An alternative general preparation of 2-alkyl-1-benzostannepines and their conversion into 1-benzostibepines and 1-benzoborepines *via* a tin-metal exchange †

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The 2-alkyl-1-benzostannepines 4a-g were prepared by the intramolecular hydrostannation of the tin intermediates 3 to an acetylenic moiety in one pot from (Z)-1-(o-bromophenyl)but-1-en-3-ynes 1. The obtained stannepines 4 were easily converted into the 1-benzostibepines 9, 10, 11, 12 and the 1-benzoborepines 14, 15 by tin-antimony and tin-boron exchange reactions in moderate to good yields, respectively. The 1-benzoborepines 14 and 15 are hitherto unknown heterocyclic ring systems.

Introduction

There has been considerable interest in the chemistry of heterocycles containing a tin atom. The chemistry of the stannole ring system,^{1,2} stannacyclopentadiene, has been reviewed and a large number of compounds has been prepared. Although the chemistry of the six-membered tin-containing heterocycles³ has also been widely studied, the corresponding seven-membered heterocycles (stannepines) have only occasionally been studied. The C-unsubstituted 3-benzostannepine IIA,⁴ the fully unsaturated heterocycle containing a tin atom at the C-3 position, was prepared by the intermolecular hydrostannation of o-diethynylbenzene I more than 35 years ago. The thiophene ring- IIB^{5a} and IIC,5b the pyrrole ring- IID⁶ and the cyclopentane ring-fused stannepines IIE⁷ have also been synthesized by the extension of this annellation reaction. Furthermore, monocyclic stannepines IV have been obtained by not only the above hydrostannation⁸ but also by ring enlargement⁹ of the carbene intermediate from the 1,4-dihydrostannabenzene III (Scheme 1).

On the one hand, it is well known that these parent stannepines can be transformed into the corresponding derivatives of borepines^{4b,5-7,8b,10} and stibepines¹¹ by the tin-metal exchange reaction. Stannepines are thus useful as the key starting materials for the preparation of other heteroepines. However, only two reports of the synthesis of the 1-benzostannepines V,^{12,13} theoretically possible structural isomers, have been known in very recent years. The C-unsubstituted 1-benzostannepine¹² and the 2-trimethylsilyl derivative¹² have been prepared by the coupling of dimethyltin dichloride and the 1,6-dilithium compound, generated from (Z,Z)-1-bromo-4-(2-bromophenyl)-1-trimethylsilylbuta-1,3-diene. 2-tert-Butyland 2-n-butyl-1-benzostannepines^{13,14} have also been obtained by the reaction of the corresponding 1-benzotellurepines¹⁵ with tert-butyllithium, followed by treatment with di-n-butyltin dichloride. However, these routes are fairly limited and not general; in particular, the former method provides no variety of 2-alkyl substituted 1-benzostannepines.

Previously, we reported the synthesis of the 1-benzotellurepines¹⁵ and the 1-benzoselenepines,¹⁵ which are novel seven-

[†] The yields obtained for compounds **4**, **5** and **6**, together with ¹H and ¹³C NMR measurements for the 1-benzostannepines **4**, are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p1/b0/b000900h/



membered heterocycles containing a tellurium or selenium element, *via* the successive intramolecular addition of telluroles or selenoles to a triple bond. Moreover, for several years we





have focused on the synthesis of various heterocyclic ring systems¹⁶ using efficient intramolecular cyclization reactions involving an acetylenic group. In this paper, we describe the novel route for preparation of the stable 2-alkyl-1-benzo-stannepines by a similar cyclization and the transformation of stannepines into 1-benzoborepines and 1-benzostibepines *via* the replacement of tin with antimony or boron.¹⁴

