New Methods for the Synthesis of Proximally Functionalized Arylboranes and -silanes

Howard Edan Katz

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

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The synthesis of ten novel disubstituted aromatic compounds is reported. New methods that were developed for the syntheses include (1) single I–Li exchange of 1,8-diiodonaphthalene, (2) use of $Me_3SiOSO_2CF_3$ to form C–Si bonds in sterically hindered situations, and (3) protection of an organoborane as an ethoxy ate complex during halogen–metal exchange and substitution on the organic residue. In addition, the dimethylborylation of aryllithium reagents with Me_2BOEt was generalized to include labile nucleophiles. The methods are geared to the synthesis of peri-substituted naphthalenes as anion receptors but should be of more general utility as well. Finally, some special properties of the newly synthesized compounds are discussed.

The construction of multidentate Lewis acids for anion complexation continues to be an important goal of organic and organometallic chemists. Previous work[1] in this laboratory has introduced the 1,8-diborylnaphthalene unit as a bidentate receptor for small anions. Other recent efforts have utilized organomercurials[2] and organotins[3] in the construction of anion binders. We would like to expand the scope of our own investigation to encompass borane–silane cooperativity and other multidentate effects in anion complexation. In order to do so, it will be necessary to synthesize a variety of novel organometalloids.

Just as the diversity of condensation and functionalization reactions available for Lewis basic molecules (ethers, amines, sulfides, carbonyls, etc.) has made possible the synthesis of a multitude of interesting cation binders,[4] the possibilities for anion binders would be greatly augmented if the applicable synthetic methodology were increased. Unfortunately, the number of options one has in synthesizing oligo-Lewis acids is severely limited in comparison to the Lewis bases. In the preparation of boron- and silicon-based anion receptors, two difficulties with the current methods are that (1) many methods are geared to the eventual conversion of the metalloidal group into another functionality,[5] rather than preserving the metalloid in the final product, and (2) methods which work in general cases may not be appropriate when several metalloids are in close proximity on one molecule,[6] interacting sterically or via complexed anions.

This paper describes a set of synthetic reactions that are useful in constructing proximally substituted boranes and silanes. An improved technique for the one-at-a-time peri substitution of naphthalene is reported. Our previously described[1] dimethylborylation methodology is generalized to include labile or sterically hindered organolithium compounds, and a new trimethylsilylation method is suggested for such species as well. Finally, the first example of a protection–deprotection sequence for functionalization of the organic residue of an organoborane is developed.

Although these methods are geared to the synthesis of 1,8-difunctional naphthylboranes and -silanes, the more general applicability of these techniques is considered as well. Also, some unusual properties of the newly synthesized molecules are noted.

Results

Monolithiation of 1,8-Diiodonaphthalene. Treatment of a solution of 1,8-diiodonaphthalene[7] in Et_2O with n-BuLi at −30 °C resulted in the selective formation of 1 with little or no contamination by 1,8-dilithionaphthalene. Undesired lithium–iodine exchange during the subsequent reaction of 1 with electrophiles was minimized when the substitution reaction was conducted below −50 °C; however, the reaction with less active electrophiles probably did not go to completion at this temperature. Solid substitution products 3–5 were obtained analytically pure. Although the liquid products 2 and 6 were not purified to the same extent as the solids, they were suitable for further transformations. Distillation of 2 caused partial migration of the Me_3Si group. In the NMR spectrum of the ethyl ester of 5, 5′, the CH_2 protons appeared diastereotopic, indicating that rotation about the C–B bond of 5′ was hindered on the NMR time scale.

