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Synthesis and Lewis acidity of triorganosilyl and triorganostannyl esters of orthoboric, metaboric, and arylboronic acids

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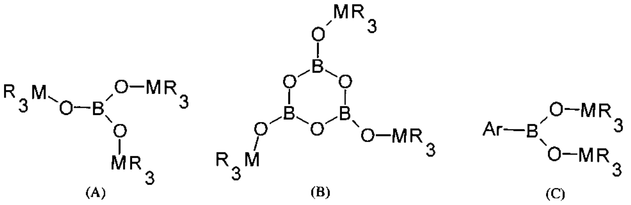
Abstract

The synthesis of 30 new triorganosilyl and triorganostannyl esters of orthoboric, metaboric, and arylboronic acids are described: $(R_3SiO)_3B$ $\{R_3 = {}^nBuMe_2$, $PhMe_2$, [2-(3-cyclohexenyl)ethyl]Me_2, (^{n}Octadecyl)Me_2, $^nHex_3\}$; $(R_3MO)_3B_3O_3$ $\{M = Si$: $R_3 = {}^nPr_3$, $^nBu_3$, $^nHex_3$, $EtMe_2$, $^nBuMe_2$, [2-(3-cyclohexenyl)ethyl]Me_2, $[(Me_2HC)(Me)_2C]Me_2$, (^{n}Octadecyl)Me_2, $PhMe_2$, Ph_2Me, Ph_3. $M = Sn$, $R = Ph$, $Me\}$; $(R_3MO)_2BAr$ $\{M = Si$: $Ar = Ph$, $R_3 = {}^nPr_3$, $^nBu_3$, Ph_2Me; $Ar = C_6H_4Br$-4, $R = Ph$, ^nPr; $Ar = C_6H_4Me$-2, $R = Ph$, ^nPr. $M = Sn$: $R = Ph$, $Ar = Ph$, C_6H_4Br-4, C_6H_4Me-2; $R = {}^nBu$, $Ar = Ph$, C_6H_4Br-4$\}$. The esters were characterised by elemental analysis, m.p./b.p., ^1H-, ^{13}C-, and ^{11}B-NMR and IR spectroscopy; solids were characterised by solid-state ^{11}B MAS NMR spectroscopy. The Lewis acidity of liquid compounds was determined by Gutmann's acceptor number (AN) method and well-defined ranges were observed for the compound classes $\{(R_3MO)_3B$, 23–36; $(R_3MO)_2BAr$, 23–31; $(R_3MO)_3B_3O_3$, 44–81$\}$. The effect of the R_3Si or R_3Sn group was to enhance the Lewis acidity at boron relative to organic esters. Increasing the steric bulk of the R_3M moiety significantly reduced AN values and there was little differentiation in AN values between R_3Si and R_3Sn derivatives. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Acceptor number; Borate esters; Lewis acidity; Group 4 elements

1. Introduction

Lewis acidity plays an important role in stoichiometric and catalytic reactions and trivalent boron compounds with a sextet of electrons around the boron are considered archetypal Lewis acids [1]. Information concerning the Lewis acidity of particular compounds and the subtle factors that affect Lewis acidity are of interest to academics and industrialists alike, since knowledge of the Lewis acidity of a particular compound allows an assessment of that compound to be made with regard to its ability to function as a Lewis acid in both laboratory and industrial settings. Thus, for example, epoxide resins may be cured by the addition of BF_3 or $(MeO)_3B_3O_3$, and the rate of the Lewis acid initiated polymerisation of the epoxide monomer phenylglycidyl ether (PGE) has been correlated with the acid strength of the initiator [2]. We have become interested in determining the Lewis acidity of compounds containing one or more B–O–M (M = Si, Sn) linkages and assessing the effect of Si or Sn atom on Lewis acidity at B. Compounds containing the B–O–M (M = Si, Sn) linkage are represented in the literature [3–13] as the triorganosilyl and triorganostannyl esters of orthoboric (structure A), metaboric (structure B), and arylboronic (structure C) acids; other compounds containing this structural motif are described in Ref. [9].



This paper reports on the synthesis and characterisation of series of new and previously reported derivatives containing B–O–Si or B–O–Sn links. The Lewis acidity of liquid products have been estimated by Gutmann's acceptor number (AN) method [14], and the effects of Si and Sn are noted and discussed.

