

Article

Synthesis and Reactivity of Novel Boranes Derived from Bulky Salicylaldimines: The Molecular Structure of a Maltolato Compound

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Abstract: Reductive amination of salicylaldehyde or 3,5-di-*tert*-butylsalicylaldehyde and 1-adamantylamine using NaBH₄ gave the corresponding aminoalcohols in high yields. Subsequent addition of one equivalent of H₃B·SMe₂ to the aminoalcohols, with loss of two equivalents of dihydrogen, resulted in the formation of adamantanyl oxazaborinanes (**1a**,**b**). The molecular structure of **1b** was studied by a single crystal X-ray diffraction study. Crystals were obtained from a saturated Et₂O solution and belong to the triclinic space group P $\bar{1}$ with unit cell parameters $a = 9.1267(4)$ Å; $b = 11.676(2)$ Å; $c = 12.240(3)$ Å; $\alpha = 66.840(3)^\circ$; $\beta = 78.529(3)^\circ$; and $\gamma = 67.354(3)^\circ$. The molecular structure of the addition product (**2a**) arising from maltol and **1a** was also confirmed by single crystal X-ray diffraction. Crystals were obtained from a saturated 1:2 mixture of toluene/Et₂O and belong to the orthorhombic space group Pna2(1) with unit cell parameters $a = 18.519(6)$ Å; $b = 17.315(5)$ Å; and $c = 12.680(4)$ Å. The asymmetric unit contains two molecules that differ slightly in some of the dihedral angles.

Keywords: adamantylamine; adduct; borane; hydroboration; maltol

1. Introduction

The hydroboration reaction involves the addition of a B–H bond in hydroboranes to unsaturated molecules and has become an important method of reducing alkenes, alkynes, ketones and imines in organic synthesis [1]. The resulting organoboron products are remarkably versatile synthons that can be transformed into diverse families of important compounds (Figure 1). However, difficulties associated with synthesis, cost, handling and storage of hydroboranes have continued to plague their practical use at an industrial scale [2]. As such, there has been a considerable amount of research addressed at synthesizing novel boranes for the hydroboration reaction [3]. Commonly used boranes in both unanalyzed and catalyzed hydroboration reactions are pinacolborane ($\text{HBO}_2\text{C}_2\text{Me}_4$) and catecholborane ($\text{HBO}_2\text{C}_6\text{H}_4$), both of which are derived from 1,2-diols. Likewise, our recent efforts in this area have involved the synthesis of sterically-encumbered dioxaborolanes derived from commercially-accessible 1,2-diols that are easily handled and stored for the selective addition to alkenes and alkynes [4,5]. Much less studied, however, are hydroboranes based on amines and aminoalcohols. As part of this present study, we have begun to generate a family of oxazaborinanes derived from readily-prepared aminoalcohols based upon the salicylaldimine structural motif. Related oxazaborolidines containing a B–H bond are of interest as these simple compounds can act as either hydroboration reagents, or as Lewis-acid catalysts for a wide range of transformations, especially in the Corey–Bakshi–Shibata reduction of ketones using borane [6]. Fine-tuning the electronic and steric component of the aminoalcohol backbone will allow us to alter the behavior of the resulting oxazaborinane. We have initially prepared novel oxazaborinanes derived from 1-adamantylamine where the large adamantyl group should provide steric protection for the Lewis acidic boron atom; the results of our study are described herein.

