1-Aminoboratabenzene Complexes of Scandium Group Metals[‡]

Bing Wang,[a] Xiaolai Zheng,[a] and Gerhard E. Herberich*[a]

Keywords: Boron / Group 3 metals / Metallocenes / Boratabenzene / Lithium

The syntheses of the new lithium boratabenzenes Li(3,5-$\text{Me}_2\text{C}_5\text{H}_3\text{BN}i\text{Pr}_2$), Li(**3**), and Li_2[(3,5-$\text{Me}_2\text{C}_5\text{H}_3\text{BNMe})_2$-$(\text{CH}_2)_2$], Li_2(**5**), via the dicarbanion route are described. Lithium 1-aminoboratabenzenes react with metal trihalides in toluene (110 °C, 3 d) to give the stepped ladder dimers [(3,5-$\text{Me}_2\text{C}_5\text{H}_3\text{BNMe}_2)_2\text{Y}(\mu\text{-Cl})_2\text{Li}]_2$, (**12**), [(3,5-$\text{Me}_2\text{C}_5\text{H}_3\text{BNMe}_2)_2$-$\text{Lu}(\mu\text{-Cl})_2\text{Li}]_2$ (**13**), and the mononuclear complexes YCl[3,5-$\text{Me}_2\text{C}_5\text{H}_3\text{BN}(\text{SiMe}_3)_2]_2$ (**18**), LuCl[3,5-$\text{Me}_2\text{C}_5\text{H}_3\text{BN}(\text{SiMe}_3)_2]_2$ (**19**), and ScCl(3,5-$\text{Me}_2\text{C}_5\text{H}_3\text{BN}i\text{Pr}_2)_2$ (**20**). When donor solvents such as THF or THP are used, analogous reactions take place at ambient temperature, giving solvates such as (3,5-$\text{Me}_2\text{C}_5\text{H}_3\text{BNMe}_2)_2\text{Sm}(\mu\text{-Cl})_2\text{Li(THF)}$ (**15**), (3,5-$\text{Me}_2\text{C}_5\text{H}_3\text{BNMe}_2)_2\text{Y}(\mu\text{-Cl})_2\text{Li(THP)}$ (**16**), (3,5-$\text{Me}_2\text{C}_5\text{H}_3\text{BN}i\text{Pr}_2)_2\text{Y}(\mu\text{-Cl})_2\text{Li(THF)}_2$ (**21**), (3,5-$\text{Me}_2\text{C}_5\text{H}_3\text{BN}i\text{Pr}_2)_2\text{Sm}(\mu\text{-Cl})_2\text{Li(THF)}_2$ (**22**), and the ansa complexes [(3,5-$\text{Me}_2\text{C}_5\text{H}_3\text{BNMeCH}_2)_2]\text{Lu}(\mu\text{-Cl})_2\text{Li(THF)}_2$ (**23**) and [(3,5-$\text{Me}_2\text{C}_5\text{H}_3\text{BNMeCH}_2)_2]\text{Lu}(\mu\text{-Cl})_2\text{Li(THP)}_2$ (**24**). The bridge cleavage product Y(acac)(3,5-$\text{Me}_2\text{C}_5\text{H}_3\text{BNMe}_2)_2$ (**14**) is obtained from **12** and Na(acac) in toluene at ambient temperature. The complexes **12**, **14**, **16**, **18**·PhMe, **19**·PhMe, **20** (as two polymorphs **α-20** and **β-20**), **21**, and **24** (as the *rac*-stereomer) are characterized by single-crystal structure determinations. In all structures except those of the mononuclear complexes **18** and **19**, the ring-ring rotational positions are close to 180°, cf. e.g. **14**, or to 60°, cf. e.g. **20**; these conformations minimize transannular ligand-ligand repulsions. The internal coordination of a *B*-NMe_2 sidearm, which is unprecedented, is found in the structures of the stepped ladder dimers **12** and **13**, and in the mononuclear complexes **15** and **16**. According to solution NMR spectroscopy, all complexes are dynamic with respect to ring-ring rotation and, in the cases with internal coordination, they are dynamic with respect to the interchange between free and coordinated *B*-NMe_2 sidearms.