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2. Results and discussion

2.1. Synthesis and characterisation

Silyl and stannyl esters of orthoboric, metaboric, and arylboronic acids are conveniently prepared by the azeotropic removal of water from the corresponding mixtures of boron acid and triorganyosilanol or triorganyostannyl derivatives [3] and the previously reported compounds $(R_3MO)_3B$ {M = Si: R_3 = Et_3 [4–8] (**1**), ^{n}Pr_3 [6] (**2**), ^{n}Bu_3 [7] (**3**), Ph_3 [4,9] (**4**). M = Sn: R_3 = ^{n}Bu_3 [10] (**5**), Ph_3 [10] (**6**)}, $(Et_3SiO)_3B_3O_3$ [8] (**7**), $(^nBu_3SnO)_3B_3O_3$ [10] (**8**), and $(Ph_3SiO)_2BPh$ [9] (**9**) were prepared by these methods. Similarly, the new triorganosilyl esters of orthoboric acid (**10**–**14**), metaboric acid (**15**–**25**), and arylboronic acids (**26**–**32**) were prepared from the triorganosilanol as shown in Eqs. (1)–(3) and the triorganostannyl esters of metaboric acid (**33**, **34**) and arylboronic acids (**35**–**39**) were synthesised as shown in Eqs. (2)–(4) with $(^nBu_3Sn)_2O$ being used as an alternative for ^{n}Bu_3SnOH (Eq. (4)) for the tributylstannyl derivatives. Compounds **15**, **19** and **23** were prepared also by a method described for **7** [8] from a 1:1 stoichiometric reaction of B_2O_3 and the corresponding orthoborate esters (**2**, **10**, **11**) at high temperature (250°C, 22 h) in a sealed reaction vessel, in yields of $\sim 85\%$.

$$3R_3SiOH + H_3BO_3 \rightarrow (R_3SiO)_3B + 3H_2O \qquad (1)$$

{R_3 = ^{n}$BuMe_2$ (**10**), $PhMe_2$ (**11**), [2-(3-cyclohexenyl)ethyl]Me_2 (**12**), (^{n}Octadecyl)Me_2 (**13**), ^{n}Hex_3 (**14**)}

$$3R_3MOH + 3H_3BO_3 \rightarrow (R_3MO)_3B_3O_3 + 6H_2O \qquad (2)$$

{M = Si, R_3 = ^{n}Pr_3 (**15**), ^{n}Bu_3 (**16**), ^{n}Hex_3 (**17**), $EtMe_2$ (**18**), ^{n}$BuMe_2$ (**19**), [2-(3-cyclohexenyl)ethyl]Me_2 (**20**) [$(Me_2HC)(Me)_2C$]Me_2 (**21**), (^{n}Octadecyl)Me_2 (**22**), $PhMe_2$ (**23**), Ph_2Me (**24**), Ph_3 (**25**); M = Sn, R = Ph (**33**), Me (**34**)}

$$2R_3MOH + ArB(OH)_2 \rightarrow (R_3MO)_2BAr + 2H_2O \qquad (3)$$

{M = Si, Ar = Ph, R_3 = ^{n}Pr_3 (**26**), ^{n}Bu_3 (**27**), Ph_2Me (**28**); Ar = C_6H_4Br-4, R = Ph (**29**), ^{n}Pr (**30**); Ar = C_6H_4Me-2, R = Ph (**31**), ^{n}Pr (**32**); M = Sn, R = Ph, Ar = Ph (**36**), C_6H_4Br-4 (**37**), C_6H_4Me-2 (**39**)}

$$(^nBu_3Sn)_2O + ArB(OH)_2 \rightarrow (^nBu_3SnO)_2BAr + H_2O \qquad (4)$$

{Ar = Ph (**35**), C_6H_4Br-4 (**38**)}

All new compounds were prepared in high yield as colourless high boiling liquids or as colourless crystalline solids and were air-stable but generally water-sensitive. Yields, m.p./b.p., and elemental analysis data for the new compounds **10**–**39** are reported in Table 1.

Solution ^{11}B-NMR spectra ($CDCl_3$, RT) were obtained on all compounds (Table 2) and the signals for the R_3Si derivatives were observed within well-defined ranges: δ 14.4–15.4, $(R_3SiO)_3B$; δ 17.2–19.0, $(R_3SiO)_3B_3O_3$; δ 25.9–27.9, $ArB(OSiR_3)_2$; chemical shifts of 15.1 (CCl_4) and 19.6 (CCl_4) have been reported previously [15] for $(Me_3SiO)_3B$ and $(Me_3SiO)_3B_3O_3$, respectively. The increased shielding at boron of 2–3 ppm for $(Me_3SiO)_3B$ relative to organic esters derived from primary or secondary alcohols can be seen to quite general for all the $(R_3SiO)_3B$ derivatives and this has been attributed to steric interactions inducing a higher probabilty of favourable conformations for B–O π-bonding [16]. Fewer R_3Sn esters were prepared, but the solution $\delta(^{11}B)$ data obtained suggest a slight deshielding of the B nuclei for the orthoborate and metaborate esters relative to the R_3Si derivatives. The arylboronic triorganostannyl acid esters (**35**–**39**) had resonances within the range δ 18.2–22.1 and the boron nuclei were significantly more shielded ($\Delta\delta$ ca. 7 ppm) than those in the R_3Si esters and in most other arylboronic acids derivatives [15]. Solid state ^{11}B-MAS-NMR data were also obtained on most solid samples and these are reported in Table 2. All spectra were characterised by a broad complex signal that was simulated as described previously [17,18]; the δ_{iso} values so obtained were in good agreement with the solution δ values discussed above and confirmed the relative upfield shifts for the B nuclei of $ArB(OSnR_3)_2$ in relation to $ArB(OSiR_3)_2$ derivatives. ^{1}H- and ^{13}C-NMR data were obtained on all new compounds and these are presented in Section 3; observed spectra had chemical shifts, multiplicities, and relative intensities as expected with ^nJ(HH) coupling constants of 7–10 Hz.

