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The stereochemistry of aziridine borane lithiation: diastereoselectivity and enantioselectivity

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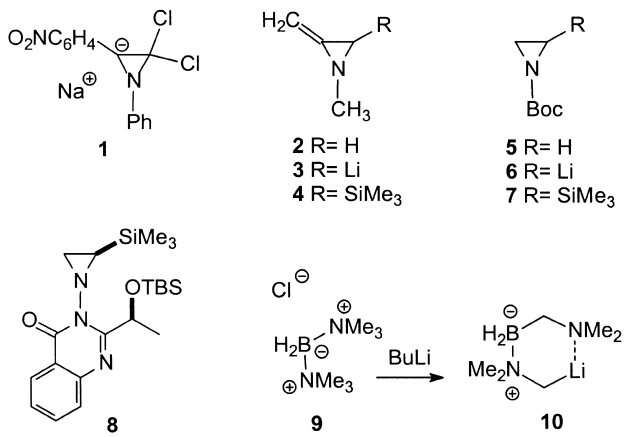
Abstract—Lithiation of 1-methylaziridine borane, 1-(*tert*-butyldimethylsiloxyethyl)aziridine borane, or 1-(*tert*-butyldimethylsiloxyethyl)-2-methylaziridine borane occurs *syn* to the boron substituent, while lithiation of 1-(*tert*-butyldimethylsiloxyethyl)-2-trimethylstannylaziridine borane occurs *anti* to boron as well as silicon due to the steric effect of trimethylsilyl group (*s*-butyllithium was used in all cases). Kinetically controlled lithiation in the first three cases results from a combination of steric and electrostatic effects. Enantioselective lithiation occurs in the presence of (−)-sparteine, with product enantioselectivities near 70% ee.

1. Introduction

Direct metallation of aziridines has been known since the first report by Rubottom et al. in 1972, describing the surprisingly stable anion **1**.[1] Soon thereafter, Quast et al. reported the lithiation of methyleneaziridine **2** to generate **3**, and were able to demonstrate an enantioselective modification of this process by lithiation in the presence of a chiral lithium complexing agent at −120°C, followed by trapping with TMSCl to afford **4** (12.4% ee).[2] Anion trapping was conducted at temperatures below −50°C to avoid decomposition of **2**.[2a] Lithiation of *N*-*t*-butoxycarbonylaziridine **5** has been reported by Beak et al., but in this case the anion **6** decomposes more rapidly and trapping with Me_3SiCl to afford **7** requires an in situ technique.[3] The most extensive studies have involved the 2-magnesioaziridines generated by Satoh et al. by reductive desulfinylation.[4,5] Many other interesting reports of metallated aziridines have appeared over the years.[6] However, beyond the original study by Quast et al.,[2b] there have been no reports describing enantioselective aziridine lithiation to our knowledge. On the other hand, diastereoselective lithiations directed by covalently bound chiral auxiliaries at nitrogen are known in the case of a 2-iso-propylideneaziridine, or with aziridines containing a carbonyl group at the C(2) position.[7] Furthermore, a chiral aziridinyl anion equivalent has been generated from **18** by fluoride-induced desilylation.[8]

We became interested in the aziridine lithiation problem in connection with a synthetic project where access to enantioenriched monosubstituted aziridines was desired.[6j,k] A number of other projects in our laboratory had encountered situations where lithiation of amine borane complexes was facile,[9] and related observations have been reported by several other groups using amine boranes[10,11] and amine BF_3 complexes,[12] respectively. To our knowledge, the first relevant report is the 1966 paper by Miller, demonstrating the conversion from **9** to **10**.[13] (Scheme 1) Based on some of the early analogies,[10–13] we wondered whether direct lithiation of simple aziridine boranes[14] would be possible, and whether an enantioselective version of this process might be achieved. Our preliminary report established the feasibility of aziridine borane lithiation and briefly summarized evidence for the relative stereochemistry of the reaction.[15] Recently, Simpkins et al. have described the



Scheme 1.

Keywords: 2-lithioaziridine; aziridine; enantioselective lithiation; sparteine.
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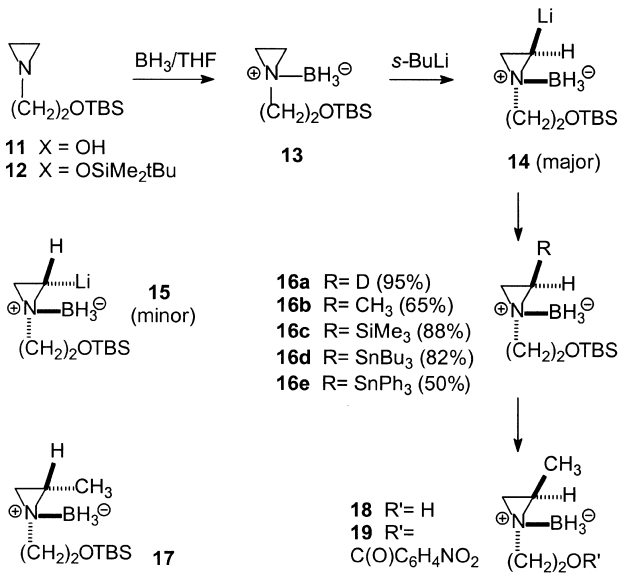
lithiation of *N*-methylisoindoline borane in the presence of sparteine. Products of electrophilic trapping were obtained with up to 89% ee,[16] depending on the electrophile. Interesting issues of relative stereochemistry were also encountered in the Simpkins study.[16] We have now carried out similar experiments in the aziridine series to evaluate the prospects for enantioselective lithiation. This work is described below, along with an account of relevant aspects of relative stereocontrol.

2. Results and discussion

The first lithiation experiments were carried out with **13**, prepared from commercially available *N*-(2-hydroxyethyl)-aziridine **11** (Scheme 2). After hydroxyl protection as the TBS ether **12**, the stable borane complex **13** was prepared using fresh BH_3–THF solution[6c,d] and was isolated by flash chromatography (82% overall). Treatment of **13** with *s*-BuLi for 0.5–1 h in THF at −78°C was sufficient for lithiation, based on the results of trapping with D_2O quenching (>97% deuterium incorporation, complete within the limits of NMR assay). However, the stereochemistry of the intermediate lithioaziridines (**14** or **15**) could not be determined unambiguously at this stage. Assignment of the structure **16a** was made by analogy to the examples described below.