Introduction

Boratabenzenes are close relatives of the more familiar cyclopentadienides; this is particularly true of the systematic aspects of their salts and complexes.[2] The boratabenzene chemistry of the scandium group metals is still relatively unexplored, despite an early communication in this field.[2b] We have described the first bis(boratabenzene)scandium chlorides, which were synthesized from ScCl_3 and lithium boratabenzenes.[2b,3] Bazan et al. demonstrated that Fu's borabenzene trimethylphosphane adduct $\text{C}_5\text{H}_5\text{BPMe}_3$ [4] reacts with $\text{Sc(THF)}_2\text{Ph}_3$ to give (1-phenylboratabenzene)scandium complexes.[5] More recently we reported on the synthesis and structural chemistry of the dinuclear (1-methylboratabenzene)yttrium complex [Y(μ-Cl)(3,5-$\text{Me}_2\text{C}_5\text{H}_3\text{BMe})_2]_2$.[6]

Closely related works involve compounds of magnesium in group 2,[7] and a very large variety of complexes of group 4 metals, mainly of zirconium.[4a,5,8] It was decided to study these compounds as they are novel, and because they are thought to mimic catalyst systems of modern Ziegler−Natta olefin polymerization processes that are derived from CpZr and CpTi complexes. Some of the catalyst systems so obtained are rather similar to those derived from ZrCl_2Cp_2,[8m] and others display considerably modified properties,[5,8f−8l] thus widening the range of the potential applications of these complexes. A similar parallel between cyclopentadienyl and boratabenzene complexes may be expected for catalysts of the scandium group metals,[9] providing a further incentive to explore the chemistry of boratabenzene complexes of the Sc group metals.

The goal of the present paper is to report on the syntheses and structures of Sc, Y, Sm, and Lu bis(boratabenzene) complexes that bear a *B*-amino group. It will be seen that the presence of a *B*-amino group provides a remarkably rich structural chemistry to this class of complexes.

Results and Discussion

Lithium Boratabenzenes

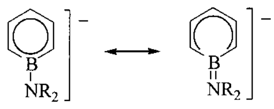
Lithium boratabenzenes are the most common source of boratabenzene ligands. Their properties are greatly influenced by the *B*-bonded substituents. *B*-(dialkylamino)boratabenzenes differ from boratabenzenes with innocent substituents at boron such as $\text{Li}(\text{C}_5\text{H}_5\text{BPh})$,[10] $\text{Li}(\text{C}_5\text{H}_5\text{BMe})$,[11a] $\text{Li}(\text{C}_5\text{H}_5\text{B}t\text{Bu})$,[11a] and $\text{Li}(\text{C}_5\text{H}_5\text{BH})$.[4a]

[‡] Borabenzene Derivatives, 37. − Part 36: Ref.[1a]

[a] Institut für Anorganische Chemie, Technische Hochschule Aachen
52056 Aachen, Germany
Fax: (internat.) + 49-(0)241/809-2288
E-mail: gerhard.herberich@ac.rwth-aachen.de

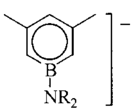
1434−1948/02/0101−0031 $ 17.50+.50/0

The dialkylamino group strongly perturbs the aromatic π-electron system of the boratabenzene ring. This was first demonstrated for the parent compound Li($C_5H_5BNMe_2$), Li(**1**),[11] and was later brought into a wider perspective.[12] Furthermore, and as will be detailed below, the amino functionality may also act as a Lewis base towards the Li^+ ions.



1⁻

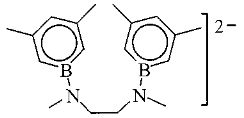
We prefer the more easily accessible 3,5-dimethyl derivatives and use Li($3,5\text{-}Me_2C_5H_3BNMe_2$), Li(**2**),[3] the diisopropylamino compound Li($3,5\text{-}Me_2C_5H_3BNiPr_2$), Li(**3**), the bis(trimethylsilyl)amino compound Li[$3,5\text{-}Me_2C_5H_3BN(SiMe_3)_2$],[3] Li(**4**), and the bifunctional boratabenzene $Li_2[(3,5\text{-}Me_2C_5H_3BNMeCH_2)_2]$, Li_2(**5**).



2⁻: R = Me

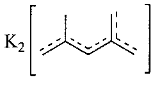
3⁻: R = *i* Pr

4⁻: R = SiMe₃

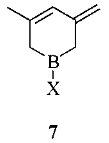


5²⁻

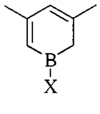
The syntheses of these ligand systems were based on what we call the dicarbanion route.[13] Double potassiation of 2,4-dimethylpenta-1,3-diene (and double bond isomers) gave the dipotassio derivative $K_2[CH_2CMeCHC(CH_2)_2]$ (**6**), which on treatment with BCl_2NMe_2 afforded the 1,2,3,6-tetrahydroborinine (**7a**). After distillation, **7a** is partially isomerized to the dihydroborinine isomers (**8a**) and (**9a**). Treatment with strong bases such as LDA or $LiN(SiMe_3)_2$ resulted in double bond migration and deprotonation to give the boratabenzene as the TMEDA solvate Li(TMEDA)(**2**),[13] or as the donor-free salt Li(**2**).[3] This synthesis is readily reproduced with much better yields than originally published. The new salt Li(**3**) and its TMEDA solvate were obtained analogously. Attempted preparation of Li(**4**) by this method resulted in a low yield (22%) of the ring closure product **7c**, and the subsequent deprotonation by $LiN(SiMe_3)_2$ failed altogether.[14]



