Borabenzene Derivatives. 28. Pinene-Fused Dihydroborinines, Boratabenzenes, and a Borabenzene−Pyridine Adduct[1]

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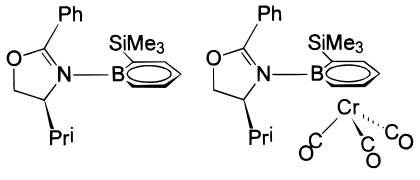
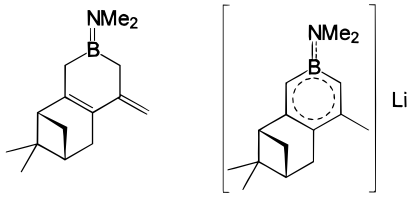
The known enantiomerically pure, (1*S*,5*S*)-(−)-α-pinene-derived tetrahydroborinine (1*R*,9*R*)-4-(dimethylamino)-10,10-dimethyl-6-methylene-4-boratricyclo[7.1.1.$0^{2,7}$]undec-2(7)-ene (**3**) is used as starting material for the synthesis of enantiomerically pure, pinene-fused borabenzene derivatives. In the presence of catalytic amounts of HCl compound **3** can be isomerized to the corresponding dihydroborinine **5a** (120 °C, 3 days, 100%). Treatment of **5a** with BCl_3 in CH_2Cl_2 at −60 °C affords the *B*-chloro derivative **5b** (85%). Compound **5b** reacts with $ZnMe_2$ in toluene to produce the *B*-methyl derivative **5c** (84%), and with Me_3SiOMe in CH_2Cl_2 to give the *B*-methoxy compound **5d** (91%). The compounds **5a**−**d** are 2,6-dienes and are free of double-bond isomers. Lithiation of **5c** with $LiN(SiMe_3)_2$ in hexane and of **5d** with LDA in THF affords the corresponding boratabenzenes Li(**8**) (83%) and Li(**9**) (∼100%). The structure of the crystalline solvate Li(TMEDA)(**8**) (≡**10**) is of the same type as that of Li(TMEDA)(**4**) with a $Li(TMEDA)^+$ ion attached to the *exo*-face of the anion $\mathbf{8}^-$. The reaction of Li(**4**) with CuI in toluene gives oxidative coupling products **11** with a C5−C5′ bond and some dihydroborinine **5a** (up to 25%). The mixture **11** consists essentially of diastereomeric *exo*,*exo*- and *endo*,*exo*-isomers in a 4:1 ratio, respectively. The major isomer, *exo*,*exo*-**11,** can be isolated as crystalline clathrate *exo*,*exo*-**11**·1/2C_6H_6 (≡**12**); the structure of **12** (as determined by X-ray single-crystal structure analysis) proves the C_2-symmetric *exo*,*exo*-linkage across the 5,5′-C−C bond with the 2,6-position of the double bonds as in **5a**−**d**. Silylation of Li(**4**) gives a 4:1 mixture **14** of 5-*exo*- and 5-*endo*-(trimethylsilyl) derivatives (∼100%). This mixture reacts with BCl_3 to give the *B*-chloro derivatives **15** (again as a 4:1 mixture of stereoisomers, 93%). Treatment of **15** with pyridine affords red crystals of the pyridine adduct **16** (43%) as the first Lewis base adduct of an enantiomerically pure borabenzene. The structure of **16** is very similar to that of borabenzene−pyridine; the angle between the borabenzene best plane and the pyridine best plane amounts to 33.02(14)°.

Introduction

Considerable efforts have been devoted over the years to the development of chiral and often also enantiomerically pure cyclopentadienyl ligands and complexes.[4] The analogous chemistry of borabenzene and boratabenzene derivatives has remained essentially untouched. G. C. Fu et al. recently made the borabenzene adduct **1** of an enantiomerically pure oxazoline and subsequently added a $Cr(CO)_3$ group diastereoselctively; this sequence gave compound **2** as the first enantiomerically pure borabenzene complex.[5] We used enantiomerically enriched (−)-α-pinene[6] (ee 95−98%) as starting material for the synthesis of the tetrahydroborinine **3** and the first enantiomerically pure boratabenzene salt Li(**4**).[2]



1 **2**



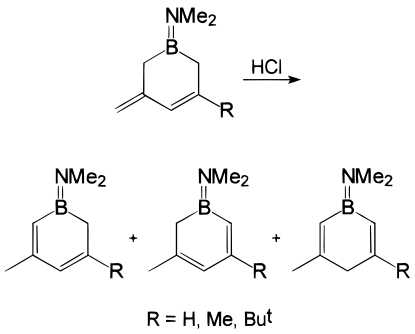
3 **Li (4)**

The aim of this paper is to document the further development of enantiomerically pure pinene-fused borabenzene and boratabenzene derivatives. We shall describe (i) the synthesis of compounds with boron-bonded substituents other than the NMe_2 group of **3** and **4**, (ii) the first example of an oxidative coupling of a

(1) Part 27: See ref 2.
(2) Herberich, G. E.; Ganter, B.; Pons, M. *Organometallics* **1998**, *17*, 1254.
(3) Pons, M. Doctoral Dissertation, Technische Hochschule Aachen, Aachen, Germany, 1999.
(4) (a) Halterman, R. L. *Chem. Rev.* **1992**, *92*, 965. (b) *Metallocenes*; Togni, A., Halterman, R. L., Eds.; Wiley-VCH: Weinheim, 1998; Vols. 1 and 2.
(5) Tweddell, J.; Hoic, D. A.; Davis, W. M.; Fu, G. C. *J. Org. Chem.* **1997**, *62*, 8286.
(6) Bir, G.; Kaufmann, D. *Tetrahedron Lett.* **1987**, *28*, 777.

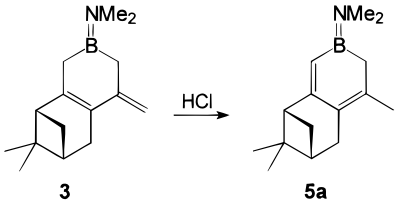
10.1021/om990310u CCC: $18.00
Publication on Web 07/24/1999

Scheme 1



R = H, Me, Bu^t

Scheme 2

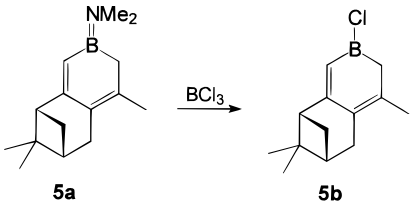


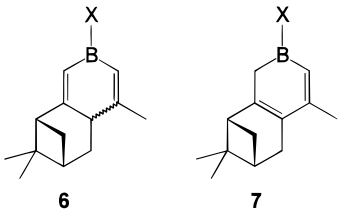
boratabenzene ion, and (iii) a pinene-fused borabenzene−pyridine adduct.

