

# Borabenzene Derivatives. 23.<sup>1</sup> New Synthetic Entry into Borabenzene Chemistry via Doubly Kalkiated Pentadienes: Synthesis of 1-(Dimethylamino)-3-methylene-1,2,3,6-tetrahydroborinines and Lithium 1-(Dimethylamino)boratabenzene Derivatives

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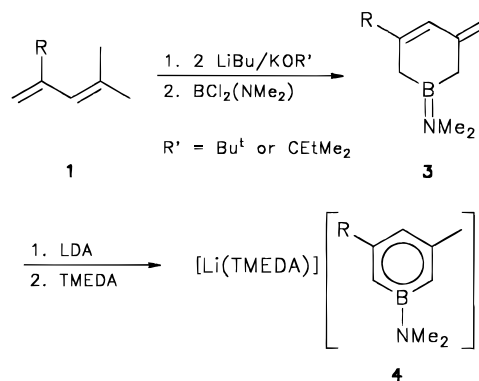
Dicarbaniions obtained by dikalkiation from suitable dienes **1** such as (*E*)-2-methyl-1,3-pentadiene, 2,4-dimethyl-1,3-pentadiene, and 2-*tert*-butyl-4-methyl-1,3-pentadiene react with  $\text{BCl}_2(\text{NMe}_2)$  to form 1-(dimethylamino)-3-methylene-1,2,3,6-tetrahydroborinines **3a** (5-R = H), **3b** (5-R = Me), and **3c** (5-R = Bu<sup>t</sup>) in moderate yields. The compounds **3a–c** dimerize reversibly to give crystalline dimers (**3a**)<sub>2</sub>, (**3b**)<sub>2</sub>, and (**3c**)<sub>2</sub> as  $C_{2v}$  and  $C_{2h}$  isomers. The structure of  $C_{2v}$ -(**3a**)<sub>2</sub> was determined by X-ray diffraction. In solution a monomer/dimer equilibrium is established with  $K = 49.0 \text{ mol L}^{-1}$  for dissociation at 22.0 °C,  $\Delta H = (70 \pm 2) \text{ kJ mol}^{-1}$ , and  $\Delta S = (270 \pm 8) \text{ J K}^{-1} \text{ mol}^{-1}$ . The methylene-1,2,3,6-tetrahydroborinines **3** isomerize thermally at 100–120 °C to give dihydroborinines. Thus **3b** affords a mixture (3/2) of 3,5-dimethyl-1,2-dihydroborinine **5b** and 3,5-dimethyl-1,4-dihydroborinine **6b**. The isomerization is catalyzed by acids as HCl in Et<sub>2</sub>O and then may take place at ambient temperature. Metalation of **3a–c** with LDA in THF gives high yields of lithium 1-(dimethylamino)boratabenzene salts which can be isolated as TMEDA solvates **4a–c**. The structure of  $[\text{Li}(\text{TMEDA})](3\text{-Bu}^t\text{-5-MeC}_5\text{H}_3\text{BNMe}_2)$  (**4c**) is that of a contact ion pair.

## Introduction

At present essentially three synthetic entries into borabenzene and boratabenzene chemistry are known:<sup>3</sup> the cobaltocene route,<sup>4</sup> Ashe's tin route<sup>5</sup> with a recent ramification,<sup>6</sup> and our recently developed synthesis via metalation and ring closure of suitable pentadienylboranes.<sup>2</sup> We present here a further synthetic method which is a variation of the metalation/borylation theme.

Our new synthesis is essentially a three-step procedure (Scheme 1).<sup>7</sup> Double kalkiation of suitable pentadiene derivatives **1a–c**<sup>8</sup> gives the dipotassio compounds

## Scheme 1



<sup>®</sup> Abstract published in *Advance ACS Abstracts*, May 1, 1996.

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$\text{K}_2(\mathbf{2a-c})$ . Subsequent ring closure with dichloro(dimethylamino)borane,  $\text{BCl}_2(\text{NMe}_2)$ , affords the 3-methylene-1,2,3,6-tetrahydroborinines **3a–c**. By a combination of double-bond migration and deprotonation these new  $\text{C}_5\text{B}$  heterocycles are transformed to give Li(TMEDA) 1-(dimethylamino)boratabenzene salts **4a–c**. The use of the dipotassio compounds  $\text{K}_2(\mathbf{2a-c})$  as intermediates implies the presence of a methyl group in the position  $\beta$  to the boron atom of **4a–c**.

## Results and Discussion

**Double Kalkiation and Ring Closure.** A vast body of information on polymetalation of olefinic and aro-

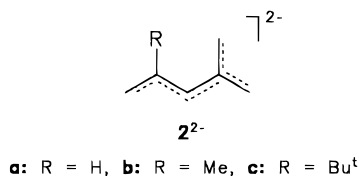
(7) Standt, R. Doctoral Dissertation, Technische Hochschule Aachen, Aachen, Germany, 1995.

(8) The various 1,3-isomers seem to be equally suitable. For details see the Experimental Section.

matic hydrocarbons is available.<sup>9</sup> 2-Methyl-1,4-pentadiene has been lithiated with LiBu/TMEDA to give the dilithio derivative Li<sub>2</sub>(**2a**) in near quantitative yield (96%);<sup>10</sup> the lithiation of 2,4-dimethyl-1,4-pentadiene is apparently much less favorable.<sup>10a</sup>

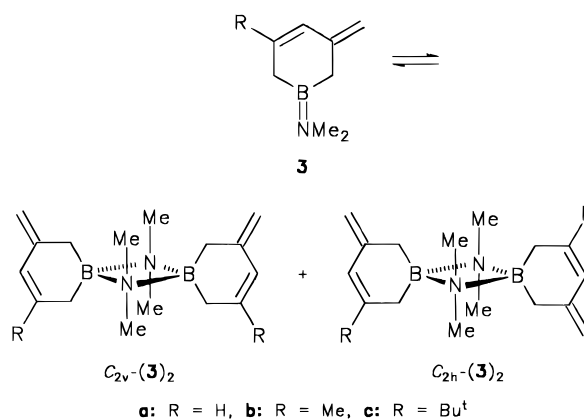
In our hands, the kallation of conjugated pentadienes proved to be preferable, partly because the conjugated dienes are more readily available and partly because the dipotassio compounds gave better yields in the subsequent ring closure step. As bases we used the Lochmann–Schlosser base,<sup>11</sup> LiBu/KOBU<sup>t</sup>, or the modified base LiBu/KOCeMe<sub>2</sub>.<sup>12</sup> The products K<sub>2</sub>(**2a–c**) are insoluble in hexane and can be purified by washing with hexane; this process is not completely successful but works better with the modified base.