Scheme 2.

When **13** was treated with *s*-BuLi followed by iodomethane (6 h, −78°C), a dominant methylation product **16b** was formed. NMR assay of the crude product revealed trace signals probably due to the minor diastereomer **17b**. Purification of **17b** was not achieved, but the product ratio could be established as 22:1 by comparison of the major (δ 1.51 ppm) and minor (δ 1.42 ppm) methyl doublets. To prove the stereochemistry of the major product **16b**, the TBS group was removed using Bu_4NF/THF at rt. The resulting alcohol **18** was converted without isolation to the crystalline *p*-nitrobenzoate **19** using *p*-nitrobenzoyl chloride at room temperature (59% overall). The structure and relative stereochemistry of **19** were established by X-ray crystallography (Fig. 1),[17] and the *cis* relationship between the methyl and borane subunits was confirmed. Assuming retention of configuration from the C–Li intermediate through the C–C bond forming step to form **16b**, initial lithiation occurs *syn* to boron and favors **14** over **15** by a ratio of at least 20:1.

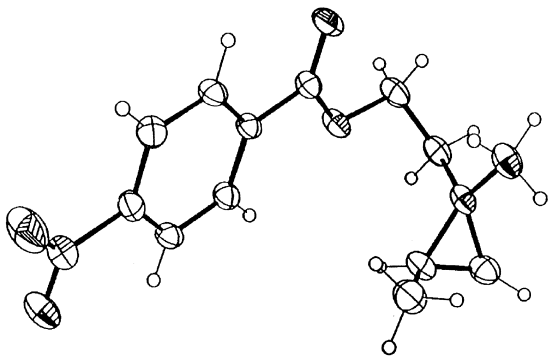


Figure 1. Crystal structure of *p*-nitrobenzoate ester aziridine borane complex **19**.

Trapping experiments with other electrophiles were performed, and similar results were obtained. Thus, lithiation as before, followed by addition of Me_3SiCl, Bu_3SnCl, and Ph_3SnCl at −78°C gave products **16c**, **16d**, and **16e**, respectively. Comparisons of NMR data for **16b**–**16e** indicated that all four products have the same dominant configuration. No evidence for the minor diastereomers **17c** or **17d** was detected in either of the most efficient silylation or stannylation examples, but up to ca. 5% of **17** may have been missed. The Ph_3SnCl experiment was more complex and was not studied in detail. However, the product **16e** proved to be highly crystalline and confirmation of the structure and stereochemistry was obtained by X-ray crystallography (Fig. 2).[18]

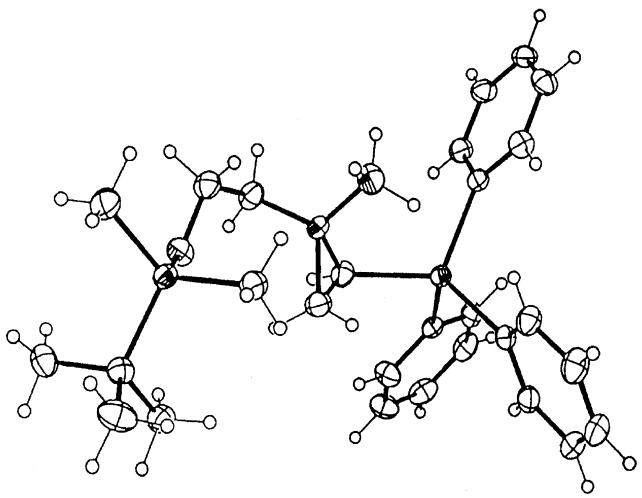
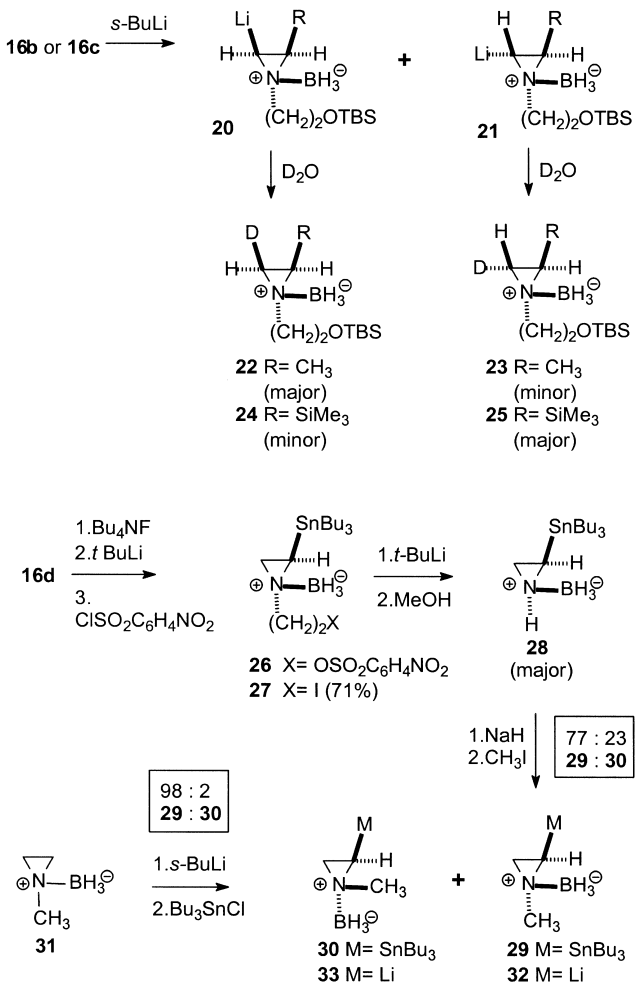


Figure 2. Crystal structure of 2-triphenylstannylaziridine borane complex **16e**.

The sequence of lithiation and deuteration of **16b** and **16c** was investigated to gain further insights regarding lithiation preferences (Scheme 3). Treatment of **16b** with *sec*-butyllithium followed by D_2O resulted in the formation of



Scheme 3.

