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9-Hetero-10-boraanthracene-derived borinic acid catalysts for regioselective activation of polyols†

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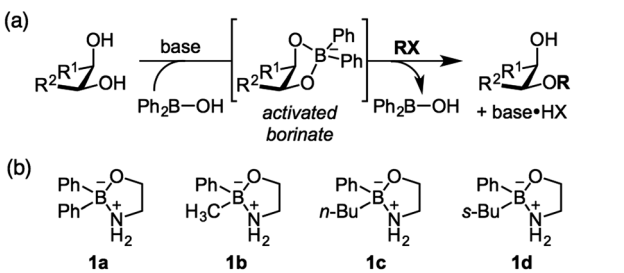
Heteraborinine-derived borinic acids serve as efficient catalysts for regioselective monofunctionalization of di- and polyols. Arylborinic acids of this type, wherein the B–OH group is incorporated into a 6π electron system, display both improved catalytic activity for functionalization of diols and enhanced stability towards air oxidation relative to the 'parent' diphenylborinic acid (Ph_2BOH). These properties enable their applications at loadings as low as 0.1 mol% and without the need for a stabilizing precatalyst ligand (*e.g.*, ethanolamine). Complexation studies, computation and kinetic data suggest that while the heteraborinine-derived borinic acids show significantly lower association constants with substrates than Ph_2BOH, this effect is more than compensated for by the increased nucleophilicity of their tetracoordinate diol adducts.

Introduction

The development of catalysts able to influence the regio- or chemoselectivity of organic reactions is an area of active investigation.[1] Selective functionalization of hydroxyl (OH) groups in di- or polyols is of particular interest, with applications ranging from manipulation of simple hydroxylated feedstocks[2] to the preparation of carbohydrate-[3] and inositol-based targets[4] and the derivatization of complex natural products.[5] Approaches for catalyst-controlled regioselective activation of OH groups include Lewis base,[6] Lewis acid[7] and transition metal catalysis.[8]

Our group has explored applications of organoboron compounds as catalysts for regioselective activation of OH groups in 1,2- and 1,3-diol motifs. The use of borinic (R_2BOH) rather than boronic acid ($RB(OH)_2$) catalysts was an important consideration, with the former providing direct access to the tetracoordinate adducts that were proposed to serve as activated nucleophiles. Accordingly, aminoethyl diphenylborinate **1a** is an efficient precatalyst (see below) for acylation,[9] alkylation,[10] sulfonylation[11] and glycosylation[12,13] of numerous substrates, including carbohydrate derivatives (Scheme 1).[14] This mode of catalysis results in high levels of selectivity for equatorial OH groups belonging to *cis*-1,2-diol motifs in pyranoside substrates and is applicable to classes of electrophiles for which Lewis base activation has been challenging (*e.g.*, alkyl and glycosyl halides). It exploits the strong, selective and reversible covalent interactions between organoboron compounds and diols that have been employed extensively in the molecular recognition field.[15]

In considering how to identify organoboron compounds having improved properties as diol activation catalysts, we faced a set of issues that appeared to present divergent requirements. Tosylation of *cis*-1,2-cyclohexanediol displayed apparent zero-order (saturation) kinetics in substrate, first-order kinetics in catalyst **1a** and first-order kinetics in TsCl, consistent with sulfonylation of the borinate ester being turnover-limiting.[11] This finding suggested that a more electron-rich borinic acid would display higher catalytic activity due to the enhanced nucleophilicity of its tetracoordinate borinate derivative. Experiments employing substituted arylborinic acids, although consistent with this hypothesis, did not lead to improvements in catalyst activity: incorporation of *para*-methoxy substituents resulted in a less active diarylborinic acid catalyst, apparently reflecting the inductively electron-withdrawing nature of these groups.[11] Moreover, the magnitude of the observed substituent effects



Scheme 1 (a) Borinic acid catalyzed diol activation; and (b) structures of borinic ester precatalysts **1a–d**.

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† Electronic supplementary information (ESI) available: Experimental procedures, characterization data, crystallographic data for the diboroxanes derived from **2b** and **2c** (.cif) and computational details. CCDC 935003 and 935004. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3sc51172c

was modest and it appeared that significantly more electron-rich variants would be needed to effect useful levels of rate acceleration.