Silylation of the metalation products with Me<sub>3</sub>SiCl in combination with analytical gas chromatography and NMR spectroscopy confirmed high yields in the dikaliation step.<sup>13</sup> Metalation of **1a**<sup>8</sup> [(*E*)-2-methyl-1,3-pentadiene and 4-methyl-1,3-pentadiene (7/3)] with LiBu/KOCeMe<sub>2</sub> (2 equiv) gave disilylated product in >95% yield. The 2,4-dimethyl-1,3-pentadiene (**1b**) gave 37, 52, and 11% of mono-, di-, and trisilylated product, respectively, when treated with LiBu/KOBU<sup>t</sup>; these yields were 22, 74, and 4% with the more reactive and more selective base LiBu/KOCeMe<sub>2</sub> (2 equiv). Finally, the *tert*-butyl compound **1c** [2-*tert*-butyl-4-methyl-1,3-pentadiene and (*E*)-2,4,5,5-tetramethyl-1,3-hexadiene (3/7)] yielded 81% of disilylated products and 19% of monosilylated products upon treatment with LiBu/KOBU<sup>t</sup> (2.5 equiv). The generally high yields of dikaliation products reflect the comparatively high stabilities of the anions (**2a–c**)<sup>2–9</sup>



To effect ring closure, a suspension of the potassium compounds K<sub>2</sub>(**2a–c**) is added to a solution of dichloro(dimethylamino)borane, BCl<sub>2</sub>(NMe<sub>2</sub>), in a hexane/THF mixture. The salt formed (KCl) is filtered off, and flash distillation of the filtrate separates the volatile products from much polymeric material. The <sup>11</sup>B NMR spectra of the raw products **3a–c** so obtained show the presence of admixtures which, on the basis of the observed chemical shifts δ(<sup>11</sup>B), are presumed to be BCl(OR)-(NMe<sub>2</sub>) and B(OR)<sub>2</sub>(NMe<sub>2</sub>) with R = Bu<sup>t</sup> or CEtMe<sub>2</sub>.<sup>14</sup> Further purification by fractionating distillation is

### Scheme 2



**Table 1. Typical Results of the Syntheses of **3a–c** and Their Dimers (**3a–c**)<sub>2</sub>**

olefin no.	amt (mmol)	amt of BCl <sub>2</sub> (NMe <sub>2</sub> ) (mmol)	after distillation		crystalline dimer yield (%)
			yield (%)	purity (%)	
<b>1a</b>	109	109	19 (17) <sup>a</sup>	50 (68) <sup>a</sup>	12
<b>1b</b>	116	104	25 (24) <sup>a</sup>	46 (70) <sup>a</sup>	21
<b>1c</b>	54	54	47	63	35

<sup>a</sup> First entry for vacuum flash distillation, second entry for result after distillation using a Vigreux column.

accompanied by high losses of product because of similar boiling points of the products and impurities. We also note that occasionally olefin isomerization reactions take place during distillation (see below).

Upon standing at ≤25 °C, the liquid products **3a–c** slowly solidify. This is due to a slow and, as will be seen below, reversible formation of crystalline dimers (**3a**)<sub>2</sub>, (**3b**)<sub>2</sub>, and (**3c**)<sub>2</sub>. In each case these dimers exist as C<sub>2v</sub> and C<sub>2h</sub> isomers (Scheme 2). The two isomers can easily be distinguished by their <sup>1</sup>H NMR spectra. The four *N*-methyl groups are chemically equivalent for the C<sub>2h</sub> dimers giving rise to one singlet whereas the C<sub>2v</sub> dimers possess two types of *N*-methyl groups and hence display a conspicuous pair of singlets.

The formation of these crystalline materials greatly eased the problem of product purification. Table 1 shows a summary of representative preparative results. As all allylic boranes, the compounds **3a–c** as well as their dimers are highly sensitive to air and traces of water. Therefore, we did not attempt to obtain elemental analyses and essentially used their NMR spectra for characterization.

**Dimers of **3a–c**.** The dimerization of aminoboranes is a long known phenomenon and seems to be especially favored for aminodihaloboranes bearing small substituents at boron and nitrogen.<sup>15,16</sup> However, we are not aware of previous observations of peralkylated aminoborane dimers.<sup>17</sup>

As already mentioned, the dimers of **3a–c** form as mixtures of C<sub>2v</sub> and C<sub>2h</sub> isomers, and the isomer ratios

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(13) For details see ref 7.

(14) For reference data see: (a) Nöth, H.; Wrackmeyer, B. In *NMR Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer Verlag: Berlin, 1978; Vol. 14. (b) Wrackmeyer, B. *Annu. Rep. NMR Spectrosc.* **1988**, *20*, 61. (c) Siedle, A. R. *Annu. Rep. NMR Spectrosc.* **1988**, *20*, 205.

(15) (a) Nöth, H.; Fritz, P. *Z. Anorg. Allg. Chem.* **1963**, *324*, 270. (b) Nöth, H. In *Progress in Boron Chemistry*; Brotherton, R. J., Steinberg, H., Eds.; Pergamon Press: Oxford, U.K., 1970; Vol. 3, p 211. (c) Becher, H. J.; Goubeau, J. *Z. Anorg. Allg. Chem.* **1952**, *268*, 133. (16) Nöth, H.; Vahrenkamp, H. *Chem. Ber.* **1967**, *100*, 3353.

**Table 2. Selected Bond Distances (pm) and Bond Angles (deg) for  $C_{2v}$ (**3a**)<sub>2</sub>**

(a) Distances			
N1–B1	163.5(4)	N2–B1	163.3(4)
N1–B2	163.4(4)	N2–B2	162.8(4)
N1–C17	148.2(4)	N2–C27	148.3(4)
N1–C18	147.9(4)	N2–C28	148.4(4)
B1–C11	160.3(4)	B2–C21	160.6(4)
B1–C15	161.3(4)	B2–C25	160.4(4)
C11–C12	150.7(4)	C21–C22	150.3(4)
C12–C13	132.8(4)	C22–C23	132.8(4)
C13–C14	144.6(4)	C23–C24	145.0(4)
C14–C15	151.4(4)	C24–C25	151.5(4)
C14–C16	132.3(5)	C24–C26	132.7(4)