1, R = Li
2, R = SiMe₃
5, R = B(OH)₂
5′, R = B(OEt)₂
6, R = BMe₂

3, X = Me, Y = H
4, XY = CH₂CH₂CH₂
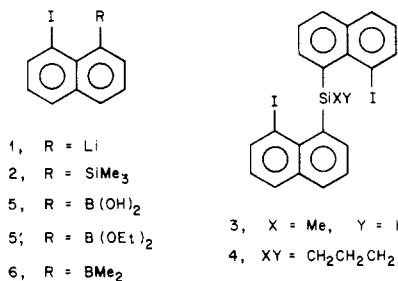
Dimethylborylation of Labile Aryllithiums. The condensation[1] of an aryllithium with Me_2BOEt to form an ate complex followed by reaction with BF_3OEt_2 was used to synthesize boranes 6–8. In all three cases, substitution of B for Li occurred under conditions mild enough to prevent the gross decomposition of the aryllithium via coupling or halogen–metal exchange. The major impediment to the isolation of higher yields of 7 and 8 was their high volatility, with boiling points only slightly above that of PhBr. The latter impurity thwarted our efforts to obtain high-resolution mass spectra (HRMS) of 7 and 8.

Trimethylsilylation of Less Reactive Aryllithiums. Trimethylsilyl trifluoromethanesulfonate (TMSTF) reacted with aryllithiums even in cases where Me_3SiCl did

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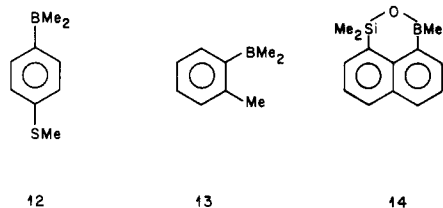(7) House, H. O.; Koepsell, D. G.; Campbell, W. J. *J. Org. Chem.* **1972**, *37*, 1003–1011.

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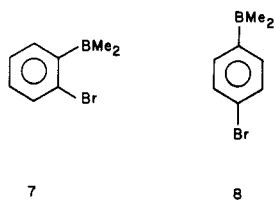
not. Thus, silanes 2 and 11 (method 1) were obtained in 75% and 24% yields, respectively, whereas Me₃SiCl gave none of the desired products. Furthermore, the reaction of TMSTF with o-BrC₆H₄Li[8] gave a 79% isolated yield of >95% pure o-BrC₆H₄SiMe₃ (a benzyne precursor[9]), vs. 39% with Me₃SiCl.[8] Even [8-(trimethylsilyl)-1-naphthyl]lithium and TMSTF gave a product mixture containing 30% of the extremely crowded 1,8-bis(trimethylsilyl)naphthalene[10] (identified by ^{1}H NMR), in contrast to the behavior of Me₃SiCl in an analogous situation,[11] where Li migration was observed.

Protection–Metalation–Substitution of Haloaryl-boranes. Addition of 6 to excess LiOEt in (CH₂)₄O converted the borane to its ethoxy borate. It was then possible to metalate at the iodo carbon and substitute with an electrophile, and compounds 9–11 were synthesized in this

9, R = Me

10, R = SMe

11, R = SiMe₃
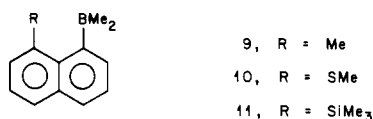
manner. Tetrahydrofuran was superior to Et₂O for this reaction, and the products decomposed if the reaction mixtures were left above 10 °C for prolonged periods. The use of an acidic quench (BF₃OEt₂ or MeSO₃H) before product isolation would have improved the material balances but also was found to cause some product decomposition; instead, the LiOEt was precipitated during the concentration and extraction steps, thereby decomposing the complexes. Anomalously low chemical shifts were noted for the B and the CH₃ protons in 10.

We briefly attempted to generalize this procedure by synthesizing p-MeSC₆H₄BMe₂ (12) from 8, analogous to the preparation of 10. This was somewhat successful, using s-BuLi for 1 h at -35 °C to perform the halogen–metal exchange; however, the presence of unreacted 8 in the product mixture indicated that the metalation step was much more sluggish than in the case of 6. The attempted synthesis of o-MeC₆H₄BMe₂ (13) from 7 (analogous to the procedure for 9) was completely unsuccessful. The reaction of protected, transmetallated 6 with Me₂SiHCl or Me-SiHCl₂ gave mixtures of products, including 14, containing the heretofore unknown naphthoxasilaborin ring.

