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Borabenzene Derivatives. 29. Synthesis and Structural Diversity of Bis(boratabenzene)scandium Complexes. Structures of $[ScCl(C_5H_5BMe)_2]_2$, $[ScCl(3,5\text{-}Me_2C_5H_3BNMe_2)_2]_2$, and $ScCl[3,5\text{-}Me_2C_5H_3BN(SiMe_3)_2]_2$[1]

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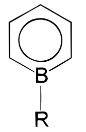
The bis(boratabenzene)scandium complexes **3**−**5** are synthesized from solvent-free lithium boratabenzenes and $ScCl_3$ in toluene (110 °C, 3 days). Complex $[ScCl(C_5H_5BMe)_2]_2$ (**3**) possesses a doubly chloro-bridged dinuclear structure with four facially coordinated boratabenzene ligands. Compound $[ScCl(3,5\text{-}Me_2C_5H_3BNMe_2)_2]_2$ (**4**) differs from **3** in that each scandium atom binds to one boratabenzene in an unprecedented N−B−C-2 coordination mode and facially to the second boratabenzene ligand; in solution **4** is fluxional, displaying only one type of boratabenzene ligand with effective lateral symmetry. Complex $ScCl[3,5\text{-}Me_2C_5H_3BN(SiMe_3)_2]_2$ (**5**) is mononuclear because of the bulkiness of its boratabenzene. Metalation of the 1,2,3,6-tetrahydroborinine $3\text{-}CH_2\text{-}5\text{-}MeC_5H_5BNMe_2$ (**9**) affords the solvent-free boratabenzene $Li(3,5\text{-}Me_2C_5H_3BNMe_2)$ (**7**). The mixture of 1,2- and 1,4-dihydroborines $3,5\text{-}Me_2C_5H_4BNMe_2$ (**10a**,**b**) (accessible from **9** by isomerization) can be transformed into the solvent-free boratabenzene $Li[3,5\text{-}Me_2C_5H_3BN(SiMe_3)_2]$ (**8**) by (i) treatment with BCl_3 to give the chloro derivatives **11a**,**b**, (ii) subsequent amination with $NH(SiMe_3)_2/NEt_3$, and (iii) metalation with $LiN(SiMe_3)_2$.

Introduction

Scandium and its higher homologues possess a rich cyclopentadienyl chemistry.[2] Complexes of the type $[MXCp_2]_n$ (M = scandium group metal; X = Cl, Br; n = 1, 2) have been studied in much detail. In most cases they form dimeric structures as in $[Sc(\mu\text{-}Cl)Cp_2]_2$, which has two μ-Cl bridges and a pseudotetrahedral coordination around the Sc atom.[3] The use of bulky ligands such as Cp* often hinders dimerization, and complexes $ScXCp^*_2$ (X = Cl, Me) are mononuclear.[4] The metallocenes of the scandium group metals have proven to be highly efficient catalysts for olefin and alkyne transformations.[5,6]

Boratabenzenes[7] **1** are most closely akin to the cyclopentadienide Cp^- (**2**). But in contrast to (cyclopentadienyl)scandium chemistry, the analogous boratabenzene chemistry of scandium and all other group 3 metals is in its infancy.[8] In this paper we report on the synthesis and structure of three bent-sandwich complexes **3**−**5** of scandium which, quite remarkably, represent three different types of structure.



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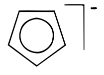

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3: $[ScCl(C_5H_5BMe)_2]_2$[8]
4: $[ScCl(3,5\text{-}Me_2C_5H_3BNMe_2)_2]_2$
5: $ScCl[3,5\text{-}Me_2C_5H_3BN(SiMe_3)_2]_2$

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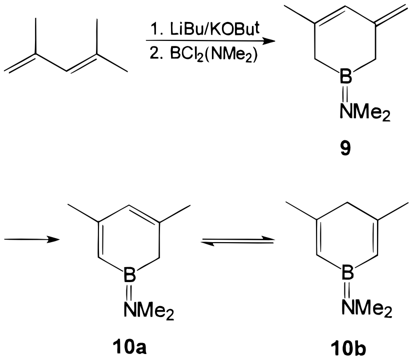
Results and Discussion

Syntheses of Lithium Boratabenzenes. The ligands used in this work were made in the form of solvent-free lithium boratabenzenes **6**−**8**.