On the other hand, the propensity of diarylborinic acids – especially electron-rich congeners – to undergo oxidation, generating phenols and boronic acids, presented practical limitations. Long-term storage of most diarylborinic acids in their pure form is problematic, and instead they are generally handled as their crystalline, tetracoordinate ethanolamine esters.[16] We have shown that the latter may be employed as precatalysts for diol activation, as the ligand undergoes electrophilic functionalization (*e.g.*, *N*,*O*-bis-acetylation or -sulfonylation) and displacement by substrate. However, avoiding the use of a precatalyst and the generation of the resulting ligand-derived by-products could be advantageous. In addition, the rate profiles of certain reactions (particularly those in which Ag_2O was employed as the halide-abstracting reagent), and our inability to recover diphenylborinic acid from product mixtures, suggested that the catalyst could be susceptible to oxidation under the reaction conditions. Borinic acids displaying improved stability towards oxidation might thus be useful candidates as catalysts.

Our preliminary structure–activity relationships for borinic acid catalysts illustrated the difficulties in simultaneously fulfilling the criteria of enhanced borinate nucleophilicity and improved stability towards oxidation. Unsymmetric borinic acid $Ph(CH_3)BOH$ underwent more rapid oxidation than Ph_2BOH, necessitating careful exclusion of oxygen during workup and immediate complexation with ethanolamine.[17] The resulting tetracoordinate adduct **1b** was stable towards storage, but did not show improved activity relative to **1a** in acylation, sulfonylation, alkylation and glycosylation reactions of representative substrates. Variation of the alkyl group in alkyl/arylborinate esters $Ph(R)B(OCH_2CH_2NH_2)$ (**1c**: R = *n*-Bu; **1d**: R = *s*-Bu) did not provide improved results, and the challenges associated with preparation and handling of the free borinic acids rendered the systematic evaluation of such compounds challenging.

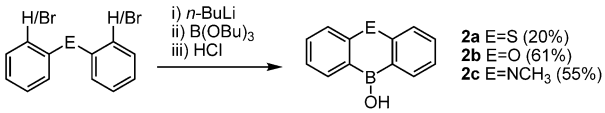
We became interested in the possibility that borinic acids based on oxa-, thia- or azaborinine frameworks might possess unique properties that could simultaneously address the two criteria discussed above. Incorporation of the borinic acid group into a 6π electron system was expected to decrease its Lewis acidity,[18] potentially generating a more nucleophilic tetracoordinate borinate adduct. Literature data also suggested that members of this class of compounds would be resistant to oxidation.[19–21] Heteraborinines have been the subject of numerous studies aimed at probing their structure and bonding, and their potential applications as components of chemical sensors, organic electronics, ligands and hydrogen storage materials have generated interest in recent years.[22–24] However, the reversible covalent interactions between heteraborinine-derived borinic acids and diols have not been studied quantitatively, and it was not clear whether compounds of this type would be useful diol activation catalysts. Herein, we describe experiments indicating that 9-oxa-, thia- and aza-10-boraanthracene-derived borinic acids, while interacting weakly with 1,2-diols, display high activities as catalysts for the monofunctionalization of such substrates, allowing loadings as low as 0.1 mol%. Their improved stability towards oxidation obviates the need for an amino alcohol-derived precatalyst (and the generation of ligand-derived byproducts) and enables their recovery upon completion of catalytic reactions. Modification of the heteroatom tether also provides a means to optimize turnover frequency and/or number for a given reaction type.