(b) Angles			
B1–N1–B2	87.8(2)	B1–N2–B2	88.1(2)
N1–B1–N2	90.5(1)	N1–B2–N2	90.7(1)
C17–N1–C18	106.5(2)	C27–N2–C28	106.1(3)
C11–B1–C15	108.2(3)	C21–B2–C25	107.8(2)

observed depend on the crystallization temperature. If the crystallization of the crude liquid takes place at low temperatures (–25 °C) the solids obtained are 1/1 mixtures of the  $C_{2v}$  and  $C_{2h}$  isomers. In contradistinction to this situation, slow crystallization at 25 °C produces almost pure samples (>98%) of the  $C_{2v}$  isomers  $C_{2v}$ (**3a**)<sub>2</sub> and  $C_{2v}$ (**3c**)<sub>2</sub>. In the case of (**3b**)<sub>2</sub> no such preferential crystallization of the  $C_{2v}$  isomer is observed. It seems that in this case the two isomers can cocrystallize as a solid solution because both isomers possess almost the same shape. Examples for cocrystallization of organic compounds with similar molecular shape have been documented in the literature.<sup>18</sup>

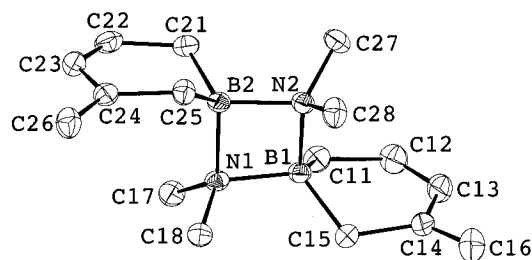
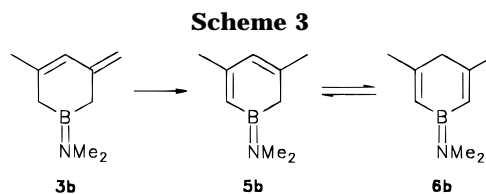
When the dimers are dissolved in CDCl<sub>3</sub>, the equilibria between the two dimers and the monomers are established. In solution the isomer ratio of the dimers of (**3a–c**) is always close to 1/1, as one would expect, and the monomers dominate, especially at higher temperatures. At low concentrations no dimers can be seen in the NMR spectra, and so the crystalline dimers are good sources of the pure monomers **3a–c**. For **3a** the equilibrium constant (eq 1) is e.g.  $K = 49.0 \text{ mol L}^{-1}$  at

$$K = \frac{[\mathbf{3a}]^2}{[C_{2v}\text{-}(\mathbf{3a})_2] + [C_{2h}\text{-}(\mathbf{3a})_2]} \quad (1)$$

22.0 °C and  $K = 15.2 \text{ mol L}^{-1}$  at 10.5 °C. From the temperature dependence of the equilibrium constant we deduce  $\Delta H = (70 \pm 2) \text{ kJ mol}^{-1}$  and  $\Delta S = (270 \pm 8) \text{ J K}^{-1} \text{ mol}^{-1}$  (cf. ref 16).

**Structure of  $C_{2v}$ (**3a**)<sub>2</sub>.** The colorless crystals obtained from **3a** by slow preferential crystallization at ambient temperature were characterized by X-ray crystallography (Table 2, Figure 1). The crystals were those of the  $C_{2v}$  dimer, as deduced earlier from the <sup>1</sup>H NMR spectrum of freshly redissolved crystals.

The molecules of  $C_{2v}$ (**3a**)<sub>2</sub> show a nearly square central B<sub>2</sub>N<sub>2</sub> ring with a slight ring twist; the vertical displacements from the best ring plane are 9.0(4) pm for the boron and the nitrogen atoms. The planes C11, B1, C15 and C21, B2, C25 are perpendicular [90.2(2) and 89.5(2)°] to the central ring and span dihedral angles

**Figure 1.** Thermal ellipsoid plot (PLATON)<sup>19</sup> of the molecule  $C_{2v}$ (**3a**)<sub>2</sub>. Ellipsoids are scaled to 30% probability.

of 44.4(3) and 44.0(3)° with the planes C11·C15 and C21·C25, respectively. Quite remarkable is that the two planes C11, B1, C15 and C21, B2, C25 coincide (maximum vertical displacement 0.9(3) pm). The observed bond lengths and angles are altogether unexceptional. The four independent B–C bond lengths are not significantly different [range: 160.3(4)–161.3(4) pm] and are rather long. A known and closely related structure is that of the dimer of 2,5-dihydro-2-methyl-1*H*-1,2-azaborole.<sup>20</sup>

**Isomerization Reactions.** All three tetrahydroborinines **3a–c** undergo thermal olefin isomerization reactions. We give details only for **3b**, the simplest case.<sup>21</sup> Heating **3b** at 100 °C for 5 h effects conversion to the unsymmetrical dihydroborinine **5b** and more slowly to the symmetrical isomer **6b**. After 24 h an equilibrium ratio of **5b**/**6b** = 3/2 is reached (Scheme 3). Similar equilibria have been observed previously between *C*-unsubstituted 1,2- and 1,4-dihydroborinines.<sup>2a,5d</sup> Acids such as HCl (in Et<sub>2</sub>O, 0.02–1.0 equiv) induce isomerization of **3b** at room temperature. In NMR tube experiments we see the formation of **5b** and **6b** within minutes but also decomposition of the ring compounds with concomitant consumption of the acid HCl.<sup>21</sup> This type of isomerization is even observed when NMR spectra are measured in CDCl<sub>3</sub> because this solvent usually contains traces of HCl; the reaction can be suppressed by addition of a trace of NEt<sub>3</sub>. For **3a** the thermal as well as the catalyzed isomerization reactions are less smooth and decomposition predominates.

**Metalation of the Boracarbycles **3a–c**.** The tetrahydroborinines **3a–c** undergo slow base-catalyzed isomerization and metalation with LDA in THF (1 equiv, ambient temperature, 3 d). Quaternization [ $\delta$ (<sup>11</sup>B) = –8] and decomposition are also observed, especially if an excess of LDA is used. After addition of TMEDA to the reaction mixture and crystallization, the corresponding lithium boratabenzene salts can be isolated as TMEDA solvates **4a–c** in good yields (60–90%). The dihydroborinine isomers as e.g. **5b** and **6b** react in the same way.

(17) Dimerization of Me<sub>2</sub>BNMe<sub>2</sub> at very low temperature has been mentioned in passing: Boese, R.; Niederprüm, N.; Bläser, D. *Struct. Chem.* **1992**, *3*, 399.

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(20) Schulze, J.; Boese, R.; Schmid, G. *Chem. Ber.* **1981**, *114*, 1297.

(21) For more details of the isomerization reactions and NMR data of the dihydroborinine isomers of **3a,c** so formed, see ref 7.