Results and Discussion

Isomerization of 3. The tetrahydroborinine **3** contains the structural element of a diallylborane and therefore is particularly sensitive. It was readily destroyed, presumably by a ring-opening reaction, when we attempted to exchange the substituent at boron. On the other hand, it was known that simple 3-methylenetetrahydroborinines can readily be isomerized to less reactive 3-methyldihydroborinines (Scheme 1),[7] for instance by trace impurities such as $BCl_2(NMe_2)$ or by deliberately added hydrogen chloride. In the case of **3**, the isomerization works particularly well (Scheme 2). This is due to the higher degree of alkyl substitution of **3** that should greatly facilitate the addition of electrophiles (i.e., protons in the case of HCl-catalyzed isomerization). However, in contrast to the general case of Scheme 1, the isomerization of **3** produces only isomer **5a**, while the conceivable isomers **6a** (two stereoisomers) and **7a** are not observed. The ^{13}C NMR spectrum of **5a** displays two $^{11(10)}B$ quadrupole-broadened signals. Of these, one belongs to an sp^3-C and one to an sp^2-C atom. We also see only one olefinic proton. These spectral details exclude divinylborane isomers **6a**. Furthermore, NOE difference spectra show that the 6-Me group is close to the dihydroborinine CH_2 group and 1-H to the olefinic borinine CH group. Both findings identify unambiguously the constitution as that of **5a** and exclude the alternative formula **7a**. Thus we here have the same preferential disposition of the two double bonds that is also observed, for example, in isodicyclopentadienes (tricyclo[5.2.1.0^{2,6}]deca-2,5-dienes).[8] Isomer **5a** is favored thermodynamically (i) by a higher degree of substitution (as compared to **6a**) and (ii) by the greater length of the bond C2−C7 (as compared to **7a**), which reduces the ring strain of the pinane skeleton. These qualitative considerations are supported by semiempirical calculations.[9a] After geometry optimization with the AM1 Hamiltonian[9b] with published parameters for boron[9c] the lowest heat of formation was found for isomer **5a**.[10]

Scheme 3





a: X = NMe_2; **b**: X = Cl; **c**: X = Me; **d**: X = OMe

Substitution at Boron. In olefin polymerization reactions with catalyst systems $ZrCl_2(C_5H_5BX)_2$/MAO the outcome is rather strongly influenced by the substituent at boron (X = NPr^i_2, Ph, OEt).[11] These observations motivated us to study the substitution of the NMe_2 group of **5a**. We chose the chloro compound **5b** as our first goal. Treatment of **5a** with BCl_3 in CH_2Cl_2 at −60 °C for a few minutes affords the desired chloro compound **5b** in high yield (85%) (Scheme 3); longer reaction times and/or higher temperatures result in ring opening and decomposition. We note that again only isomer **5b** is found.

The highly reactive chloro compound **5b** can readily be methylated with $ZnMe_2$ in toluene to give **5c** (Scheme 4). Deprotonation of **5c** by an excess of the reagent was not observed, and so the ratio of the reactands **5b**/$ZnMe_2$ is not critical. In general, the replacement of an electronegative, boron-bonded group in dihydroborinines with a hydrocarbyl substituent is not so simple as in the present case, and only very few examples have been described previously.[12] A variety of further substitution processes is feasible. Treatment of **5b** with Me_3SiOMe results in smooth formation of the methoxy compound **5d** (Scheme 4).

Lithiation of 5a, 5c, and 5d. We have already described the synthesis of the boratabenzene salt Li(**4**)

(7) Herberich, G. E.; Englert, U.; Schmidt, M. U.; Standt, R. *Organometallics* **1996**, *15*, 2707.

(8) (a) Alder, K.; Flock, F. H.; Janssen, P. *Chem. Ber.* **1956**, *89*, 2689. (b) Katz, T. J.; Rosenberger, M.; O'Hara, R. K. *J. Am. Chem. Soc.* **1964**, *86*, 249. (c) Rosenblum, M. *J. Am. Chem. Soc.* **1957**, *79*, 3179. (d) Cookson, R. C.; Isaacs, N. S.; Szelke, M. *Tetrahedron* **1964**, *20*, 717.

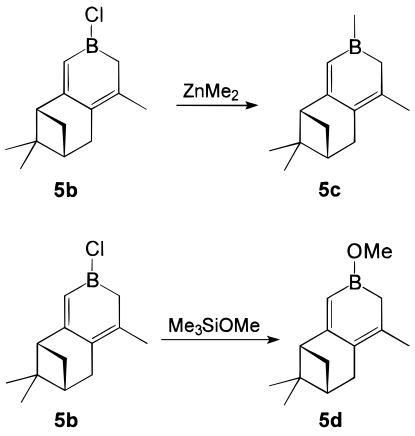
(9) (a) *CAChe*, Version 4.0 for Power Macintosh; Oxford Molecular: Oxford, U.K., 1996. (b) Dewar, M. J. S.; Zoebisch, E. G.; Healey, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902. (c) Dewar, M. J. S.; Jie, C.; Zoebisch, E. G. *Organometallics* **1988**, *7*, 513.

(10) The following values for the heat of formation were obtained: for **5a** 30.6, for the energetically more favorable stereoisomer of **6a** (with 7-H in *endo*-disposition) 82.0, and for **7a** 43.2 kJ/mol.

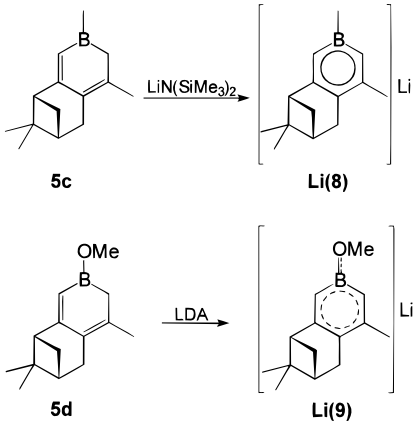
(11) (a) Bazan, G. C.; Rodriguez, G.; Ashe, A. J., III; Al-Ahmad, S.; Müller, C. *J. Am. Chem. Soc.* **1996**, *118*, 2291. (b) Bazan, G. C.; Rodriguez, G.; Ashe, A. J., III; Al-Ahmad, S.; Kampf, J. W. *Organometallics* **1997**, *16*, 2492. (c) Rogers, J. S.; Bazan, G. C.; Sperry, C. K. *J. Am. Chem. Soc.* **1997**, *119*, 9305. (d) Barnhart, R. W.; Bazan, G. C.; Mourey, T. *J. Am. Chem. Soc.* **1998**, *120*, 1082.

(12) (a) Herberich, G. E.; Schmidt, B.; Englert, U. *Organometallics* **1995**, *14*, 471. (b) Maier, G.; Wolf, H.-J.; Boese, R. *Chem. Ber.* **1990**, *123*, 505.

Scheme 4



Scheme 5



by base-induced isomerization and deprotonation of **3**.[2] Lithiation of **5a** with LDA in THF affords, of course, the same salt Li(**4**). In a similar way the dihydroborinines **5c** and **5d** can be lithiated to give the corresponding boratabenzene salts Li(**8**) and Li(**9**) (Scheme 5). In the methyl series it is preferable to use $LiN(SiMe_3)_2$ in hexane as base. In this case the powdery product Li(**8**) is barely soluble in hexane and thus can readily be isolated while excess base remains in solution.

In several cases lithium boratabenzenes have been isolated from reaction mixtures by addition of TMEDA and crystallization from concentrated solutions in hexane. In the case of the pinene-fused boratabenzenes, the TMEDA solvates are rather soluble in hexane. They are therefore less useful for synthetic purposes. However, the solvate Li(TMEDA)(**8**) (≡**10**) was obtained as good crystals that were suitable for crystallographic work.

Structure of 10. The solvate **10** crystallizes in the orthorhombic space group $P2_12_12_1$ with $Z = 8$. There are two independent molecules in the elemental cell. Their structural data do not differ significantly; selected data are given for one of the two molecules (Figure 1, Table 1).

The structure of **10** is of the same type as that of Li(TMEDA)(**4**).[2] It consists of ion-pairs with $[Li(TMEDA)]^+$ attached to the less hindered *exo*-face of the anion **8**$^-$. The boratabenzene ring is approximately planar [largest vertical distance of 0.035(4) Å for C51]. The lithium atom is placed 1.904(7) Å below the best boratabenzene plane; its projection onto this plane coincides with the geometrical center of the ring [slip distortion 0.000 Å].