Results and discussion

Synthesis of 1-benzostannepines

The synthesis of the 2-alkyl-1,1-dibutyl-1-benzostannepines 4 is shown in Scheme 2. (Z)-1-(o-Bromophenyl)but-1-en-3-ynes 1, which were obtained in our previous study,^{15b} were lithiated with 2.2 equiv. of Bu'Li in the presence of N,N,N',N'-tetramethylethylenediamine (TMEDA) in anhydrous hexane at -80 °C, and then treated with 1.1 equiv. of di-n-butylchlorotin hydride (Buⁿ₂ClSnH),¹⁷ which was freshly generated from an equal amount of di-n-butyltin dichloride (Buⁿ₂SnCl₂) and di-nbutyltin dihydride (Buⁿ₂SnH₂), giving the desired 2-alkyl-1benzostannepines 4a-g as stable colorless oils, together with the debrominated (Z)-1-(phenyl)but-1-en-3-ynes 5 and the bis[(Z)o-(but-1-en-3-ynyl)phenyl]dibutylstannanes 6. These materials could be separated by silica gel column chromatography. The enyne compounds 5 were probably produced by the hydrolysis of the lithio derivatives 2. The formation of the diarylstannanes 6 could be easily explained by the process involving a 1:2 coupling of Buⁿ₂Cl₂Sn and 2. Treatment of the trimethylsilyl derivative 1h with Bu'Li in a similar manner gave a complex mixture without any detectable compounds, and lithiation of the phenyl derivative 1i resulted in 5-exo-dig cyclization to afford 1-benzylideneindene 7 in low yield without producing any tin-containing compounds. A similar cyclization of the lithio compound having a phenylacetylene moiety 18 that produced a five-membered compound has already been reported.

It is well known that the intermolecular addition of organotin hydride compounds to a carbon–carbon triple bond induced by radical initiators (*e.g.*, AIBN, Et₃B),¹⁹ transition metal catalysts (*e.g.*, Pd(PPh₃)₄),²⁰ base catalysts⁴ or Lewis acid catalysts (*e.g.*, ZrCl₄, HfCl₄)²¹ gives the hydrostannylation products, and this addition frequently proceeds in the absence of a catalyst.²² Therefore, the stannepines **4** may probably be obtained by the intramolecular *7-endo-dig* ring closure of the tin hydride intermediates **3** at the sp carbon of the triple bond, as shown in Scheme 2. Compounds **4** are quite stable and are not sensitive to air, light or even moisture. 2-Methyl- **4c**, 2-*n*propyl- **4d**, 2-*n*-hexyl- **4e**, 2-*n*-octyl- **4f** and 2-cyclohexyl-1 benzostannepine **4g** are new compounds, although 2-*tert*-butyl **4a** and 2-*n*-butyl derivative **4b** have been prepared in our recent work.¹³ These results are summarized in the electronic supplementary data (Table 1). The structural assignment of the products **4**, **5** and **6** could be made from the ¹H and ¹³C NMR and HRMS spectra (electronic supplementary data, Table 2, and Experimental section). No six-membered *6-exo-dig* products **8** were formed by this ring closure reaction, although in the case of intramolecular hydrotelluration and hydroselenation at a carbon–carbon triple bond, as described in our previous paper,¹⁵ both the *7-endo-dig* and the *6-exo-dig* reactions took place. Furthermore, a similar hydrosilylation gave only the *6-exo-dig* products.^{16*i*} The reason for the differences caused by changing the element is not clear at present.

Conversion of stannepines into stibepines

C-unsubstituted 1-benzostibepine¹² and the 2-tert-butyl and 2-n-butyl derivatives¹³ have been previously obtained. The tin-antimony exchange reactions of 3-benzostannepine¹¹ and the six-membered tin-containing heterocyclic compounds ^{3a,3h,23} have been extensively studied. These reactions prompted us to examine a similar replacement reaction using the 1-benzostannepines obtained in this work for the purpose of producing the 1-benzostibepines. The stannepines 4a,b readily reacted with 1.0 equiv. of antimony trichloride (SbCl₃) in CHCl₃ at 0 °C to almost quantitatively afford the corresponding 1-chloro-1benzostibepines 9a,b, but these compounds were too unstable to be isolated. Thus, we planned the transformation of 9 into the Sb-phenyl or -alkyl substituted derivatives. Treatment of the 1-chlorostibepines 9 (freshly prepared without purification after removal of the solvent and the generated Buⁿ₂SnCl₂ under reduced pressure) with a small excess of phenyllithium in ether at -20 °C afforded the 1-phenyl-1-stibepines 10 in moderate yields (Scheme 3). The methyl 11 and 1-n-butyl derivatives 12 were also obtained in a similar manner by using methyllithium and n-butyllithium instead of phenyllithium, respectively. Compounds 10, 11 and 12 were more stable than the 1-chlorostibepines 9 and could easily be purified by normal silica gel chromatography.