12　　　　　　13　　　　　　14

Halogen–Metal Exchange of 4. The dilithiation reaction of 4 with n-BuLi (Et₂O–(CH₂)₄O, 2:1, -78 °C; 5 min)

was clean as evidenced by NMR and GC–MS of the D₂O-quenched product 15. Unfortunately, attempts to trap the dilithiate from 4 with Me₂BOEt consistently led to ate complexes that could neither be characterized nor cleanly decomposed.

Discussion

The synthesis of peri-substituted naphthalenes, particularly the "permethylelement"-substituted compounds[12] such as 10 and 11, is of interest for a variety of physical organic chemical studies. The use of 1,8-diiodonaphthalene as a starting material for the stepwise introduction of peri substituents has two advantages over the previously employed reagents, 1,8-dibromonaphthalene[13] and 1-bromo-8-iodonaphthalene.[14] The diiodide is the easiest to prepare in large quantities, and the iodide remaining after the first substitution is much more reactive than bromide toward both halogen–metal exchange[15] and organometallic coupling.[16]

It is interesting to contrast the behavior of Me₂BOEt and Me₃SiCl in reactions with organolithium reagents. It appears that the former can be used to incorporate the dimethylboryl group onto a wide range of substituted aromatics, including those with sensitive substituents or sterically hindered lithiated carbons. It is possible to view the Me₂B group as the anionophilic antipode of the MeO group, which is a common ligand in benzocrown cation binders.[17]

On the other hand, Me₃SiCl₂ was surprisingly problematic in view of its reputation as a reagent for quantitatively trapping aryllithiums, even in sterically hindered situations.[18] The trimethylsilylation of heteroatoms under mild conditions has long been accomplished with TMSTF;[19] however, we have found no precedent for the use of TMSTF to form C–Si bonds with lithiated organics. Clearly, there are situations where the use of the more reactive TMSTF is called for instead of Me₃SiCl in the synthesis of carbon-substituted trimethylsilanes,[20] especially where a low reaction temperature must be maintained.

Although there are a few examples of borates as synthetic intermediates,[21] the present results provide the first instance of a borate complex prepared deliberately for borane protection during the functionalization of an organic residue on the borane. The method should also work for other boranes containing an easily metalated carbon, although extension to bromoaromatics would require careful optimization, since Li–Br exchange is retarded in the presence of inductively donating substituents.[22] The protection–substitution procedure would be especially valuable for the synthesis of homologous series of sub-

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stituted boranes to study substituent–property relationships,[23] and provides additional access to boranes "not available by hydroboration".[24] The procedure may also be of use in assembling oligomers of boranes.

The substituents on some of the presently described compounds display special interactions. For example, the [11]B chemical shifts of 9, 11, 6, and 10 are 81, 75, 70, and 16 ppm, respectively. The dramatic upfield shift in 10 is compelling evidence[25] that the boron and sulfur atoms in 10 are intramolecularly complexed. This is a clear case of the complex being formed because of preorganization,[26] in that the complexing groups are brought together during the synthesis of 10. On the contrary, 13 (δ([11]B) 78) showed no sign of existing as an intermolecular S–B complex. The slight upfield shifts observed for 11 and 6 may be the result of very weak bonding between the substituents or else may reflect distortion of the naphthalene ring[12] because of a steric effect.

Diethyl ester 5′ was generated as an intermediate in the synthesis of 5 and was also synthesized by reesterifying 5. When 5′ was dissolved in $CDCl_3$, a "clean" quartet for the CH_2 protons was never observed, but instead a complex multiplet was noted. The multiplet broadened slightly but did not coalesce upon heating the sample to 60 °C. Therefore, the CH_2 protons of 5′ must be diastereotopic, and exchange of the CH_2 proton environments by rotation about the C–B bond of the ester must overcome a barrier of $\geq$18 kcal/mol. The ester thus provides an unusual example of chirotopicity[27] near a boron atom.[28] Theoretically, a mixed ester of 5 would be resolvable into enantiomers.