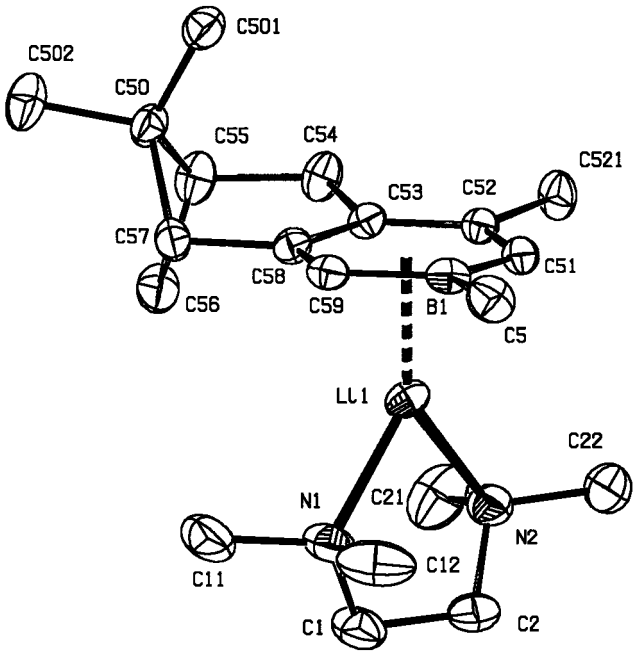


Figure 1. Displacement ellipsoid plot (PLATON)[13] of the molecule **10**. Ellipsoids are scaled to 30% probability.

Table 1. Selected Bond Lengths and Bond Angles for 10

(a) Bond Distances (Å)			
B1−C51	1.513(7)	B1−C59	1.519(6)
C51−C52	1.380(5)	C58−C59	1.395(6)
C52−C53	1.410(5)	C53−C58	1.411(5)
B1−C5	1.581(7)		
N1−Li1	2.137(8)	N2−Li1	2.116(7)
B1−Li1	2.454(8)	C51−Li1	2.344(8)
C52−Li1	2.383(8)	C53−Li1	2.394(8)
C58−Li1	2.360(7)	C59−Li1	2.376(7)
(b) Bond Angles (deg)			
C5−B1−C51	124.8(4)	C5−B1−C59	122.9(4)
C51−B1−C59	112.2(4)		

The fusion of the pinene skeleton to the boratabenzene ring is characterized by a torsional angle C57−C58−C53−C54 of 7.4(6)°, which places C54 above and C57 below the boratabenzene plane. This torsion is possibly caused by a 1,5-interaction between C53 and the *endo*-Me group with C501. The precision of the observed bond lengths of the boratabenzene fragment is not sufficient to justify a detailed comparison with the closely related and more precise structures of $[Li(TMPDA)](C_5H_5BNMe_2)$,[14] $NMe_3Ph(C_5H_5BMe)$,[12a] $[Li(TMEDA)](3\text{-}Bu^t\text{-}5\text{-}MeC_5H_3BNMe_2)$,[7] and Li(TMEDA)(**4**).[2]

Oxidative Coupling of Anion 4$^-$. During the exploration of the reaction chemistry of Li(**4**) we stumbled onto large colorless crystals. These turned out to be the coupling product *exo,exo*-**11** cocrystallized with 0.5 equiv of benzene, *exo,exo*-**11**·$1/2C_6H_6$ (≡**12**). Since oxidative coupling of a boratabenzene ion has not yet been reported, we decided to make this product in a rational way. The reaction of CuI with Li(**4**) in toluene gave black elemental copper and a raw product which contained a mixture of coupling products **11** and the dihydroborinine **5a** (up to 25%). The ^{13}C and ^1H NMR spectra of the

(13) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.
(14) Herberich, G. E.; Schmidt, B.; Englert, U.; Wagner, T. *Organometallics* **1993**, *12*, 2891.

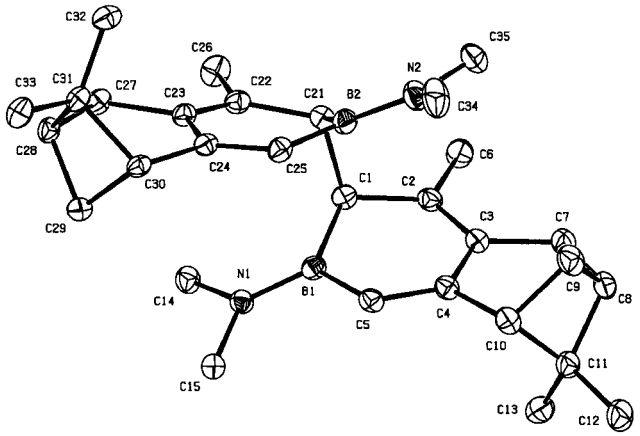
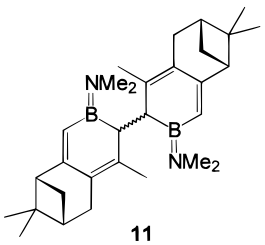


Figure 2. Displacement ellipsoid plot (PLATON)[13] of the molecule *exo,exo*-**11** of clathrate **12**. Ellipsoids are scaled to 30% probability.

mixture **11** showed the presence of two main isomers in a 4:1 ratio and traces (3%) of a third species, all three species having spectra that were closely related to those of **5a**. Crystallization of the mixture from benzene afforded the clathrate **12** of the C_2-symmetric major isomer *exo,exo*-**11**. The minor isomer displays a doubled set of signals and hence must be C_1-symmetric *endo,exo*-**11**.



11

The oxidative coupling reaction creates a C−C linkage, and quite remarkably, only the 5-position of the pinene-fused dihydroborinine is amenable to this bond formation. We suggest that this regioselectivity is related to the energetic preference of dihydroborinine **5a** over its isomers **6a** and **7a** discussed above and also avoids the greater steric congestion that would result from alternative coupling modes with participation of the 3- or the 7-positions.

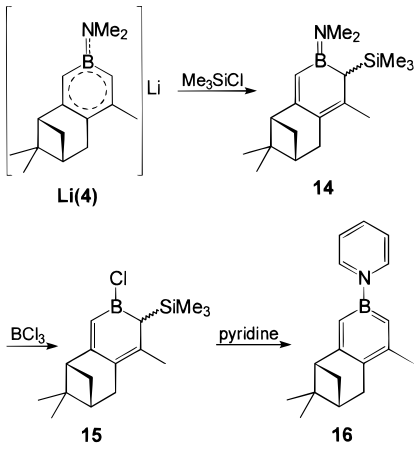
Structure of 12. The molecule *exo,exo*-**11** shows the C_2-symmetric structure of a two-bladed propeller (Figure 2, Table 2). The C−C linkage between C-5 and C-5′ is remarkably long [C1−C21 1.618(3) Å], and the torsional angle C2−C1−C21−C22 amounts to 160.14(16)°. In the dihydroborinine rings the C(sp^3)−B bonds [1.590 Å av] are significantly longer than the C(sp^2)−B bonds [1.548 Å av]. The C−C single bonds [1.481(3)−1.515(3) Å] and the C−C double bonds [1.343(3)−1.354(3) Å] show that the diene system is localized, and the double bonds are found in the 2,6-position as in the dihydroborinines **5a**−**d**. In contrast to this situation the dihydroborinines 2-(Me_3E)C_5H_5BMe show a partial delocalization in the ring which increases from E = Si to E = Pb.[15]

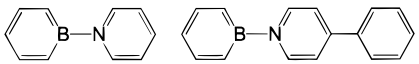
Borabenzene−Pyridine Adduct. In 1985 Maier, Paetzold, Schmid et al. described borabenzene−pyridine adduct **13a** as the first borabenzene adduct with an uncharged Lewis base.[16] Recent work by G. C. Fu et al. described several further examples,[5,17] including a PMe_3 adduct,[17b] a 4-phenylpyridine adduct **13b**,[17a] and the chiral oxazoline derivative **1**.[5]