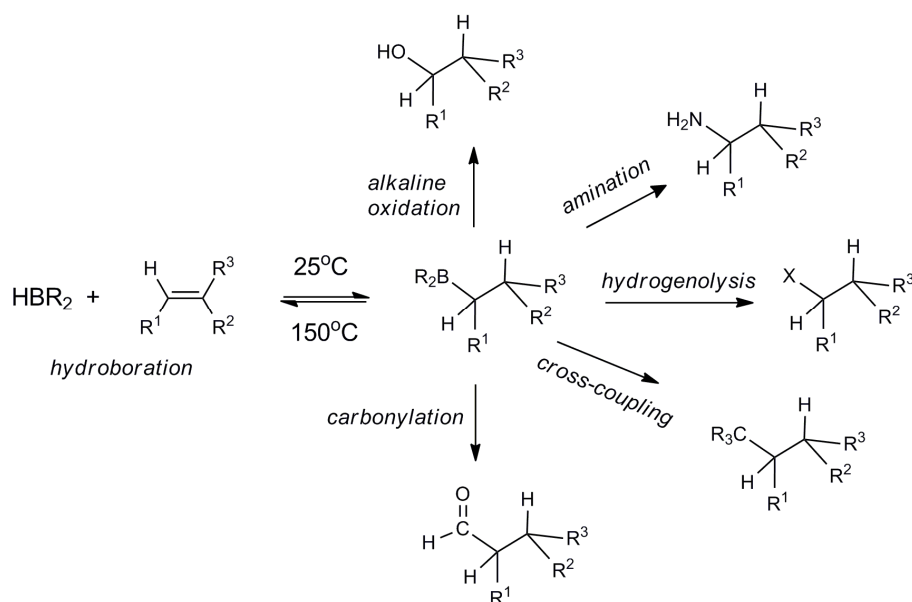


Figure 1. Hydroboration of alkenes and subsequent transformation to generate a wide array of compounds.

2. Results and Discussion

2.1. Synthesis and Reactivity

Addition of salicylaldehyde, or 3,5-di-*tert*-butylsalicylaldehyde, to 1-adamantylamine followed by a reductive amination step using excess sodium borohydride in methanol gave the corresponding aminoalcohols in high yields [7,8]. Drop-wise addition of a solution of $\text{H}_3\text{B}\cdot\text{SMe}_2$ at room temperature in toluene to the aminoalcohols gave the desired oxazaborinanes **1a,b** selectively (Figure 2). Compounds **1a** and **1b** have been characterized using a number of physical methods including multinuclear NMR spectroscopy. For instance, oxazaborinane **1a** displays a doublet in the ^{11}B -NMR spectrum at δ 25.5 ppm with a B–H bond coupling of $J = 150.2$ Hz, similar to that reported previously for the related oxazaborolidine derived from (1*R*, 1*S*)-(–)-ephedrine which is observed at δ 25 as a doublet with a B–H coupling of $J = 160$ Hz [9]. Interestingly, only a broad singlet is observed in the ^{11}B -NMR spectrum for **1b**, suggesting a dynamic behavior presumably arising from the large butyl groups. Proton and carbon NMR data are as expected and do not change much upon formation of the corresponding oxazaborinanes.

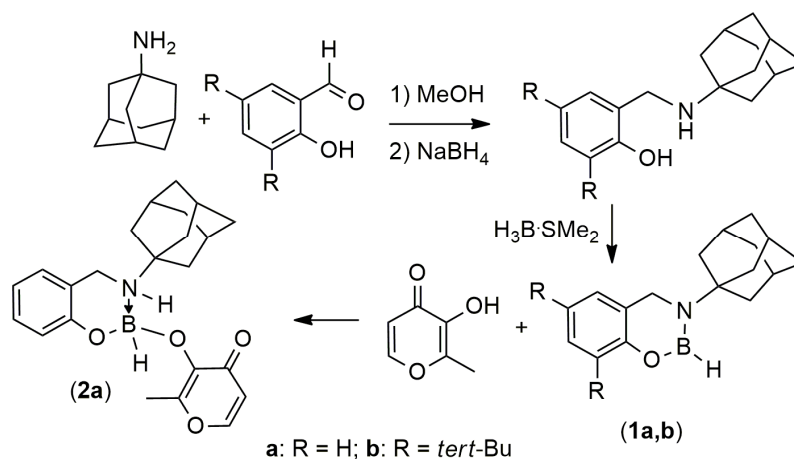


Figure 2. Synthesis of novel oxazaborinanes **1a,b** and their reactivity with maltol.

Initial reactivity studies were conducted on the less-hindered compound **1a** and this species failed to add to ketones, alkenes or alkynes, even in reactions using elevated temperatures or those done in a microwave reactor. Conversely, reactions of **1a** with benzaldehyde slowly gave the corresponding addition product albeit conversions were remarkably low, limiting its use as a borane for the hydroboration reaction. Attempts to use a number of transition metals to facilitate this reaction also proved unsuccessful [10].