(22) Keller, E. *SCHAKAL 88, a Fortran Program for the Representation of Molecular and Crystallographic Models*; Kristallographisches Institut der Universität Freiburg: Freiburg, Germany, 1980.

**Table 3. Selected Bond Distances (pm) and Bond Angles (deg) for 4c**

(a) Distances			
N1–C11	144.5(2)	N1–C12	144.7(2)
B–C2	151.8(2)	B–C6	152.0(2)
C2–C3	139.5(2)	C3–C4	141.0(2)
C4–C5	140.6(2)	C5–C6	138.9(2)
C3–C7	154.6(2)	C5–C8	151.3(2)
Li–B	245.1(4)	Li–C2	238.9(3)
Li–C3	240.8(5)	Li–C4	238.7(3)
Li–C5	237.0(3)	Li–C6	235.6(3)
Li–N2	213.9(3)	Li–N3	213.4(3)
N1–B	144.8(2)		

(b) Angles			
B–C2–C3	122.2(1)	C2–C3–C4	119.9(1)
C3–C4–C5	121.9(1)	C4–C5–C6	121.5(1)
C5–C6–B	120.8(1)	C6–B–C2	113.5(1)
C2–B–N1	123.2(1)	C6–B–N1	123.2(1)
B–N1–C11	123.3(1)	B–N1–C12	122.6(1)
C11–N1–C12	112.7(1)		

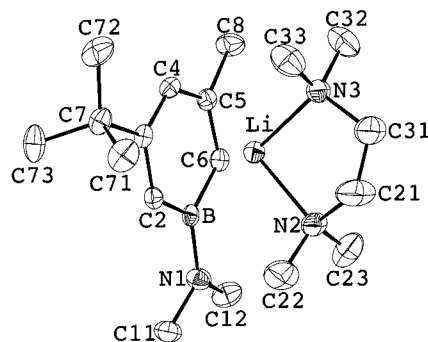
**Structure of 4c.** The *tert*-butyl compound **4c** crystallizes as a van der Waals crystal (Table 3, Figures 2 and 3). The molecule of **4c** is a contact ion pair of [Li(TMEDA)]<sup>+</sup> ions and boratabenzene counterions. Thus the overall structural type is the same as previously found for Li(TMEDA)(C<sub>5</sub>H<sub>5</sub>BNMe<sub>2</sub>) (**7**).<sup>2b</sup>

The structural parameters of the anion are very similar to those found for **7**, confirming once more the presence of a delocalized aromatic anion with a strong perturbation by the exocyclic *B*-amino substituent. However, two features of the structure are noteworthy. The [Li(TMEDA)]<sup>+</sup> in **4c** is more tightly bound to the counterion as compared to [Li(TMEDA)]<sup>+</sup> in **7**. The vertical displacement of the Li atom from the best C<sub>5</sub>B ring plane amounts to 191 pm for **4c** and is 205 pm for **7**. We note that the *N*-methyl groups of the cations bend toward the counterion. This bending is less pronounced in the five-membered ring of [Li(TMEDA)]<sup>+</sup> as compared to the six-membered ring of [Li(TMEDA)]<sup>+</sup> and thus creates less repulsion allowing the cation to approach the counterion more closely. Furthermore, in contrast to the situation in **7**, there is little slip distortion in the lithium ring interaction. The Li–C bond distances (235–241 pm) vary much less than in **7** (238–262 pm).

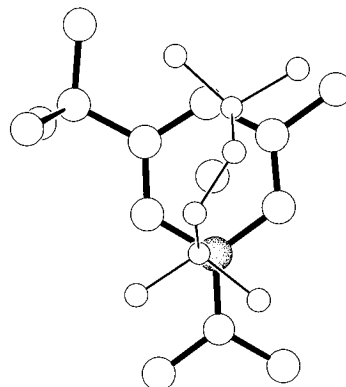
**Concluding Remarks.** We finally discuss advantages and limitations. Our new synthesis is straightforward requiring only three steps, but gives only moderate overall yields: 7–12% for **4a**, 18–21% for **4b**, and 32–42% for **4c**. It is limited to dialkylamino substituents at boron, and only the syntheses of dimethylamino compounds have been worked out. However, it offers the first chance to introduce *C*-substituents in the 3-/5-positions and presumably also in the 4-position. This feature should be of future interest keeping in mind the enormous and varied effects of peralkylation in cyclopentadienyl chemistry.

## Experimental Section

**General Procedures.** Reactions were carried out under an atmosphere of dinitrogen by means of conventional Schlenk techniques. Pentane and hexane were distilled from Na/K alloy, and THF was distilled from sodium benzophenone ketyl. Kieselgur was heated in a high vacuum at 300 °C prior to use. Melting points were measured in sealed capillaries and are uncorrected. NMR spectra were used to judge the purity of the new compounds; elemental analyses were not attempted because of the reactivity of the compounds prepared.



**Figure 2.** Thermal ellipsoid plot (PLATON)<sup>19</sup> of the molecule **4c**. Ellipsoids are scaled to 30% probability.



**Figure 3.** SCHAKAL<sup>22</sup> representation of the molecule **4c** looking onto the anion plane.

NMR spectra were recorded on a Bruker WP 80 PFT spectrometer (<sup>1</sup>H, 80 MHz), a Bruker WH 270 PFT (<sup>13</sup>C, 67.9 MHz; <sup>11</sup>B, 86.6 MHz), a Jeol NM-PS-100 (<sup>11</sup>B, 32.1 MHz), a Varian VXR 300 (<sup>1</sup>H, 300 MHz; <sup>13</sup>C, 75.4 MHz), and a Varian Unity 500 spectrometer (<sup>1</sup>H, 500 MHz; <sup>13</sup>C, 125.7 MHz). Mass spectra were recorded on a Varian MAT CH-5 and on a Finnigan MAT-95 spectrometer. DTA measurements were carried out in an argon atmosphere using a tantalum sample holder, an alumina reference, and Ni–Cr/Ni thermoelements.