Table 2. Selected Bond Lengths and Bond Angles for 12

(a) Bond Distances (Å)			
N1−B1	1.407(3)	N2−B2	1.405(4)
C1−B1	1.590(4)	C21−B2	1.589(4)
C1−C2	1.507(3)	C21−C22	1.515(3)
C2−C3	1.354(3)	C22−C23	1.343(3)
C3−C4	1.481(3)	C23−C24	1.488(3)
C4−C5	1.347(3)	C24−C25	1.350(3)
C5−B1	1.549(4)	C25−B2	1.547(4)
C1−C21	1.618(3)		
(b) Bond Angles (deg)			
C1−B1−C5	114.7(2)	C21−B2−C25	114.7(2)
C1−B1−N1	123.0(2)	C21−B2−N2	123.1(2)
C5−B1−N1	122.2(2)	C25−B2−N2	122.0(2)
C2−C1−B1	112.5(2)	C21−C1−B1	111.3(2)
C2−C1−C21	109.0(2)		

Scheme 6





13a **13b**

In this work we used Li(**4**) to synthesize the first Lewis base adduct of an enantiomerically pure borabenzene (Scheme 6). Silylation of Li(**4**) with Me_3SiCl gave **14** as a 4:1 mixture of two *exo*/*endo*-isomers with the $SiMe_3$ group in the 5-position. These isomers are dihydroborinines of type **5**, thus displaying again the strong preference for the 2,6-position of the double bonds. The corresponding chloro derivatives **15** were obtained by treatment of the mixture **14** with BCl_3, and the *exo*/*endo*-isomer ratio was unchanged. Addition of pyridine at ambient temperature effected a markedly exothermic reaction and formation of the desired pyridine adduct **16**. The product can be isolated as beautifully red crystals; in solution it is rather sensitive to air.

The pyridine adduct **13a** is deep yellow,[16] and the analogous 4-phenylpyridine adduct **13b** is described as

(15) Herberich, G. E.; Rosenplänter, J.; Schmidt, B.; Englert, U. *Organometallics* **1997**, *16*, 926.

(16) Boese, R.; Finke, N.; Henkelmann, J.; Maier, G.; Paetzold, P.; Reisenauer, H. P.; Schmid, G. *Chem. Ber.* **1985**, *118*, 1644.

(17) (a) Qiao, S.; Hoic, D. A.; Fu, G. C. *Organometallics* **1997**, *16*, 1501. (b) Hoic, D. A.; Wolf, J. R.; Davis, W. M.; Fu, G. C. *Organometallics* **1996**, *15*, 1315.

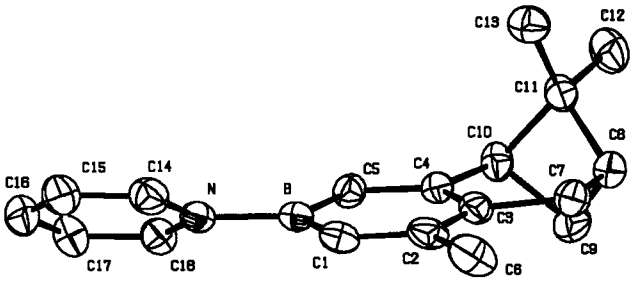


Figure 3. Displacement ellipsoid plot (PLATON)[13]of the molecule **16**. Ellipsoids are scaled to 30% probability.

Table 3. Selected Bond Lengths and Bond Angles for Adduct 16

(a) Bond Distances (Å)			
C1−B	1.476(4)	C5−B	1.488(5)
C1−C2	1.398(4)	C4−C5	1.397(4)
C2−C3	1.405(4)	C3−C4	1.397(4)
N−B	1.556(4)		
N−C14	1.339(4)	N−C18	1.335(4)
C14−C15	1.379(5)	C17−C18	1.382(4)
C15−C16	1.368(5)	C16−C17	1.370(5)
(b) Bond Angles (deg)			
N−B−C1	120.9(3)	C14−N−B	121.1(3)
N−B−C5	120.6(2)	C18−N−B	121.0(3)
C1−B−C5	118.5(3)	C14−N−C18	117.9(3)

orange to orange-red.[17a] The color of **13a** has been interpreted as due to a $\pi-\pi^*$ transition with pronounced charge-transfer character. This transition transfers a π-electron from the HOMO (essentially located in the borabenzene part) to the LUMO (essentially in the pyridine moiety).[16] In **16** the 3-fold alkyl substitution pushes the HOMO to higher energies, thus causing a bathochromic shift of the charge-transfer band. In solution, the color of **16** varies from blue in the nonpolar pentane to deep red in the more polar dichloromethane. The nonpolar solvent destabilizes the polar ground state, thereby causing a further shift to longer wavelengths.

Structure of 16. Adduct **16** crystallizes in the orthorhombic space group $P2_12_12_1$ with $Z = 4$ (Figure 3, Table 3). The structure is very similar to those of **13a** and **13b**. The borabenzene ring is planar [maximum deviation from best plane of 0.007(3) Å for C4], and the same is true for the pyridine moiety [maximum deviation from best plane of 0.003(2) Å for N, 0.003(3) Å for C14, C16, and C17]. The interplanar angle spanned by the two planes amounts to 33.02(14)° and is somewhat smaller than for **13a** (43.3°)[16] and **13b** (48.7°).[17a] A recent AM1 calculation on **13a** gave an interplanar angle of 35° and a barrier to internal rotation of 10 kJ/mol.[18] Thus the ring−ring torsional mode is rather soft and will allow considerable variation of the interplanar angle under the influence of packing forces.

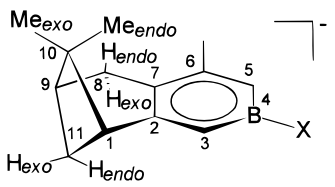
Concluding Remarks

In our preceding communication we had shown that the pinene-fused salt Li(**4**) can be made with remarkable yield and efficiency and represents a complexity of the skeleton that seemed out of reach until then.[2] This situation has allowed us to develop a chemistry of enantiomerically pure derivatives, based on a cheap starting material from the chiral pool. This paper concentrates on organoboron chemistry; in a later paper we shall describe transition metal complexes of the pinene-fused boratabenzene ligands.

Experimental Section

General Procedures. Reactions were carried out under an atmosphere of dinitrogen by means of conventional Schlenk techniques. Hexane was distilled from potassium, CH_2Cl_2 from CaH_2, and Et_2O from sodium benzophenone ketyl. Electron impact mass spectra were recorded on a Finnigan MAT-95 spectrometer with a nominal electron energy of 70 eV. Elemental analyses were performed by Analytische Laboratorien Prof. Dr. H. Malissa und G. Reuter GmbH, D-51789 Lindlar. Melting points were determined in sealed capillaries on a Büchi 510 melting point apparatus and are uncorrected.

NMR Spectra. NMR spectra were recorded on a Varian Unity 500 spectrometer (^{1}H, 500 MHz;^{13}C{^{1}H}, 125.7 MHz; ^{11}B{^{1}H}, 160.4 MHz). Chemical shifts are given in ppm; they were measured at ambient temperature and are relative to internal TMS for ^{1}H and ^{13}C and relative to $BF_3{\cdot}Et_2O$ as external reference for ^{11}B. The ^{1}H and ^{13}C NMR spectra show a fairly constant pattern for the pinane skeleton. Assignments are based on numerous COSY, HETCOR, HMQC, HMBC, and NOE difference spectra which are not documented here. Typical (unsigned) coupling constants $J(^1H-^1H)$ are as follows: $^4J_{1,9} = 5.8$, $^3J_{1,11exo} = 5.8$, $^3J_{3,5} = 3.1$, $^2J_{8endo,8exo} = 14.7$; $^3J_{8endo,9} = 2.8$ and $^3J_{8exo,9} = 3.1$, assignment possibly has to be interchanged; $^4J_{8endo,11exo} = 0-2$, $^3J_{9,11exo} = 5.5$, $^2J_{11endo,11exo} = 8.5$ Hz.