6: $Li(C_5H_5BMe)$[9]
7: $Li(3,5\text{-}Me_2C_5H_3BNMe_2)$
8: $Li[3,5\text{-}Me_2C_5H_3BN(SiMe_3)_2]$

In previous work we have described the synthesis of the TMEDA solvate **7**·TMEDA via a dicarbanion route.[10] To this end 2,4-dimethyl-1,3-pentadiene was doubly kaliated, and subsequent ring closure with BCl_2NMe_2[11] gave the 1,2,3,6-tetrahydroborinine **9**, sometimes partially isomerized to the dihydroborinines **10a** and **10b** (Scheme 1). The isomerization **9** → **10** can take place in a number of ways. If unconsumed $BCl_2(NMe_2)$ is present during distillative workup of the ring closure product, this impurity effects a catalytic isomerization.[10] Isomerization may also be effected in a separate workup step with HCl in diethyl ether[10] and also takes place during metalation, e.g., with LDA in THF.[10] In our earlier work we added TMEDA after the metalation step and isolated the solvate **7**·TMEDA by crystallization from hexane.[10] In this work we used $LiN(SiMe_3)_2$ in hexane as the metalating agent and obtained the solvent-free lithium salt **7** as a barely soluble, white powder (Scheme 2).

Scheme 1



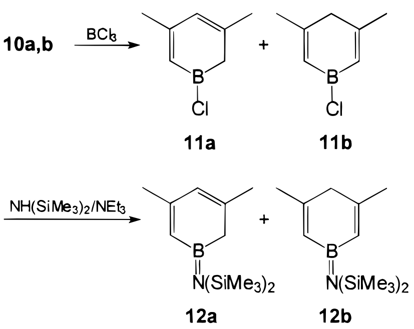
Scheme 2

$$\mathbf{9} \text{ or } \mathbf{10} + LiN(SiMe_3)_2 \rightarrow \mathbf{7} + NH(SiMe_3)_2$$

Since it turned out later that the NMe_2 group of the scandium complex **4** (see below) may coordinate to the scandium center, we decided to synthesize an analogue of **7** with a bulkier amino substituent and chose the boratabenzene **8** as our target. Replacement of the NMe_2 group with a $N(SiMe_3)_2$ group requires two steps (Scheme 3).

It would seem most logical and desirable to effect this substitution with the 1,2,3,6-tetrahydroborinine **9** as starting material. However, we learned quickly that **9** is much more inclined to suffer a destructive ring-opening than its more robust dihydroborinine isomers **10a**,**b**. Therefore we first isomerized **9** to the mixture **10a**,**b**.[10] Then the dihydroborinines **10a**,**b** were treated with boron trichloride in dichloromethane to give a mixture of the chloro derivatives **11a**,**b**. The subsequent transformation into the bis(trimethylsilyl)amino derivatives **12a**,**b** was readily effected with $NH(SiMe_3)_2/NEt_3$. Finally, metalation of **12a**,**b** with $LiN(SiMe_3)_2$ in hexane afforded the solvent-free boratabenzene **8**.

Scheme 3



The new species **11**, **12**, and **8** were characterized by NMR. We note in passing that the isomer ratio **a**/**b** in **10**−**12** varies considerably, depending on subtle details of the working conditions.

Syntheses of Scandium Complexes 3−5. Treatment of $ScCl_3$ with a suitable source of Cp^- (in a 1:2 ratio) in THF gives the solvate $Cp_2ScCl(THF)$;[12] sublimation (220 °C/10^{-6} bar) of the solvate in small batches results in loss of THF and formation of the dimer $[ScClCp_2]_2$.[12a]

We decided to use a different approach. Many lanthanide trihalides react with NaCp in benzene suspension (20 °C, 4−5 days) to give the solvent-free products $[LnXCp_2]_n$ directly.[13] However, the reaction of $ScCl_3$ with the appropriate salts **6**, **7**, or **8** in toluene required heating to 110 °C and prolonged reaction times (Scheme 4). The solids (mainly LiCl formed) were then removed by filtration, and the desired products **3**−**5** were obtained as brilliant orange crystals by crystallization from toluene or toluene/hexane at −30 °C. The remarkably low nucleophilic reactivity of $Li(C_5H_5BMe)$ (**6**) had already been noted in reactions with main group electrophiles[14] and is the cause for the harsher reaction conditions required here.

Scheme 4

$$n\ ScCl_3 + 2n\ \underset{\mathbf{6-8}}{LiL} \rightarrow \underset{\mathbf{3-5}}{[ScClL_2]_n} + 2n\ LiCl$$

6 and **3**: $L = C_5H_5BMe$, $n = 2$

7 and **4**: $L = 3,5\text{-}Me_2C_5H_3BNMe_2$, $n = 2$

8 and **5**: $L = 3,5\text{-}Me_2C_5H_3BN(SiMe_3)_2$, $n = 1$

Crystal Structure Determinations. Compound **3** crystallizes in the form of monoclinic rods. The molecule **3** is dinuclear and displays crystallographic centrosymmetry (Table 1, Figures1 and 2).