**Kaliation and Ring Closure. General Procedure.** A solution of LiBu (2.0–2.5 equiv) in hexane was added to a suspension of KOR (R = Bu<sup>t</sup> or C<sub>6</sub>H<sub>5</sub>) in hexane (≥1 mL/mmol) at 0 °C. After the mixture was stirred at room temperature for 1 h, the diene (1.0 equiv) was added, and the reaction mixture was heated under reflux for 20 h. The precipitate of potassium compounds was filtered off and washed thoroughly three times with hot hexane. Then the solid was suspended in hexane (1 mL/mol) and was added slowly to BCl<sub>2</sub>(NMe<sub>2</sub>)<sup>23</sup> in hexane/THF (4/1, 2 mL/mmol) at 10 °C. After the mixture was stirred at room temperature for 14 h KCl was removed by filtration, and all volatiles were pumped off in a vacuum. Flash distillation gave the products together with byproducts BCl(OR)(NMe<sub>2</sub>) and B(OR)<sub>2</sub>(NMe<sub>2</sub>) (R = Bu<sup>t</sup> or C<sub>6</sub>H<sub>5</sub>). Further purification could be achieved by a careful vacuum distillation using a Vigreux column (10 cm). Upon standing at or below 25 °C, colorless crystals of the dimers formed. The crystals were collected and washed three times with a small volume of cold pentane. Removing the pentane from the washings and cooling afforded a further crop of the dimers.

**1-(Dimethylamino)-3-methylene-1,2,3,6-tetrahydroborinine (3a) and Dimers (3a)<sub>2</sub>.** Reaction of **1a** [9.00 g, 109.5 mmol, as 7/3 mixture of (*E*)-2-methyl-1,3-pentadiene and

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4-methyl-1,3-pentadiene<sup>24</sup>], KOCeMe<sub>2</sub><sup>12b</sup> (27.66 g, 219 mmol), LiBu (1.6 M in hexane, 137 mL, 219 mmol), and BCl<sub>2</sub>(NMe<sub>2</sub>)<sup>23</sup> (13.71 g, 109 mmol) gave, after flash distillation, a pale yellow liquid (5.59 g, containing 50% **3a**, 21 mmol, 19%). Vacuum distillation using a Vigreux column gave a colorless liquid (3.73 g, containing 68% **3a**, 19 mmol, 17%). Upon standing at room temperature colorless crystals of pure C<sub>2v</sub>-(**3a**)<sub>2</sub> (1.77 g, 7 mmol, 12%) formed while crystallization at -25 °C gave a 1/1 mixture of C<sub>2v</sub> and C<sub>2h</sub>-(**3a**)<sub>2</sub>.

**3a**: bp 70 °C/9 mbar; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 6.16 (dm, *J* = 9.8 Hz, 1H, 4-H), 5.85 (dt, *J* = 9.8, 4.0 Hz, 1H, 5-H), 4.80 (m, 1H, CH<sub>2</sub>=), 4.73 (m, 1H, CH<sub>2</sub>=), 2.75 (s, 3H, NMe), 2.69 (s, 3H, NMe), 1.96 (br, s, 2H, 2-H), 1.55 (dd, *J* = 4.1, 2.2 Hz, 2H, 6-H); <sup>13</sup>C-NMR (68 MHz, CDCl<sub>3</sub>, -50 °C) δ 145.40 (m, C-3), 131.20 (dm, *J* = 154.7 Hz) and 130.80 (dm, *J* = 149.9 Hz) (C-4,5), 111.24 (t, *J* = 154.3 Hz, CH<sub>2</sub>=), 38.84 (q, *J* = 134.4 Hz, NMe), 38.46 (q, *J* = 134.3 Hz, NMe), 23.34 (br, t, *J* = 113 Hz) and 16.85 (br, t, *J* = 119 Hz) (C-2,6); <sup>11</sup>B-NMR (32 MHz, CDCl<sub>3</sub>, BF<sub>3</sub>·OEt<sub>2</sub> external) δ 46; MS (70 eV) *m/z* (*I*<sub>rel</sub>) 135 (1, M<sup>+</sup>), 79 (100, C<sub>6</sub>H<sub>7</sub><sup>+</sup>).

C<sub>2v</sub>-(**3a**)<sub>2</sub>: mp 56 °C with heating rate of 1.0 °C/min (DTA), 70 °C with heating rate of 5.0 °C/min (DTA); a corresponding exothermal peak is not observed upon cooling; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 6.00 (dt, *J* = 9.8, 1.8 Hz, 2H, 4-H), 5.88 (dt, *J* = 9.5, 4.6 Hz, 2H, 5-H), 4.69 (br, s, 4H, CH<sub>2</sub>=), 2.28 (s, 6H, NMe<sub>2</sub>), 2.14 (s, 6H, NMe<sub>2</sub>), 1.67 (br, s, 4H, 2-H), 1.28 (br, d, *J* = 4 Hz, 4H, 6-H); <sup>11</sup>B-NMR (32 MHz, CDCl<sub>3</sub>, BF<sub>3</sub>·OEt<sub>2</sub> external) δ 5; MS (70 eV) *m/z* (*I*<sub>rel</sub>) 270 (40, M<sub>2</sub><sup>+</sup>), 135 (100, M<sup>+</sup>), 99 (100, Me<sub>2</sub>NBNMe<sub>2</sub><sup>+</sup>).

C<sub>2h</sub>-(**3a**)<sub>2</sub> (only in mixture with C<sub>2v</sub> isomer, several signals superimposed): <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 6.00 (m, 2H, 4-H), 5.88 (m, 2H, 5-H), 4.68 (br, s, 2H, CH<sub>2</sub>=), 4.66 (br, s, 2H, CH<sub>2</sub>=), 2.20 (s, 12H, NMe<sub>2</sub>), 1.63 (br, s, 4H, 2-H), 1.33 (br, d, *J* = 4 Hz, 4H, 6-H).

**1-(Dimethylamino)-5-methyl-3-methylene-1,2,3,6-tetrahydroborinine (3b) and Dimers (3b)<sub>2</sub>**. Reaction of 2,4-dimethyl-1,3-pentadiene<sup>25</sup> (**1b**) (11.14 g, 116 mmol), KOCeMe<sub>2</sub><sup>12b</sup> (29.26 g, 232 mmol), LiBu (1.6 M in hexane, 145 mL, 232 mmol), and BCl<sub>2</sub>(NMe<sub>2</sub>)<sup>23</sup> (13.13 g, 104 mmol) gave, after flash distillation, a pale yellow liquid (9.21 g, containing 46% **3b**, 28 mmol, 25%). Vacuum distillation using a Vigreux column gave a colorless liquid (5.98 g, containing 70% **3b**, 27 mmol, 24%). Upon standing at room temperature, colorless crystals of a 1/1 mixture of C<sub>2v</sub>-(**3b**)<sub>2</sub> and C<sub>2h</sub>-(**3b**)<sub>2</sub> (3.67 g, 13 mmol, 21%) formed.