IR spectra were obtained for all samples and the strongest bands in all samples were in the 1393–1300 cm^{-1} region and due to B–O stretches (Table 2). The orthoborate $(R_3SiO)_3B$ derivatives (**10**–**14**) had ν_{max} in the range 1336–1325 cm^{-1}, consistent with **1** [8], and the metaborate $(R_3SiO)_3B_3O_3$ derivatives (**15**–**25**) had maxima at higher wavenumber and in the range 1393–1350 cm^{-1} in accord with **7** [8]. Absorption bands at 732 and 720 cm^{-1} [8] or 742 and 735 cm^{-1} [10], described as diagnostic for the B_3O_3 ring system, were observable in our systems but this area of the spectrum generally appeared more as a medium intensity singlet at 730 cm^{-1} with a shoulder at 745 cm^{-1}, or less frequently vice versa, rather than as a well resolved doublet. The arylboronate esters $ArB(OSiR_3)_2$ (**26**–**32**) had their B–O stretches in the range 1335–1315 cm^{-1}, in agreement with **9** [9] whilst the $ArB(OSnR_3)_2$ esters (**35**–**39**) had diagnostic bands at ca.1375 and 1301 cm^{-1} for R = ^{n}Bu (**35**, **38**) and Ph (**36**, **37**, **39**), respectively. Additionally, the R_3Sn esters displayed a strong band at 1290–1280 cm^{-1} (R = ^{n}Bu) or 1270 cm^{-1} (R = Ph) which has been previously assigned to the $\nu_{(asym)}$(B–O–Sn) stretch [10]. This band was always weaker than that of the B–O band shown in Table 2 except for **5** where it was the strongest band in the spectrum.

2.2. Acceptor number (AN) values

Gutmann and co-workers have described a quantitative parameter (Acceptor number, AN), derived from the ^{31}P-NMR shifts produced in Et_3PO by electrophilic solvent interactions that lead to deshielding of the P atoms by inductive effects involving electron donation from O to the solvent, as a measure of the Lewis acidity of the solvent [14]. For comparative purposes this AN scale has arbitrary fixed points for hexane (0) and $SbCl_5$ (100). In relation to the Lewis acidity of trigonal boron compounds, the AN value is a measure of how well the O donor atom of the Et_3PO competes with the heteroatoms bound to boron for its acceptor orbital; thus BF_3 has an AN value of 89 whereas $B(NMe_2)_3$ has an AN value of 9 [2]. The liquid triorganosilyl and triorganostannyl orthoborate esters and arylboronic acid esters are poor Lewis acids (AN values 23–36, and 23–31, respectively) whilst the liquid esters of metaboric acid are considerably stronger Lewis acids (AN = 44–81). These AN values for the esters with B–O–Si or B–O–Sn linkages are in the same general ranges as those observed [2] for organic esters, e.g. $(MeO)_3B$ and $(MeO)_3B_3O_3$ have AN values of 23 and 79, respectively. The most highly acidic of those derivatives measured was **23** {$(PhMe_2SiO)_3B_3O_3$, AN = 81} whose Lewis acidity approaches that of BF_3 and is greater than that of $(MeO)_3B_3O_3$. As was found for the organic esters [2], increasing the steric bulk of the R_3M moiety significantly reduces the AN value for a particular compound, and there also appears to be little differentiation between corresponding R_3Si and R_3Sn derivatives, e.g. orthoborates: **1** > **2** > **3** ~ (**5**), metaborates: **18** > **7** > **15** > **16** ~ (**8**) > **17** (R_3Sn derivatives are in parentheses).