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Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for 3

(a) Bond Distances			
Sc−Cl	2.5653(5)	Sc−Cl′	2.5902(5)
Sc−C12	2.603(1)	Sc−C22	2.746(1)
Sc−C13	2.535(1)	Sc−C23	2.616(1)
Sc−C14	2.507(1)	Sc−C24	2.502(1)
Sc−C15	2.577(1)	Sc−C25	2.550(1)
Sc−C16	2.703(1)	Sc−C26	2.592(1)
Sc−B1	2.854(1)	Sc−B2	2.826(1)
C12−B1	1.510(2)	C22−B2	1.517(2)
C12−C13	1.392(2)	C22−C23	1.380(2)
C13−C14	1.398(2)	C23−C24	1.399(2)
C14−C15	1.408(2)	C24−C25	1.399(2)
C15−C16	1.388(2)	C25−C26	1.393(2)
C16−B1	1.526(2)	C26−B2	1.511(2)
C17−B1	1.581(2)	C27−B2	1.582(2)
(b) Bond Angles			
Sc−Cl−Sc′	100.40(1)	Cl−Sc−Cl′	79.60(1)
C12−B1−C16	112.3(1)	C22−B2−C26	112.4(1)
C12−B1−C17	123.6(1)	C22−B2−C27	124.3(1)
C16−B1−C17	124.1(1)	C26−B2−C27	123.3(2)

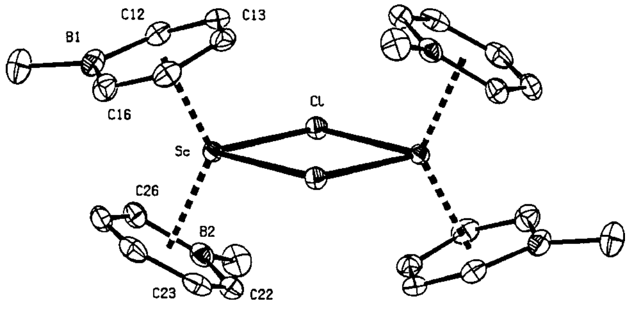

Figure 1. PLATON plot[15] of the molecule **3**. Displacement ellipsoids are scaled to 30% probability. Designations of symmetry-related atoms are omitted for clarity.

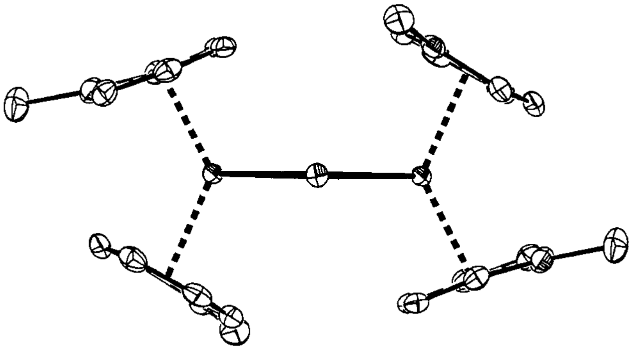

Figure 2. Side-view of the molecule **3**.

The structure of complex **3** is of a very common type. Two bent sandwich units with two facially bonded ring ligands are joined by two bridging ligands. Representative examples are $[Sc(\mu\text{-}Cl)Cp_2]_2$,[3] $[Y(\mu\text{-}Cl)(C_5H_4Me)_2]_2$,[16] and $[Ti(\mu\text{-}X)(C_5H_4R)_2]_2$ (X = Cl, R = H, Me; X = Br, R = Me).[17]

In **3** the central Sc_2Cl_2 ring is planar by symmetry with a nonbonding Sc···Sc′ distance of 3.961(1) Å. The Sc−Cl distances average to 2.5778(5) Å, which is not different from the value observed for $[Sc(\mu\text{-}Cl)Cp_2]_2$ [Sc−Cl (av) 2.575(2) Å].[3]

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for 4

(a) Bond Distances			
Sc−C12	2.563(2)	Sc−Cl	2.599(1)
Sc−C13	2.555(2)	Sc−Cl′	2.530(1)
Sc−C14	2.482(2)	Sc−N2	2.316(2)
Sc−C15	2.517(2)	Sc−C22	2.457(2)
Sc−C16	2.549(2)	Sc−B2	2.569(2)
Sc−B1	2.819(2)		
N1−B1	1.417(3)	N2−B2	1.514(3)
N1−C10	1.440(3)	N2−C20	1.469(3)
N1−C11	1.449(3)	N2−C21	1.487(3)
C12−B1	1.537(3)	C22−B2	1.492(3)
C12−C13	1.396(3)	C22−C23	1.414(3)
C13−C14	1.407(3)	C23−C24	1.385(3)
C14−C15	1.415(3)	C24−C25	1.402(3)
C15−C16	1.388(3)	C25−C26	1.379(3)
C16−B1	1.537(3)	C26−B1	1.507(3)
(b) Bond Angles			
Sc−Cl−Sc′	101.50(2)	Cl−Sc−Cl′	78.50(1)
C10−N1−C11	111.6(2)	C20−N2−C21	108.3(2)
C10−N1−B1	124.0(2)	C20−N2−B2	115.9(2)
C11−N1−B1	124.3(2)	C21−N2−B2	113.1(2)
C12−B1−C16	111.9(1)	C22−B2−C26	116.9(2)
N1−B1−C12	124.0(2)	N2−B2−C22	116.1(2)
N1−B1−C16	124.0(2)	N2−B2−C26	126.3(1)