Results and discussion

Catalyst synthesis and properties

Compounds **2a–c** were prepared by cyclization of the bis-*ortho*-lithiated precursors with tributyl borate, followed by hydrolysis with aqueous acid, in analogy to reported methods (Scheme 2).[20,25]

Recrystallization yielded the dehydrated, dimeric borinates, which showed no evidence of decomposition upon storage for months in closed vials under ambient conditions. The solid-state structures of the dimeric forms of **2b** and **2c** (Fig. 1) indicate that the central oxa- and azaborinine rings are planar, with trigonal planar geometries for the boron atoms ($\Sigma_{angles,2b} = 360.0°$; $\Sigma_{angles,2c} = 360.0°$) and, in the case of **2c**, the nitrogen atoms ($\Sigma_{angles} = 360.0°$). Trends in bond length are consistent with a degree of cyclic delocalization in both the 6π azaborinine and, to a lesser extent, oxaborinine ring systems. The average B–C_{ipso} bond distances are 1.527 Å and 1.538 Å for the diboroxanes derived from **2c** and **2b**, respectively; these are both shorter than the corresponding average B–C bond distances in $(Ph_2B)_2O$ (1.571 Å).[26] The B–O bond distances show the reverse



Scheme 2 Preparation of 9-hetero-10-boraanthracene-derived borinic acids. (i) *n*-BuLi (2.2 equiv.), THF, –30 °C → 23 °C, 18 h; (ii) $B(OBu)_3$ (1.1 equiv.), reflux, 2 h; and (iii) 4 N HCl, 15 min, 23 °C.

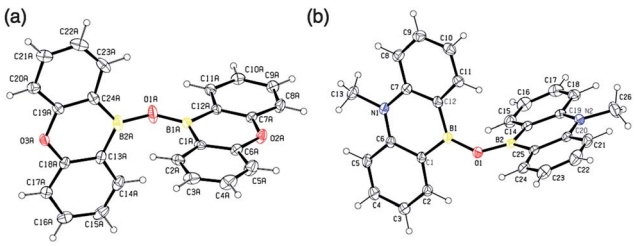


Fig. 1 X-Ray structures of the dimeric borinates derived from (a) **2b** and (b) **2c**. Selected bond lengths (Å) and angles (°): (a) O(1)–B(1) 1.358(3), B(1)–C(1) 1.540(3), C(1)–C(6) 1.392(3), C(6)–O(2) 1.377(2), O(2)–C(7) 1.380(2), C(7)–C(12) 1.386(3), C(12)–B(1) 1.540(3), C(1)–B(1)–C(12) 115.85(18), C(12)–B(1)–O(1) 119.9(2), O(1)–B(1)–C(1) 124.15(19), B(1)–O(1)–B(2) 145.8(2); and (b) O(1)–B(1) 1.376(2), B(1)–C(1) 1.528(2), C(1)–C(6) 1.419(2), C(6)–N(1) 1.393(2), N(1)–C(7) 1.402(2), C(7)–C(12) 1.414(2), B(1)–O(1)–B(2) 136.15(14), C(1)–B(1)–C(12) 115.79(15), C(12)–B(1)–O(1) 123.53(16), O(1)–B(1)–C(1) 120.63(16), C(6)–N(1)–C(7) 122.87(13), C(7)–N(1)–C(13) 118.23(14), C(13)–N(1)–C(6) 118.85(14).

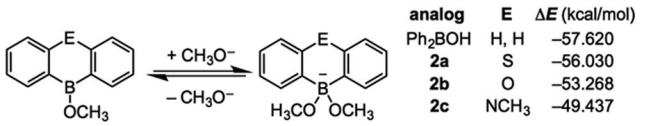
trend, with the diboroxanes of **2c** and **2b** having average B–O distances of 1.376 and 1.368 Å, both of which are longer than that of tetraphenyldiboroxane (1.346 Å). This latter trend is consistent with reduced B–O bond orders due to delocalization in the aza- and oxaborinane rings. Computational modelling (B3LYP/6-31+G(d,p), gas phase) revealed shorter C–B and longer B–O bond distances for the diboroxane derived from **2c** relative to that from **2b**, consistent with the solid-state structural data (see the ESI†).

A comparison of the rates of oxidation of **2b** and Ph_2BOH was carried out by nuclear magnetic resonance (NMR) spectroscopic analysis of solutions in air-saturated CD_3OD/D_2O (3 : 1 v/v) (Fig. 2). Whereas oxidative fragmentation of Ph_2BOH to phenol and phenylboronic acid was evident within 24 h, the spectrum of **2b** showed no detectable change after 140 h. These results are consistent with qualitative observations of Maitlis concerning a similar 9-aza-10-boraanthracene-derived borinic acid.[20] Electronic effects arising from incorporation of the boron substituent into a 6π electron system, as well as structural constraints of the fused-ring architecture that suppress Lewis base coordination or C–B bond migration,[21] may contribute to the resistance of **2b** towards oxidation.