**3b**: bp 80 °C/8 mbar; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 5.99 (m, 1H, 4-H), 4.71 (m, 1H, CH<sub>2</sub>=), 4.64 (m, 1H, CH<sub>2</sub>=), 2.75 (s, 3H, NMe), 2.70 (s, 3H, NMe), 1.89 (br, s, 2H) and 1.46 (br, s, 2H) (2-/6-H), 1.80 (br, s, 3H, Me); <sup>13</sup>C-NMR (68 MHz, CDCl<sub>3</sub>, -50 °C) δ 145.92 (s, C-3), 139.66 (q, *J* = 6.7 Hz, C-5), 126.47 (d, *J* = 151.6 Hz, C-4), 108.98 (t, *J* = 155.3 Hz, CH<sub>2</sub>=), 38.59 (q, *J* = 134.4 Hz, NMe), 38.54 (q, *J* = 134.4 Hz, NMe), 26.69 (q, *J* = 124.1 Hz, 5-Me), 22.80 (t, *J* = 117.2 Hz) and 22.21 (t, *J* = 114.2 Hz) (C-2,6); <sup>11</sup>B-NMR (32 MHz, CDCl<sub>3</sub>, BF<sub>3</sub>·OEt<sub>2</sub> external) δ 46; MS (70 eV) *m/z* (*I*<sub>rel</sub>) 149 (100, M<sup>+</sup>).

Mixture of C<sub>2v</sub>-(**3b**)<sub>2</sub> and C<sub>2h</sub>-(**3b**)<sub>2</sub> (1/1): mp 58 °C with heating rate of 0.5 °C/min, 80 °C with heating rate of 20 °C/min; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 5.85 (m, 2H, 4-H), 4.59 (s, 2H, CH<sub>2</sub>=), 4.58 (s, 2H, CH<sub>2</sub>=); signals of C<sub>2v</sub>-(**3b**)<sub>2</sub>, δ 2.29 (s, 6H, NMe<sub>2</sub>), 2.09 (s, 6H, NMe<sub>2</sub>), 1.80 (br, s, 6H, 2 Me), 1.59 (br, s, 4H) and 1.23 (br, s, 4H) (2-/6-H); signals of C<sub>2h</sub>-(**3b**)<sub>2</sub>; δ 2.18 (s, 12H, NMe<sub>2</sub>), 1.81 (br, s, 6H, 2 Me), 1.57 (br, s, 4H) and 1.25 (br, s, 4H) (2-/6-H); <sup>11</sup>B-NMR (32 MHz, CDCl<sub>3</sub>, BF<sub>3</sub>·OEt<sub>2</sub> external) δ 5; MS (70 eV) *m/z* (*I*<sub>rel</sub>) 298 (10, M<sub>2</sub><sup>+</sup>), 149 (100, M<sup>+</sup>).

**1-(Dimethylamino)-5-tert-butyl-3-methylene-1,2,3,6-tetrahydroborinine (3c) and Dimers (3c)<sub>2</sub>**. Reaction of diene **1c** [7.42 g, 54 mmol, as 3/7 mixture of 2-tert-butyl-

methyl-1,3-pentadiene and (*E*)-2,4,5,5-tetramethyl-1,3-hexadiene<sup>26</sup> (**1c**), KOBu<sup>t</sup> (16.31 g, 145 mmol), LiBu (1.6 M in hexane, 91 mL, 145 mmol), and BCl<sub>2</sub>(NMe<sub>2</sub>)<sup>23</sup> (6.92 g, 55 mmol) gave, after a simple vacuum distillation, a colorless liquid (7.64 g, containing 63% **3c**, 25 mmol, 47%). At room temperature pure C<sub>2v</sub>-(**3c**)<sub>2</sub> (3.61 g, 19 mmol, 35%) formed slowly. Crystallization at -25 °C gave a 1/1 mixture of C<sub>2v</sub>-(**3c**)<sub>2</sub> and C<sub>2h</sub>-(**3c**)<sub>2</sub>.

**3c**: bp 49 °C/0.04 mbar; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 6.11 (m, 1H, 4-H), 4.77 (m, 1H, CH<sub>2</sub>=), 4.70 (m, 1H, CH<sub>2</sub>=), 2.75 (s, 3H, NMe), 2.71 (s, 3H, NMe), 1.89 (m, 2H) and 1.52 (br, s, 2H) (2-/6-H), 1.08 (s, 9H, Bu<sup>t</sup>); <sup>13</sup>C-NMR (68 MHz, CDCl<sub>3</sub>) δ 150.13 (s, C-5), 146.71 (s, C-3), 123.56 (d, *J* = 151.5 Hz, C-4), 110.02 (t, *J* = 155.2 Hz, CH<sub>2</sub>=), 38.91 (qm, *J* = 134.3 Hz, NMe), 38.76 (qm, *J* = 134.1 Hz, NMe), 36.28 (s, CMe<sub>3</sub>), 29.20 (qm, *J* = 125.3 Hz, CMe<sub>3</sub>), 23.7 (br, t) and 16.3 (br, t) (C-2,6); <sup>11</sup>B-NMR (32 MHz, CDCl<sub>3</sub>, BF<sub>3</sub>·OEt<sub>2</sub> external) δ 45; MS (70 eV) *m/z* (*I*<sub>rel</sub>) 191 (94, M<sup>+</sup>).

C<sub>2v</sub>-(**3c**)<sub>2</sub>: mp 69 °C with heating rate of 0.5 °C/min, 95 °C with heating rate of 20 °C/min; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 5.95 (s, 2H, 4-H), 4.66 (s, 4H, CH<sub>2</sub>=) 2.28 (s, 6H, NMe<sub>2</sub>), 2.13 (s, 6H, NMe<sub>2</sub>), 1.62 (s, 4H) and 1.27 (s, 4H) (2-/6-H), 1.08 (s, 18H, 2 Bu<sup>t</sup>); <sup>11</sup>B-NMR (32 MHz, CDCl<sub>3</sub>, BF<sub>3</sub>·OEt<sub>2</sub> external) δ 4.

C<sub>2h</sub>-(**3c**)<sub>2</sub> (only in mixture with C<sub>2v</sub> isomer, several signals superimposed): 5.96 (s, 2H, 4-H), 4.66 (s, 2H, CH<sub>2</sub>=), 4.65 (s, 2H, CH<sub>2</sub>=), 2.20 (s, 12H, NMe<sub>2</sub>), 1.60 (s, 4H) and 1.29 (s, 4H) (2-/6-H), 1.09 (s, 18H, 2 Bu<sup>t</sup>).