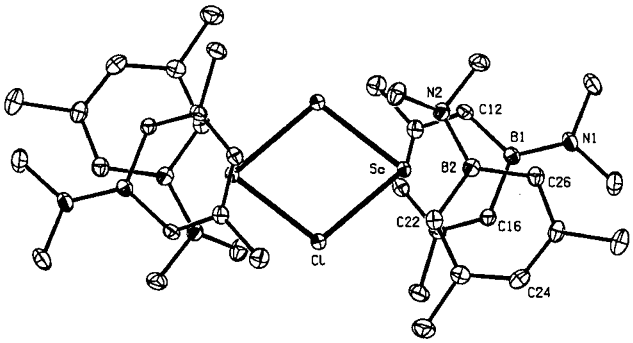

Figure 3. PLATON plot of the molecule **4**. Displacement ellipsoids are scaled to 30% probability. Designations of symmetry-related atoms are omitted for clarity.

The boratabenzene rings are approximately planar, and there is no pyramidalization at boron. In the first ring (C12···C16,B1) the MeB group is bent away from the metal by 9.1(5)°, while in the second ring (C22···C26,B2) atom C26 is bent away from the metal by 8.9(3)°. The bending angle amounts to 130.5(1)°, but the individual tilts of the best C_5B planes against the equatorial plane Sc_2Cl_2 are markedly different: 20.7(1)° for the first ring and 28.9(1)° for the second ring. The torsional positions of the rings are described by angles of 154.5° between the Sc−Sc′ vector and the projection of B−C(Me) onto the equatorial plane for the first ring and of 64.3° for the second ring.

The distances Sc−C 2.593 Å (av) [ranging from 2.502(1) to 2.746(1) Å] are longer than in $[Sc(\mu\text{-}Cl)Cp_2]_2$[3] [Sc−C (av) 2.46(1) Å] and in $ScMeCp^*_2$[4] [Sc−C 2.46(1) Å]. This difference seems to reflect the lower charge density of the C_5H_5B ring as compared to that of Cp. The distance Sc−B amounts to 2.840 Å (av).

The molecule of **4** shows crystallographic centrosymmetry (Table 2, Figure 3). It consists of a planar central Sc_2Cl_2 unit [Sc···Sc′ 3.972(1) Å, Sc−Cl (av) 2.565(1) Å], but apart from this, the structure of **4** in the crystal shows little similarity to that of **3** since the bonding of the two independent boratabenzene ligands of **4** is surprisingly different (Figure 4).

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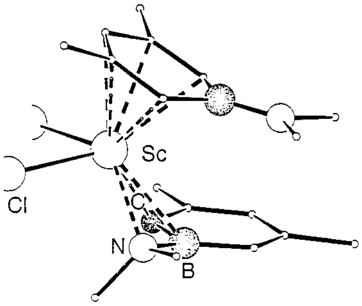

Figure 4. Coordination modes of the two nonequivalent boratabenzene ligands (SCHAKAL).[18] The atoms N1 and B1 of the facially coordinated boratabenzene ligand as well as the atoms N2, B2, and C22 of the η^3-coordinated ligand are emphasized.

In the first ring (C12···C16,B1) the five carbon atoms lie in a plane [largest perpendicular displacement of 0.018(2) Å for C13], while the boron is bent away from the metal by 17.8(4)°. The tilt of the best C_5B plane against the Sc_2Cl_2 plane is 28.1(1)° [or 31.6(1)° for the best C_5 plane]. The Sc−C distances average to 2.533 Å [ranging from 2.482(1) to 2.563(1) Å], and the distance Sc−B1 amounts to 2.819(2) Å. These distances are all slightly shorter than for **3**. We also note that the bond length B1−N1 of 1.417(3) Å is close to the distance for typical aminoboranes [1.41 Å][19] and shorter than for the lithium salts Li(TMEDA)($C_5H_5BNMe_2$) [1.448(2) Å][20] and Li(TMEDA)(3,5-$Me_2C_5H_3BNMe_2$) [1.448(2) Å].[10] A similar shortening has been observed for $ZrCl_2(C_5H_5\text{-}BNPr^i{}_2)_2$ [1.396(6) Å].[21] These observations reflect an increase of B−N π-interactions with increasing charge of the central metal (Li < Sc < Zr).