Reversible covalent interactions with diols

While previous literature suggested that **2a–c** should display attenuated Lewis acidities relative to diphenylborinic acid,[18] quantitative data regarding their reversible covalent interactions with diols were not available. Computational studies of a model system (complexation of methoxide by the methyl borinates of Ph_2BOH and **2a–c** in the gas phase) were carried out using density functional theory (DFT) with the B3LYP functional and 6-311+G(d,p) basis set (Fig. 3).[27] The calculated methoxide affinities of the heteraboraanthracene derivatives were lower than that of Ph_2BOMe, and decreased in the order **2a** > **2b** > **2c**. This pattern is in line with the expected trend of increasing delocalization in the thia-, oxa- and azaborinane rings, respectively.

Experimental determinations of the association constants between **2a–c** and catechol were carried out by UV-vis titrations in a pH 7.4 HEPES buffer (3 : 1 methanol–water). Addition of catechol was accompanied by a decrease in absorbance at the long-wavelength, anthracene-type band, consistent with interruption of conjugation upon binding (Fig. 4). Values of K_a were



analog	E	ΔE (kcal/mol)
Ph_2BOH	H, H	−57.620
2a	S	−56.030
2b	O	−53.268
2c	NCH_3	−49.437

Fig. 3 Calculated gas-phase energies of interaction between methoxide and the methylborinates derived from Ph_2BOH and **2a–c** (B3LYP/6-311+G(d,p)).

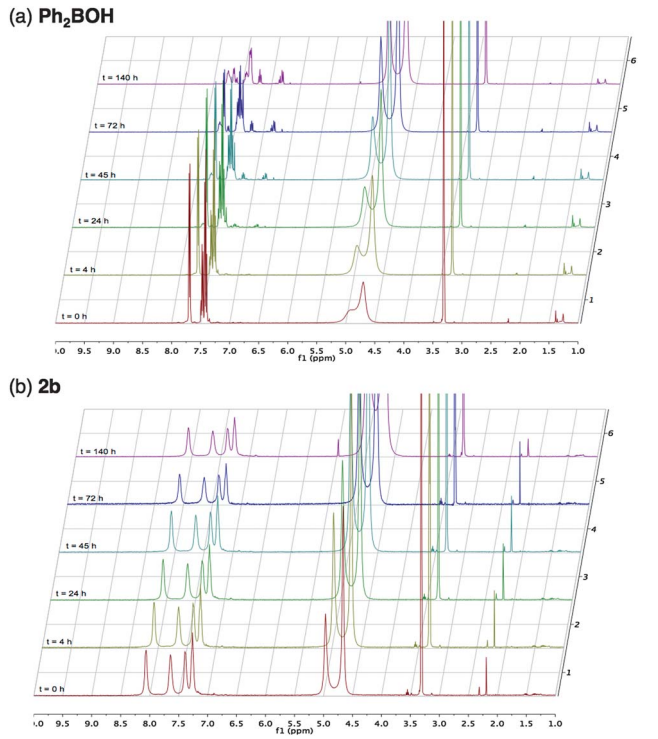
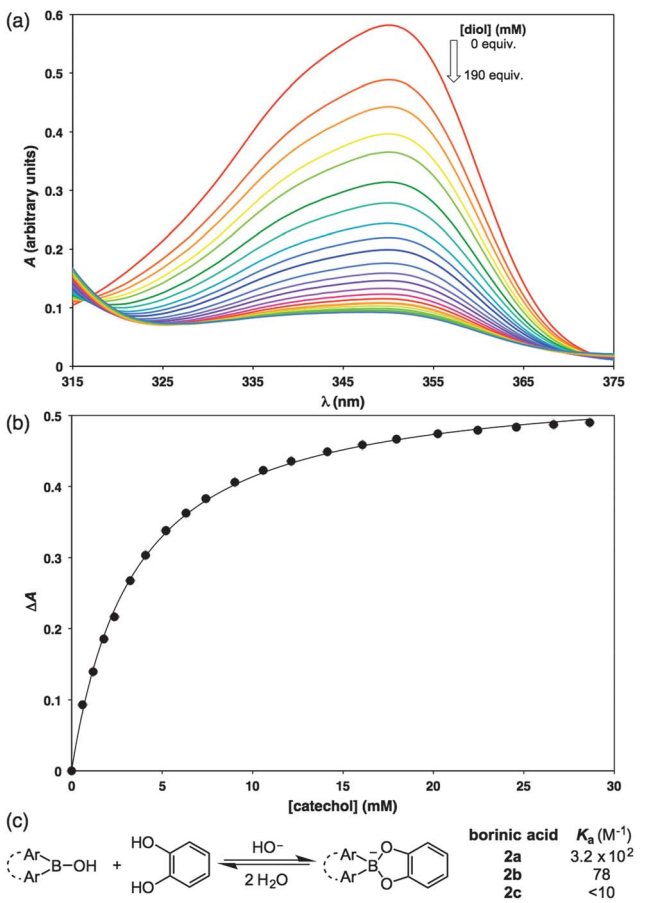