These AN values also indicate that there is an electron-withdrawing electronic effect, associated with incorporating Si or Sn atoms into the ester linkage, which results in increased Lewis acidity at B. The AN data for the orthoborate esters clearly demonstrate that the Si and Sn derivatives should be stronger Lewis acids than the isomeric C analogues, i.e. **1**, **2**, **5**, **10**, and **11** would all be expected from steric considerations to be less acidic than $(H_3CO)_3B$ (AN = 23 [2]) and yet these compounds have AN values which are higher. Similar electron-withdrawing effects associated with SiR_3 groups

Table 1
Elemental analysis [a] of new triorganosilyl and triorganylstannyl borate esters

Compound		Yield/%	M.p. (b.p./mmHg)/°C	C	H
10	$(^{n}BuMe_2SiO)_3B$	72	(170/15)	53.5(53.4)	11.5(11.2)
11	$(PhMe_2SiO)_3B$	75	(151–154/5.0)	62.2(62.1)	7.2(7.2)
12	$(CyclohexenylEt)Me_2SiO]_3B$	83	(>250/1.5)	63.8(64.2)	10.1(10.2)
13	$(^{n}OctadecylMe_2SiO)_3B$	87	37–39	72.7(72.5)	12.9(13.1)
14	$(^{n}Hex_3SiO)_3B$	83	(250/1.0)	71.9(71.3)	13.0(13.0)
15	$(^{n}Pr_3SiO)_3B_3O_3$	81	(260/1.5)	54.3(54.0)	10.8(10.6)
16	$(^{n}Bu_3SiO)_3B_3O_3$	77	(238–241/0.15)	59.7(59.5)	11.4(11.2)
17	$(^{n}Hex_3SiO)_3B_3O_3$	83	(250/0.1)	66.5(66.4)	11.7(12.0)
18	$(EtMe_2SiO)_3B_3O_3$	80	(185–190/0.08)	37.0(37.0)	8.5(8.5)
19	$(^{n}BuMe_2SiO)_3B_3O_3$	69	(170–175/0.1)	46.0(45.7)	9.7(9.6)
20	$[(CyclohexenylEt)Me_2SiO]_3B_3O_3$	83	Visc. liq [b]	57.1(57.2)	9.4(9.1)
21	$[(Me_2HC)(Me)_2C]Me_2SiO)_3B_3O_3$	69	(>260/0.1)	51.5(51.6)	10.6(10.3)
22	$(^{n}OctadecylMe_2SiO)_3B_3O_3$	72	39–42	67.6(67.8)	12.4(12.2)
23	$(PhMe_2SiO)_3B_3O_3$	81	(>250/0.1)	54.0(54.0)	6.5(6.2)
24	$(Ph_2MeSiO)_3B_3O_3$	67	(>250/0.1)	64.2(65.0)	6.1(5.5)
25	$(Ph_3SiO)_3B_3O_3$	91	165–8	71.8(71.6)	5.1(5.0)
26	$(^{n}Pr_3SiO)_2BPh$	66	Visc. liq [b]	66.6(66.3)	11.1(10.9)
27	$(^{n}Bu_3SiO)_2BPh$	66	Visc. liq [b]	69.6(69.5)	11.4(11.5)
28	$(Ph_2MeSiO)_2BPh$	71	(>250/0.1)	74.9(74.7)	5.9(6.1)
29	$(Ph_3SiO)_2B(C_6H_4Br\text{-}4)$	63	121–4	69.9(70.2)	5.2(4.9)
30	$(^{n}Pr_3SiO)_2B(C_6H_4Br\text{-}4)$	85	Visc. liq [b]	55.9(56.2)	9.4(9.1)
31	$(Ph_3SiO)_2B(C_6H_4Me\text{-}2)$	86	88–92	79.4(79.1)	5.9(5.7)
32	$(^{n}Pr_3SiO)_2B(C_6H_4Me\text{-}2)$	51	Visc. liq [b]	66.6(66.9)	11.2(11.0)
33	$(Ph_3SnO)_3B_3O_3$	89	118–122	55.0(55.0)	4.2(3.9)
34	$(Me_3SnO)_3B_3O_3$	94	98–102	17.3(17.4)	4.7(4.4)
35	$(^{n}Bu_3SnO)_2BPh$	74	(250/1.0)	50.9(51.2)	8.6(8.6)
36	$(Ph_3SnO)_2BPh$	80	115–19	61.3(61.5)	4.3(4.3)
37	$(Ph_3SnO)_2B(C_6H_4Br\text{-}4)$	90	104–111	55.8(56.1)	4.1(3.8)
38	$(^{n}Bu_3SnO)_2B(C_6H_4Br\text{-}4)$	81	(250/1.0)	46.0(46.1)	7.4(7.5)
39	$(Ph_3SnO)_2B(C_6H_4Me\text{-}2)$	85	110–14	62.1(61.9)	4.8(4.5)

[a] Calculated in parenthesis.
[b] Did not distill.