Preparation of Dihydroborinine 5a. To a sample of tetrahydroborine **3**[2] (e.g., 11.5 g, 50 mmol) was added approximately 20 drops of a saturated solution of hydrogenchloride in Et_2O. The reaction mixture was kept at 120 °C for 3 days. The completion of the rearrangement reaction was then ascertained by NMR. The product is a yellowish oil which slowly solidifies to give an almost colorless solid in quantitative yield, moderately soluble in hexane: $[\alpha]_D^{23}$ +36.4° (*c* 75 mmol/L, THF). Anal. Calcd for $C_{15}H_{24}BN$: C, 78.62; H, 10.56; N, 6.11. Found: C, 78.18; H, 10.70; N, 6.13.

Data for 5a: MS *m*/*z* (I_{rel}) 229 (71, M^+), 70 (100, $C_3H_9BN^+$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.53 (s, 3-H), 2.83 (s, NMe), 2.68 (s, NMe), 2.54 (dd, $J = 5.8$, 5.5 Hz, 1-H), 2.51 (m, 2H, 8-H$_{endo}$, 8-H$_{exo}$), 2.44 (dddd, $J = 9.5$, 6.1, 5.5, 0.6 Hz, 11-H$_{exo}$), 2.11 (dddd, $J = 6.1$, 5.8, 3.0, 2.7 Hz, 9-H), 1.83 (s br, 6-Me), 1.77 (s br, 2H, 5-H$_{endo}$, 5-H$_{exo}$), 1.28 (s, 10-Me$_{exo}$), 1.14 (d, $J = 9.5$ Hz, 11-H$_{endo}$), 0.75 (s, 10-Me$_{endo}$); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 164.6 (C-2), 137.3 (C-6), 125.9 (C-7), 117.8 (br, C-3), 53.8 (C-1), 39.9 (C-9), 39.5 (C-10), 38.7 (NMe), 38.6 (NMe), 31.6 (C-8), 30.9 (C-11), 27.4 (br, C-5), 26.2 (10-Me$_{exo}$), 21.9 (6-Me), 21.3 (10-Me$_{endo}$); ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) δ 40.

Preparation of *B*-Chloro Compound 5b. A solution of BCl_3 in CH_2Cl_2 (19.5 mL, 1.70 M, 33.2 mmol) was added to **5a** (5.56 g, 24.3 mmol) in CH_2Cl_2 (40 mL) at −60 °C. The mixture turned red. Stirring was continued at −60 °C for 5 min. Then the volatiles were thoroughly pumped off under vacuum at the same temperature. Only after complete removal of the BCl_3 was the temperature allowed to rise, and the solid residue was sublimed at 100 °C/10^{-6} bar to give **5b** (4.57 g, 85%) as a white to slightly yellow, somewhat sticky solid: moderately soluble

(18) Bock, H.; Nick, S.; Näther, C.; Bensch, W. *Chem. Eur. J.* **1995**, *1*, 557.

in hexane, can be stored under argon at −30 °C. Anal. Calcd for $C_{13}H_{18}BCl$: C, 70.80; H, 8.23. Found: C, 70.51; H, 8.40.

Data for 5b: MS *m*/*z* (I_{rel}) 220 (76, M^+), 177 (100, $M^+ - C_3H_7$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.87 (s, 3-H), 2.69 (dd, J = 5.8, 5.5 Hz, 1-H), 2.59 (m, 2H, 8-H$_{endo}$, 8-H$_{exo}$), 2.52 (ddd, J = 9.8, 5.8, 5.5 Hz, 11-H$_{exo}$), 2.26 (m, 2H, 5-H$_{endo}$, 5-H$_{exo}$), 2.20 (dddd, J = 5.8, 5.8, 3.0, 3.0 Hz, 9-H), 1.95 (m, 6-Me), 1.33 (s, 10-Me$_{exo}$), 1.19 (d, J = 9.8 Hz, 11-H$_{endo}$), 0.75 (s, 10-Me$_{endo}$); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 177.0 (C-2), 144.7 (C-6), 127.9 (C-7), 124.0 (br, C-3), 53.9 (C-1), 39.6 (C-9, C-10), 37.2 (br, C-5), 31.4 (C-8), 30.2 (C-11), 26.0 (10-Me$_{exo}$), 21.7 (6-Me), 21.3 (10-Me$_{endo}$); ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) δ 61.

Preparation of *B*-Methyl Compound 5c. A solution of $ZnMe_2$ in toluene (4.90 mL, 1.5 M, 7.35 mmol) was added dropwise to **5b** (2.69 g, 12.2 mmol) in toluene (30 mL) at −78 °C. The solution was allowed to warm to room temperature overnight. The reaction mixture was filtered through a frit (covered with kieselguhr) to remove the solid formed. Then the volatiles were pumped off under vacuum, and the product was collected by condensation at 80 °C/10^{-6} bar to give **5c** (2.04 g, 84%) as a yellowish solid: soluble in hexane, can be stored at −30 °C. Anal. Calcd for $C_{14}H_{21}B$: C, 84.02; H, 10.58. Found: C, 83.87; H, 10.79.

Data for 5c: MS *m*/*z* (I_{rel}) 200 (45, M^+), 157 (100, $M^+ - C_3H_7$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.93 (s, 3-H), 2.62 (dd, J = 5.8, 5.5 Hz, 1-H), 2.57 (m, 2H, 8-H$_{exo}$, 8-H$_{endo}$), 2.48 (ddd, J = 9.5, 5.8, 5.5 Hz, 11-H$_{exo}$), 2.16 (dddd, J = 5.8, 5.8, 3.1, 2.8 Hz, 9-H), 2.13 and 2.09 (dd, J = 12.4, 1.2 Hz, 1H each, 5-H$_{endo}$, 5-H$_{exo}$), 1.92 (m, 6-Me), 1.31 (s, 10-Me$_{exo}$), 1.16 (d, J = 9.5 Hz, 11-H$_{endo}$), 0.73 (s, 10-Me$_{endo}$), 0.71 (m, BMe); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.7 (C-2), 144.5 (C-6), 127.5 (C-7), 126.2 (br, C-3), 53.7 (C-1), 39.8 (C-9), 39.4 (C-10), 38.9 (br, C-5), 31.5 (C-8), 30.6 (C-11), 26.2 (10-Me$_{exo}$), 21.8 (6-Me), 21.3 (10-Me$_{endo}$), 8.5 (br, BMe); ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) δ 68.

Preparation of *B*-Methoxy Compound 5d. Methoxytrimethylsilane (4.3 mL, 31 mmol) was added to **5b** (2.80 g, 12.7 mmol) in CH_2Cl_2 (15 mL). The mixture was kept at ambient temperature for 50 h. Shorter reaction times and/or a lower excess of silane would result in incomplete conversion. After removal of the volatiles under vacuum the product was collected by condensation at 90 °C/10^{-6} bar to give **5d** (2.50 g, 91%) as a slightly yellow oil: rather soluble in hexane, can be stored at −30 °C. Anal. Calcd for $C_{14}H_{21}BO$: C, 77.80; H, 9.79. Found: C, 78.03; H, 9.92.

Data for 5d: MS *m*/*z* (I_{rel}) 216 (100, M^+); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.45 (s, 3-H), 3.70 (s, OMe), 2.60 (dd, J = 5.8, 5.8 Hz, 1-H), 2.54 (m, 2H, 8-H$_{endo}$, 8-H$_{exo}$), 2.46 (ddd, J = 9.8, 5.8, 5.8 Hz, 11-H$_{exo}$), 2.13 (dddd, J = 5.8, 5.8, 3.1, 2.7 Hz, 9-H), 1.86 (s, 6-Me), 1.77 (m, 2H, 5-H$_{endo}$, 5-H$_{exo}$), 1.29 (s, 10-Me$_{exo}$), 1.15 (d, J = 9.8 Hz, 11-H$_{endo}$), 0.74 (s, 10-Me$_{endo}$); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 171.9 (C-2), 138.9 (C-6), 126.6 (C-7), 116.7 (br, C-3), 53.9 (C-1), 53.3 (OMe), 39.8 (C-9), 39.5 (C-10), 31.6 (C-8), 30.6 (C-11), 28.1 (br, C-5), 26.1 (10-Me$_{exo}$), 21.8 (6-Me), 21.3 (10-Me$_{endo}$); ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) δ 48.