The second ring (C22···C26,B2) is planar [largest perpendicular displacement of 0.019(2) Å for C25]. Only the atoms N2, B2, and C22 are within bonding distance to Sc with distances Sc−N2 of 2.316(2) Å, Sc−B2 of 2.569(2) Å, and Sc−C22 of 2.457(2) Å. The bonding to scandium is accompanied by a considerable lengthening of the B−N bond [N2−B2 1.514(3) Å] and a pronounced pyramidalization at the nitrogen center [angle sum of 337.3° at N; cf. value of 328.5° for regular tetrahedron]. The boron also shows some pyramidalization and is shifted away from the metal by 0.074(2) Å with respect to the plane N2,C22,C26. These observations establish an unprecedented η^3-coordination of an aminoboratabenzene which now bears some similarity to η^3-bonded benzyl ligands[22] in, for example, the cations $[CpMo(CO)_2(\eta^3\text{-}CH_2C_6H_4\text{-p-Me})]^{+}$ [23a] or in $[Cp^*{}_2Zr(\eta^7\text{-}CH_2Ph)(\eta^3\text{-}CH_2Ph)]^{+}$.[23b]

Finally we note that the structure of **4** in solution is dynamic, displaying one type of ligand and apparent lateral symmetry (i.e., overall apparent D_{2h} symmetry), even at −80 °C. Hence the barrier to the haptotropic automerization observed is rather low.

Table 3. Selected Bond Distances (Å) for 5

Sc−Cl	2.379(1)	N−B	1.471(3)
Sc−C1	2.611(2)	C1−B	1.527(4)
Sc−C2	2.556(2)	C1−C2	1.391(4)
Sc−C3	2.470(2)	C2−C3	1.396(4)
Sc−C4	2.574(2)	C3−C4	1.412(4)
Sc−C5	2.604(2)	C4−C5	1.377(3)
Sc−B	2.802(3)	C5−B	1.526(4)

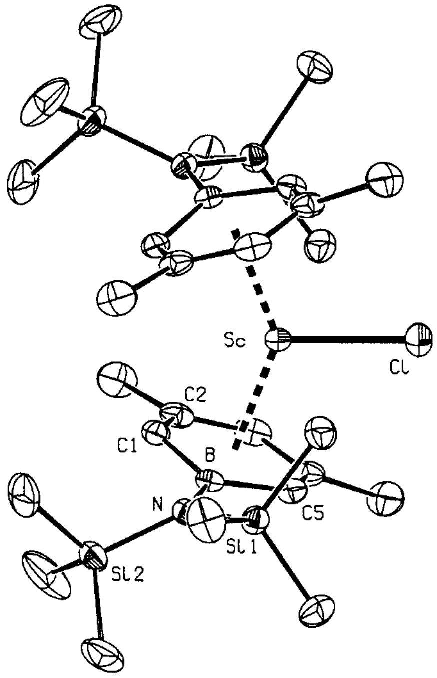

Figure 5. PLATON plot of the molecule **5**. Displacement ellipsoids are scaled to 30% probability. Designations of symmetry-related atoms are omitted for clarity.

Compound **5** is mononuclear and, being a 14e species, is coordinatively more unsaturated than **3** and **4**. The molecule **5** displays the shape of a two-bladed propeller and possesses crystallographic C_2 symmetry (Table 3, Figure 5).

As expected, the distance Sc−Cl of 2.379(1) Å is much shorter than in the dinuclear complexes with bridging Cl ligands. The ring carbon atoms (C1···C5) lie in a plane [largest perpendicular deviation 0.033(2) Å for C4], while the boron is bent away from the metal by 9.2(6)°. The slip distortion[24] is 0.19 Å, and the bending angle amounts to 140.8°. The rotational position of the rings can be described by an angle of 105.1° between the vector B−N and the projection of the Sc−Cl vector onto the best C_5B plane.

The distances Sc−C average to 2.630 Å [ranging from 2.470(2) to 2.611(2) Å], and the distance Sc−B is 2.802(3) Å. These distances are all a little shorter than in **3**. The B−N distance of 1.471(3) Å is comparatively long, presumably because of steric congestion and the polarizing influence of the positive Si centers.

The steric influence of the $N(SiMe_3)_2$ group disfavors both the dimerization of **5** to a coordinatively more

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saturated dimer, as in **3** and **4**, and the development of a lower ligand hapticity as in **4**.