One of the key intermediates in the use of oxazaborolidines as Lewis-acid catalysts in the Corey–Bakshi–Shibata reduction of ketones using borane involves coordination of the ketone to boron's empty p-type orbital. To investigate the use of **1a** as a potential Lewis-acid catalyst, we then examined the addition of maltol (3-hydroxy-2-methyl-4-pyran-4-one), a natural food additive, to see if any adduct formation was observed. Indeed, we were surprised to observe small shifts in the both the ^1H and ^{13}C -NMR spectra, but more diagnostic, was the change in the ^{11}B -NMR spectra which now showed a peak at δ 0.4 ppm, signifying the boron atom lies in a four-coordinate environment. The observation that the doublet is still present with a B–H coupling of $J = 108.1$ Hz demonstrates that the B–H bond does not react with the alcohol O–H group to give a new borate with an NBO_2 environment, along with

evolution of dihydrogen. This result suggests the potential of using these new oxazaborinanes as Lewis-acid catalysts.

2.2. Molecular Structures

Although we were unable to get single crystals of **1a** suitable for a single crystal X-ray diffraction study, crystals of **1b** were obtained readily from Et₂O at −30 °C, the molecular structure of which is shown in Figure 3a. Bond distances within the aromatic and adamantyl rings are as expected and crystallographic data is listed in Table 1. Of note are the B(1)–N(1) distance of 1.3944(17) and the B(1)–O(1) length of 1.3953(16) Å, which are typical for related oxazaborolidines [11]. The angles around boron with N(1)–B(1)–O(1) of 120.90(11)° indicate that the boron atom is still trigonal planar (Figure 3b). The angles around the nitrogen atom with B(1)–N(1)–C(1) 116.80(10), B(1)–N(1)–C(16) 126.88(10), and C(1)–N(1)–C(16) 116.32(9)° suggest the amine group is between a tetrahedral and trigonal planar environment, which is expected if there is some degree of dative bonding between the nitrogen lone pair into the empty p-type orbital of boron.

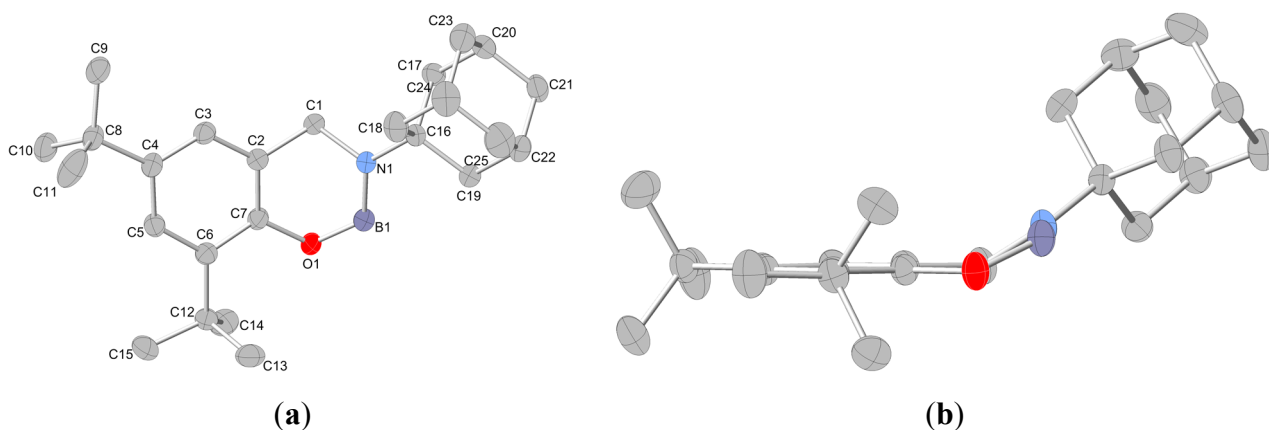


Figure 3. Two views of the molecular structure of **1b** with ellipsoids drawn at 50% probability level with hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°) for **1b**: B(1)–N(1) 1.3944(17), B(1)–O(1) 1.3953(16), N(1)–C(1) 1.4753(15), N(1)–C(16) 1.4829(15), O(1)–C(7) 1.3848(14), C(1)–C(2) 1.5051(16); N(1)–B(1)–O(1) 120.90(11), B(1)–N(1)–C(1) 116.80(10), B(1)–N(1)–C(16) 126.88(10), C(1)–N(1)–C(16) 116.32(9), C(7)–O(1)–B(1) 118.97(9), N(1)–C(1)–C(2) 111.38(10).