After the reaction of the stannepine 4a with dichlorophenylstibine (Cl₂SbPh) in CHCl₃, 4a was recovered together with a small amount of the diene compound 13.^{15b} Although the *Sb*-phenyl substituted stibepines are described in the literature, the *Sb*-alkyl derivatives could not be obtained due to the thermal instability of the reagents (dihaloalkylstibines). Thus, compounds 11 and 12 are the first isolated examples of 1-alkyl-1-benzostibepines.



Scheme 3 Reagents and conditions: i, SbCl₃ (1 equiv.), CHCl₃, 0 °C, 30 min; ii, PhLi (1.2 equiv.), ether, -20 °C, 30 min (for 10); iii, MeLi (1.2 equiv.), ether, -20 °C, 30 min (for 11); iv, *n*-BuLi (1.2 equiv.), ether, -20 °C, 30 min (for 12); v, PhSbCl₂, CHCl₃, 0 °C; vi, BCl₃ (1 equiv.), hexane, room temp., 1 h (for 14); vii, PhBCl₂ (1 equiv.), hexane, room temp., 1 h (for 15).

Conversion of stannepines into borepines

We next examined the tin-boron exchange reaction 24 in order to form the novel 1-benzoborepines using the more stable and easily available 2-*tert*-butyl-1-benzostannepine **4a**. The reaction of 1-stannepine **4a** with 1.0 equiv. of boron trichloride (BCl₃) in *n*-hexane at room temperature resulted in the desired tin-boron exchange to give 2-*tert*-butyl-1-chloro-1-benzoborepine **14a**, which could be purified by distillation under reduced pressure in spite of its being air- and moisture-sensitive. The treatment of 1-chloroborepine **14a** with phenyllithium or alkyllithium resulted in decomposition and afforded no products. However, the air- and moisture-sensitive 1-phenyl derivative **15a** was obtained by the reaction of **4a** with dichlorophenylborane (PhBCl₂) under similar conditions.

The monocyclic fully unsaturated borepines,^{8,25} 3-benzoborepines^{4,10} and other ring-fused derivatives^{5-7,26} have now been recognized and established as aromatic compounds by ¹H and ¹³C NMR spectroscopic studies, molecular orbital calculations and X-ray crystal analyses. It is well known^{4,8} that the olefinic protons of these borepines appear at lower field because of a diamagnetic ring current induced by cyclic conjugation through the boron atom, and/or the decrease in electron densities on the olefinic protons due to the overlap between the boron vacant p orbital and π systems.^{3e,27} The ¹H NMR spectra of the 1-benzoborepines 14 and 15 show signals arising from the borepine ring protons (3-H, 4-H and 5-H) at lower field than those of the 1-benzostannepines 4 and the 1-benzostibepines 9, 10, 11 and 12 obtained in this work. In particular, the proton signals of 4-H are shifted 0.34-0.64 ppm downfield, and appeared 0.25-0.62 ppm more downfield in comparison to those of the Sn-di-n-butyl substituted 1-benzostannepines 4. In addition, the observed coupling constants, $J_{3,4}$ (14a: 8.4 Hz, 15a: 7.0 Hz) are somewhat large, while the values of $J_{4.5}$ of 11.0 and 11.7 Hz observed in 14a and 15a are smaller than those of the normal seven-membered 1-benzoheteroepines containing a heavier element.^{12,13,15,28} In the ¹³C NMR of **15**, three sp² α carbon atoms, appearing at δ 141.6 (s), 148.4 (s) and 159.3 (s), are almost identically deshielded while the signals of the other sp^2 doublet γ carbons are in the normal region for aromatic and olefinic carbon atoms. These observations indicate that the 1-benzoborepines obtained in this work are aromatic.