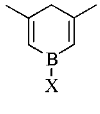
6



7



8



9

a: X = NMe_2, **b**: X = NPr^i_2, **c**: $N(SiMe_3)_2$, **d**: X = Cl

As an alternative, the substituent at boron may be modified. This has previously been described for the compounds of the series **a**,[3] and for our pinene-fused boratabenzenes.[15] Three steps are required: i) isomerization of **7a** with HCl to give the less sensitive isomers **8a/9a**; ii) treatment of the mixture **8a/9a** with BCl_3 to produce the chloro compounds **8d/9d**; iii) introduction of the desired new substituent, i.e. in the present case the $N(SiMe_3)_2$ group was introduced by the reaction of the chloro compounds **8d/9d** with a mixture of the secondary amine $NH(SiMe_3)_2$ and NEt_3, to give **8c/9c**, which was then metalated in the usual way.[3]

In a straightforward adaptation of this procedure the chloro compounds **8d/9d** were treated with $(CH_2NHMe)_2/NEt_3$ (1:1) to produce a mixture of ethylene-linked bis(aminodihydroborinines) **10**. Subsequent metalation with $LiN(SiMe_3)_2$ gave the new salt Li_2(**5**) in a high yield. The closely related bis(boratabenzene) $Li_2[(C_5H_5BNMeCH_2)_2]$ has recently been synthesized in a similar manner.[8a]

Complexes: General Comments

The most common cyclopentadienyl complexes of the scandium group metals are the bis(cyclopentadienyl)metal halides.[9] The smaller central metals usually form dinuclear complexes, such as $[Sc(\mu\text{-}Cl)Cp_2]_2$,[16a] and $Yb[(\mu\text{-}Cl)(C_5H_4Me)_2]_2$,[16b] and the larger central metals have a tendency to form higher aggregates. If the Cp ligand is sterically demanding as in the case of the pentamethylcyclopentadienyl ligand Cp*, mononuclear complexes such as $ScClCp^*_2$[17] are favored, despite their coordinative unsaturation. Larger central metals allow the formation of oligomers. For example, $(YClCp^*)_2$ displays a half-bridged dimeric structure $Cp^*_2YCl(\mu\text{-}Cl)YCp^*_2$,[18a] and the corresponding Sm complex is a cyclotrimer $[Sm(\mu\text{-}Cl)Cp^*_2]_3$.[18b] Thus, a subtle interplay of electronic requirements, steric hindrance, and presumably of the (often ignored) lattice energy of the crystal (cf. ref.[6]) determines the structural type observed for a particular compound.

At the outset of this work we decided to study simple metathetical reactions of scandium group metal trihalides with lithium boratabenzenes in a 1:2 ratio. In the related cyclopentadienyl chemistry, refluxing benzene has occasionally been used as the reaction medium[19] to prevent the formation of solvates that is common when the reactions are carried out in THF. In NMR spectroscopic tube experiments we found that higher reaction temperatures were required; heating the suspension of the reactants in toluene at 110 °C for 3 days gave satisfactory results in most cases. In the case of $SmCl_3$/Li(**2**), ill-defined reactions took place above 40 °C; thus THF was used. Other reactions were also carried out in ethereal solvents. Table 1 gives an overview of all products, isolated and characterized; of these, the complexes **11** and **17** have been described in previous work.[3]

Table 1. 1-Aminoboratabenzene complexes

11	$[Sc(\mu\text{-}Cl)(3,5\text{-}Me_2C_5H_3BNMe_2)_2]_2$[3]
12	$[(3,5\text{-}Me_2C_5H_3BNMe_2)_2Y(\mu\text{-}Cl)_2Li]_2$
13	$[(3,5\text{-}Me_2C_5H_3BNMe_2)_2Lu(\mu\text{-}Cl)_2Li]_2$
14	$Y(acac)(3,5\text{-}Me_2C_5H_3BNMe_2)_2$
15	$(3,5\text{-}Me_2C_5H_3BNMe_2)_2Sm(\mu\text{-}Cl)_2Li(THF)$
16	$(3,5\text{-}Me_2C_5H_3BNMe_2)_2Y(\mu\text{-}Cl)_2Li(THP)$
17	$ScCl[3,5\text{-}Me_2C_5H_3BN(SiMe_3)_2]_2$[3]
18	$YCl[3,5\text{-}Me_2C_5H_3BN(SiMe_3)_2]_2$
19	$LuCl[3,5\text{-}Me_2C_5H_3BN(SiMe_3)_2]_2$
20	$ScCl(3,5\text{-}Me_2C_5H_3BN\textit{i}Pr_2)_2$
21	$(3,5\text{-}Me_2C_5H_3BN\textit{i}Pr_2)_2Y(\mu\text{-}Cl)_2Li(THF)_2$
22	$(3,5\text{-}Me_2C_5H_3BN\textit{i}Pr_2)_2Sm(\mu\text{-}Cl)_2Li(THF)_2$
23	$[(3,5\text{-}Me_2C_5H_3BNMeCH_2)_2]Lu(\mu\text{-}Cl)_2Li(THF)_2$
24	$[(3,5\text{-}Me_2C_5H_3BNMeCH_2)_2]Lu(\mu\text{-}Cl)_2Li(THP)_2$