We were also fortunate enough to obtain single crystals from the reaction of **1a** with maltol to give **2a**, the molecular structure is shown in Figure 4. Two independent molecules of **2a** were found within the unit cell. Although co-crystallization has been the subject of recent interest lately, particularly in the area of pharmaceutical chemistry [12], it appears that **1a** has reacted with maltol via O–H bond activation. Indeed, coordination of the maltol group to the Lewis-acidic boron atom occurs through the alcohol oxygen atom and not the ketone group. The angles around boron within one molecule are O(5)–B(2)–O(6) 111.1(4), O(5)–B(2)–N(2) 110.2(4) and O(6)–B(2)–N(2) 104.6(4)°, which deviate significantly from a trigonal planar geometry whereupon angles closer to 120° would be expected. Similar trends are observed in the other molecule. The two boron-oxygen bond distances differ slightly from one another with B(2)–O(5) bond being 1.454(6) Å and the B(2)–O(6) bond is 1.478(7) Å. The

angles around the nitrogen atom in the same molecule are C(1)–N(1)–C(8) 114.6(4), C(1)–N(1)–B(1) 107.5(4) and C(8)–N(1)–B(1) 121.0(4)°. More important, however, is that the boron-nitrogen bond distance in this molecule is significantly elongated, with a distance of B(1)–N(1) 1.634(8) Å compared to 1.3944(17) Å found in **1b**. These data all support at a structural form where the O–H bond of the alcohol has been broken and either a formal positive charge could be placed on the nitrogen atom and a formal negative charge would reside on the four coordinate boron atom or, more likely, the molecule exists as a Lewis acid-base adduct (Figure 5). For comparison, the boron-nitrogen bond distance in a structurally-related compound derived from B(OMe)₃, 3,5-di-*tert*-butylsalicylaldehyde and aniline is 1.628(4) Å, which contains a true dative bond [13]. Hydrogen atoms were found in Fourier difference maps and refined. These clearly indicate N–H bonds with distances of N(1)–H(1D) 0.91(6) and N(2)–H(2D) 0.96(7) Å, respectively. Intramolecular hydrogen bonding with the corresponding oxygen atoms is present, leading to near linear hydrogen bonds with distances of B(1)–H(1C) 1.14(5) and B(2)–H(2C) 1.21(5) Å, respectively. The formation of **2a** presumably arises from initial coordination of the alcohol oxygen to the Lewis acidic boron atom.

Table 1. Crystal data and structure refinement details for compounds **1b** and **2a**.

Complex	1b	2a
Formula	C ₂₅ H ₃₈ BNO	C ₂₃ H ₂₈ BNO ₄
Molecular weight	379.37	393.27
Crystal system	Triclinic	Orthorhombic
Space group	Pī	Pna2(1)
<i>a</i> /Å	9.1267(19)	18.519(6)
<i>b</i> /Å	11.676(2)	17.315(5)
<i>c</i> /Å	12.240(3)	12.680(4)
α/°	66.840(3)	90
β/°	78.529(3)	90
γ/°	67.354(3)	90
<i>V</i> /Å ³	1105.0(4)	4066(2)
<i>Z</i>	2	8
ρ _{calc} /Mg·m ^{−3}	1.140	1.285
Crystal size/mm ³	0.60 × 0.45 × 0.20	0.45 × 0.20 × 0.10
Temp/K	198(1)	188(1)
Radiation	Mo- <i>K</i> _α (λ = 0.71073 Å)	Mo- <i>K</i> _α (λ = 0.71073 Å)
μ/mm ^{−1}	0.067	0.086
Total reflections	7700	27270
Total unique reflections	4799	4981
No. of variables	405	541
θ Range/°	1.81 to 27.50	1.61 to 28.48
Largest difference peak/hole/e Å ^{−3}	0.359 and −0.160	0.350 and −0.259
S (GoF) on F ²	1.042	1.082
<i>R</i> 1 ^a (<i>I</i> > 2σ(<i>I</i>))	0.0427	0.0618
w <i>R</i> 2 ^b (all data)	0.1256	0.1780