Fig. 2 Relative oxidative stability of (a) Ph_2BOH and (b) **2b** in CD_3OD–D_2O (3 : 1 v/v), as evaluated by ^1H NMR over 140 h.



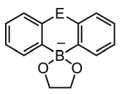
borinic acid	K_a (M^{-1})
2a	3.2×10^2
2b	78
2c	<10

Fig. 4 (a) Overlay of absorption spectra of **2a** (0.15 mM) upon addition of catechol in a 10 mM HEPES (3 : 1 CH_3OH : H_2O), pH 7.4 solution. (b) Data from (a) fitted to a 1 : 1 binding isotherm. (c) Average K_a of duplicate trials (±20%) for borinic acids **2a–c**.

determined by fitting the concentration dependence of the absorbance data to 1 : 1 binding isotherms by standard methods.[28] Each measurement was conducted in duplicate with an estimated uncertainty of 20%. In agreement with the calculations described above, the trend in catechol affinities of the cyclic borinic acids was **2a** > **2b** > **2c**, each of which was lower than that of Ph_2BOH.[29] The magnitude of this variation is significant, with the association constant between **2c** and catechol being at least three orders of magnitude lower than that of Ph_2BOH.

Catalytic activities for diol activation

The catalytic activities of **2a–c** were evaluated for sulfonylation of 1-phenyl-1,2-ethanediol with *para*-toluenesulfonyl chloride (TsCl) at 0.1 mol% loading, using ^{1}H NMR spectroscopy to monitor reaction progress (Fig. 5).[30] Despite its markedly reduced affinity for diols, oxaboraanthracene **2b** displayed superior catalytic activity to **1a** under these conditions, while maintaining a high level of selectivity for formation of the mono-sulfonylated product. This observation suggests that the **2b**–diol adduct is significantly more nucleophilic than that derived from Ph_2BOH. Indeed, calculated Mulliken charges at the oxygen atoms of tetracoordinate borinate esters derived from **2a–c** are greater than those of the corresponding diphenylborinate (Fig. 6). Caveats regarding the interpretation of these computational results are numerous: Mulliken charges are not directly related to nucleophilicity, and the gas-phase calculations ignore counterion and solvent effects (which we have found to be significant for this class of catalytic transformations). Nonetheless, our previous studies have revealed several instances in which calculated trends are consistent with observed regiochemical outcomes and catalyst structure–activity relationships.[9,11]



analog	E	Mulliken charge at O
Ph_2BOH	H, H	–0.388
2a	S	–0.521
2b	O	–0.515
2c	NCH_3	–0.528

Fig. 6 Calculated average Mulliken atomic charges on *O* for borinate esters of ethylene glycol (B3LYP/6-311+G(d,p)).