Table 2
Acceptor number (AN) values and spectroscopic (solution/solid-state MAS-^{11}B-NMR and IR) data

Compound	AN [a]	$\delta(^{11}B)$ [b] /ppm	$\delta_{iso}(^{11}B)$ [c] /ppm	ν_{max}(B–O) [d] /cm^{-1}
1	34	14.6	[e]	1329
2	28	15.4	[e]	1328
3	23	15.4	[e]	1329
4	[f]	15.1	16.1 [g]	1320
5	25	18.1	[e]	1300
6	[f]	22.7	21.4 [g]	1301
7	72	17.7	[e]	1393
8	54	20.2	[e]	1377
9	[f]	27.1	27.9 [h]	1322
10	36	14.4	[e]	1326
11	29	15.0	[e]	1336
12	23	14.7	[e]	1335
13	[f]	15.4	[i]	1332
14	[i]	15.0	[e]	1325
15	63	15.4	[e]	1385
16	56	19.0	[e]	1386
17	44	17.2	[e]	1381
18	74	17.2	[e]	1375
19	71	18.1	[e]	1380
20	70	17.2	[e]	1381
21	59	18.2	[e]	1383
22	[f]	17.9	[i]	1381
23	81	17.7	[e]	1372
24	74	17.3	[e]	1350
25	[f]	19.0	[i]	1390
26	23	26.6	[e]	1332
27	[i]	26.2	[e]	1335
28	[i]	26.3	[e]	1322
29	[f]	27.4	28.7 [h]	1315
30	[i]	25.9	[e]	1325
31	[f]	27.9	29.2 [h]	1320
32	31	26.3	[e]	1326
33	[f]	21.5	[i]	1301
34	[f]	19.5	[i]	1301
35	30	18.2	[e]	1376
36	[f]	22.1	21.0 [g]	1304
37	[f]	19.0	20.7 [g]	1301
38	30	18.2	[e]	1374
39	[f]	18.5	21.0 [g]	1301

[a] Calculated from $\delta(^{31}P)$ of Et_3PO dissolved in neat (liquid) compound from $AN = (\delta_{(sample)} - 41.0) \times \{100/(86.14 - 41.0)\}$ [2].

[b] From proton-decoupled solution spectra in $CDCl_3$ at room temperature.

[c] Solid state MAS-NMR: isotropic shift, $\delta_{iso} = \delta_{cg} - \sigma_{qs}$ (δ_{cg} is the centre of gravity of the observed signal), $\sigma_{qs} = \nu_{CG} - \nu_L = -10^6(Cq)^2(1 + 0.33\eta^2)/40(\nu_L)^2$ ($\nu_L = 96.234$ MHz) [18].

[d] Recorded as thin film between NaCl plates (liquids) or KBr discs (solids).

[e] Liquid at room temperature.

[f] Solid at room temperature.

[g] Simulated data: $\sigma_{qs} = -17.3$, $Cq = 2.53$ MHz, $\eta = 0.0$.

[h] Simulated data: $\sigma_{qs} = -27.2$, $Cq = 3.05$ MHz, $\eta = 0.5$.

[i] Not recorded.

are well documented [19] and have been observed as enhanced Brønsted acidity of hydroxy groups on Si, reduced donor properties of silyl ethers, and stabilization of α-silylcarbanions. Current interpretation of experimental data concerning O–Si bonds favours $(p-\sigma^*)_\pi$ hyperconjugation as the mechanism of the electronic interaction in silyl ethers and hydroxysilyl compounds [20]. The availability of an empty, low energy C–Si σ* orbital on Si is a consequence of its low electronegativity and a similar situation should arise for Sn which is equally less electronegative. The enhanced Lewis acidity at B is thus due to O–M $(p-\sigma^*)_\pi$ bonding competing with, and reducing O–B $(p-p)_\pi$ bonding. As might be expected, the electronic effect at B is moderated in the metaborate esters where the M:B ratio is reduced to 1:1. However, the effect is still observable and compounds **15**, **18**, **19**, **20**, **23** and **24** have AN values higher or similar to that for $(^nPrCH_2O)_3B_3O_3$ (AN = 65 [2]) whereas their acidities would be expected to be lower if the steric factor were dominating.

2.3. Conclusions

The synthesis and Lewis acidity of a series of triorganosiyl and triorganostannyl esters of orthoboric, metaboric and arylboronic acids have been reported with AN ranges for the classes of compound shown to be 23–36, 44–81 and 23–31, respectively. The Lewis acidity at B in $B–O–MR_3$ (M/Si, Sn) derivatives was enhanced relative to isomeric organic esters, and the most highly acidic of those derivatives measured was $(PhMe_2SiO)_3B_3O_3$ (AN = 81) whose Lewis acidity approaches that of BF_3 and is greater than that of $(MeO)_3B_3O_3$ or $(^nBuO)_3B_3O_3$.