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR2 = (\sum [w(F_o^2 - F_c^2)^2] / \sum [wF_o^4])^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0629 P)^2 + (0.3052 P)]$ (**1b**), $1/[\sigma^2(F_o^2) + (0.0644 P)^2 + (2.4663 P)]$ (**2a**), where $P = (\max(F_o^2, 0) + 2 F_c^2)/3$.

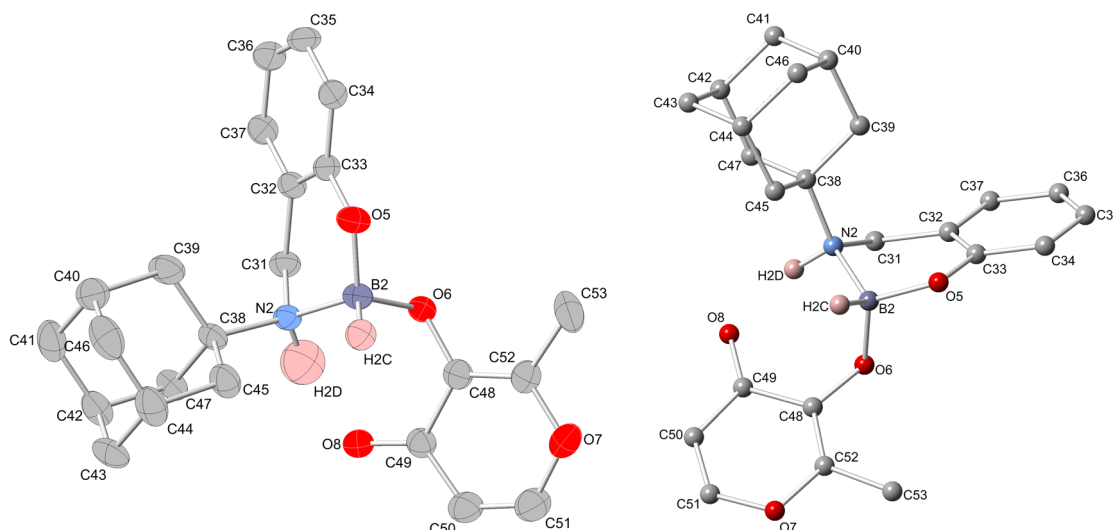


Figure 4. Two views of one of the molecules of **2a** within the unit cell with ellipsoids (left) drawn at the 50% probability level and hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°) for **2a**: B(1)–O(1) 1.452(7), B(1)–O(2) 1.478(7), B(1)–N(1) 1.634(8), B(2)–O(5) 1.454(6), B(2)–O(6) 1.478(7), B(2)–N(2) 1.634(7); O(1)–B(1)–O(2) 109.3(4), O(1)–B(1)–N(1) 110.1(4), O(2)–B(1)–N(1) 104.8(4), O(5)–B(2)–O(6) 111.1(4), O(5)–B(2)–N(2) 110.2(4), O(6)–B(2)–N(2) 104.6(4), C(1)–N(1)–C(8) 114.6(4), C(1)–N(1)–B(1) 107.5(4), C(8)–N(1)–B(1) 121.0(4), C(31)–N(2)–C(38) 115.1(4), C(31)–N(2)–B(2) 107.7(4), C(38)–N(2)–B(2) 122.0(4).