Conclusions

In the present work, the general synthesis of 2-alkyl-1-benzostannepines by an intramolecular hydrostannation reaction with a triple bond was achieved. The parent stannepines were transformed into the corresponding 1-benzostibepines and 1-benzoborepines by a tin-metal exchange. Further reactions and applications of the stannepines including other tin-metal exchanges are now under investigation.

Experimental

Melting points were measured on a Yanagimoto micro melting point hot stage apparatus and are uncorrected. IR spectra were recorded on a Hitachi 270–30 spectrometer. Mass spectra (MS) and HR-MS were recorded on a JEOL JMS-DX300 instrument. ¹H NMR spectra were recorded on a JEOL PMX-60SI (60 MHz), JEOL EX-90A (90 MHz) or JEOL JNM-GSX 400 (400 MHz) spectrometer in CDCl₃ using tetramethylsilane as internal standard and *J* values are given in Hz. ¹³C NMR spectra were recorded on a JEOL JNM-GSX 400 (400 MHz) spectrometer.

General procedure for the reaction of (Z)-1-(o-lithiophenyl)but-1-en-3-ynes with Bu^{*}₂SnHCl: formation of 2-alkyl-1,1-dibutyl-1benzostannepines 4, (Z)-1-(phenyl)but-1-en-3-ynes 5 and bis[(Z)o-(but-1-en-3-ynyl)phenyl]dibutylstannane 6

To a stirred solution of (Z)-1-(o-bromophenyl)but-1-en-3-yne 1 (5 mmol) and TMEDA (1.8 ml, 10 mmol) under an argon atmosphere was slowly added Bu'Li (1.6 mol in pentane solution, 7.5 ml, 12 mmol). After the reaction mixture had been stirred at the same temperature for 30 min, di-n-butylchlorotin hydride (5.5 mmol, freshly prepared from di-nbutyltin dihydride and one equivalent of di-n-butyltin dichloride at room temperature in quantitative yield) was added. The reaction mixture was allowed to warm to room temperature during 3-4 h with stirring. Saturated aqueous NH₄Cl (50 ml) was added, and the layers were separated. The aqueous layer was extracted with ether (50 ml \times 2). The organic layers were washed with brine (50 ml \times 2), dried (MgSO₄), and concentrated in vacuo. The resulting residue was chromatographed on silica gel eluted with *n*-hexane to give 4, 5 and 6. The results are summarized in Table 1 and the spectral data for the stannepines 4 are listed in Table 2 (see electronic supplementary information). The absorption due to C=C of compounds 5 could not be observed in the IR spectrum.

(*Z*)-5,5-Dimethyl-1-phenylhex-1-en-3-yne 5a. Colorless oil, $\delta_{\rm H}$ (90 MHz, CDCl₃) 1.30 (9H, s, Bu'), 5.68 (1H, d, *J* 11.8, Ph-CH=CH-), 6.56 (1H, d, *J* 11.8, Ph-CH=CH-), 7.30–7.45 and 7.83–8.00 (3H, m and 2H, m, Ph-H) (HRMS *m*/*z* Calc. for C₁₄H₁₆: 184.1253. Found 184.1258).

(*Z*)-1-Phenyloct-1-en-3-yne 5b. Colorless oil, $\delta_{\rm H}$ (90 MHz, CDCl₃) 0.80–1.69 and 2.24–2.57 (7H, m and 2H, m, Buⁿ), 5.70 (1H, dt, *J* 12.0, 2.4, Ph-CH=CH-), 6.58 (1H, d, *J* 12.0, Ph-CH=CH-), 7.22–7.47 and 7.80–8.04 (3H, m and 2H, m, Ph-H) (HRMS *m*/*z* Calc. for C₁₄H₁₆: 184.1253. Found: 184.1250).