3. Experimental section

3.1. General

Reactions were carried out under N_2. IR spectra were recorded on a Perkin–Elmer FT-IR 1600 spectrometer as KBr discs. Multi-element solution NMR were recorded on a Bruker AC 250 CP/MAS-NMR spectrometer operating at 250 MHz for ^{1}H, 62.9 MHz for ^{13}C-{^{1}H}, 31 P-{^{1}H) and 80.2 MHz for ^{11}B-{^{1}H). Chemical shifts (δ) are given in ppm with positive values towards high frequency (downfield) from $SiMe_4$ (^{1}H and ^{13}C), $BF_3{\cdot}OEt_2$ (^{11}B) or 85% H_3PO_4 (^{31}P). Elemental analyses (C, H) were obtained on a Carlo Erba MOD-1106 instrument using helium as carrier gas. AN values for liquid samples were obtained as described previously and were referenced against PPh_3 ($\delta = -6.0$) dissolved in the $CDCl_3$ used as a lock [2]. R_3SiOH derivatives [21,22], 2-$MeC_6H_4B(OH)_2$ [23] and Me_3SnOH [24] were prepared by literature procedures. Et_3PO, H_3BO_3, $ArB(OH)_2$ (Ar = Ph, 4-BrC_6H_4), Me_3SnCl, R_3SiCl, and $(^nBu_3Sn)_2O$ were obtained commercially and used as supplied. Details of the preparations of **10**, **15**, **26** and **35**, typical of those shown in

Eqs. (1)–(4) are given below together with ^{1}H- and ^{13}C-NMR data ($CDCl_3$, RT) of compounds **10**–**39**.

3.2. Preparation of (^{n}BuMe$_2$SiO)$_3$B (**10**)

^{n}BuMe$_2$SiOH (3.73 g, 0.03 mol) was added to H_3BO_3 (0.58 g, 0.01 mol) in MePh (100 ml) and heated in a Dean–Stark apparatus for 20 h until H_2O (0.5 ml, 0.03 mol) had separated. The PhMe was removed from the resulting solution by rotary evaporation leaving the product as an analytically pure clear colourless liquid (3.24 g, 72%) which distilled at 170°C/15 mmHg.

3.3. Preparation of (^{n}Pr$_3$SiO)$_3$B$_3$O$_3$ (**15**)

^{n}Pr$_3$SiOH (4.50 g, 0.026 mol) was added to H_3BO_3 (1.59 g, 0.026 mol) in MePh (100 ml) and heated in a Dean–Stark apparatus for 20 h until H_2O (0.94 ml, 0.052 mol) had separated. The PhMe was removed from the resulting solution by rotary evaporation leaving the crude product (5.04 g, 83%). The crude product was dissolved in the minimum amount of Et_2O and filtered to removed unreacted H_3BO_3 (0.12 g, 0.002 mol). The Et_2O was then removed under vacuum to yield a clear colourless liquid (4.92 g, 81%) which distilled at 260°C/1.5 mmHg.

3.4. Preparation of (^{n}Pr$_3$SiO)$_2$BPh (**26**)

^{n}Pr$_3$SiOH (3.04 g, 0.017 mol) was added to PhB(OH)$_2$ (1.06 g, 0.00872 mol) in MePh (100 ml) and heated in a Dean–Stark apparatus for 20 h until H_2O (0.31 ml, 0.017 mol) had separated. The PhMe was removed from the resulting solution by rotary evaporation leaving the product as an analytically pure clear colourless liquid (2.7 g, 66%).

3.5. Preparation of (^{n}Bu$_3$SnO)$_2$BPh (**35**)

(^{n}Bu$_3$Sn)$_2$O (3.0 g, 0.0051 mol) was added to PhB(OH)$_2$ (0.63 g, 0.0051 mol) in MePh (100 ml) and heated in a Dean–Stark apparatus for 20 h until H_2O (0.1 ml, 0.0051 mol) had separated. The PhMe was removed from the resulting solution by rotary evaporation leaving the product as an analytically pure clear colourless liquid (2.61 g, 74%) which distilled at 250°C/1 mmHg.