Concluding Remarks

In this paper we give a simple entry into the boratabenzene chemistry of scandium group metals. Our results demonstrate once more the close analogy between the cyclopentadienyl and boratabenzene ligands. On the other hand, the boratabenzene compounds are more complex structurally, and the discovery of the novel η^3-N−B−C coordination mode should be an incentive to investigate this area more deeply.

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 toluene from sodium; Et_2O and THF were distilled from sodium and benzophenone ketyl. Melting points were determined in sealed capillaries on a Büchi 510 melting point apparatus and are uncorrected.

NMR spectra were recorded on a Varian Unity 500 (^{1}H, 500 MHz; ^{13}C, 125.7 MHz; ^{11}B, 160.4 MHz), a Varian VXR 300 (^{1}H, 300 MHz; ^{13}C, 75.4 MHz), and a PMR-Firenze (^{11}B, 27.9 MHz). Chemical shifts were measured at ambient temperature. They are given in ppm and are relative to internal TMS for ^{1}H and ^{13}C and relative to external $BF_3{\cdot}OEt_2$ for ^{11}B. Mass spectra were recorded on a Finnigan MAT-95 spectrometer.

Solvent-Free Lithium 1-(Dimethylamino)boratabenzene (7). Lithium bis(trimethylsilyl)amide in hexane (1 M, 48.5 mL, 48.5 mmol) was added dropwise with stirring to a solution of **9**[10] (7.28 g, 48.8 mmol) in ether (70 mL) at −78 °C. After completion of the addition, the reaction mixture was kept stirring at −78 °C for 2 h, then allowed to warm to ambient temperature, and stirring was continued for 3 days. The volatiles were removed in a vacuum. Hexane (100 mL) was added to the residue, and the mixture was stirred for 2 h. The white solid was collected by filtration, washed with hexane (3 × 40 mL), and dried in a vacuum to afford **7** (4.85 g, 65%) as a white powder: ^{1}H NMR (500 MHz, THF-d_8) δ 5.14 (s, 2-/6-H), 5.09 (s, 4-H), 2.64 (s, NMe_2), 2.01 (s, 3-/5-Me); ^{13}C NMR (126 MHz, THF-d_8) δ 142.6 (C-3,5), 107.9 (br, C-2,6), 102.8 (C-4), 40.0 (NMe_2), 25.9 (3-/5-Me); ^{11}B NMR (160 MHz, d_8-THF) δ 31.6.

1-Chloro-3,5-dimethyldihydroborinine (11). Boron trichloride in CH_2Cl_2 (1.73 M, 40 mL, 69 mmol) was added dropwise with stirring to 3,5-dimethyl-1-(dimethylamino)-dihydroborinine[10] (**10**) (9.80 g, 65.8 mmol) at −78 °C. When the addition was completed, the mixture was slowly warmed to 0 °C, and stirring was continued at this temperature for 2 h. The volatiles were then removed under reduced pressure, and the residue was distilled under vacuum to afford **11** (7.13 g, 77%); bp 65−70 °C/10 mbar. Isomer ratios from **a**/**b** = 4:1 to **a**/**b** = 1:3 were observed (NMR).

11a: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.06 (m, 4-H), 6.03 (s, 6-H), 2.13 (s, 5H, CH_2 + 5-Me), 2.01 (s, 3-Me); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1 (C-5), 150.8 (C-3), 126.5 (C-4), 126.0 (br, C-6), 35.0 (br, C-2), 26.9 (5-Me), 25.5 (3-Me); ^{11}B NMR (160 MHz, $CDCl_3$) δ 62.1.

11b: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.18 (s, 2-/6-H), 3.00 (s, CH_2), 2.07 (s, 3-/5-Me); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4 (C-3,5), 130.0 (br, C-2,6), 44.6 (C-4), 25.9 (3-/5-Me); ^{11}B NMR (160 MHz, $CDCl_3$) δ 51.8.

1-[Bis(trimethylsilyl)amino]-3,5-dimethyldihydroborinine (12). A mixture of bis(trimethylsilyl)amine (7.68 g, 47.6 mmol) and triethylamine (4.82 g, 47.6 mmol) was added dropwise with stirring to 1-chloro-3,5-dimethyldihydroborinine (**11**) (6.69 g, 47.6 mmol) in hexane (150 mL) at ambient temperature, and stirring was continued overnight. The white solid formed (presumed to be $NHEt_3Cl$) was removed by filtration, washed with hexane (3 × 20 mL) and discarded. The combined filtrate was evaporated to dryness in a vacuum to afford **12** (11.4 g, 90%) as a slightly yellow solid; mp 58−59 °C, isomer ratio **a**/**b** = 94:6 (NMR). Anal. Calcd for $C_{13}H_{28}BNSi_2$ (**12**): C, 58.84; H, 10.64; N, 5.28. Found: C, 58.59; H, 10.85; N, 5.12.