(*Z*)-1-Phenylhept-1-en-3-yne 5d. Colorless oil, $\delta_{\rm H}$ (90 MHz, CDCl₃) 1.05, 1.40–1.75 and 2.42 (3H, *t*, *J* 7.6, 2H, m and 2H, tq, *J* 6.8, 2.4, Pr^{*n*}), 5.69 (1H, dt, *J* 11.9, 2.4, Ph-CH=CH-), 6.55 (1H, d, *J* 11.9, Ph-CH=CH-), 7.25–7.45 and 7.81–7.92 (3H, m and 2H, m, Ph-H) (HRMS *m*/*z* Calc. for C₁₃H₁₄: 170.1096. Found: 170.1098).

(*Z*)-1-Phenyldec-1-en-3-yne 5e. Colorless oil, $\delta_{\rm H}$ (90 MHz, CDCl₃) 0.79–1.73 and 2.23–2.38 (11H, m and 2H, m, *n*-C₆H₁₃), 5.69 (1H, dt, *J* 12.0, 2.2, Ph-CH=CH-), 6.56 (1H, d, *J* 12.0, Ph-

CH=CH-), 7.20–7.50 and 7.79–7.98 (3H, m and 2H, m, Ph-H) (HRMS m/z Calc. for C₁₆H₂₀: 212.1566. Found: 212.1560).

(*Z*)-4-Cyclohexyl-1-phenylbut-1-en-3-yne 5g. Colorless oil, $\delta_{\rm H}$ (90 MHz, CDCl₃) 0.90–1.95 and 2.61 (10H, m and 1H, m, Cy), 5.70 (1H, dd, *J* 12.1, 2.2, Ph-CH=C*H*-), 6.55 (1H, d, *J* 12.1, Ph-C*H*=CH-), 7.25–7.35 and 7.53–7.94 (3H, m and 2H, m, Ph-H) (HRMS *m*/*z* Calc. for C₁₆H₁₈: 210.1409. Found: 210.1400).

Bis[(Z)-o-(5,5-dimethylhex-1-en-3-ynyl)phenyl]di-n-butyl-

stannane 6a. Pale yellow oil, $v_{max}(neat)/cm^{-1}$ 2225 (C=C); $\delta_{\rm H}$ (90 MHz, CDCl₃) 0.65–1.08 and 1.30–1.56 (6H, m and 12H, m, Buⁿ × 2), 1.26 (18H, s, Bu' × 2), 5.58 (2H, d, J 11.8, Ph-CH=CH-× 2), 6.53 (2H, d, J 11.8, Ph-CH=CH-× 2), 7.05–7.57 and 8.34–8.56 (6H, m and 2H, m, Ph-H) (HRMS *m*/*z* Calc. for C₃₂H₃₉Sn (M⁺ – Buⁿ, 57): 543.2074. Found: 543.2070).

Bis[(*Z*)-*o*-(oct-1-en-3-ynyl)phenyl]di-*n*-butylstannane 6b. Pale yellow oil, v_{max} (neat)/cm⁻¹ 2200 (C=C); $\delta_{\rm H}$ (90 MHz, CDCl₃) 0.66–1.63 and 2.20–2.53 (32H, m and 4H, m, Bu^{*n*} × 4), 5.60 (2H, dt, *J* 11.8, 2.2, Ph-CH=CH-× 2), 6.57 (2H, d, *J* 11.8, Ph-CH=CH-× 2), 7.10–7.59 and 8.33–8.53 (6H, m and 2H, m, Ph-H) (HRMS *m*/*z* Calc. for C₃₆H₄₈Sn: 600.2778. Found: 600.2794).