(^{n}BuMe$_2$SiO)$_3$B (**10**): ^{1}H: $\delta = 0.05$ (s, 18H), 0.55 (t, 6H), 0.85 (t, 9H), 1.3 (m, 12H). ^{13}C: $\delta = 0.3$, 13.7, 17.2, 24.4, 26.5. *(PhMe$_2$SiO)$_3$B* (**11**): ^{1}H: $\delta = 0.25$ (s, 18H), 7.3 (d, 9H), 7.5 (m, 6H). ^{13}C: $\delta = 1.3$, 128.1, 129.7, 133.4, 140.1. *(2-{3-cyclohexenyl}Et)Me$_2$SiO]$_3$B* (**12**): ^{1}H-NMR: $\delta = 0.0$ (t, 18H), 0.6 (m, 6H), 1.0–2.0 (m, 27H), 5.5 (q, 6H). ^{13}C-NMR: $\delta = 0.7$, 15.3, 25.2, 28.6, 29.7, 31.7, 36.9, 126.7, 127.0. *(^{n}OctadecylMe$_2$SiO)$_3$B* (**13**): ^{1}H-NMR: $\delta = 0.0$ (s, 18H), 0.5 (t, 6H),) 0.8 (t, 9H), 1.2 (m, 96H). ^{13}C-NMR: $\delta = 0.0$, 14.1, 17.5, 17.8, 22.7, 23.2, 29.4, 29.7, 31.9, 33.5. *(^{n}Hex$_3$SiO)$_3$B* (**14**): ^{1}H-NMR: $\delta = 0.4$ (t, 18H), 0.7 (t, 27H), 1.1 (m, 72H). ^{13}C-NMR: $\delta = 14.1$, 14.8, 22.7, 23.2, 31.7, 33.6. *(^{n}Pr$_3$SiO)$_3$B$_3$O$_3$* (**15**): ^{1}H-NMR: $\delta = 0.55$ (m, 18H), 0.80 (t, 27H), 1.3 (m, 18H). ^{13}C-NMR: $\delta = 16.6$, 17.5, 18.3. *(^{n}Bu$_3$SiO)$_3$B$_3$O$_3$* (**16**): ^{1}H-NMR: $\delta = 0.7$ (t, 27H), 0.8 (m, 18H), 1.2 (m, 36H). ^{13}C-NMR: $\delta = 13.7$, 15.4, 25.4, 26.7. *(^{n}Hexyl$_3$SiO)$_3$B$_3$O$_3$* (**17**): ^{1}H-NMR: $\delta = 0.7$ (t, 18H), 0.9 (t, 27H), 1.3 (m, 72H). ^{13}C-NMR: $\delta = 14.1$, 14.5, 22.6, 22.9, 31.6, 33.2. *(EtMe$_2$SiO)$_3$B$_3$O$_3$* (**18**): ^{1}H-NMR: $\delta = 0.2$ (s, 18H), 0.65 (q, 6H), 1.0 (t, 9H). ^{13}C-NMR: $\delta = 0.1$, 6.4, 8.9. *(^{n}BuMe$_2$SiO)$_3$B$_3$O$_3$* (**19**): ^{1}H-NMR: $\delta = 0.25$ (s, 18H), 0.7 (t, 6H), 0.95 (t, 9H), 1.35 (q, 12H). ^{13}C-NMR: $\delta = 0.0$, 13.7, 17.1, 25.4, 26.4. *[(2-{3-cyclohexenyl}Et)Me$_2$SiO]$_3$B$_3$O$_3$* (**20**): ^{1}H-NMR: $\delta = 0.2$ (s, 18H), 0.7 (m, 6H), 1.15–2.15 (m, 27H), 5.65 (q, 6H). ^{13}C-NMR: $\delta = 0.0$, 14.2, 25.3, 28.1, 29.6, 31.6, 36.3, 126.6, 126.7. *[(Me$_2$HC)(Me)$_2$C]Me$_2$SiO)$_3$B$_3$O$_3$* (**21**): ^{1}H-NMR: $\delta = 0.2$ (s, 18H), 0.9 (s, 36H), 1.7 (sept, 3H). ^{13}C-NMR: $\delta = 0.0$, 18.5, 20.0, 24.8, 34.1. *(^{n}OctadecylMe$_2$SiO)$_3$B$_3$O$_3$* (**22**): ^{1}H-NMR: $\delta = 0.2$ (s, 18H), 0.65 (q, 6H), 0.9 (t, 9H), 1.25 (m, 96H). ^{13}C-NMR: $\delta = 0.0$, 14.1, 17.2, 17.5, 22.7, 23.0, 29.4, 29.7, 31.9, 33.4. *(PhMe$_2$SiO)3B$_3$O$_3$* (**23**): ^{1}H-NMR: $\delta = 0.5$ (s, 18H), 7.4 (d, 9H), 7.6 (m, 6H). ^{13}C-NMR: $\delta = 0.0$, 128.1, 130.0, 133.4, 139.0. *(Ph$_2$MeSiO)$_3$B$_3$O$_3$* (**24**): ^{1}H-NMR: $\delta = 0.9$ (s, 9H), 7.6 (m, 18H), 7.85 (m, 12H). ^{13}C-NMR: $\delta = 0.0$, 127.8, 128.0, 130.1, 134.2. *(Ph$_3$SiO)$_3$B$_3$O$_3$* (**25**): ^{1}H-NMR: $\delta = 7.1$–7.6 (m, 45H). ^{13}C-NMR: $\delta = 127.6$, 129.7, 135.3. *(^{n}Pr$_3$SiO)$_2$BPh* (**26**): ^{1}H-NMR: $\delta = 0.85$ (m, 12H), 1.0 (t, 18H), 1.55 (m, 12H), 7.5 (d, 3H), 7.9 (t, 2H). ^{13}C-NMR: $\delta = 16.8$, 18.1, 18.3, 125.1, 127.4, 129.0, 134.9. *(^{n}Bu$_3$SiO)$_2$BPh* (**27**): ^{1}H-NMR: $\delta = 0.55$ (m, 12H), 0.75 (t, 18H), 1.25 (m, 24H), 7.25 (d, 3H), 7.5 (t, 2H). ^{13}C-NMR: $\delta = 13.7$, 15.0, 25.6, 26.6, 125.2, 127.2, 130.2, 134.9. *(Ph$_2$MeSiO)$_2$BPh* (**28**): ^{1}H-NMR: $\delta = 0.7$ (s, 6H), 7.3–7.55 (m, 20H), 7.65 (m, 5H). ^{13}C-NMR: $\delta = 0.8$, 125.3, 127.7, 127.9, 129.6, 130.3, 135.3, 134.2, 137.0. *(Ph$_3$SiO)$_2$B(C$_6$H$_4$Br-4)* (**29**): ^{1}H-NMR: $\delta = 7.2$–7.8 (m, 34H). ^{13}C-NMR: $\delta = 128.0$, 128.3, 130.0, 130.2, 135.0, 135.2, 137.5. *(^{n}Pr$_3$SiO)$_2$B(C$_6$H$_4$Br-4)* (**30**): ^{1}H-NMR: $\delta = 0.75$ (t, 12H), 1.05 (t, 18H), 1.4 (m, 12H), 7.55 (d, 2H), 7.65 (d, 2H). ^{13}C-NMR: d = 16.8, 18.0, 18.3, 125.3, 130.7, 136.5. *(Ph$_3$SiO)$_2$B(C$_6$H$_4$Me-2)* (**31**): ^{1}H-NMR: $\delta = 2.55$ (s, 3H), 7.25 (m, 4H), 7.5 (m, 18H), 7.65 (t, 12H). ^{13}C-NMR: $\delta = 22.5$, 124.1, 127.6, 129.8, 130.1, 132.5, 135.0, 135.1, 135.3. *(^{n}Pr$_3$SiO)$_2$B(C$_6$H$_4$Me-2)* (**32**): ^{1}H-NMR: $\delta = 0.5$ (t, 12H), 0.8 (t, 18H), 1.3 (m, 12H), 2.2 (s, 3H), 6.9–7.2 (m, 4H). ^{13}C-NMR: $\delta = 16.7$, 17.8, 18.3, 28.4, 124.3, 128.5, 129.2, 132.2, 140.6. *(Ph$_3$SnO)$_3$B$_3$O$_3$* (**33**): ^{1}H-NMR: $\delta = 7.2$–7.45 (m, 45H). ^{13}C-NMR: $\delta = 128.3$, 129.3, 136.2, 139.6. *(Me$_3$SnO)$_3$B$_3$O$_3$* (**34**): ^{1}H-NMR: $\delta = 0.4$ (27H). ^{13}C-NMR: $\delta = -2.7$. *(^{n}Bu$_3$SnO)$_2$BPh* (**35**): ^{1}H-NMR: $\delta =$