12a: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.83 (t, J = 1.3 Hz, 4-H), 5.74 (s, 6-H), 2.00 (s, 5-Me), 1.92 (s, 3-Me), 1.87 (s, CH_2), 0.19 (s, 2 $SiMe_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.5 (C-3), 146.5 (C-5), 127.4 (br, C-6), 124.4 (C-4), 35.1 (br, C-2), 26.6 (5-Me), 26.0 (3-Me), 8.6 ($SiMe_3$); ^{11}B NMR (160 MHz, $CDCl_3$) δ 52.9.

12b: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.94 (s, 2-/6-H), 2.78 (s, CH_2), 1.96 (s, 3-/5-Me), 0.21 (s, 2 $SiMe_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.8 (C-3,5), 130.8 (br, C-2,6), 42.3 (C-4), 26.4 (3-/5-Me), 4.4 ($SiMe_3$); ^{11}B NMR (160 MHz, $CDCl_3$) δ 43.2.

Lithium 1-[Bis(trimethylsilyl)amino]-3,5-dimethylboratabenzene (8). Lithium bis(trimethylsilyl)amide in hexane (1 M, 36.8 mL, 36.8 mmol) was added dropwise with stirring to a solution of **12** (9.76 g, 36.8 mmol) in ether (100 mL) at −78 °C. The reaction mixture was kept stirring at −78 °C for 2 h, then allowed to warm to ambient temperature, and stirring was continued for 2 days. The volatiles were removed in a vacuum. Hexane (100 mL) was added to the residue, and the mixture was stirred for 2 h. The white solid formed was collected by filtration, washed with hexane (3 × 40 mL), and dried in a vacuum to afford **8** (6.82 g, 68%) as a white powder: ^{1}H NMR (500 MHz, THF-d_8) δ 5.53 (s, 2-/6-H), 5.49 (s, 4-H), 2.07 (s, 3-/5-Me), 0.07 (s, 2 $SiMe_3$); ^{13}C NMR (126 MHz, THF-d_8) δ 141.6 (C-3,5), 121.0 (br, C-2,6), 105.6 (C-4), 25.6 (3-/5-Me), 4.9 ($SiMe_3$); ^{11}B NMR (160 MHz, THF-d_8) δ 34.5.

Di-μ-chlorotetrakis(1-methylboratabenzene)discandium (3). A suspension of $ScCl_3$ (1.00 g, 6.6 mmol) and **6** (1.30 g, 13.3 mmol) in toluene (20 mL) was stirred at 110 °C for 3 days. The solid material was filtered off, and the orange filtrate was cooled to −30 °C to give **3** as orange rod-shaped crystals; a further crop was obtained by concentrating the mother liquor and again cooling to −30 °C (total: 1.0 g, 58%); mp 160−161 °C, no dec up to 250 °C; can be sublimed at 130 °C/10^{-6} bar; extremely sensitive to traces of oxygen or humidity; very soluble in toluene, barely soluble in hexane. Anal. Calcd for $C_{24}H_{32}B_4Cl_2Sc_2$ (**3**): C, 54.95; H, 6.15. Found: C, 54.64; H, 6.29. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.58 (dd, 3-/5-H), 7.24 (dd, 2-/6-H), 6.64 (tt, 4-H), J_{23} = 10.5, J_{34} = 7.1, J_{24} = 1.7 Hz, 0.89 (s, Me); ^{13}C NMR (76 MHz, CD_2Cl_2) δ 142.9 (C-3,5), 134.2 (br, C-2,6), 113.0 (C-4), 7 (br, Me); ^{11}B NMR (27.9 MHz, C_6D_6/CD_2Cl_2) δ 48.

Di-μ-chlorotetrakis[1-(dimethylamino)-3,5-dimethylboratabenzene]discandium (4). A suspension of $ScCl_3$ (449 mg, 2.97 mmol) and **7** (956 mg, 6.17 mmol) in toluene (15 mL) was stirred at 100 °C for 1 day. The solid material was removed by filtration and washed with toluene (2 × 2 mL). The deep red filtrate was evaporated to dryness at reduced pressure to afford **4** (853 mg, 76%) as orange solid; mp 97−98 °C. The material can be recrystallized from toluene. Anal. Calcd for $C_{36}H_{60}B_4Cl_2N_4Sc_2$ (**4**): C, 57.43; H, 8.03; N, 7.44. Found: C, 57.16; H, 8.27; N, 7.39. ^{1}H NMR (500 MHz, C_6D_6) δ 6.02 (s, 4-H), 5.39 (s, 2-/6-H), 2.85 (s, NMe_2), 1.92 (s, 3,5-Me), with sharp signals at +23 °C and at −80 °C; some line-broadening is seen at intermediate temperatures, but no changes of the chemical shifts (possibly indicating an equilibrium with a monomer in low concentration). ^{13}C NMR (126 MHz, C_6D_6) δ 153.3 (C-3,5), 113.3 (C-4), 113.1 (br, C-2,6), 38.7 (NMe_2), 26.3 (3-/5-Me); ^{11}B NMR (160 MHz, C_6D_6) δ 35.2.