Bis[(*Z*)-*o*-(pent-1-en-3-ynyl)phenyl]di-*n*-butylstannane 6c. Pale yellow oil, v_{max} (neat)/cm⁻¹ 2210 (C≡C); $\delta_{\rm H}$ (90 MHz, CDCl₃) 0.63–1.04 and 1.33–1.60 (6H, m and 12H, m, Bu^{*n*} × 2), 1.98 (6H, d, *J* 2.6, Me × 2), 5.58 (2H, dt, *J* 11.4, 2.6, Ph-CH=CH-× 2), 6.51 (2H, d, *J* 11.4, Ph-CH=CH-× 2), 7.14–7.56 and 8.30–8.46 (6H, m and 2H, m, Ph-H) (HRMS *m*/*z* Calc. for C₃₀H₃₆Sn: 516.1876. Found: 516.1839).

Bis[(*Z*)-*o*-(hept-1-en-3-ynyl)phenyl]di-*n*-butylstannane 6d. Pale yellow oil, v_{max} (neat)/cm⁻¹ 2200 (C≡C); $\delta_{\rm H}$ (90 MHz, CDCl₃) 0.84–1.07, 1.36–1.70 and 2.26–2.42 (12H, m, 16H, m and 4H, m, Bu^{*n*} × 2 and Pr^{*n*} × 2), 5.59 (2H, dt, *J* 12.1, 2.4, Ph-CH=CH-× 2), 6.50 (2H, d, *J* 12.1, Ph-CH=CH-× 2), 7.17–7.40 and 8.38 (6H, m and 2H, d, *J* 7.7, Ph-H) (HRMS *m*/*z* Calc. for C₃₀H₃₅Sn (M⁺ − Bu^{*n*}, 57): 515.1761. Found: 515.1753).

Bis[(*Z*)-*o*-(dec-1-en-3-ynyl)phenyl]di-*n*-butylstannane 6e. Pale yellow oil, v_{max} (neat)/cm⁻¹ 2205 (C=C); $\delta_{\rm H}$ (90 MHz, CDCl₃) 0.84–0.88, 1.29–2.02 and 2.31–2.38 (total 44H, m, Bu^{*n*} × 2 and *n*-C₆H₁₃ × 2), 5.59 (2H, dt, *J* 11.7, 2.4, Ph-CH=CH-× 2), 6.51 (2H, d, *J* 12.1, Ph-CH=CH-× 2), 7.12–7.57 and 8.38 (6H, m and 2H, d, *J* 7.3, Ph-H) (HRMS *m/z* Calc. for C₃₆H₄₇Sn (M⁺ – Bu^{*n*}, 57): 599.2700. Found: 599.2706).

Bis[(Z)-o-(1-cyclohexylbut-1-en-3-ynyl)phenyl]di-n-butyl-

stannane 6g. Pale yellow oil, v_{max} (neat)/cm⁻¹ 2200 (C=C); $\delta_{\rm H}$ (90 MHz, CDCl₃) 0.77–1.76 and 2.58 (38H, m, and 2H, m, Buⁿ × 2 and Cy-H × 2), 5.61 (2H, dt, *J* 11.7, 2.2, Ph-CH=CH- × 2), 6.50 (2H, d, *J* 11.7, Ph-CH=CH- × 2), 7.17–7.47 and 8.43 (6H, m and 2H, d, *J* 8.1, Ph-H) (HRMS *m*/*z* Calc. for C₃₆H₄₃Sn (M⁺ – Buⁿ, 57): 595.2387. Found: 595.2362).

Conversion of 4a into 2-tert-butyl-1-chloro-1-benzostibepine 9a

The reaction of **4a** with SbCl₃ was carried out in an NMR tube; $\delta_{\rm H}$ (400 MHz, CDCl₃) 1.25 (9H, s, Bu'), 6.41 (1H, dd, J 5.5, 12.7, 4-H), 6.68 (1H, d, J 5.5, 3-H), 7.07 (1H, d, J 12.7, 5-H), 7.25–7.59 and 7.92 (3H, m and 1H, d, J 6.4, Ph-H).