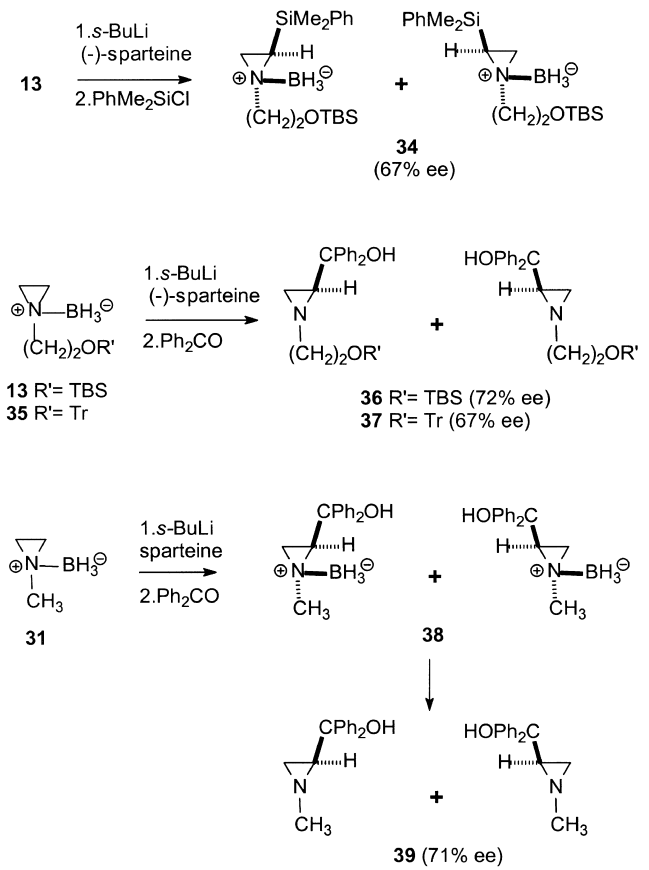
22 (R=CH_3) as the major diastereomer (90–95% by NMR integration). The assignment is based on disappearance of that C_3–H signal which has the smaller vicinal coupling constant (6.3 Hz) to C_2–H in **16b**. This requires a *trans* relationship between C_2–H and the kinetically more acidic C_3–H in **16b** according to literature data for aziridine couplings, and shows that once again, lithiation had occurred preferentially *syn* to the borane subunit to generate **20**.[19] Evidently, the *syn*-directing effect of BH_3 is still dominant even though the influence of the exocyclic N–CH_2 group should now be countered by the steric effect of a C_2–CH_3 group.

A similar lithiation/D_2O quenching sequence was carried out starting from **16c**. In contrast to **16b**, deuterium replaced that C_3–H signal which has the larger vicinal coupling constant (9.3 Hz) to C_2–H in the starting **16c**. This finding indicates that the major product is **25**, derived from the lithioaziridine **21**, and that a C_2–$SiMe_3$ substituent is large enough to overcome the *syn*-directing effect of the N–BH_3 group. The NMR spectra of the deuterated product were not resolved sufficiently to establish the ratio of **24**:**25** in this experiment, but were sufficient to conclude that **25** is the dominant isomer.

To gain additional evidence regarding configurational stability of 2-lithioaziridine borane complexes, methods were considered that might provide access to both diastereomers corresponding to **14** and **15**, or closely related structures. In principle, this might be done by tin lithium exchange if **17d** could be isolated. However, we had been unable to detect the minor diastereomer. The decision was made to target a different pair of organotin diastereomers **29** and **30** in the hope that access to both diastereomers would be simplified (Scheme 3). Part of the motivation was the realization that it should be possible to prepare **29** and **30** by removing the siloxyethyl substituent from aziridine nitrogen in **16d**, and replacing it with a methyl group. Thus, the tributylstannyl complex **16d** was deprotected (Bu_4NF), converted to the *p*-nitrobenzenesulfonate **26**, and the latter was treated with NaI/acetone to afford the iodide **27** (71% overall). Reductive cleavage of **27** using *t*-butyllithium (2.2 equiv., −78°C) then gave the N-deprotected aziridine borane **28** (92%), and *N*-methylation (NaH/CH_3I) produced a 77:23 mixture of diastereomers **29** and **30** (stereochemistry of **29** assigned by comparison of coupling constant data with **16d**). The diastereomer mixture could not be separated. However, the NMR spectra were easy to interpret, and the isomer ratio could be assigned with confidence.

A very different 98:2 ratio of the same diastereomers **29** and **30** was obtained by lithiation of the known *N*-methylaziridine borane complex (**31**)[14b] with *s*-butyllithium followed by quenching with Bu_3SnCl. With two distinct diastereomer mixtures of **29** and **30** in hand, it became possible to probe configurational stability of the corresponding organolithium derivatives. First, a control experiment was carried out to show that the 77:23 mixture of **29** and **30** undergoes complete exchange to **32**+**33** upon treatment with *n*-butyllithium at −78°C. After quenching with water, the destannylated **31** was obtained, but none of the starting **29** or **30** was recovered. With tin–lithium exchange confirmed, the procedure was repeated starting with the same mixture of **29** and **30**, but the intermediate organolithium species were quenched with Bu_3SnCl. This gave **29** and **30** in a ratio of 82:18 (90%), together with destannylated **31** (10%). The small change in diastereomer ratios in the recovered **29**/**30** (82:18) compared to the starting ratio (77:23) is consistent with a small kinetic advantage for trapping of **33** by protic impurities to generate the destannylated byproduct **31**, but not with an equilibrium between **32** and **33**. Because the product ratio does not resemble the 98:2 ratio of diastereomers **29** and **30** obtained via lithiation of **31**, we conclude that the intermediate 2-lithioaziridines **32** and **33** are configurationally stable on the time scale of the experiments.

Attention was turned to the enantioselective lithiation of **13** using (−)-sparteine as the chiral ligand for lithium.[20] The original subset of aziridine products **16** proved difficult to assay for enantiomeric excess, so the reaction of the lithioaziridine **14** with additional electrophiles was explored. Eventually, two examples were encountered where the enantiomers could be resolved using HPLC methods (Scheme 4). In both cases, it was important to use phenyl-substituted electrophiles to facilitate assay. Thus, **13** was lithiated in ether in the presence of (−)-sparteine, and the resulting **14** was trapped with $ClSiMe_2Ph$. The product



Scheme 4.