A rationale for the relative activities of **2a**, **2b** and **2c** is not evident in the absence of kinetic data for each catalyst. (For example, it appears that catalyst **2c** undergoes deactivation as the reaction progresses. Catalyst oxidation is unlikely given the resistance of **2c** to this pathway (see below), and we found no evidence to suggest that **2c** is unstable in the presence of TsCl and *i*-Pr_2NEt. We also note that the activity of **2c** as a sulfonylation catalyst is not inhibited by product **3a** or by *i*-Pr_2NEt·HCl.) However, preliminary kinetics experiments employing **2b** as catalyst were consistent with the hypothesis of enhanced rate of catalyst turnover at the expense of substrate binding: in the presence of excess TsCl and *i*-Pr_2NEt, consumption of *cis*-1,2-cyclohexanediol followed first-order kinetics. This behavior stands in contrast to the apparent zero-order (saturation) kinetics observed using catalyst **1a** under these conditions. The contrasting kinetic profiles of the sulfonylation reactions catalysed by **1a** and **2b** are depicted in Fig. 7. Under optimized conditions, diol monotosylates **3a** and **3b** were isolated in 90% and 95% yields, respectively, using catalyst **2b** at 0.1 mol% loading.[31]

The utility of the heteraborinane catalysts extends to reactions of more complex, carbohydrate-derived triol substrates.

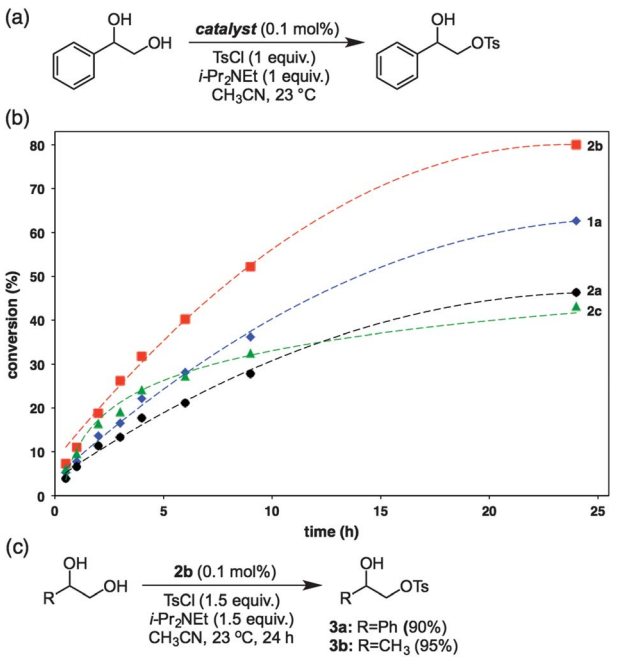


Fig. 5 (a) Monosulfonylation of 1-phenyl-1,2-ethanediol with catalysts **1a** and **2a–c**; (b) Yield of product **3a** *versus* reaction time as a function of catalyst structure. Yields were determined by ^{1}H NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard. Lines connecting the points are not fits to kinetic expressions, and are provided only as guides for the eye. (c) Preparation of tosylates **3a** and **3b** using catalyst **2b** (0.1 mol%).

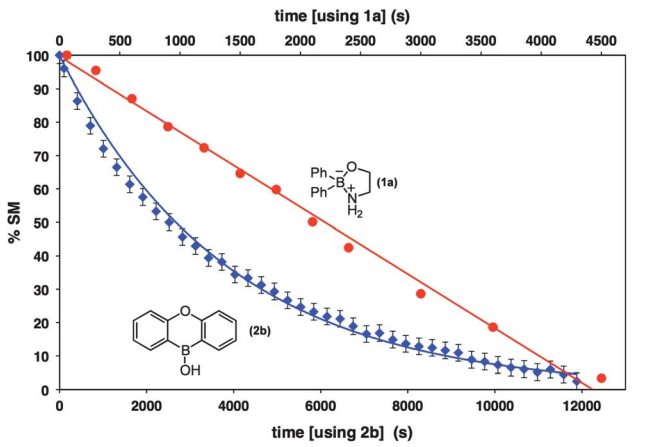
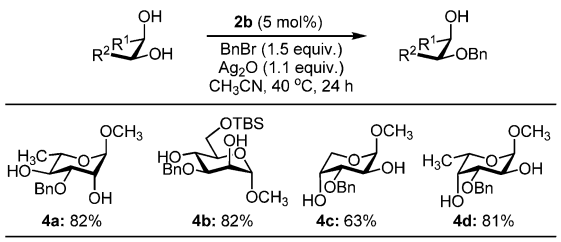