**Monomer/Dimer Equilibrium for 3a**. A sample of pure C<sub>2v</sub>-(**3a**)<sub>2</sub> (0.2896 g, 1.072 mmol) was dissolved in CDCl<sub>3</sub> (total volume 0.86 mL, formal total concentration of **3a** 2.49 mol L<sup>-1</sup>). After equilibration at a chosen temperature, the ratio of total dimer to monomer concentrations was estimated by means of the <sup>11</sup>B NMR spectra. Each measurement was repeated at 1 day intervals to ensure equilibrium conditions. This resulted in equilibrium constants *K* (eq 1) of 49.0 (22.0 °C), 40.4 (20.0 °C), 22.2 (14.0 °C), 17.3 (11.5 °C), and 15.2 (10.5 °C) mol L<sup>-1</sup> and thermodynamic data Δ*H* = (70 ± 2) kJ mol<sup>-1</sup> and Δ*S* = (270 ± 8) J K<sup>-1</sup> mol<sup>-1</sup>.

**Thermal Isomerization of 3b**. A sample of (**3b**)<sub>2</sub> in a sealed NMR tube was heated to 120 °C for 24 h, and gave a 3/2 mixture of **5b** and **6b**. At 100 °C the ratio **3b**/**5b**/**6b** was 77/23/0 after 1 h, 13/72/15 after 3 h, 0/68/32 after 5 h, and 0/62/38 after 24 h. The isomers **5b** and **6b** of the equilibrium mixture form a crystalline solid: mp 60–68 °C; MS (70 eV) *m/z* (*I*<sub>rel</sub>) 149 (63, M<sup>+</sup>), 70 (100, Me<sub>2</sub>NBCH<sub>3</sub><sup>+</sup>).

**5b**: <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 5.72 (sept, *J* ≈ 1.5 Hz, 1H, 4-H), 5.71 (br, s, 1H, 6-H), 2.81 (s, 3H, NMe), 2.67 (s, 3H, NMe), 1.96 (d, *J* = 1.5, 3H, Me), 1.87 (br, s, 3H, Me), 1.62 (br, s, 2H, 2-H); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>, TMS) δ 155.17 (C-5), 143.73 (C-3), 124.78 (C-4), 120.0 (br, C-6), 38.84 (NMe), 38.69 (NMe), 26.58 (Me), 26.15 (Me), 25.1 (br, C-2); <sup>11</sup>B-NMR (32 MHz, CDCl<sub>3</sub>, BF<sub>3</sub>·OEt<sub>2</sub> external) δ 41.

**6b**: <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 5.94 (m, 2H, 2-/6-H), 2.85 (s, 6H, NMe<sub>2</sub>), 2.76 (br, s, 2H, 4-H), 1.93 (s, 6H, 2 Me); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) δ 154.19 (C-3,5), 124.0 (br, C-2,6), 42.43 (C-4), 39.03 (NMe<sub>2</sub>), 26.44 (2 Me); <sup>11</sup>B-NMR (32 MHz, CDCl<sub>3</sub>, BF<sub>3</sub>·OEt<sub>2</sub> external) δ 34.

**Acid-Catalyzed Isomerization of 3b**.<sup>21</sup> (**3b**)<sub>2</sub> was dissolved in CDCl<sub>3</sub> and kept standing for 1 h to ensure that mainly monomer **3b** was present. After addition of HCl (0.02–1.0 equiv) in Et<sub>2</sub>O the solution was kept at ambient temperature, and <sup>1</sup>H NMR spectra were recorded at times ranging from 6 min to 5 d. Decomposition amounted to 60 and 35% with 1.0 and 0.6 equiv of HCl, respectively. If <0.3 equiv of HCl was used, the isomerization reaction stopped before equilibrium was reached.

**Preparation of 4a**. LiBu (1.6 M in hexane, 3.1 mL, 5.0 mmol) was added to diisopropylamine (0.61 g, 6.0 mmol) in THF (10 mL) at 0 °C. After the mixture was stirred at ambient

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temperature for 1 h, the LDA solution so formed<sup>27</sup> was cooled to  $-78\text{ }^{\circ}\text{C}$ , and **(3a)<sub>2</sub>** (0.68 g, 5.0 mmol) in THF (5 mL) was added dropwise. The mixture was allowed to warm to room temperature, and stirring was continued for 2–3 d. The volatiles were then removed in a vacuum, and the residue was dissolved in TMEDA (0.58 g, 5.0 mmol) and pentane. The solution was filtered to remove insoluble material and then kept at  $-30\text{ }^{\circ}\text{C}$ . The solid formed was collected, washed with pentane ( $3 \times 3\text{ mL}$ ), and dried in a vacuum to give **4a** (0.80 g, 3.1 mmol, 62%) as a white solid.

**4a:** <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.40 (dd,  $J = 10.7, 7.0\text{ Hz}$ , 1H, 5-H), 6.00 (ddm,  $J = 10.7, 2.8\text{ Hz}$ , 1H, 6-H), 5.95 (t,  $J = 2.2\text{ Hz}$ , 1H, 2-H), 5.75 (dm,  $J = 7.0\text{ Hz}$ , 1H, 4-H), 3.07 (s, 6H, NMe<sub>2</sub>), 2.38 (s, 3H, Me); 1.66 (br, s, 12H, 4 Me) and 1.43 (br, s, 4H, 2 CH<sub>2</sub>) (TMEDA); <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  142.53 (C-3), 134.55 (C-5), 111.5 (br, C-6), 107.3 (br, C-2), 100.36 (C-4), 39.57 (NMe<sub>2</sub>), 26.10 (3-Me); 55.59 (CH<sub>2</sub>) and 44.78 (Me) (TMEDA); <sup>11</sup>B NMR (32 MHz, C<sub>6</sub>D<sub>6</sub>, BF<sub>3</sub>·OEt<sub>2</sub> external)  $\delta$  32.

**Preparation of 4b.** Treatment of **(3b)<sub>2</sub>** (0.75 g, 5.0 mmol) as described above for **(3a)<sub>2</sub>** produced **4b** (1.14 g, 4.2 mmol, 84%) as a white solid. The mixture of isomers **5b** and **6b** obtained by heating **(3b)<sub>2</sub>** at  $100\text{ }^{\circ}\text{C}$  for 17 h gave similar results.

