	5542(5)	6212(2)	7268(2)	64(1)
C(10)	5264(1)	8316(1)	5102(1)	34(1)
C(11)	3740(1)	8722(1)	4557(1)	38(1)
C(12)	4243(1)	9349(1)	4039(1)	36(1)
C(13)	6303(1)	9574(1)	4053(1)	31(1)
C(14)	7843(1)	9195(1)	4612(1)	35(1)
C(15)	7320(2)	8572(1)	5129(1)	36(1)
C(16)	6870(2)	10180(1)	3454(1)	37(1)
N(17)	5523(1)	10475(1)	2841(1)	44(1)
O(17)	5523(1)	10475(1)	2841(1)	44(1)
C(18)	6730(2)	10960(1)	2383(1)	43(1)
C(19)	6175(3)	11395(1)	1648(1)	63(1)
C(20)	7762(3)	11795(1)	1327(1)	70(1)
C(21)	9782(3)	11766(1)	1716(1)	67(1)
C(22)	10355(2)	11333(1)	2450(1)	57(1)
C(23)	8756(2)	10932(1)	2769(1)	41(1)
N(24)	8831(1)	10424(1)	3463(1)	39(1)
O(24)	8831(1)	10424(1)	3463(1)	39(1)

Note: U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

sensitive functional groups. We found that $Mn(OAc)_3$ can also be used with **1a**–**c** to give the corresponding boron-containing benzoxazoles **3a**–**c** in low to moderate yield. A proposed mechanism for the manganese promoted intramolecular cyclization of Schiff bases **1a**–**c** is shown in Scheme 4 (61, 62). An alternate mechanism exists whereby initial coordination of the Schiff base to the metal centre occurs via the imine nitrogen atom followed by nucleophilic attack of the oxygen atom to the imine carbon. The formation of these heterocycles can be monitored by the disappearance of the aldimine N=CH functionality in the ^{1}H NMR spectra. The ^{11}B NMR spectra show a broad peak at 31 ppm for the three-coordinate boron atom. The molecular structure of **3c** is shown in Fig. 3 and crystallographic data provided in Table 1. Selected bond distances and angles are shown in Table 5, and atomic coordinates provided in Table 6. Bond distances are similar to those observed for **1b** and **2** and once again no considerable intermolecular interaction is observed between the imine nitrogen and the boron atom. As expected, the imine C(16)=N(24) bond distance (1.341(1) Å) is somewhat shorter than the C(23)—N(24) distance (1.393(1) Å). Unfortunately, attempts to generate the 2-Bpin derivative **3a** using either **1a** or **2** gave only minor amounts of the desired product (by ^{1}H NMR spectroscopy) along with a number of unidentified products.

Experimental

General

All reagents and solvents used were obtained from Aldrich. NMR spectra were recorded on a JEOL JNM-GSX270 FT NMR spectrometer. ^{1}H NMR chemical shifts are reported in ppm and referenced to residual protons in deuterated solvent at 270.1 MHz. ^{11}B{^{1}H} NMR chemical shifts are referenced to external $F_3B{\cdot}OEt_2$ at 86.6 MHz. ^{13}C{^{1}H} NMR chemical shifts are referenced to solvent carbon resonances as internal standards at 67.8 MHz. Multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), broad (br), and overlapping (ov). Infrared spectra were obtained using a Mattson Genesis II FT-IR spectrometer and reported in cm^{-1}. Melting points were measured uncorrected with a Mel-Temp apparatus. Microanalyses for C, H, and N were carried out at Desert Analytics (Tucson, AZ). The synthesis of pinacolated derivatives of formylphenylboronic acids has been described elsewhere

(25). All reactions were carried out in the air and products are stable indefinitely under such conditions.