1.0 (t, 18H), 1.2 (t, 12H), 1.45 (m, 12H), 1.65 (m, 12H), 7.3 (d, 3H), 7.5 (t, 2H). ^{13}C-NMR: $\delta = 9.6$, 13.7, 27.4, 29.2, 128.0, 131.6, 136.5, 141.9. $(Ph_3SnO)_2BPh$ (**36**): ^{1}H-NMR: $\delta = 7.2$–7.8 (m, 35H). ^{13}C-NMR: $\delta = 128.3$, 128.8, 129.1, 129.2, 136.8, 137.3, 139.6, 156.5. $(Ph_3SnO)_2B(C_6H_4Br\text{-}4)$ (**37**): ^{1}H-NMR: $\delta = 7.2$–7.7 (m, 34H). ^{13}C-NMR: $\delta = 127.1$, 127.6, 127.8, 128.3, 128.4, 128.6, 129.0, 138.3. $(^nBu_3SnO)_2BC_6H_4Br\text{-}4$ (**38**): ^{1}H-NMR: $\delta = 0.65$ (t, 18H), 0.95 (t, 12H), 1.2 (m, 12H), 1.4 (m, 12H), 7.15 (d, 2H), 7.25 (d, 2H). ^{13}C-NMR: $\delta = 9.6$, 13.7, 27.2, 29.0, 122.8, 131.0, 137.0, 140.5. $(Ph_3SnO)_2BC_6H_4Me\text{-}2$ (**39**): ^{1}H-NMR: $\delta = 2.4$ (s, 3H), 7.3 (t, 12H), 7.4 (d, 18H), 7.6 (m, 4H). ^{13}C-NMR: $\delta = 21.1$, 128.3, 128.6, 129.0, 129.3, 136.8, 137.2, 139.6.

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