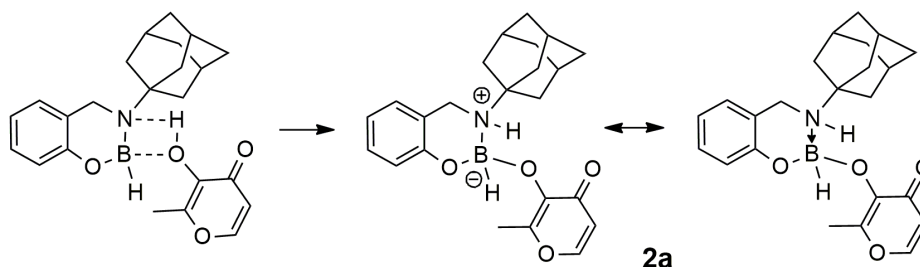


Figure 5. Formation of **2a**.

3. Experimental Section

3.1. General

Reagents and solvents were purchased from Aldrich Chemicals (Oakville, ON, Canada) and used as received. NMR spectra were recorded either on a Varian Mercury 200 Plus FT NMR spectrometer (^1H : 200 MHz; ^{13}C : 50 MHz; Varian Medical Systems, Inc., Palo Alto, CA, USA) or a JEOL JNM-GSX400 FT NMR spectrometer (^1H : 400 MHz; ^{11}B : 128 MHz; ^{13}C : 100 MHz; JEOL USA, Inc., Peabody, MA, USA) spectrometer. Chemical shifts (δ) are reported in ppm [relative to residual solvent peaks (^1H and ^{13}C) and external $\text{BF}_3 \cdot \text{OEt}_2$ (^{11}B)] and coupling constants (J) in Hz. Multiplicities are reported as singlet (s), doublet (d), triplet (t), multiplet (m), overlapping (ov), and broad (br). Melting points were determined using a Stuart SMP30 apparatus (Bibby Scientific Ltd., Stone, Staffordshire, UK) and are uncorrected. Microwave reactions were performed using a CEM Discover SP system (CEM,

Matthews, NC, USA) in standard closed vessels with the reaction temperature monitored by the internal IR pyrometer (CEM, Matthews, NC, USA). The Schiff base and aminoalcohol ligands were synthesized according to known literature procedures [7,8].

3.2. Synthesis of 3-(adamantan-1-yl)-3,4-dihydro-2H-benzo[e][1,3,2]oxazaborinane (**1a**)

H₃B·SMe₂ (2.6 mL of a 2 M toluene solution, 5.2 mmol) was added dropwise to a stirred solution of 2-((adamantan-1-ylamino)methyl)phenol (1.22 g, 4.73 mmol) in toluene (2 mL). Gas evolved upon addition of the borane and a white precipitate formed. The mixture was heated at reflux for 7 h. Upon cooling to RT, the solvent was removed under vacuum to afford **1a** as a white solid. Yield: 1.22 g (96%) of a white solid. M.p. 121–123 °C. ¹H-NMR (200 MHz, CDCl₃): δ 7.19–7.10 (br m, 1H, Ar), 7.01–6.90 (ov m, 3H, Ar), 4.25 (s, 2H, ArCH₂N), 3.95 (br m, 1H, B–H), 2.15 (br s, 3H, adamantyl), 1.91–1.89 (ov m, 6H, adamantyl), 1.76–1.62 (ov m, 6H, adamantyl). ¹¹B NMR (128 MHz, CDCl₃): δ 25.5 (d, *J* = 150.2 Hz, B–H). ¹³C{¹H} NMR (50 MHz, CDCl₃): δ 150.4, 128.1, 127.2, 122.8, 122.4, 117.7, 53.7, 42.5, 40.4, 36.7, 30.0.