34 was isolated by chromatography and was shown to have 67% ee by HPLC on a chiral support. The absolute configuration was not assigned in any of the lithiations, but the enantiomerically enriched products were compared with racemic products using HPLC to confirm the assignment of peaks corresponding to each enantiomer.

In a second series of experiments, **13** was lithiated in the presence of sparteine, followed by trapping with benzophenone. When the reaction was subjected to aqueous workup, the aziridine **36** was obtained. In contrast to the analogous **16** and **34**, the intermediate borane complex had not survived the workup and isolation. Apparently, the combination of steric hindrance and incorporation of electronegative substituents in the Ph_2COH subunit results in a borane complex that is easily dissociated and decomposes during the isolation procedure.

In an attempt to improve enantioselectivity by varying the oxygen protecting group, the trityl ether **35** was used as a substrate. The same sparteine-mediated lithiation and benzophenone trapping was carried out as described for **13**. The reaction proved unexpectedly complex, apparently due to partial cleavage of the trityl protecting group during lithiation, and only 8% of the expected trapping product **37** was obtained. As before, the borane complex in the hindered product had decomposed during isolation. Enantioselectivity assay using HPLC indicated that **37** was formed with 67% ee. Although this value is lower than in the corresponding experiment with **13** to form **36** (72% ee), it is likely that the apparent difference is due to non-ideal peak shapes for the product enantiomers and systematic error in the assay.

One final series of enantioselective (−)-sparteine-mediated lithiation experiments was performed using **31** as the substrate. Lithiation and benzophenone trapping worked well in toluene, but the reaction gave the borane complex **38** as well as some of the free aziridine **39**. The complex **38** could be isolated in modest yield by crystallization, but the material was not stable enough for ee assay, so the borane was cleaved by treatment with ethanol–dichloromethane. The resulting **39** (21% overall from **31**) had >99% ee according to HPLC assay. However, when the crystallization step was omitted, the ee of **39** dropped to 71%. This result shows that high ee in the prior experiment resulted from an upgrade during crystallization.

The 71% ee value for **39** is in the same range as observed for the other (−)-sparteine-mediated aziridine lithiations, and suggests that the nature of the nitrogen substituent is not an important factor in the enantioselective lithiations. This would be no surprise if the lithiation occurs *syn* to boron, as in the corresponding reactions in the absence of sparteine, because the alkyl group attached to nitrogen would be on the opposite side of the aziridine compared to the site of lithiation. In view of these considerations, further variation of the nitrogen alkyl substituent appears unlikely to improve enantioselectivity beyond the ca. 70% ee level.

3. Conclusion

All of the experiments described above are consistent with dominant aziridine lithiation *syn* to the BH_3 subunit. This conclusion is supported by two X-ray structures (Figs. 1 and 2), and by NMR correlations in the case of **16**, **22**, **29**, **34**, and **38**. Similar lithiation diastereoselectivity results were encountered by Simpkins et al.,[16] although they also observed electrophile-dependent diastereoselectivity in the subsequent trapping reactions.

The *syn* directing effect of the borane can be regarded as a non-covalent version of the complexation-induced proximity effect.[21] We believe that the primary interactions responsible for *syn*-direction are electrostatic in nature, resulting from the attraction between partially negative hydridoborate bonds and the partially positive lithium in the transition state for lithiation. Similar lithium–hydride interactions are well known in the solid state structure of the lithium borohydride–TMEDA complex.[22]

Practical levels of enantioselection were not achieved with the aziridine boranes.[23] Attempts to vary the nitrogen substituent were unproductive, probably because the *N*-alkyl group is on the remote side of the aziridine ring compared to the site of lithiation. However, the results were sufficient to confirm that enantioselection is possible in the aziridine boranes. As in the Simpkins experiments with the *N*-methylisoindoline borane substrate,[16] the directing effect of (−)-sparteine is compatible with *syn*-direction by the borane subunit.

4. Experimental

4.1. General

HPLC analysis was performed on a Gilson system with detection by UV. All lithiations were run under nitrogen flow in oven or flame dried glassware. Tetrahydrofuran and diethyl ether were freshly distilled from sodium benzophenone ketyl under N_2. Commercial reagents were used as received unless noted.

4.1.1. 1-(*tert*-Butyldimethylsiloxyethyl)aziridine borane (13). A solution of 2-aziridineethanol (Aldrich, 1.30 mL, 16.2 mmol) in 20 mL of dry THF was cooled to −78°C and treated with 10.0 mL (16.0 mmol) of a 1.60 M solution of *n*-BuLi in hexane. After 20 min a solution containing 2.40 g (16.0 mmol) of *t*-butyldimethylsilyl chloride (Aldrich) in 5 mL of THF was added by cannula. The reaction mixture was maintained at −78°C for 3 h and then was allowed to warm slowly (12 h) to rt. The mixture was then treated with 16.0 mL (16.0 mmol) of a 1 M solution of borane–THF complex in THF (Aldrich). After 30 min the solvent was removed (aspirator), and the crude complex was taken up in 50 mL of ether. The ethereal solution was washed with water (2×10 mL), brine (1×10 mL), and dried ($MgSO_4$). After removal of solvent (aspirator), the residue was purified by flash chromatography on silica gel (10×3 cm), 1:3 EtOAc/hexane eluent to give 2.85 g (82%) of **13** as a colorless oil; analytical TLC on silica gel, 1:4 EtOAc/hexane, R_f=0.35. IR (neat, cm^{-1}) 2318, 2380, B–H; 300 MHz NMR ($CDCl_3$, ppm) δ 4.03 (2H, t, J=5.1 Hz) 2.74 (2H, t, J=5.1 Hz) 2.3–2.1 (4H, m) 2.1–1.0 (3H, br q, J=95.0 Hz) 0.91 (9H, s) 0.10 (6H, s). HRMS (EI): $M-H^+$ found 214.1802. $C_{10}H_{25}BNOSi$ requires 214.1799.