2-tert-Butyl-1-phenyl-1-benzostibepine 10a

A solution of 4a (71 mg, 0.17 mmol) in CHCl₃ (2 ml) was added in one portion with stirring to SbCl₃ (39 mg, 0.17 mmol) in CHCl₃ (10 ml) under an argon atmosphere at 0 °C. The reaction mixture was vigorously stirred at room temperature for 30 min. After removal of the solvent at room temperature in vacuo, followed by exclusion of BuSnCl₂ at 100-110 °C/2 mmHg using a semimicro distillation apparatus, the resulting residue was dissolved in hexane (10 ml). To this hexane solution of crude 9a at -20 °C was added PhLi (1.14 mol 1⁻¹, 0.25 ml, 0.17 mmol). The mixture was stirred under the above conditions for 30 min, quenched by the addition of aqueous NH_4Cl (10 ml) and extracted with hexane (30 ml \times 3). The organic layer was washed with brine (30 ml \times 2), dried (MgSO₄) and evaporated. The resulting residue was chromatographed on silica gel using hexane as eluent to give 10a (23 mg, 36% from 4a) as a colorless oil. This compound was identical with the authentic sample prepared in our previous paper.13

2-*n*-Butyl-1-phenyl-1-benzostibepine 10b

The stannepine **4b** was treated with SbCl₃ and worked up as described for the preparation of **10a** to give **10b** (27 mg, 41% from **4b**) as a colorless oil. This compound was identical with the authentic sample prepared in our previous paper.¹³

2-tert-Butyl-1-methyl-1-benzostibepine 11a

The stannepine **4a** was treated with MeLi instead of PhLi and worked up as described for the preparation of **10a** to give **11a** (31 mg, 57% from **4a**) as a colorless oil; $\delta_{\rm H}$ (400 MHz, CDCl₃) 0.95 (3H, s, Sb-Me), 1.18 (9H, s, Bu'), 6.28 (1H, dd, *J* 6.0, 13.2, 4-H), 6.69 (1H, d, *J* 6.0, 3-H), 6.82 (1H, d, *J* 13.2, 5-H), 7.29–7.49 and 7.61–7.71 (3H, m and 1H, m, Ph-H); $\delta_{\rm C}$ (100 MHz, CDCl₃) –6.2 (q), 30.6 (q), 39.4 (s), 127.4 (d), 127.9 (d), 128.1 (d), 129.4 (d), 129.6 (d), 132.6 (d), 133.8 (s), 137.1 (d), 142.8 (s), 157.2 (s) (HRMS *m*/*z* Calc. for C₁₅H₁₉Sb: 320.0525. Found: 320.0533).

2-n-Butyl-1-methyl-1-benzostibepine 11b

The stannepine **4b** was treated with MeLi instead of PhLi and worked up as described for the preparation of **10a** to give **11b** (22 mg, 41% from **4b**) as a colorless oil; $\delta_{\rm H}$ (400 MHz, CDCl₃) 1.13 (3H, s, Sb-Me), 0.90, 1.22–1.58 and 2.36 (3H, t, *J* 7.5, 4H, m and 2H, t, *J* 7.3, Buⁿ), 6.30 (1H, dd, *J* 5.3, 12.3, 4-H), 6.46 (1H, d, *J* 5.3, 3-H), 6.92 (1H, d, *J* 12.3, 5-H), 7.23–7.35 and 7.46–7.50 (3H, m and 1H, m, Ph-H); $\delta_{\rm C}$ (100 MHz, CDCl₃) – 5.5 (q), 14.0 (q), 22.3 (t), 32.3 (t), 38.4 (t), 127.5 (d), 128.2 (d), 128.6 (d), 130.7 (d), 130.8 (d), 132.3 (d), 133.9 (s), 136.0 (d), 142.0 (s), 144.9 (s) (HRMS *m*/*z* Calc. for C₁₅H₁₉Sb: 320.0525. Found: 320.0526).