The effect of a nearby silyl substituent on naphthylborane anion complexes, such as in the fluoride complex of 11, is substantial and will be treated in a forthcoming paper.

In summary, we have developed a number of synthetic procedures that are of particular relevance to the synthesis of borane and silane anion receptors and may be of more general utility as well. In so doing, we have prepared a series of novel substituted aromatic compounds, some of which exhibited uncommon properties. Further studies of the synthesis and properties of polydentate Lewis acids are in progress.

Experimental Section

General Data. Reactions of organolithiums and organoboranes were conducted with stirring under Ar, and borane products were stored under Ar at −20 °C. Solvents for organometallics were distilled from the usual drying agents; other reagents were used as received. Nuclear magnetic resonance spectra were recorded on a JEOL FX-90Q spectrometer containing a variable-temperature probe. Chemical shifts are in ppm vs. Me_4Si (^{1}H, ^{13}C) or BF_3·OEt_2 ([11]B). Some ^{1}H and ^{13}C spectra were referenced to residual protons or deuterated carbons in the solvents. Mass spectra (MS) are listed as m/e (relative intensity). High-resolution mass spectra (HRMS) were obtained by using a Nicolet FT/MS-1000 Fourier transform mass spectrometer with a magnetic field strength of 3.0 T. Elemental analyses were determined by

Galbraith Laboratories, Knoxville, TN. Purities of liquids assayed by ^{1}H NMR and by GC, expressed as mol %, were in agreement to ±<5%.

General Procedure for (8-Iodo-1-naphthyl)lithium (1). A 0.08 M solution of 1,8-diiodonaphthalene in Et_2O was cooled to −30 °C, and exactly 1 equiv of *n*-BuLi was added. After being stirred for 20 min at −30 °C, the solution was cooled to −80 °C and treated with an electrophile at this temperature.

(8-Iodo-1-naphthyl)trimethylsilane (2). Trimethylsilyl trifluoromethanesulfonate (3.1 mL, 16 mmol) and $(CH_2)_4O$ (30 mL) were added to a solution of 1 (13.2 mmol). The solution was allowed to warm to room temperature overnight, washed with concentrated aqueous NaCl buffered with $NaHCO_3$, dried, filtered, and concentrated. The residue represented ~90% material balance and contained 83% product and 17% of other isomers and monosubstituted naphthalenes. Distillation, column chromatography, and preparative GC did not improve the purity of the product. However, the crude material was suitable for conversion to 11: ^{1}H NMR ($CDCl_3$) δ 0.63 (s, 9, CH_3), 7.1 (t, 1, J = 7 Hz), 7.4 (t, 1, J = 7 Hz), 7.70, 7.80, 7.95, 8.25 (4 d of d, 4, J = 7 Hz, J′ = 1 Hz); ^{13}C NMR ($CDCl_3$) δ 5.7 (CH_3), 96.7 (CI), 124.8, 126.0, 130.2, 130.8, 138.1, 140.7 (tertiary), 135.8, 141.2 (quaternary); MS 326 (12, M^+), 311 (93), 183 (100).