4.1.2. 1-(*tert*-Butyldimethylsiloxyethyl)-2-deuterioaziridine borane (16a). A solution of **13** (0.115 g, 0.535 mmol) in 5 mL of dry THF was cooled to −78°C under nitrogen and was treated with 2.80 mL (2.71 mmol) of 0.97 M *sec*-BuLi in cyclohexane (Aldrich). After 35 min the reaction mixture was quenched with a solution of 0.16 mL D_2O in 2 mL of THF. After the same workup as for non-deuterated **13**, **16a** was obtained in quantitative yield. Characteristic changes were observed in relevant NMR signals compared to **13**; ($CDCl_3$, ppm) δ 2.3–2.1 (3H, m) 2.1–1.0 (3H, br s). Monodeuteration was confirmed by HRMS (EI): $M-H^+$ found 215.1858. $C_{10}H_{24}BDNOSi$ requires 215.1861.

4.1.3. 1-(*tert*-Butyldimethylsiloxyethyl)-2-methylaziridine borane (16b). A solution of **13** (0.599 g, 2.78 mmol) in 15 mL of dry THF was cooled to −78°C and then treated with 13.8 mL (13.4 mmol) of a 0.97 M solution of *sec*-BuLi in cyclohexane (Aldrich). After 35 min a solution of 1.7 mL (27.3 mmol) methyl iodide in 3 mL THF was added by cannula. The reaction was maintained at −78°C for 6 h and allowed to warm slowly to rt. The solvent was removed (aspirator) and the residue taken up in ether (50 mL). The ethereal solution was washed with water (2×5 mL), brine (1×5 mL), and dried ($MgSO_4$). After removal of solvent (aspirator), the residue was purified by flash chromatography on silica gel (15×2 cm, 3×6 mL then 46×2 mL fractions, 5:95 EtOAc/hexane eluent) to give **16b** (0.415 g, 65%) followed by recovered **13** (50 mg, 8%); **16b**: colorless oil, analytical TLC on silica gel, 1:4 EtOAc/hexane, R_f=0.43. IR (neat, cm^{-1}) 2375, B–H; 300 MHz NMR ($CDCl_3$, ppm) δ 4.2–4.1 (1H, m) 3.9–3.8 (1H, m) 3.1–3.0 (1H, m) 2.5–2.4 (1H, m) 2.4–2.3 (1H, m) 2.12 (1H, d, J=7.2 Hz) 2.01 (1H, d, J=6.3 Hz) 2.0–1.0 (3H, br s) 1.47 (3H, d, J=6.3 Hz) 0.87 (9H, s) 0.07 (3H, s) 0.06 (3H, s). HRMS (EI): $M-H^+$ found 228.1962. $C_{11}H_{27}BNOSi$ requires 228.1955.

4.1.4. 1-(*tert*-Butyldimethylsiloxyethyl)-2-trimethylsilylaziridine borane (16c). Using the same procedure as for **16b**, the product **16c** was isolated in 88% yield as a colorless, unpleasant smelling oil; analytical TLC on silica gel, 1:4 EtOAc/hexane, R_f=0.53. IR (neat, cm^{-1}) 2377, B–H; 300 MHz NMR ($CDCl_3$, ppm) δ 4.1–3.9 (2H, m) 3.0–2.9 (1H, m) 2.6–2.5 (1H, m) 2.28 (1H, d, J=9.3 Hz) 2.14 (1H, d, J=7.8 Hz) 2.1–0.8 (3H, br s) 1.55 (1H, dd, J=9.3, 7.8 Hz) 0.88 (9H, s) 0.22 (9H, s) 0.07 (3H, s) 0.06 (3H, s). HRMS (EI): $M-H^+$ found 286.2194. $C_{13}H_{33}BNOSi_2$ requires 286.2194.

4.1.5. 1-(*tert*-Butyldimethylsiloxyethyl)-2-tri-*n*-butylstannylaziridine borane (16d). Using the same procedure as for **16b**, the product **16d** was isolated in 82% yield as a colorless oil; **16d**, analytical TLC on silica gel, 1:4 EtOAc/hexane, R_f=0.70. IR (neat, cm^{-1}) 2370, B–H; 300 MHz NMR ($CDCl_3$, ppm) δ 4.2–3.8 (2H, m) 2.9–2.6 (2H, m) 2.38 (1H, d, J=9.3 Hz) 2.15 (1H, d, J=7.8 Hz) 2.0–1.0 (3H, br s) 1.76 (1H, dd, J=9.3, 7.8 Hz) 1.6–1.2 (12H, m) 1.1–1.0 (6H, m) 0.90 (9H, s) 0.90 (9H, t, J=6.9 Hz) 0.09 (3H, s) 0.08 (3H, s). HRMS (EI): $M-H^+$ found 504.2883. $C_{22}H_{51}BNOSiSn$ requires 504.2855.

4.1.6. 1-(*tert*-Butyldimethylsiloxyethyl)-2-triphenylstannylaziridine borane (16e). Using the same procedure as for **16b**, the product **16e** was isolated as a colorless oil that solidified (50%). Crystallization from dichloromethane–hexane gave colorless prisms, mp 102–104°C, suitable for X-ray crystallography; analytical TLC on silica gel, 3:7 EtOAc/hexane, R_f=0.62. IR (neat, cm^{-1}) 2368, B–H; 300 MHz NMR ($CDCl_3$, ppm) δ 7.8–7.3 (15H, m) 4.1–4.0 (2H, m) 2.9–2.8 (2H, m) 2.60 (1H, d, J=8.7 Hz) 2.45 (1H, dd, J=8.7, 6.9 Hz) 2.34 (1H, d, J=6.9 Hz) 2.2–1.2 (3H, br s) 0.83 (9H, s) 0.03 (3H, s) 0.01 (3H, s). HRMS (EI): $M-H^+$ found 564.1926. $C_{28}H_{39}BNOSiSn$ requires 564.1917.