2-tert-Butyl-1-n-butyl-1-benzostibepine 12a

The stannepine **4a** was treated with Bu"Li instead of PhLi and worked up as described for the preparation of **10a** to give **12a** (14 mg, 23% from **4a**) as a colorless oil; $\delta_{\rm H}$ (400 MHz, CDCl₃) 1.20 (9H, s, Bu'), 0.81 and 1.23–1.73 (3H, t, *J* 7.3 and 6H, m, Bu"), 6.24 (1H, dd, *J* 6.0, 13.2, 4-H), 6.76 (1H, d, *J* 6.0, 3-H), 6.78 (1H, *J* 13.2, 5-H), 7.28–7.32 and 7.60–7.72 (3H, m and 1H, m, Ph-H) (HRMS *m*/*z* Calc. for C₁₈H₂₅Sb: 362.0995. Found: 362.0994.

1,2-Di-n-butyl-1-benzostibepine 12b

The stannepine **4a** was treated with Bu"Li instead of PhLi and worked up as described for the preparation of **10a** to give **12b** (15 mg, 25% from **4b**) as a colorless oil; $\delta_{\rm H}$ (400 MHz, CDCl₃) 0.85–1.20, 1.20–1.60 and 2.22–2.35 (8H, m, 8H, m and 2H, m, Bu" × 2), 6.25 (1H, dd, J 6.0, 13.0, 4-H), 6.50 (1H, d, J 6.0,

3-H), 6.88 (1H, d, *J* 13.0, 5-H), 7.30–7.33 and 7.60–7.75 (3H, m and 1H, m, Ph-H) (HRMS *m*/*z* Calc. for $C_{18}H_{25}Sb$: 362.0995. Found: 362.0999).

Conversion of 4a into 2-tert-butyl-1-chloro-1-benzoborepine 14a

A solution of **4a** (71 mg, 0.17 mmol) in CHCl₃ (2 ml) was added in one portion with stirring to BCl₃ (20 mg, 0.17 mmol) in CHCl₃ (10 ml) under an argon atmosphere at 0 °C. The reaction mixture was vigorously stirred at room temperature for 30 min. After evaporation of the solvent, the resulting residue was distilled under reduced pressure to give **14a** (17 mg, 44%) as a pale yellow oil, bp 90–100 °C (2 mmHg); $\delta_{\rm H}$ (400 MHz, CDCl₃) 1.43 (9H, s, Bu'), 6.75 (1H, dd, *J* 8.4, 11.9, 4-H), 7.25 (1H, d, *J* 8.4, 5-H), 7.49 (1H, d, *J* 11.9, 3-H), 7.40–7.60 and 8.30–8.40 (3H, m and 1H, m, Ph-H) (HRMS *m/z* Calc. for C₁₄H₁₆BCl: 230.1034, 232.1004. Found: 230.1031, 232.1011).

Conversion of 4a into 2-tert-butyl-1-phenyl-1-benzoborepine 15a

The stannepine **4a** was treated with PhBCl₂ instead of BCl₃ and worked up as described for the preparation of **14a** to give **15a** (25 mg, 54%) as a colorless oil, bp 80–100 °C (4 × 10⁻⁶ mmHg); $\delta_{\rm H}$ (400 MHz, CDCl₃) 1.19 (9H, s, Bu'), 6.50 (1H, dd, J 7.0, 11.7, 4-H), 6.75 (1H, d, J 7.0, 3-H), 6.88 (1H, d, J 11.7, 5-H), 7.32–7.52 and 7.71–7.80 (6H, m and 3H, m, Ph-H); $\delta_{\rm C}$ (100 MHz, CDCl₃) 32.4 (q), 36.9 (s), 124.8 (d), 126.8 (d), 127.0 (d), 127.3 (d), 127.4 (d), 127.5 (d), 128.6 (d), 131.0 (d), 131.3 (d), 135.8 (d), 136.6 (s), 141.6 (s), 148.4 (s), 159.3 (s) (HRMS *m*/*z* Calc. for C₂₀H₂₁B: 272.1736. Found: 272.1734).

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