Bis(8-iodo-1-naphthyl)methylsilane (3). Tetrahydrofuran (100 mL) and $MeSiHCl_2$ (0.68 mL, 6.6 mmol) were added to 1 (13.2 mmol), and the solution was allowed to warm to ambient temperature. After 1 h at ambient temperature, the mixture was washed with dilute HCl and concentrated aqueous NaCl, dried, filtered, and concentrated to 4.2 g of an oil. Crystallization from CH_2Cl_2–hexane gave 1.8 g (50%) of brown prisms: mp 131–133 °C; ^{1}H NMR ($CDCl_3$) δ 0.91 (d, 3, J = 3.5 Hz, CH_3), 7.02 (t, 2, J = 8 Hz), 7.3 (t, 2, J = 7 Hz), 7.7 (2 d of d, 4, J = 8 Hz, J′ = 1 Hz), 7.79 (m, 1, SiH), 7.97 (d of d, 2, J = 7 Hz, J′ = 1 Hz), 8.20 (d of d, 2, J = 8 Hz, J′ = 1 Hz); ^{13}C NMR ($CDCl_3$) δ 2.43 (CH_3), 97.0 (CI), 125.2, 126.3, 130.3, 131.3, 139.4, 141.2 (tertiary), 135.6, 140.2 (C_1 and C_{4a}), 139.2 (C_{8a}); MS 550 (M^+), 535 (10), 423 (30), 297 (30), 252 (35), 169 (100). Anal. C, H, I, Si.[28]

1,1-Bis(8-iodo-1-naphthyl)silacyclobutane (4). Tetrahydrofuran (150 mL) and $(CH_2)_3SiCl_2$ (1.2 mL, 10 mmol) were added to 1 (19.8 mmol). The solution was allowed to warm to −50 °C over 2 h and then to room temperature. The mixture was washed with concentrated aqueous NaCl, dried, filtered, and concentrated to 6 g of viscous brown oil. Trituration with 20 mL of petroleum ether followed by crystallization from CH_2Cl_2–Et_2O–hexane gave 3.3 g (58%) of brown solid; mp 139–141 °C; ^{1}H NMR (CD_2Cl_2) δ 2.2 (m, 6, CH_2), 6.87 (t, 2, J = 8 Hz), 7.4–7.9 (m, 8), 8.49 (d of d, 2, J = 7 Hz, J′ = 1 Hz); ^{13}C NMR (CD_2Cl_2) δ 17.5 (CCH_2C), 24.3 (CH_2Si), 97.5 (CI), 125.8, 126.2, 129.7, 131.7, 139.3, 140.6 (tertiary), 136.0, 140.9 (quaternary); MS 576 (2, M^+), 449 (100), 407 (42), 321 (40), 293 (58), 279 (70), 272 (58), 252 (85), 155 (64). Anal. C, H, I, Si.[28]

8-Iodo-1-naphthaleneboronic Acid (5). Triethyl borate (1.8 mL, 11 mmol) was added to 1 (6.6 mmol), and the mixture was allowed to warm to ambient temperature overnight. The solution was washed with dilute HCl and dilute aqueous Na_2CO_3, dried, filtered and concentrated to an oil that contained 5′. The oil was dissolved in 50 mL of CH_2Cl_2 and vigorously stirred[30] with aqueous NaOH (60 mL, 0.5 M) and $PhCH_2NEt_3Br$ (20 mg). After 24 h, the aqueous layer was brought to pH 2 and the white precipitate collected. The yield of boronic acid was 0.8 g (41%): mp 140 °C dec, ^{1}H NMR (CD_3CN) δ 6.12 (s, 2, OH), 7.21 (t, 1, J = 7 Hz), 7.4–8.0 (m, 4), 8.19 (d of d, 1, J = 7 Hz, J′ = 1 Hz); ^{13}C NMR (CD_3SOCD_3) δ 100.2 (CI), 125.6, 126.6, 128.9, 129.5, 132.0, 138.5 (tertiary), 135.9 (quaternary); ^{11}B NMR δ 31.0; MS 298 (19, M^+), 171 (43), 127 (100). Anal. C, H, I, B.[28]

(8-Iodo-1-naphthyl)dimethylborane (6). Ethyl dimethylborinate (2.4 mL, 22.1 mmol) was dissolved in 30 mL of Et_2O at −80 °C. To this solution was added a solution of 1 (15.8 mmol). The combined solution was allowed to warm to +10 °C and then recooled to −80 °C. Boron trifluoride etherate (1.94 mL, 15.7 mmol) was added, and the mixture was allowed to warm to room temperature overnight. The solvents were removed in vacuo, and the residue was extracted with 25 mL of hexane. The extract was