**4b:** <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  5.75 (d,  $J = 1.7\text{ Hz}$ , 2H, 2-/6-H), 5.57 (t,  $J = 1.7\text{ Hz}$ , 1H, 4-H), 3.07 (s, 6H, NMe<sub>2</sub>), 2.36 (s, 6H, CH<sub>3</sub>); 1.68 (br, s, 12H, 4 Me) and 1.44 (br, s, 4H, 2 CH<sub>2</sub>) (TMEDA); <sup>13</sup>C NMR (68 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  142.88 (s, C-3,5), 107.8 (br, C-2,6), 101.60 (dm,  $J = 153.2\text{ Hz}$ , C-4), 39.65 (qq,  $J = 130.6, 4.6\text{ Hz}$ , NMe<sub>2</sub>), 26.04 (q,  $J = 124.2\text{ Hz}$ , Me); 56.03 (t,  $J = 130.6\text{ Hz}$ , CH<sub>2</sub>) and 44.88 (q,  $J = 134.4\text{ Hz}$ , Me) (TMEDA); <sup>11</sup>B NMR (32 MHz, C<sub>6</sub>D<sub>6</sub>, BF<sub>3</sub>·OEt<sub>2</sub> external)  $\delta$  32.

**Preparation of 4c.** Treatment of **(3c)<sub>2</sub>** (or the mixture of isomers obtained by heating **(3c)<sub>2</sub>** at  $100\text{ }^{\circ}\text{C}$  for 17 h) (0.96 g, 5.0 mmol) as described above for **(3a)<sub>2</sub>** gave **4c** (1.41 g, 4.5 mmol, 90%) as colorless crystals.

**4c:** <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  5.95 (t,  $J = 2\text{ Hz}$ , 1H), 5.75 (t,  $J = 2\text{ Hz}$ , 1H), and 5.71 (t,  $J = 2\text{ Hz}$ , 1H) (2-/4-/6-H), 3.05 (s, 6H, NMe<sub>2</sub>), 2.37 (s, 3H, Me), 1.44 (s, 9H, Bu<sup>t</sup>); 1.70 (br, s, 12H, 4 Me) and 1.44 (br, s, 4H, 2 CH<sub>2</sub>) (TMEDA); <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  156.25 (C-5), 142.92 (C-3), 106.5 (br) and 103.2 (br) (C-2,6), 97.36 (C-4), 39.58 (NMe<sub>2</sub>), 36.02 (CMe<sub>3</sub>), 32.56 (CMe<sub>3</sub>), 26.98 (Me); 55.92 (br, CH<sub>2</sub>) and 45.16 (br, Me) (TMEDA); <sup>11</sup>B NMR (32 MHz, C<sub>6</sub>D<sub>6</sub>, BF<sub>3</sub>·OEt<sub>2</sub> external)  $\delta$  31.

**X-ray Structure Determinations.** Geometry and intensity data were collected on ENRAF Nonius CAD4 diffractometers equipped with graphite monochromators. A summary of crystal data, data collection parameters, and convergence results is given in Table 4. The structures were solved by direct methods<sup>28</sup> and refined on structure factors with the SDP program system.<sup>29</sup> In the case of *C*<sub>2v</sub>-**(3a)<sub>2</sub>**, all hydrogen atoms were refined with isotropic displacement parameters; only *B*<sub>iso</sub> for H15b tended to small negative values and was fixed at  $1.0 \times 10^4\text{ pm}^2$ .<sup>30</sup> In the case of **4c**, only the hydrogen atoms bonded

**Table 4. Crystallographic Data, Data Collection Parameters, and Refinement Parameters for *C*<sub>2v</sub>-**(3a)<sub>2</sub>** and **4c****

	<i>C</i> <sub>2v</sub> - <b>(3a)<sub>2</sub></b>	<b>4c</b>
formula	C <sub>16</sub> H <sub>28</sub> B <sub>2</sub> N <sub>2</sub>	C <sub>18</sub> H <sub>37</sub> BN <sub>3</sub> Li
fw	270.04	313.27
cryst system	monoclinic	triclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14)	<i>P</i> 1̄ (No. 2)
<i>a</i> , pm	837.0(6)	884.86(9)
<i>b</i> , pm	1263.4(6)	1450.2(2)
<i>c</i> , pm	1533(1)	831.7(3)
$\alpha$ , deg		94.48(2)
$\beta$ , deg	97.04(6)	100.30(2)
$\gamma$ , deg		87.87(1)
<i>V</i> , nm <sup>3</sup>	1.609(3)	1.0466(4)
<i>D</i> <sub>calcd</sub> , g cm <sup>-3</sup>	1.114	0.994
<i>Z</i>	4	2
<i>F</i> (000)	592.0	348.0
$\mu$ , cm <sup>-1</sup>	0.59	0.38
cryst dimens, mm	0.7 × 0.6 × 0.6	0.5 × 0.5 × 0.5
radiation ( $\lambda$ , pm)	Mo K $\alpha$ (71.07)	Cu K $\alpha$ (154.18)
<i>T</i> , K	253	228
scan mode	$\omega$	$\omega/\theta$
scan range, deg	$3 \leq \theta \leq 27$	$5 \leq \theta \leq 70$
tot. data	3407	2934
unique obsd data	2010 ( $I > \sigma(I)$ )	2456 ( $I > \sigma(I)$ )
sec extinction coeff		$0.494 \times 10^{-5}$
no. of variables	292	233
<i>R</i> , <i>R</i> <sub>w</sub> <sup>a</sup>	0.083, 0.078	0.068, 0.083
max resid density,	0.31	0.33
	$10^{-6}\text{ e pm}^{-3}$	

<sup>a</sup> Refinement on *F*;  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $R_w = [\sum w(|F_o| - |F_c|)^2]^{1/2} / \sum w(F_o)^2$ ;  $w = 1/\sigma^2(F_o)$ .

to ring carbon atoms and C8 were refined; all others were located in difference Fourier syntheses, idealized (C–H = 98 pm, *B*<sub>H</sub> = 1.3*B*<sub>C</sub>), and included in the refinement as riding atoms. The unsatisfactory *R*<sub>w</sub> is mainly due to a certain degree of disorder in the TMEDA moiety as indicated by anisotropic displacement parameters for the atoms in this group.<sup>30</sup>

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**Supporting Information Available:** <sup>1</sup>H and <sup>13</sup>C NMR spectra for **3a–c**, for the dimers **(3a)<sub>2</sub>**, **(3b)<sub>2</sub>**, and **(3c)<sub>2</sub>**, and for **4a–c**, **5b**, and **6b** and tables of bond distances and angles, anisotropic thermal parameters, and atom coordinates and *B* values for *C*<sub>2v</sub>-**(3a)<sub>2</sub>** and **4c** (77 pages).<sup>30</sup> Ordering information is given on any current masthead page.

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(30) Further details of the crystal structure analyses 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-405009 for *C*<sub>2v</sub>-**(3a)<sub>2</sub>** and CSD-405010 for **4c**, the names of the authors, and this journal citation.

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