3.3. Synthesis of 3-(adamantan-1-yl)-6,8-di-tert-butyl-3,4-dihydro-2H-benzo[e][1,3,2]oxazaborinane (**1b**)

H₃B·SMe₂ (0.8 mL of a 2 M toluene solution, 1.60 mmol) was added dropwise to a stirred solution of 2-((adamantan-1-ylamino)methyl)-4,6-di-tert-butylphenol (515 mg, 1.39 mmol) in toluene (3 mL). Gas evolved upon addition of the borane, and the reaction was heated gently for 12 h, at which point a white precipitate formed and was collected by suction filtration. Yield: 408 mg (77%) of a white solid. M.p. 144–146 °C. ¹H-NMR (400 MHz, CDCl₃): δ 7.16 (d, *J* = 2.3 Hz, 1H, Ar), 6.84 (d, *J* = 2.3 Hz, 1H, Ar), 4.21 (s, 2H, ArCH₂N), 2.12 (br s, 3H, adamantyl), 1.88 (s, 6H, adamantyl), 1.67 (br m, 6H, adamantyl), 1.40 (s, 9H, *t*Bu), 1.28 (s, 9H, *t*Bu). ¹¹B-NMR (128 MHz, CDCl₃): δ 26 (br s, B–H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 146.8, 143.9, 137.2, 122.3, 122.1, 121.7, 53.4, 42.4, 40.8, 36.7, 35.0, 34.4, 31.6, 29.9, 29.5.

3.4. Synthesis of **2a**

A solution of maltol (47 mg, 0.37 mmol) in toluene (3 mL) was added dropwise to a stirred solution of **1a** (100 mg, 0.37 mmol) in toluene (1 mL). The mixture was stirred at RT for 18 h, at which point the solvent was removed under vacuum, affording an oily brown solid. The residue was dissolved in THF (2 mL) and cooled to −30 °C for several hours. The solution was then filtered quickly to remove impurities and the filtrate brought to dryness. Yield: 141 mg (96%) of a waxy yellow solid. ¹H-NMR (200 MHz, CDCl₃): δ 7.62 (d, *J* = 5.6 Hz, 1H, C=CH), 7.43 (br s, 1H, C–OH), 7.12 (m, 1H, Ar), 6.96 (d, *J* = 7.4 Hz, 1H, Ar), 6.81–6.75 (ov m, 2H, Ar), 6.29 (d, *J* = 5.6 Hz, 1H, HC=C), 4.55 (dd, *J* = 15.3, 4.8 Hz, 1H, ArCHHN), 4.03 (dd, *J* = 15.3, 1.6 Hz, 1H, ArCHHN), 2.37 (s, 3H, C=C–CH₃), 2.03–1.90 (br m, 9H, adamantyl), 1.58 (ov m, 6H, adamantyl). ¹¹B-NMR (128 MHz, CDCl₃): δ 0.4 (d, *J* = 108.1 Hz, B–H). ¹³C{¹H} NMR (50 MHz, CDCl₃): δ 178.6, 159.3, 155.4, 153.6, 146.4, 129.0, 126.7, 120.3, 119.0, 118.2, 115.6, 57.4, 43.4, 39.7, 36.1, 29.7, 15.2.

3.5. X-ray Crystallography

Single crystals of **1b** and **2a** were coated with Paratone-*N* oil, mounted using a polyimide MicroMount and frozen in the cold nitrogen stream of the goniometer. A hemisphere of data was collected on a Bruker AXS P4/SMART 1000 diffractometer using ω and ϕ scans with a scan width of 0.3° and 10 s (**1b**) and 30 s (**2a**) exposure times. The detector distance was 5 cm. The data were reduced (SAINT) [14] and corrected for absorption (SADABS) [15]. The structures were solved by direct methods and refined by full-matrix least squares on F^2 (SHELXTL) [16]. All non-hydrogen atoms were refined using anisotropic displacement parameters. For **2a** the N–H and B–H hydrogen atoms were found in Fourier difference maps and refined using isotropic displacement parameters. The remainder of the hydrogen atoms for **2a** were included in calculated positions and refined using a riding model. Due to the light atom nature of the compound, determination of absolute configuration was impossible and Friedel opposites merged in final refinement runs. The asymmetric unit contains two independent molecules that differ slightly in some of the dihedral angles. Crystallographic data for **1b** and **2a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 1039702 and 1039703, respectively.

4. Conclusions

We have readily prepared two new salicylaldehyde-based oxazaborinanes derived from adamantylamine and characterized them using multinuclear NMR spectroscopy as well as a single crystal X-ray diffraction study for one compound. While initial results show the potential for these oxazaborinanes as reagents for the hydroboration reaction, it is obvious the steric and electronic environments of the molecules must be altered to improve efficacy. Future work will concentrate on trying to make the boron atom more electrophilic by using salicylaldehydes and amines containing electron-withdrawing groups. We also provide evidence for coordination and activation of alcohols to these oxazaborinanes and we will examine chiral variants of these compounds as catalysts for the Corey–Bakshi–Shibata reduction of ketones, the results of which will be presented in due course.