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cooled to –70 °C, filtered, concentrated, and distilled to give product (3.0 g, 65% yield, 80–90% pure); bp 130–140 °C (0.1 torr); mp ~15 °C; ^{1}H NMR (CD$_2$Cl$_2$) δ 1.32 (s, 6, CH$_3$), 7.1–8.2 (m, 6); ^{13}C NMR (CD$_2$Cl$_2$) δ 18 (br, CH$_3$), 102.3 (CI), 125.7, 126.7, 127.2, 127.8, 129.6, 135.9 (tertiary), 136.0, 139.1 (quaternary); ^{11}B NMR (CD$_2$Cl$_2$ or toluene-d_8) δ 70.0; MS 294 (14, M$^+$), 279 (100), 150 (60); HRMS calcd for C$_{12}$H$_{12}$BI 294.0071, found 294.0063.

(2-Bromophenyl)dimethylborane (7). To a solution of 2-bromophenyllithium[8] (7.6 mmol) at –100 °C was added Me$_2$BOEt (1.25 mL, 11.4 mmol). After 1 h at –100 °C, the temperature was raised to –75 °C, and BF$_3$OEt$_2$ (0.94 mL, 7.6 mmol) was added. The mixture was allowed to warm to room temperature overnight. The solvents were removed in vacuo, the residue extracted with 15 mL of hexane, and the extract separated, concentrated, and distilled. The fraction distilling at 80 °C (0.2 torr) consisted of 0.57 g (38%) of product: 90% pure; ^{1}H NMR (toluene-d_8) δ 1.06 (s, 6, CH$_3$), 6.8–7.4 (m, 4, ArH); ^{11}B NMR (toluene-d_8) δ 82.5; MS 198/196 (25, m$^+$), 183/181 (100).

(4-Bromophenyl)dimethylborane (8). A solution of 4-bromo-1-iodobenzene (2.54 g, 9.0 mmol), Et$_2$O (60 mL), and (CH$_2$)$_4$O (60 mL) was cooled to –100 °C and *n*-BuLi (9.2 mmol) was added. The mixture was stirred at –100 °C for 30 min and then allowed to warm to –80 °C as a precipitate formed. Ethyl dimethylborinate (0.63 mL, 11.6 mmol) was added at –100 °C, followed by warming to –50 °C. Finally, the mixture was recooled to –80 °C, treated with BF$_3$OEt$_2$ (9.0 mmol), and worked up as for 7. The yield was 0.80 g (45%) of a solid melting near room temperature: 90% pure; ^{1}H NMR (CD$_2$Cl$_2$) δ 1.11 (s, 6, CH$_3$), 7.58 and 7.78 (AB q, 4, *J* = 8.2 Hz, ArH); ^{13}C NMR (CD$_2$Cl$_2$) δ 11.6 (br, CH$_3$), 127.7 (CBr), 131.4, 136.6; ^{11}B NMR (CD$_2$Cl$_2$) δ 77.5; MS 198/196 (17, M$^+$), 183/181 (100).

General Procedure for Substitution of (8-Iodo-1-naphthyl)dimethylborane. A solution of LiOEt (0.03 M) was prepared from EtOH and *n*-BuLi in (CH$_2$)$_4$O. The solution was cooled to –70 °C, and 6 (0.8 equiv) was added. The mixture was allowed to warm to –10 °C and then recooled to –70 °C, whereupon an additional equivalent of *n*-BuLi was added. After 1 h at –70 °C, an electrophile was added, and the mixture was maintained at –70 °C for 1 additional hour, then allowed to warm to +10 °C, and concentrated at 2 torr. The residue was extracted with 5–10 mL of hexane, and the extract was concentrated and distilled.