4.1.7. 1-(*p*-Nitrobenzoyloxyethyl)-2-methylaziridine borane (19). To a stirred solution of **16b** (65.0 mg, 0.284 mmol) in 1 mL of THF at room temperature was added tetrabutylammonium fluoride (0.28 mL of a 1.0 M solution in THF, 0.28 mmol). TLC analysis revealed that desilylation was complete after 15 min. The solvent was removed under a stream of N_2 at room temperature. The residue was dissolved in 1 mL of CH_2Cl_2 and *p*-nitrobenzoyl chloride (54.5 mg, 0.293 mmol) in 1 mL of CH_2Cl_2 was added via cannula. The reaction was stirred at room temperature for 2 h. The solvent was removed (aspirator), and the residue dissolved in 8 mL of Et_2O. The ether solution was washed with 1 M aqueous $NaHCO_3$ (1×2 mL), H_2O (1×2 mL) and brine (1×2 mL) and dried ($MgSO_4$). The solvent was removed to give 45 mg (59%) of crude **19** as a

yellow solid; analytical TLC on silica gel, 1:4 EtOAc/hexane, R_f=0.10. Pure material was obtained by crystallization from hexane/ether, mp 109–110°C, yellow prisms, suitable for X-ray crystallography. IR ($CDCl_3$, cm^{-1}) 2375, B–H; 1727, C=O; 300 MHz NMR ($CDCl_3$, ppm) δ 8.35 (2H, d, J=9.0 Hz) 8.23 (2H, d, J=9.0 Hz) 5.0–4.7 (2H, m) 3.4–3.3 (1H, m) 2.7–2.6 (1H, m) 2.5–2.4 (1H, m) 2.22 (2H, d, J=7.2 Hz) 2.2–1.0 (3H, br s) 1.55 (3H, d, J=6.0 Hz). HRMS (EI): M^+ found 264.12811. $C_{12}H_{17}BN_2O_4$ requires 264.12810.

4.1.8. Lithiation of 16b and 16c followed by deuterium oxide quench; conversion to 1-(*tert*-butyldimethylsiloxyethyl)-2-methyl-3-deuterioaziridine borane (22) and 1-(*tert*-butyldimethyl-siloxyethyl)-2-trimethylsilyl-3-deuterioaziridine borane (25). The same procedure for lithiation; deuteration was used as described for preparation of **16a**, and the workup and purification followed the methods described for **16b** and **16c**. Starting from **16b**, the product consisted of ca. 95% of **22** (NMR assay). IR (neat, cm^{-1}) 2954, C–H; 2377, B–H; 300 MHz NMR ($CDCl_3$, ppm) δ 4.2–4.1 (1H, m) 3.9–3.8 (1H, m) 3.1–3.0 (1H, m) 2.5–2.4 (1H, m) 2.4–2.3 (1H, m) 2.11 (1H, d, J=7.8 Hz) 2.1–1.0 (3H, br s) 1.48 (3H, d, J=6.0 Hz) 0.89 (9H, s) 0.08 (3H, s) 0.07 (3H, s). HRMS (EI): $M-H^+$ found 229.2013. $C_{11}H_{26}BDNOSi$ requires 229.2018.

Starting from **16c**, the product was **25**. IR (neat, cm^{-1}) 2954, C–H; 2371, B–H; 300 MHz NMR ($CDCl_3$, ppm) δ 4.1–4.0 (2H, m) 3.0–2.9 (1H, m) 2.6–2.5 (1H, m) 2.14 (1H, d, J=7.8 Hz) 2.0–1.0 (3H, br s) 1.55 (1H, d, J=7.8 Hz) 0.89 (9H, s) 0.22 (9H, s) 0.08 (3H, s) 0.07 (3H, s). HRMS (EI): $M-H^+$ found 287.2250. $C_{13}H_{32}BDNOSi_2$ requires 287.2257.

4.1.9. Deprotection of 16d; conversion to 2-tri-*n*-butylstannylaziridine borane (28). A solution of **16d** (0.665 g, 1.32 mmol) in 10 mL of THF was treated at rt with 1.35 mL (1.35 mmol) of a 1 M solution of tetrabutylammonium fluoride in THF (Aldrich). After 20 min the solvent was removed (aspirator) and the crude alcohol was taken up in 40 mL of ether. The ethereal solution was washed with water (2×3 mL) and brine (1×3 mL) and dried ($MgSO_4$). After removal of solvent (aspirator), the residue was purified by flash chromatography on silica gel (15×3 cm), 2:3 EtOAc/hexane eluent to give the alcohol as a colorless oil, 0.451 g (88%); analytical TLC on silica gel, 1:4 EtOAc/hexane, R_f=0.10. IR (neat, cm^{-1}) 3400, O–H; 2370, B–H; 300 MHz NMR ($CDCl_3$, ppm) δ 4.2–3.9 (2H, m) 2.9–2.7 (2H, m) 2.6 (1H, br s) 2.33 (1H, d, J=9.3 Hz) 2.22 (1H, d, J=7.2 Hz) 2.0–1.0 (3H, br s) 1.70 (1H, dd, J=9.3, 7.2 Hz) 1.6–1.3 (12H, m) 1.1–1.0 (6H, m) 0.90 (9H, t, J=6.9 Hz). A solution of the alcohol (0.441 g, 1.13 mmol) in 5 mL THF was cooled to −78°C and treated with 0.63 mL (1.13 mmol) of a solution of 1.79 M *t*-BuLi in pentane (Aldrich). After 10 min a solution of 0.252 g (1.14 mmol) *p*-nitrobenzene–sulfonyl chloride in 2.5 mL of THF was added by cannula. The cold bath was removed and the reaction mixture was stirred at rt for 1 h. The solvent was removed (aspirator) and the residue taken up in ether (40 mL). The ethereal solution was washed with water (2×5 mL) and dried ($MgSO_4$). The solvent was removed (aspirator) to give 0.591 g (91%) of nosylate **26** which was used without further purification in the next step.