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Author Contributions

This work is part of Jeremy Bourque's undergraduate Honour's thesis and he did all of the synthetic work and catalyst screening. Chris Vogels, Steve Geier and Andreas Decken were responsible for the crystallographic aspects of the paper. All authors took part in the writing of this publication and Stephen Westcott conceived and designed this study.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Clay, J.M.; Vedejs, E. Hydroboration with pyridine borane at room temperature. *J. Am. Chem. Soc.* **2005**, *127*, 5766–5767.
2. Atkins, W.J., Jr.; Burkhardt, E.R.; Matos, K. Safe handling of boranes at scale. *Org. Process Res. Dev.* **2006**, *10*, 1292–1295.
3. Kanth, J.V.B. Borane-amine complexes for hydroboration. *Aldrichim. Acta* **2002**, *35*, 57–66.
4. Fritschi, C.B.; Wernitz, S.B.; Vogels, C.M.; Shaver, M.P.; Decken, A.; Bell, A.; Westcott, S.A. 4,4,5,5-Tetraphenyl-1,3,2-dioxaborolane: A bulky borane for the transition metal catalysed hydroboration of alkenes. *Eur. J. Inorg. Chem.* **2008**, *2008*, 779–785.
5. Hunter, N.M.; Vogels, C.M.; Decken, A.; Bell, A.; Westcott, S.A. [Cp*IrCl₂]₂ catalyzed hydroborations of alkenes using a bulky dioxaborocine. *Inorg. Chim. Acta* **2011**, *365*, 408–413.
6. Cho, B.T. Recent advances in the synthetic applications of the oxazaborolidine-mediated asymmetric reduction. *Tetrahedron* **2006**, *62*, 7621–7643.
7. Wang, Y.-C.; Tao, R. 2-[(Adamantan-1-ylamino)methyl]phenol. *Acta Cryst.* **2012**, *E68*, doi:10.1107/S1600536811056194.
8. Wang, J.; Ma, C.; Wang, J.; Jo, H.; Canturk, B.; Fiorin, G.; Pinto, L.H.; Lamb, R.A.; Klein, M.L.; DeGrado, W.F. Discovery of novel dual inhibitors of the wild-type and the most prevalent drug-resistant mutant, S31N, of the M2 proton channel from influenza A virus. *J. Med. Chem.* **2013**, *56*, 2804–2812.
9. Joshi, N.N.; Srebnik, M.; Brown, H.C. Chiral oxazaborolidines as catalysts for the enantioselective addition of diethylzinc to aldehydes. *Tetrahedron Lett.* **1989**, *30*, 5551–5554.
10. Vogels, C.M.; Westcott, S.A. Recent advances in organic synthesis using transition metal-catalyzed hydroborations. *Curr. Org. Chem.* **2005**, *9*, 687–699.
11. Corey, E.J.; Azimioara, M.; Sarshar, S. X-Ray crystal structure of a chiral oxazaborolidine catalyst for enantioselective carbonyl reduction. *Tetrahedron Lett.* **1992**, *33*, 3429–3430.
12. Shan, N.; Zaworotko, M.J. The role of cocrystals in pharmaceutical science. *Drug Discov. Today* **2008**, *13*, 440–446.
13. Mitra, A.; DePue, L.J.; Struss, J.E.; Patel, B.P.; Parkin, S.; Atwood, D.A. Mononuclear Schiff base boron halides: Synthesis, characterization, and dealkylation of trimethyl phosphate. *Inorg. Chem.* **2006**, *45*, 9213–9224.
14. *SAINT 7.23A*; Bruker AXS, Inc.: Madison, WI, USA, 2006.
15. *SADABS 2008*, George Sheldrick; Bruker AXS, Inc.: Madison, WI, USA, 2008.
16. Sheldrick, G.M. SHELXTL. A short history of SHELX. *Acta Cryst.* **2008**, *A64*, 112–122.