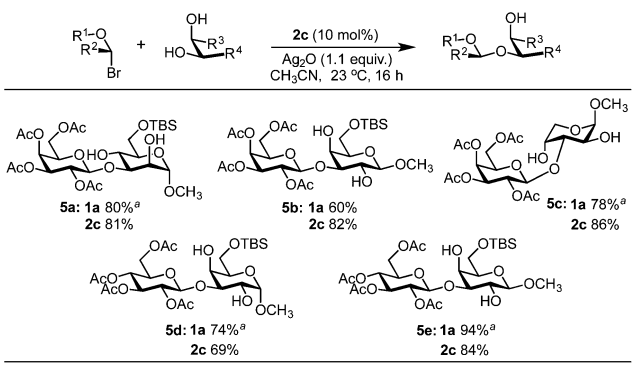
Fig. 7 Plots of diol concentration *versus* time for sulfonylation of *cis*-1,2-cyclohexanediol using catalysts **1a** and **2b**. Conditions: 1 mol% **1a**, 0.5 mmol diol, 5 equiv. TsCl and *i*-Pr_2NEt, 10 mL CH_3CN; 3 mol% **2b**, 0.2 mmol diol, 5 equiv. TsCl and *i*-Pr_2NEt, 10 mL CH_3CN. Conversions were determined by ^{1}H NMR with 1,3,5-trimethoxybenzene as internal standard. Different *x*-axis scales are used for the two catalytic reactions to emphasize the difference in the shapes of the graphs.

Using regioselective monobenzylation of α-L-rhamnopyranoside as a test reaction, the optimal catalyst was again found to be **2b** (see the ESI†). Employing the latter enabled a reduction in both the catalyst loading (from 10 mol% to 5 mol%) and the reaction time (from 48 h to 24 h) in comparison to our previously reported conditions using **1a**.[10] This observation was found to hold for regioselective benzylation of rhamno-, manno-, arabino- and fucopyranoside substrates (Scheme 3). In each case, the identity of the major regioisomer was consistent with that obtained using **1a** as precatalyst. The levels of regiocontrol exerted by **1a** and **2b** were also found to be similar. The products of manno configuration (**4a** and **4b**) were formed along with the C2-OBn regioisomers: the ratios of 3-OBn : 2-OBn isomers determined by ^{1}H NMR analysis of crude reaction mixtures using catalyst **2b** were 7.4 : 1 for **4a** and 5.0 : 1 for **4b**. With precatalyst **1a**, the corresponding ratios were 5.1 : 1 and 5.3 : 1, respectively.

Finally, **2a–c** were investigated as catalysts for regioselective activation of glycosyl acceptors. For this transformation, it was azaborinane **2c** that provided the highest yields, despite displaying the lowest catechol affinity of the three heteraborinanes (Scheme 4). This result highlights the utility of tuning the electronic properties at boron by varying the identity of the heteroatom in **2a–c**. Control experiments suggest that the utility of **2c** as a glycosylation catalyst may stem from its low rate of oxidation in the presence of Ag_2O, relative to those of **2a–b** and Ph_2BOH (see the ESI†). While Ag_2O is employed as a halide abstracting reagent and base in the glycosylation reactions, it is also known to be a mild oxidant. Consistent with the idea that **2c** resists oxidation by Ag_2O, it was recovered intact from glycosylation reaction mixtures (70% average yield of recovered catalyst for the glycosylations shown in Scheme 4).



Scheme 3 Selective monobenzylation of pyranoside substrates catalyzed by **2b**.



Scheme 4 Regioselective glycosylations catalysed by **2c**. [a]Yields from ref. 12.

Conclusions

The improved stability towards oxidation and enhanced activity for diol activation that characterizes the heteraborinine-derived borinic acids constitutes a useful set of properties, and one that has previously been elusive. Opportunities exist to explore other members of this interesting class of arene analogs, to further fine-tune their catalytic activity by heteroatom and substituent variation, and to develop chiral variants.

Acknowledgements

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