The nosylate **26** was dissolved in 10 mL of acetone and treated with 0.77 g (5.2 mmol) of sodium iodide. The reaction mixture was stirred at rt for 6 h. The solvent was removed (aspirator) and the residue taken up in ether (40 mL). The ethereal solution was washed with water (3×5 mL) and dried ($MgSO_4$). Removal of the solvent (aspirator) afforded 0.458 g (89%) of **27** as a yellow oil which was used directly in the next step; **27**: analytical TLC on silica gel, 1:4 EtOAc/hexane, R_f=0.40. IR (neat, cm^{-1}) 2956, C–H; 2368, B–H; 300 MHz NMR ($CDCl_3$, ppm) δ 3.52 (2H, t, J=8.1 Hz) 3.2–3.1 (1H, m) 2.9–2.8 (1H, m) 2.31 (1H, d, J=9.6 Hz) 2.23 (1H, d, J=7.5 Hz) 2.0–1.0 (3H, br s) 1.78 (1H, dd, J=9.6, 7.5 Hz) 1.6–1.3 (12H, m) 1.1–1.0 (6H, m) 0.90 (9H, t, J=6.0 Hz). A solution of **27** (0.458 g, 0.920 mmol) in 15 mL of a 3:2 (v/v) solution of pentane/ether was cooled to −78°C and treated with 1.20 mL (2.18 mmol) of a 1.78 M solution of *t*-BuLi in pentane. The reaction mixture was stirred for 35 min and.088 mL of methanol was added by syringe. The mixture was warmed to rt, the solvent removed (aspirator), and the residue was taken up in ether (40 mL). The solution was washed with water (3×4 mL) and brine (1×4 mL) and dried ($MgSO_4$). Removal of the solvent afforded 0.292 g (92%) **28** as a yellow oil; analytical TLC on silica gel, 1:4 EtOAc/hexane, R_f=0.23. IR (neat, cm^{-1}) 3259, N–H; 2360, B–H; 300 MHz NMR ($CDCl_3$, ppm) δ 2.75 (1H, br s) 2.60 (1H, dd, J=9.3, 8.7 Hz) 2.0–1.0 (3H, br s) 2.0–1.8 (2H, m) 1.6–1.3 (12H, m) 1.1–1.0 (6H, m) 0.90 (9H, t, J=6.0 Hz). HRMS (EI): $M-C_4H_9^+$ found 290.1130. $C_{10}H_{25}BNSn$ requires 290.1102.

4.1.10. *N*-Methylation of 28; preparation of isomeric 1-methyl-2-tri-*n*-butylstannylaziridine boranes 29 and 30. A flame-dried, 25 mL round-bottomed flask containing a Teflon coated stir bar was charged with 0.118 g of a 60% sodium hydride dispersion in mineral oil. The sodium hydride was washed with hexane (1×3 mL) and dried under a stream of nitrogen. The flask was then charged with 6 mL of THF. To the resultant mixture was added dropwise a solution of **28** (0.292 g, 0.846 mmol) in 6 mL of dry THF. The reaction mixture was stirred at rt for 30 min and then treated with 0.40 mL (6.4 mmol) of methyl iodide. After 3 h the solvent was removed (aspirator) and the residue taken up in ether (40 mL). The ethereal solution was washed with water (2×4 mL) and brine (1×4 mL) and dried ($MgSO_4$). Removal of the solvent (aspirator) afforded 0.28 g (92%) of an orange oil. The mixture of **29** and **30** was isolated by flash chromatography (18×2 cm column, 5×4 mL then 60×2 mL fractions) using 5:95 hexane/EtOAc as the eluent to give 0.16 g of a 77:23 mixture of **29**:**30**. After removal of solvent (aspirator), the residue was purified by flash chromatography on silica gel (15×3 cm^2, 5×7 mL, 35×4 mL then 10×10 mL fractions), 5:95 EtOAc/hexane eluent; the less polar isomer **29** was isolated containing <5% of **30** from one of the lead fractions; analytical TLC on silica gel, 1:4 EtOAc/hexane, R_f=0.35. IR (neat, cm^{-1}) 2362, B–H; 300 MHz NMR ($CDCl_3$, ppm) δ 2.68 (3H, s) 2.24 (1H, d, J=9.3 Hz) 2.19 (1H, d, J=7.5 Hz) 2.1–1.0 (3H, br s) 1.7–1.3 (13H, m) 1.1–1.0 (6H, m) 0.90 (9H, t, J=7.5 Hz). HRMS (EI): $M-C_4H_9^+$ found 304.1261. $C_{11}H_{27}BNSn$ requires 304.1259.

Late fractions from the chromatography gave a small amount of an enriched mixture, ca. 3:1 ratio of **30**:**29**,

sufficient to deduce the NMR signals for **30**; analytical TLC on silica gel, 1:4 EtOAc/hexane, R_f=0.34. IR (neat, cm^{-1}) 2360, B–H; 300 MHz NMR ($CDCl_3$, ppm) δ 2.6–2.5 (1H, m) 2.58 (3H, s) 2.0–1.9 (1H, m) 2.0–1.0 (3H, br s) 1.6–1.3 (13H, m) 1.1–1.0 (6H, m) 0.90 (9H, t, J=7.5 Hz).

4.1.11. Tin–lithium exchange experiment using 29/30. A solution of **29/30** (77:23 ratio; 0.153 g, 0.426 mmol) in 7 mL of THF was cooled to −78°C and was treated with 0.82 mL (1.27 mmol) of a 1.55 M solution of *n*-BuLi in hexane. After 1 h the reaction was quenched with a solution containing 0.345 mL (1.27 mmol) tributyl tin chloride in 3 mL of THF. The reaction mixture was allowed to warm slowly to rt. TLC revealed the presence of tetrabutyl tin, **29**, **30** and **31** (NMR assay; **31**:[**29**+**30**]=1:9). The diasteromer mixture **29/30** was isolated by flash chromatography (15×3 cm^2, 10 mL fractions) using 1:9 EtOAc/hexane as the eluent to obtain 0.102 g (66%) of **29/30** as a colorless oil, 85:15 ratio by ^{1}H NMR assay.

4.2. General procedure for lithiations in the presence of (−)-sparteine

A solution of (−)-sparteine (992 mg, 4.23 mmol) in 4 mL of dry ether or toluene was cooled to −78°C under nitrogen and treated with 1.3 M *sec*-BuLi in cyclohexane (3.30 mL, 4.29 mmol). To the yellow solution was added a solution of the aziridine–borane complex (0.70 mmol) in 1 mL of ether or toluene. After stirring for 1 h (ether) or 2 h (toluene), excess of the electrophilic quenching agent was added (benzophenone: 7 mmol; $PhMe_2SiCl$: 5 mmol) in 2 mL of ether. With benzophenone as the trapping agent, the solution became dark green. The solution was allowed to warm to rt over 1 h, and then stirred an additional 2 h. After quenching with 5 mL of water, the organic layer was separated, extracted with ether (5 mL), washed with water (1×10 mL) and brine (1×10 mL), and dried ($MgSO_4$). In the benzophenone trapping experiments, benzhydrol was formed as a sideproduct and was removed during chromatography.