Preparation of *B*-Methylboratabenzene Derivative Li(8). A solution of **5c** (2.84 g, 14.2 mmol) in hexane (35 mL) was cooled to −78 °C. A hexane solution of $LiN(SiMe_3)_2$ (15.0 mL, 1.0 M, 15.0 mmol) was added dropwise within 15 min. The mixture was then allowed to warm to room temperature overnight. The product was collected on a frit, carefully washed with hexane (3 × 5 mL), and dried under vacuum to give Li(**8**) (2.44 g, 83%) as colorless powder: only slightly soluble in hexane and toluene, soluble in ether, and very soluble in THF.

Data for Li(8): ^{1}H NMR (500 MHz, THF-d_8) δ 5.81 (m, 5-H), 5.58 (s br, 3-H), 2.72 (dd, J = 15.0, 3.1 Hz, 8-H$_{exo}$), 2.54 (ddm, J = 15.0, 2.8 Hz, 8-H$_{endo}$), 2.40 (dddm, J = 8.9, 6.1, 5.5 Hz, 11-H$_{exo}$), 2.35 (dd, J = 5.8, 5.5 Hz, 1-H), 2.14 (dddd, J = 6.1, 5.8, 3.1, 2.8 Hz, 9-H), 2.03 (s, 6-Me), 1.39 (d br, J = 8.9 Hz, 11-H$_{endo}$), 1.26 (s, 10-Me$_{exo}$), 0.51 (s, 10-Me$_{endo}$), 0.37 (s, BMe); ^{13}C{^{1}H} NMR (126 MHz, THF-d_8) δ 149.7 (C-2), 140.0 (C-6), 124.5 (br, C-5), 124.1 (br, C-3), 110.5 (C-7), 53.2 (C-1), 42.5 (C-9), 39.6 (C-10), 33.1 (C-11), 32.7 (C-8), 27.2 (10-Me$_{exo}$), 23.1 (6-Me), 21.6 (10-Me$_{endo}$), 4.3 (br, BMe); ^{11}B{^{1}H} NMR (160 MHz, THF-d_8) δ 33.

Preparation of the TMEDA Solvate 10. The warm solution of Li(**8**) (467 mg, 2.27 mmol) in hexane and THF (5 mL each) was filtered through a G4-frit. TMEDA (0.37 mL, 2.50 mmol) was added to the filtrate. Careful removal of the volatiles under vacuum left **10** (611 mg, 84%) as a slightly yellow powder: soluble in hexane and benzene. Colorless crystals for X-ray work were obtained by cooling a warm hexane solution of **10** to ambient temperature (∼50%). Anal. Calcd for $C_{20}H_{36}BLiN_2$: C, 74.54; H, 11.26; N, 8.69. Found: C, 74.70; H, 11.19; N, 8.80.

Data for 10: ^{1}H NMR (500 MHz, C_6D_6) δ 6.58 (d, J = 2.4 Hz, 5-H), 6.34 (d, J = 2.4 Hz, 3-H), 2.91 (dm, J = 15.6 Hz, 1H) and 2.81 (dd, J = 15.6, 3.1 Hz, 1H) for 8-H$_{endo}$ and 8-H$_{exo}$, 2.75 (dd, J = 5.5, 5.5 Hz, 1-H), 2.63 (ddd, J = 8.6, 5.8, 5.5 Hz, 11-H$_{exo}$), 2.39 (dddd, J = 5.8, 5.5, 3.1, 2.8 Hz, 9-H), 2.33 (s, 6-Me), 1.44 (s, 10-Me$_{exo}$), 1.23 (s, 10-Me$_{endo}$), 1.02 (d, J = 8.6 Hz, 11-H$_{endo}$), 0.90 (s, BMe); TMEDA 1.63 (s br, 2 CH_2), 1.65−1.25 (complex, 4 Me); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ 150.3 (C-2), 140.3 (C-6), 125.2 (br, C-3, C-5), 110.1 (C-7), 52.8 (C-1), 42.0 (C-9), 39.5 (C-10), 34.1 (C-11), 32.7 (C-8), 26.9 (10-Me$_{exo}$), 23.7 (6-Me), 21.7 (10-Me$_{endo}$), 4.6 (br, BMe); TMEDA 55.8 (CH_2), 45.2 (Me); ^{11}B{^{1}H} NMR (160 MHz, C_6D_6) δ 34.

Preparation of *B*-Methoxyboratabenzene Derivative Li(9). LDA was prepared from diisopropylamine (1.25 mL, 8.9 mmol) in THF (8 mL) and LiBu (5.0 mL, 1.6 M in hexane, 8.0 mmol) at 0 °C. Compound **5d** (1.57 g, 7.26 mmol) in hexane (8 mL) was added at −60 °C. The reaction mixture was allowed to warm to ambient temperature and was kept stirring for 80 h. After careful removal of the volatiles, the resulting residue was triturated with hexane (20 mL). Filtration through a frit covered with kieselguhr and removal of the volatiles under vacuum left Li(**9**) (1.92 g, 100%) as a yellowish powder which is somewhat contaminated, mainly by LDA, and retains THF in varying small quantities (NMR): moderately soluble in hexane, soluble in benzene and ether, very soluble in THF. A TMEDA solvate could not be obtained.

Data for Li(9): ^{1}H NMR (500 MHz, THF-d_8) δ 5.20 (d, J = 2.8 Hz, 5-H), 5.02 (d, J = 2.8 Hz, 3-H), 3.53 (s, OMe), 2.69 (dd, J = 14.8, 3.1 Hz, 8-H$_{exo}$), 2.59 (dd, J = 14.8, 2.8 Hz, 8-H$_{endo}$), 2.37 (m, 11-H$_{exo}$), 2.34 (dd, J = 6.1, 5.5 Hz, 1-H), 2.14 (dddd, J = 6.1, 5.8, 3.1, 2.8 Hz, 9-H), 2.02 (s, 6-Me), 1.25 (s, 10-Me$_{exo}$), 1.24 (d, J = 8.2 Hz, 11-H$_{endo}$), 0.59 (s, 10-Me$_{endo}$); ^{13}C{^{1}H} NMR (126 MHz, THF-d_8) δ 151.7 (C-2), 140.9 (C-6), 108.6 (br, C-5), 107.9 (br, C-3), 107.2 (C-7), 54.1 (C-1), 53.0 (OMe), 42.9 (C-9), 39.7 (C-10), 33.2 (C-8, C-11), 27.4 (10-Me$_{exo}$), 23.7 (6-Me), 21.8 (10-Me$_{endo}$); ^{11}B{^{1}H} NMR (160 MHz, THF-d_8) δ 35.

Oxidative Coupling of Li(4) with CuI. A solution of Li(**4**)^2 (1.09 g, 4.59 mmol) in toluene (15 mL) was added dropwise to a suspension of CuI (1.91 g, 10.0 mmol) in toluene (15 mL) at −60 °C. The cooling bath was then removed. The mixture slowly turned black. Stirring was continued for 2 h at 20 °C. After filtration through a frit covered with kieselguhr, the volatiles were removed under vacuum. The brown residue was dissolved in hexane. After a further filtration and removal of the solvent the solid residue of **11** (873 mg, 84%, contaminated by **5a**) was analyzed by NMR. Crystallization from benzene gave **12** as colorless crystals: soluble in hexane. Anal. Calcd for $C_{33}H_{49}B_2N_2$: C, 80.01; H, 9.97; N, 5.65. Found: C, 79.67; H, 9.86; N, 5.95.

Data for 11 (mixture): MS *m*/*z* (I_{rel}) 456 (2, M^+), 229 (63, $C_{15}H_{24}BN^+$), 228 (63, $C_{15}H_{23}BN^+$), 70 (100, $C_3H_9BN^+$); ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) δ 40.