Bis[1-{bis(trimethylsilyl)amino}-3,5-dimethylboratabenzene)]chloroscandium (5). A suspension of $ScCl_3$ (290 mg, 1.92 mmol) and **8** (1.08 g, 3.98 mmol) in toluene (15 mL) was stirred at 110 °C for 4 days. Workup as described for **4** afforded **5** (1.03 g, 88%) as a light orange-yellow solid; mp 124−125 °C; can be recrystallized from toluene. Anal. Calcd for

Table 4. Crystal Data, Data Collection Parameters, and Convergence Results for 3, 4, and 5

formula	$C_{24}H_{32}B_4Cl_2Sc_2$ (**3**)	$C_{36}H_{60}B_4Cl_2N_4Sc_2$ (**4**)	$C_{26}H_{54}B_2ClN_2ScSi_4$ (**5**)
fw	524.58	752.97	609.11
system	monoclinic	triclinic	monoclinic
space group (no.)	$P2_1/n$ (14)	$P\bar{1}$ (2)	$C2/c$ (15)
a, Å	6.5836(7)	9.1552(9)	20.520(1)
b, Å	13.761(1)	9.407(4)	8.6587(6)
c, Å	14.009(2)	12.252(3)	20.301(2)
α, deg		80.15	
β, deg	95.372(9)	80.46(1)	96.611(6)
γ, deg		74.58(2)	
U, Å^3	1263.6(2)	994.1(5)	3583.1(4)
Z	2	1	4
d_{calc}, g cm^{-3}	1.38	1.26	1.13
μ, cm^{-1}	7.62	5.05	4.28
θ_{max}, deg	29.0	28.0	26.0
temp, K	293	203	203
λ, Å	0.71073	0.71073	0.71073
cryst dimens, mm^3	0.68 × 0.60 × 0.48	0.64 × 0.48 × 0.32	0.6 × 0.6 × 0.4
abs corr	empirical Ψ	none	none
no. of reflns	7231	5871	4798
no. of indep obs reflns $I > 1.0\sigma(I)$	2945	4085	2846
no vars	210	337	164
R^a	0.027	0.046	0.057
$R_w{}^b$	0.038	0.048	0.059
GOF^c	1.337	1.266	1.571
res el dens, e Å^{-3}	0.25	0.48	0.42

[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.

$C_{26}H_{54}B_2ClN_2ScSi_4$ (**5**): C, 51.27; H, 8.94; N, 4.60. Found: C, 51.11; H, 8.99; N, 4.61. ^{1}H NMR (500 MHz, C_6D_6) δ 5.94 (d, J = 1.8 Hz, 2-/6-H), 5.60 (t, J = 1.8 Hz, 4-H), 1.98 (s, 3-/5-Me), 0.38 (s, 2 $SiMe_3$); ^{13}C NMR (126 MHz, C_6D_6) δ 153.0 (C-3,5), 127.4 (br, C-2,6), 110.4 (C-4), 26.7 (3-/5-Me), 5.0 ($SiMe_3$); ^{11}B NMR (160 MHz, C_6D_6) δ 40.5.

Crystal Structure Determinations of 3, 4, and 5. Geometry and intensity data were collected with Mo Kα radiation on an ENRAF-Nonius CAD4 diffractometer equipped with a graphite monochromator. Crystal data, data collection parameters, and convergence results are compiled in Table 4. Only in the case of **3** was an empirical absorption correction based on azimuthal scans[25] applied before averaging symmetry equivalent data. The structures were solved by direct methods[26] and subsequent Fourier difference syntheses. The models were refined on structure factors with the local version of the SDP[27] program suite. In the full-matrix least-squares refinement, all non-hydrogen atoms were assigned anisotropic displacement parameters. Hydrogen atoms were refined with isotropic displacement parameters in the case of **3** and **4** and included as riding on the corresponding carbon atoms [C−H = 0.98 Å, $U_{iso}(H) = 1.3U_{eq}(C)$] in the case of **5**.[28]

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Supporting Information Available: Tables of bond distances and angles, anisotropic displacement parameters, and atom coordinates for **3**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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