*Synthesis of **1a***

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (2-FPBpin) (524 mg, 2.27 mmol) was added to a solution of 2-aminophenol (248 mg, 2.27 mmol) in THF (15 mL) and magnesium sulfate (10.0 g). After four days at room temperature the yellow solution was concentrated to 5 mL and stored at 0°C for three days. A brown precipitate was filtered, washed with diethyl ether (3 × 10 mL), and dried under vacuum to give **1a**. Yield: 429 mg (59%) of a brown solid; mp 120–122°C. IR (Nujol) (cm^{-1}): 3413, 3049, 2918, 2858, 1699, 1620, 1587, 1562, 1481, 1462, 1375, 1346, 1317. ^{1}H NMR ($CDCl_3$) δ: 9.04 (s, 1H, C*H*=N), 7.95 (d, *J* = 8 Hz, 1H, Ar), 7.78 (d, *J* = 8 Hz, 1H, Ar), 7.46 (m, 2H, Ar), 7.18 (m, 2H, Ar), 7.02 (d, *J* = 8 Hz, 1H, Ar), 6.92 (ov d of d, *J* = 8 Hz, 1H, Ar), 1.34 (s, 12H, pin). ^{11}B NMR δ: 30 (br). ^{13}C NMR δ: 161.2 (*C*=N), 152.0, 140.1, 136.0, 134.4, 133 (br, *C*-B), 131.0, 130.2, 128.7, 127.9, 120.1, 117.5, 115.4, 83.7 (BO*C*), 24.9 (BOC*C*H_3).

*Synthesis of **1b***

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (3-FPBpin) (508 mg, 2.16 mmol) was added to a solution of 2-aminophenol (238 mg, 2.16 mmol) in anhydrous ethanol (10 mL). The clear yellow solution was heated at reflux for 1 h, after which the reaction mixture was stored at 5°C for 2 days. The resultant precipitate was filtered, washed with hexane (2 × 10 mL), and dried under vacuum to give **1b**. Yield: 609 mg (87%) of a pale yellow solid; mp 116–117°C. IR (Nujol) (cm^{-1}): 3408, 2924, 2856, 1626, 1462, 1365, 1252, 1140. ^{1}H NMR ($CDCl_3$) δ: 8.70 (s, 1H, C*H*=N), 8.30 (s, 1H, Ar), 8.05 (d, *J* = 8 Hz, 1H, Ar), 7.95 (d, *J* = 8 Hz, 1H, Ar), 7.51 (ov d of d, *J* = 8 Hz, 1H, Ar), 7.29 (d, *J* = 8 Hz, 1H, Ar), 7.22 (ov d of d, *J* = 8 Hz, 1H, Ar), 7.03 (d, *J* = 8 Hz, 1H, Ar), 6.93 (ov d of d, *J* = 8 Hz, 1H, Ar), 1.37 (s, 12H, pin). ^{11}B NMR δ: 32 (br). ^{13}C NMR δ: 157.2 (*C*=N), 152.3, 138.0, 135.7, 135.5, 135.1, 131.0, 130 (br, *C*-B), 128.8, 128.3, 120.1, 115.8, 115.0, 84.1 (BO*C*), 24.8 (BOC*C*H_3).

*Synthesis of **1c***

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (4-FPBpin) (1.01 g, 4.33 mmol) was added to a solution of 2-aminophenol (477 mg, 4.33 mmol) in anhydrous ethanol (25 mL) whereupon the solution was heated at reflux for 2 h. After 12 h at room temperature a bright yellow solid formed from the reaction mixture. The precipitate was filtered, washed with hexane (2 × 10 mL), and dried under vacuum to give **1c**. Yield: 1.27 g (91%) of a bright yellow solid; mp 114–115°C. IR (Nujol) (cm^{-1}): 3371, 2927, 2858, 1622, 1585, 1510, 1462, 1360, 1288, 1234, 1167, 1144, 1086. ^{1}H NMR ($CDCl_3$) δ: 8.64 (s, 1H, C*H*=N), 7.93 (ov m, 4H, Ar), 7.28 (d, *J* = 8 Hz, 1H, Ar), 7.20 (ov d of d, *J* = 8 Hz, 1H, Ar), 7.02 (d, *J* = 8 Hz, 1H, Ar), 6.90 (t, *J* = 8 Hz, 1H, Ar), 1.35 (s, 12H, pin). ^{11}B NMR δ: 31 (br). ^{13}C NMR δ: 156.9 (*C*=N), 152.4, 137.9, 135.3, 135.0, 133 (br, *C*-B), 129.0, 127.8, 120.0, 115.8, 115.0, 84.0 (BO*C*), 24.8 (BOC*C*H_3).