4.2.1. Scalemic 2-dimethylphenylsilyl-1-(*tert*-butyldimethylsiloxyethyl)aziridine (34). The general procedure was used for lithiation of **13** in the presence of (−)-sparteine in ether, followed by trapping with dimethylphenylchlorosilane. After flash chromatography, **34** (67%) was obtained as a colorless oil; HPLC assay: chiralcel OJ, 0.03% ethanol/hexane, 1 mL/min, major enantiomer eluting at 6.8 min, minor enantiomer eluting at 9 min(69% ee); analytical TLC on silica gel, 1:24 ether/dichloromethane, R_f=0.3. IR (neat, cm^{-1}) 2380, B–H; 300 MHz NMR ($CDCl_3$, ppm) δ 7.4–7.15 (5H, m) 3.95–3.75 (2H, m) 2.75–2.65 (1H, m) 2.45–2.35 (1H, m) 2.17 (1H, d, J=9.2 Hz) 2.05 (1H, d, J=7.4 Hz) 1.50 (1H, dd, J=7.4, 9.2 Hz) 0.70 (9H, s) 0.45 (3H, s) 0.35 (3H, s) −0.01 (3H, s) −0.02 (3H, s). HRMS (EI): M^+ found 349.2431. $C_{18}H_{36}BNOSi_2$ requires 349.2429.

4.2.2. Scalemic 2-diphenylhydroxymethyl-1-(*tert*-butyldimethylsiloxyethyl)aziridine (36). The general procedure was used for lithiation of **13** in the presence of (−)-sparteine in ether, followed by benzophenone trapping. After flash chromatography, **36** (78%) was obtained as a colorless oil; HPLC assay: chiralcel OD, 0.03% ethanol/hexane, 1 mL/min, major enantiomer eluting at 14.07 min, minor enantiomer eluting at 12.04 min(72% ee); analytical TLC on silica gel, 1:24 ether/dichloromethane, R_f=0.3. IR (neat, cm^{-1}) 3415, O–H; 300 MHz NMR ($CDCl_3$, ppm) δ 7.35–7.1 (10H, m) 3.75 (1H, s) 3.6–3.5 (1H, m) 3.4–3.3 (1H, m) 2.6–2.45 (1H, m) 2.35 (1H, dd, 6.2, 3.5 Hz) 1.85 (1H, d, J=3.5 Hz) 1.45 (1H, d, J=6.2 Hz) 0.75 (9H, s) −0.15 (6H, s). HRMS (EI): M^+ found 383.2286. $C_{23}H_{33}NO_2Si$ requires 383.2281.

4.2.3. Scalemic 2-diphenylhydroxymethyl-1-(triphenylmethoxyethyl)aziridine (37). The general procedure was used for lithiation of **35** in the presence of (−)-sparteine in toluene, followed by benzophenone trapping. After flash chromatography, **37** (8%) was obtained as a colorless oil; HPLC assay: chiralcel OD, 0.5% isopropanol/hexane, 1 mL/min, major enantiomer eluting at 21.6 min, minor enantiomer eluting at 16.9 min (70% ee); analytical TLC on silica gel, 5:1 hexane/ethyl acetate. IR (neat, cm^{-1}) 3447, O–H; 300 MHz NMR ($CDCl_3$, ppm) δ 7.4–7.1 (25H, m) 3.75 (1H, s) 3.20–3.14 (1H, m) 2.98–2.93 (1H, m) 2.73–2.68 (1H, m) 2.42–2.35 (1H, m) 2.0 (1H, d, J=2.7 Hz) 1.54 (1H, d, J=4.8 Hz).

4.2.4. Scalemic 2-diphenylhydroxymethyl-1-methylaziridine (39). The general procedure was carried out in toluene starting with 50 mg of **31**. After aqueous workup, the borane complex **38** was cleaved by stirring in 6 mL of 1:1 EtOH/CH_2Cl_2 at rt for 24 h. The solvent was removed (aspirator) and the residue was purified by flash chromatography on silica gel (12×3 cm, 1:3 EtOAc/hexanes, 15 mL fractions) to afford 109 mg (65%, 71% ee) of **39** as a colorless oil from fractions 26–32. HPLC assay: chiralcel AD, 1% isopropanol/hexane, 1 mL/min, major enantiomer eluting at 10.4 min, minor enantiomer at 13.6 min (71.4% ee); for characterization data, see the following entry.

4.2.5. Isolation of scalemic 2-diphenylhydroxymethyl-1-methylaziridine (39). The general procedure in toluene was repeated through the aqueous workup and solvent removal. A portion of the solid residue containing **38** (60 mg) was heated with 1:1 hexane/CH_2Cl_2 (ca. 4 mL) until all of the solid was dissolved. The resulting homogeneous solution was allowed to stand in a refrigerator for 12 h. The resulting precipitate (first crop) was collected to afford 20 mg of **38** (33% from crude **38**, 21% from **31**) of colorless solid. The crystallized material was treated with 1:1 CH_2Cl_2/EtOH (2 mL; rt for 24 h). The solvent was then removed to afford **39** as a colorless oil; HPLC assay: chiralcel AD, 0.5% isopropanol/hexane, 1 mL/min, one enantiomer (>99% ee) eluting at 12.6 min (racemic material shows a second peak eluting at 17.7 min); analytical TLC on silica gel, 2:1:1 hexane/ether/dichloromethane, R_f=0.29. IR (neat, cm^{-1}) 3181, O–H; 300 MHz NMR ($CDCl_3$, ppm) δ 7.45–7.23 (10H, m) 3.82 (1H, s) 2.43 (3H, s) 2.28 (1H, dd, J=6.3, 3.3 Hz) 1.95 (1H, d, J=3.6 Hz) 1.32 (1H, d, J=6.3 Hz). HRMS (EI): M^+ found 239.1313. $C_{16}H_{17}NO$ requires 239.1310.

5. Note added in proof

After submission of this manuscript we became aware of a report describing the conversion of *N*-tosylaziridines into chiral amine derivatives via lithiation in the presence of

sparteine (O'Brien, P.; Rosser, C. M.; Caine, D. *Tetrahedron Lett.* **2003**, *44*, 6613).

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17. The crystal structure of **19** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 216768.
18. The crystal structure of **16e** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 216966.
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