Data for *exo,exo*-11: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.29 (s, 3-H), 2.55 (s, NMe), 2.47 (s, NMe), 2.45−2.20 (complex, 4H, 1-H, 8-H$_{endo}$, 8-H$_{exo}$, 11-H$_{exo}$), 2.15 (s, 5-H), 2.05 (dddd, J = 6.1, 5.8, 3.1, 2.8 Hz, 9-H), 1.89 (s, 6-Me), 1.25 (s, 10-Me$_{exo}$), 1.06 (d, J = 8.9 Hz, 11-H$_{endo}$), 0.67 (s, 10-Me$_{endo}$); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 156.5 (C-2), 137.1 (C-6), 127.7 (C-7), 120.1 (br,

Table 4. Crystal Data, Data Collection Parameters, and Convergence Results for 10, 12, and 16

formula	$C_{20}H_{36}BLiN_2$ (**10**)	$C_{30}H_{46}B_2N_2$ 0.5C_6H_6 (**12**)	$C_{18}H_{22}BN$ (**16**)
fw	322.28	495.39	263.19
system	orthorhombic	orthorhombic	orthorhombic
space group (no)	$P2_12_12_1$ (19)	$P2_12_12$ (18)	$P2_12_12_1$ (19)
a, Å	8.788(5)	29.975(5)	9.822(1)
b, Å	15.424(8)	9.806(3)	11.420(1)
c, Å	31.288(9)	10.126(2)	13.593(1)
U, Å^3	4241(6)	2976(2)	1524.6(3)
Z	8	4	4
d_{calc}, g cm^{-3}	1.009	1.106	1.146
μ, cm^{-1}	3.93	4.32	4.55
θ_{max}, deg	65.0	70.0	75.0
temp, K	173	180	293
λ, Å	1.5418	1.5418	1.5418
crystal dimens, mm^3	0.36 × 0.56 × 0.64	0.40 × 0.68 × 0.72	0.3 × 0.3 × 0.7
no. of reflns	6615	5528	3486
no. of indep obs reflns	3801	4728	2222
$I > n\sigma(I)$	$n = 1$	$n = 2$	$n = 1$
no. of vars	434	530	270
R^a	0.070	0.053	0.057
$R_w{}^b$	0.080	0.060	0.054
GOF^c	1.676	1.835	1.088
res el dens, e Å^{-3}	0.604	0.692	0.247

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w^{-1} = \sigma^2(F_o)$. [c] GOF $= [\sum w(|F_o| - |F_c|)^2/n_{obs} - n_{var}]^{1/2}$. n_{obs}: no. of observations. n_{var}: no. of variables refined.

C-3), 52.7 (C-1), 40.5 (br, C-5), 40.0 (C-9), 39.9 (C-10), 39.0 (NMe), 38.7 (NMe), 32.0 (C-8), 30.2 (C-11), 26.2 (10-Me$_{exo}$), 21.3 (6-Me), 20.4 (10-Me$_{endo}$).

Data for *endo,exo*-11: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.46 (s, 3-H), 5.29 (s, 3′-H), 2.82 (s, NMe), 2.76 (s, NMe), 2.62 (s, NMe′), 2.57 (s, NMe′), 2.45−2.20 (complex, 8H, 1-H, 1′-H, 8-H$_{endo}$, 8′-H$_{endo}$, 8-H$_{exo}$, 8′-H$_{exo}$, 11-H$_{exo}$, 11′-H$_{exo}$), 2.05 (m, 2H, 9-H, 9′-H), 1.87 and 1.69 (s, 6-Me, 6′-Me), 1.25 (s, 10′-Me$_{exo}$), 1.24 (s, 10-Me$_{exo}$), 1.14 (d, $J = 9.1$ Hz, 1H) and 1.02 (d, $J = 9.2$ Hz, 1H) for 11-H$_{endo}$ and 11′−H$_{endo}$), 0.76 and 0.67 (s, 10-Me$_{endo}$, 10′-Me$_{endo}$); 5-H and 5′-H could not be located; note superposition of signals at 5.29, 2.45−2.20, 1.25, and 0.67; ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 161.6 and 158.3 (C-2, C-2′), 142.1 and 139.7 (C-6, C-6′), 127.7 and 125.5 (C-7, C-7′), 119.0 and 117.9 (br, C-3, C-3′), 53.5 and 52.8 (C-1, C-1′), 40.0 and 37.6 (br, C-5, C-5′), 40.0 (C-9, C-9′, C-10, C-10′), 39.4 and 38.7 (NMe$_2$, NMe$_2$′), 32.4, 32.2, 32.1 and 30.5 (C-8, C-8′, C-11, C-11′), 26.4 and 26.2 (10-Me$_{exo}$, 10′-Me$_{exo}$), 21.5 and 21.2 (6-Me, 6′-Me), 21.5 and 19.9 (10-Me$_{endo}$, 10′-Me$_{endo}$).

Preparation of 4-(Dimethylamino)-5-(trimethylsilyl) Derivatives 14. A solution of Me_3SiCl (5.2 mL, 41.2 mmol) in THF (10 mL) was cooled to 0 °C. Li(**4**) (6.62 g, 20.6 mmol, THF content determined by NMR) in pentane (90 mL) was added dropwise with stirring and cooling. Stirring was continued at 20 °C for 2 h. After careful removal of the volatiles under vacuum, pentane was added to the residue, and the resulting suspension was filtered through a frit covered with kieselguhr to remove the LiCl formed. The pentane was then pumped off to leave **14** as a 4:1 mixture of *exo*- and *endo*-isomers (6.20 g, 100%), as a colorless or, if less pure, slightly yellow oil which slowly solidified: soluble in pentane, very soluble in CH_2Cl_2; can be stored at −30 °C. Anal. Calcd for $C_{18}H_{32}BNSi$: C, 71.74; H, 10.70; N, 4.65. Found: C, 71.93; H, 10.85; N, 4.58.

Data for 14 (mixture): MS m/z (I_{rel}) 301 (44, M^+), 73 (100, $SiMe_3^+$); ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) δ 41.

Data for *exo*-14: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.46 (s, 3-H), 2.79 (s, NMe), 2.70 (s, NMe), 2.48 (dd, $J = 5.8$, 5.5 Hz, 1-H), 2.51−2.43 (complex, 2H, 8-H$_{endo}$, 8-H$_{exo}$), 2.40 (dddm, $J = 9.5$, 5.8, 5.5 Hz, 11-H$_{exo}$), 2.25 (s, 5-H$_{endo}$), 2.10 (dddd, $J = 5.8$, 5.8, 3.1, 2.8 Hz, 9-H), 1.83 (s br, 6-Me), 1.28 (s, 10-Me$_{exo}$), 1.18 (d, $J = 9.5$ Hz, 11-H$_{endo}$), 0.71 (s, 10-Me$_{endo}$), −0.03 (s, $SiMe_3$); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 163.2 (C-2), 140.0 (C-6), 123.3 (C-7), 118.6 (br, C-3), 53.2 (C-1), 40.1 (br, C-5), 40.0 (C-9), 39.8 (C-10), 39.6 (NMe), 38.3 (NMe), 31.4 (C-8), 30.4 (C-11), 26.3 (10-Me$_{exo}$), 22.9 (6-Me), 21.3 (10-Me$_{endo}$), 0.6 ($SiMe_3$).