*Synthesis of **2***

2-Formylphenylboronic acid (253 mg, 1.69 mmol) was added to a solution of 2-aminophenol (184 mg, 1.69 mmol) in anhydrous ethanol (15 mL). The clear yellow solution was heated at reflux for 3 h whereupon the solution was allowed to cool to room temperature. After 12 h a bright yellow precipitate formed, which was filtered, washed with hexane (3 × 5 mL), and dried under vacuum to give **2**. Yield: 226 mg (62%) of a bright yellow solid; mp 180°C (dec). IR (Nujol) (cm^{-1}): 2912, 2857, 1628, 1460, 1375, 1270, 1164. ^{1}H NMR ($CDCl_3$) δ: 8.71 (s, 2H, C*H*=N), 7.54 (d, *J* = 8 Hz, 2H, Ar), 7.43 (m, 2H, Ar), 7.25 (ov m, 8H, Ar), 6.95 (m, 4H, Ar). ^{11}B NMR δ: 7 (br). ^{13}C NMR δ: 160.1 (*C*=N), 158.4, 135.9, 134.5, 133.4, 133.0, 132.7, 132.1, 130 (br, *C*-B), 128.0, 118.7, 115.7, 114.4. Anal. calcd. for $C_{26}H_{18}B_2N_2O_3$: C 72.95, H 4.24, N 6.54; found: C 72.49, H 4.20, N 6.37.

*Reaction of **1a** with Mn(OAc)$_3$*

Manganese triacetate (934 mg, 3.48 mmol) was added to a solution of **1a** (563 mg, 1.74 mmol) in toluene (20 mL) and the dark brown solution was heated at reflux for 2 h. The precipitated manganese salts were removed by suction filtration and the toluene was removed under vacuum to afford a dark brown solid. The mixture was analyzed by ^{1}H NMR spectroscopy and showed the presence of minor amounts of **3a** along with a number of unidentified products. Attempts to isolate **3a** proved unsuccessful.

*Synthesis of **3b***

Manganese triacetate (1.36 g, 5.07 mmol) was added to a solution of **1b** (819 mg, 2.54 mmol) in toluene (20 mL) and the dark brown solution was heated at reflux for 2 h. The precipitated manganese salts were removed by suction filtration and the toluene was removed under vacuum to afford a dark red solid. The solid was dissolved in hexane (25 mL), filtered through alumina, and allowed to crystallize at 5°C over 72 h. The resultant solid was filtered, washed with cold hexane (3 × 5 mL), and dried to give **3b**. Yield: 314 mg (39%) of a red-brown solid; mp 131–132°C. IR (Nujol) (cm^{-1}): 2933, 2914, 2856, 2360, 1734, 1587, 1456, 1409, 1367, 1323. ^{1}H NMR ($CDCl_3$) δ: 8.70 (s, 1H, Ar), 8.34 (d, *J* = 8 Hz, 1H, Ar), 7.95 (d, *J* = 8 Hz, 1H, Ar), 7.76 (ov m, 1H, Ar), 7.57–7.53 (ov m, 2H, Ar), 7.35 (ov m, 2H, Ar), 1.37 (s, 12H, pin). ^{11}B NMR δ: 31 (br). ^{13}C NMR δ: 163.2 (*C*=N), 150.9, 142.2, 137.8, 134.0, 133 (br, *C*-B), 130.3, 128.4, 126.6, 125.1, 124.6, 120.1, 110.7, 84.2 (BO*C*), 25.0 (BOC*C*H_3). Anal. calcd. for $C_{19}H_{20}BNO_3$: C 71.04, H 6.29, N 4.36; found: C 71.24, H 6.18, N 4.59.