(8-Methyl-1-naphthyl)dimethylborane (9). Methyl iodide (400 μL, 6.4 mmol) was used as the electrophile. The mixture was allowed to reach ambient temperature before concentration. The yield from 400 mg of 6 was 180 mg (73%) (bp 130 °C (0.3 torr); 90% pure; with the impurities consisting of 1-methyl- and 1,8-dimethylnaphthalene. ^{1}H NMR (toluene-d_8) δ 1.06 (s, 6,

BCH$_3$), 2.24 (s, 3, ArCH$_3$), 7.0–7.6 (m, 6, ArH); ^{11}B NMR (toluene-d_8) δ 81; MS 182 (58, m$^+$), 167 (74), 151 (100), 139 (56); HRMS calcd for C$_{13}$H$_{15}$ B 182.1261, found 182.1257.

[8-(Methylthio)-1-naphthyl]dimethylborane (10). Dimethyl disulfide (180 μL, 2.0 mmol) was used as the electrophile. The yield from 400 mg of 6 was 160 mg (55%) (bp 145 °C (0.1 torr); 85% pure) with the impurities consisting of 1-(methylthio)- and 1,8-bis(methylthio)naphthalene: ^{1}H NMR (toluene-d_8) δ 0.62 (s, 6, BCH$_3$), 1.58 (s, 3, SCH$_3$), 7.0–7.2 (m, 2, ArH), 7.4–7.6 (m, 4, ArH); ^{13}C NMR (toluene-d_8) δ 22.7 (CH$_3$S), 123.8, 125.8, 126.5, 127.4, 128.8, 129.5 (tertiary), 133.8, 134.9, 139.4 (quaternary); ^{11}B NMR (toluene-d_8) δ 16.2, MS 214 (4, m$^+$), 199 (100), 183 (86); HRMS calcd for C$_{10}$H$_{15}$BS 214.0982, found: 214.0975.

[8-(Trimethylsilyl)-1-naphthyl]dimethylborane (11) (Method 1). Trimethylsilyl trifluoromethanesulfonate (480 μL, 2.5 mmol) was used as the electrophile. The yield from 300 mg of 6 was 97 mg of a mixture that was 60% product and 40% 1-(trimethylsilyl)naphthalene, representing a 24% yield of product: the impurity was removed by preparative GC; ^{1}H NMR (CD$_2$Cl$_2$) δ 0.30 (s, 9, CH$_3$Si), 1.07 (s, 6, CH$_3$B), 7.2–7.9 (m, 6, ArH); ^{13}C NMR (CD$_2$Cl$_2$) δ 2.4 (CH$_3$Si), 12.5 (b, CH$_3$B), 124.5, 125.0, 129.4, 130.6, 132.4, 136.5 (tertiary); 133.8, 139.8, 140.8 (quaternary); ^{11}B NMR (CD$_2$Cl$_2$) δ 74.6; MS 240 (10, M$^+$), 225 (20), 209 (55), 73 (100); HRMs calcd for C$_{15}$H$_{21}$BSi 240.1500, found 240.1499.

[8-(Trimethylsilyl)-1-naphthyl]dimethylborane (11) (Method 2). A solution of 2 (11.4 mmol) in Et$_2$O (130 mL) was treated with *n*-BuLi (12.5 mmol) for 20 min at –70 °C. The lithiate was added to a –70 °C solution of Me$_2$BOEt (1.8 mL, 16.5 mmol) in Et$_2$O (20 mL). After 1.5 h at –70 °C, the mixture was warmed to 0 °C and then cooled again to –70 °C. Boron trifluoride etherate (1.05 mL, 12.5 mmol) was added, and the solution was left to warm to room temperature overnight. Concentration, hexane extraction, filtration and concentration of the extract, and distillation gave 1.7 g (62%) of product (83% pure; bp 135 °C (0.2 torr)), as a light yellow oil, contaminated only with 1-naphthyltrimethylsilane.