Data for *endo*-14: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.54 (s, 3-H), 2.80 (s, NMe), 2.70 (s, NMe), 2.54 (dd, $J = 5.8$, 5.5 Hz, 1-H), 2.56−2.38 (complex, obscured by signals of major isomer, 3H, 8-H$_{endo}$, 8-H$_{exo}$, 11-H$_{exo}$), 2.24 (s, 5-H$_{exo}$), 2.11 (dddd, $J = 5.8$, 5.8, 3.1, 2.8 Hz, 9-H), 1.85 (s br, 6-Me), 1.28 (s, 10-Me$_{exo}$), 1.10 (d, $J = 9.5$ Hz, 11-H$_{endo}$), 0.84 (s, 10-Me$_{endo}$), 0.02 (s, $SiMe_3$), note superposition of signals at 2.70, 2.56−2.38, and 1.28; ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 163.6 (C-2), 140.6 (C-6), 123.4 (C-7), 118.3 (br, C-3), 53.6 (C-1), 40.2 (C-9), 40.1 (br, C-5), 40.0 (C-10), 39.6 (NMe), 38.4 (NMe), 32.2 (C-11), 31.6 (C-8), 26.4 (10-Me$_{exo}$), 23.2 (6-Me), 21.9 (10-Me$_{endo}$), 1.4 ($SiMe_3$).

Preparation of 4-Chloro-5-(trimethylsilyl) Derivatives 15. A solution of BCl_3 in CH_2Cl_2 (8.4 mL, 1.50 M, 12.6 mmol) was added dropwise to **14** (3.05 g, 10.1 mmol) in CH_2Cl_2 (30 mL) at −70 °C. The mixture was kept at 20 °C for 1 h, and the color turned to brown. Then the volatiles were removed under vacuum. The product was collected by condensation at 140 °C/10^{-6} bar to give **15** (2.75 g, 93%) as a yellowish oil which solidified at ambient temperature. The product can be recrystallized from hexane at −30 °C to give a colorless solid: very soluble; can be stored at −30 °C. Anal. Calcd for $C_{16}H_{26}BClSi$; C, 65.65; H, 8.95. Found: C, 65.72; H, 8.83.

Data for 15 (mixture): MS m/z (I_{rel}) 292 (11, M^+), 73 (100, $SiMe_3^+$); ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) δ 57.

Data for *exo*-15: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.86 (s br, 3-H), 3.34 (s br, 5-H$_{endo}$), 2.67 (dd, $J = 5.8$, 5.5 Hz, 1-H), 2.65−2.54 (complex, 2H, 8-H$_{endo}$, 8-H$_{exo}$), 2.50 (dddm, $J = 9.5$, 5.8, 5.5 Hz, 11-H$_{exo}$), 2.20 (dddd, $J = 5.8$, 5.8, 3.1, 2.8 Hz, 9-H), 1.98 (s, 6-Me), 1.32 (s, 10-Me$_{exo}$), 1.21 (d, $J = 9.5$ Hz, 11-H$_{endo}$), 0.68 (s, 10-Me$_{endo}$), 0.07 (s, $SiMe_3$); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 173.0 (C-2), 148.7 (C-6), 125.9 (C-7), 125.2 (br, C-3), 58.6 (br, C-5), 53.0 (C-1), 39.8 (C-9), 39.4 (C-10), 31.7 (C-8), 30.3 (C-11), 26.1 (10-Me$_{exo}$), 23.6 (6-Me), 21.2 (10-Me$_{endo}$), 0.4 ($SiMe_3$).

Data for *endo*-15: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.88 (s br, 3-H), 3.28 (s br, 5-H$_{exo}$), 2.68 (dd, $J = 5.8$, 5.5 Hz, 1-H), 2.65−2.47 (complex, obscured by signals of major isomer, 3H, 8-H$_{endo}$, 8-H$_{exo}$, 11-H$_{exo}$), 2.21 (dddd, $J = 5.8$, 5.8, 3.1, 2.8 Hz, 9-H), 1.98 (s br, 6-Me), 1.33 (s, 10-Me$_{exo}$), 1.13 (d, $J = 9.8$ Hz, 11-H$_{endo}$), 0.82 (s, 10-Me$_{endo}$), 0.12 (s, $SiMe_3$), note superposition at 2.65−2.47 and 1.98; ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 173.1 (C-2), 148.9 (C-6), 126.2 (C-7), 125.2 (br, C-3),

58.6 (br, C-5), 53.3 (C-1), 39.9 (C-9), 39.4 (C-10), 31.3 and 30.3 (C-8, C-11), 26.1 (10-Me_{exo}), 23.8 (6-Me), 21.2 (10-Me_{endo}), 1.2 ($SiMe_3$).

Preparation of (1*R*,9*R*)-6,10,10-Trimethyl-4-boratricyclo-[7.1.1.$0^{2,7}$]undeca-2,4,6-triene−Pyridine (16). Pyridine (0.30 mL, 3.72 mmol) was added to **15** (792 mg, 2.71 mmol) in ether (5 mL). At first a red-purple solid precipitated, heat evolved, and the precipitate dissolved. The purple mixture was kept at 20 °C for 1 h. Then the solvent was pumped off. The residue was dissolved in CH_2Cl_2 (3 mL). After layering with ether (10 mL) and hexane (10 mL) crystals deposited and were collected, washed with pentane, and dried under vacuum to give **16** (304 mg, 43%, not optimized) as large shiny red crystals, which slowly become turbid: dec ≈ 70 °C; slightly soluble in pentane (blue), moderately soluble in ether (purple-red), very soluble in benzene (purple) and in CH_2Cl_2 (deep red). Anal. Calcd for $C_{18}H_{22}BN$: C, 82.14; H, 8.43; N, 5.32. Found: C, 81.91; H, 8.28; N, 5.26.

Data for 16: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.06 (ddm, J = 6.7, 1.5 Hz, 2 *o*-py), 7.95 (dddd, J = 7.6, 7.6, 1.5, 1.5 Hz, *p*-py), 7.64 (ddm, J = 7.6, 6.7 Hz, 2 *m*-py), 6.44 (d, J = 2.6 Hz, 5-H), 6.20 (d, J = 2.6 Hz, 3-H), 2.94 (dd, J = 16.1, 3.1 Hz, 8-H_{exo}), 2.87 (dd, J = 16.1, 2.8 Hz, 8-H_{endo}), 2.78 (dd, J = 5.8, 5.8 Hz, 1-H), 2.61 (ddd, J = 8.9, 5.8, 5.5 Hz, 11-H_{exo}), 2.37 (dddd, J = 5.8, 5.5, 3.1, 2.8 Hz, 9-H), 2.37 (s, 6-Me), 1.44 (s, 10-Me_{exo}), 1.43 (d, J = 8.9 Hz, 11-H_{endo}), 0.81 (s, 10-Me_{endo}); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 153.1 (C-2), 143.7 (*o*-py), 142.3 (C-6), 139.1 (*p*-py), 125.9 (*m*-py), 120.1 (C-7), 117.3 (br, C-5), 114.6 (br, C-3), 52.5 (C-1), 41.1 (C-9), 38.6 (C-10), 32.5 (C-8), 32.0 (C-11), 26.4 (10-Me_{exo}), 22.7 (6-Me), 21.4 (10-Me_{endo}); $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ 32.

Crystal Structure Determinations of 10, 12, and 16. Geometry and intensity data were collected with Cu Kα radiation on an Enraf-Nonius Turbo-CAD4 diffractometer equipped with a graphite monochromator (λ = 1.5418 Å). Crystal data, data collection parameters, and convergence results are collected in Table 4. Because of the low linear absoption coefficients, no absorption corrections were applied to the experimental data. The structures were solved by direct methods[19] and refined on structure factors with the local version of the SDP program suite.[20] In the full-matrix least-squares refinement, all non-hydrogen atoms were assigned anisotropic displacement parameters. Hydrogen atoms were included as riding on the corresponding carbon atoms (C−H = 0.98 Å, $U_{iso}(H) = 1.3U_{eq}(C)$) in the case of **10** and refined isotropically for **12** and **16**.[21]

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Supporting Information Available: Tables of crystal data, bond distances and angles, positional parameters, and displacement parameters for **10**, **12**, and **16**.[21] This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD-127315 for **10**, CSD-127314 for **12**, and CSD-127313 for **16**, the names of the authors, and this journal citation.