*Synthesis of **3c***

Manganese triacetate (934 mg, 3.48 mmol) was added to a solution of **1c** (563 mg, 1.74 mmol) in toluene (20 mL) and the dark brown solution was heated at reflux for 2 h. The precipitated manganese salts were removed by suction filtration and the toluene was removed under vacuum to afford a dark brown solid. The solid was dissolved in hexane (25 mL), filtered through alumina, and allowed to crystallize at 5°C over 72 h. The resultant solid was filtered, washed with cold hexane (3 × 5 mL), and dried to give **3c**. Yield: 157 mg (28%) of a pale brown solid; mp 186–188°C. IR

(Nujol) (cm^{-1}): 2964, 2891, 1732, 1709, 1604, 1570, 1545, 1454, 1362, 1268, 1244, 1140, 1092. ^{1}H NMR ($CDCl_3$) δ: 8.28 (d, *J* = 8 Hz, 2H, Ar), 7.98 (d, *J* = 8 Hz, 2H, Ar), 7.79 (ov m, 1H, Ar), 7.60 (ov m, 1H, Ar), 7.37 (ov m, 2H, Ar), 1.38 (s, 12H, pin). ^{11}B NMR δ: 31 (br). ^{13}C NMR δ: 163.1 (*C*=N), 150.9, 142.2, 135.3, 132 (br, *C*-B), 129.4, 126.8, 125.4, 124.7, 120.2, 110.7, 84.2 (BO*C*), 25.0 (BOC*C*H_3). Anal. calcd. for $C_{19}H_{20}BNO_3$: C 71.04, H 6.29, N 4.36; found: C 71.38, H 6.39, N 4.54.

X-ray crystallography

Crystals of **1b**, **2**, and **3c** were grown from methylene chloride solutions at 5°C. Single crystals were mounted using a glass fibre and Paratone-N oil and frozen in the cold stream of the goniometer. Data were collected on a Bruker AXS P4/SMART 1000 diffractometer using ω and φ scans with a scan width of 0.3° and 30 s exposure times. The detector distance was 4 cm. The data were reduced (SAINT) (26) and corrected for absorption (SADABS) (27). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 (SHELXTL) (28). All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were located in Fourier difference maps and refined isotropically. For **2**, one molecule of CH_2Cl_2 was disordered over two positions, generated by an inversion center. For **3c**, a disorder in the oxazole ring (N/O(17) and N/O(24)) was refined by determining the occupancy using an isotropic model and fixed at 50% for consecutive cycles. A disorder in the Bpin fragment was refined by determination of the occupancy using an isotropic model and subsequently fixed at 55% for O(2), C(6), C(7), C(8), and C(9) and 45% for O(2a), C(6a), C(7a), C(8a), and C(9a).

Conclusion

We have prepared new Schiff bases containing boronate ester groups via condensation reactions with pinacolated formylphenylboronic acids (FPBpin) and 2-aminophenol. Reactions of the 2-FPBpin derivative gave a novel dimer containing a seven-membered ring with a BOB bridge. The aldimine functionality in this dimer is stabilized by an intramolecular N→B interaction. Addition of metals to the 3- and 4-Bpin Schiff-bases lead to the formation of boron-containing benzoxazoles which could be isolated in moderate yield. The use of $Mn(OAc)_3$ for these reactions provides a gentle and efficient route to making benzoxazoles that have the potential to be readily functionalized using Suzuki–Miyaura cross-coupling reactions.

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