Metallocenoids with 1-(Dimethylamino)-3,5-dimethylboratabenzene Ligands

In our earlier work, we obtained the Sc complex **11** from the reaction of $ScCl_3$ with Li(**2**) (ratio 1:2) in toluene. The crystal of complex **11** displays a unique N−B−C η^3-coordination of one boratabenzene ring and a normal, facially bonded second boratabenzene ligand. In solution, the structure is dynamic with effective D_{2h} symmetry.[3] The analogous reactions of the trihalides YCl_3 and $LuCl_3$ with Li(**2**) in toluene produced the dinuclear bis(boratabenzene) complexes **12** and **13** as pale yellow platelets, which, surprisingly, contained two equivalents of loosely bound LiCl. The attempted recrystallization from hot toluene resulted in the very slow separation of solid LiCl. Treatment of complex **12** with sodium acetylacetonate [≡ Na(acac)] gave the bridge cleavage product **14**, which crystallized from toluene as large yellow blocks.

The structure of this mononuclear complex **14** (Figure 1) is discussed in some detail. The overall structure is that of a bent sandwich with a bending angle of 136.1°, and with the acac ligand in the pseudoequatorial plane. The two boratabenzene rings are roughly planar with the boron atom bending away from the metal by 6.3° in the first ring [C11..C15,B1], and by 12.2° in the second ring [C21..C25,B2]. The Y−(C_5B) distance is 2.319 Å for the first ring and 2.355 Å for the second ring. The Y atom is shifted towards the γ ring carbon atoms, the slip distortions[21] are 0.078 Å for the first ring and 0.129 Å for the second ring.

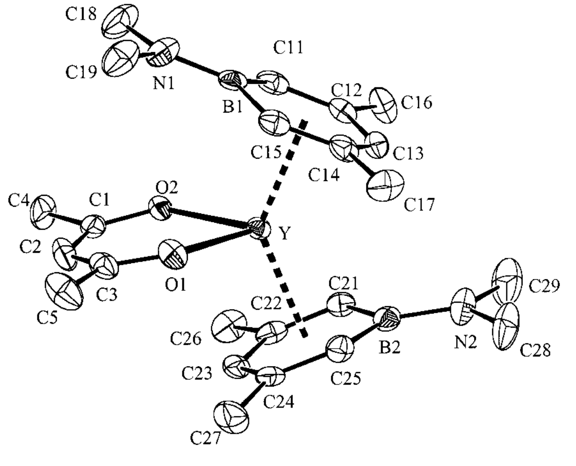


Figure 1. Molecular structure (PLATON plot, see ref.[20], at the 30% probability level) of **14** in the crystal. Selected bond lengths [Å] and bond angles [°]: Y−O1 2.205(5), Y−C1n 2.667(7) for C13 to 2.731(7) for C11, Y−B1 2.847(8), B1−N1 1.394(10), Y−O2 2.200(5), Y−C2n 2.694(7) for C23 to 2.755(7) for C21, Y−B2 2.941(8), B2−N2 1.411(10), O1−Y−O2 79.25(18).

Several details of the structure reflect the importance of intramolecular repulsive ligand-ligand interactions. The two ligands adopt an antiperiplanar conformation. Thus, the rings are eclipsed and the three ring substituents of one ring are staggered with respect to those of the other ring. This motif is found in all structures of this paper, except those of the mononuclear complexes **18** and **19** (see below). The larger folding angle, metal-to-ligand distance, and slip distortion for the second ring relative to the first ring is caused by the transannular repulsion exerted by C13 and the 3,5-methyl groups with C16 and C17. The acac ligand is almost perfectly planar, but bent along the line O1,O2 away from the nearby NMe_2 group of the first ligand; the distance of the Y atom from the acac plane is 0.33 Å. The average B−N distance of 1.403 Å is close to that of typical aminoboranes [1.41 Å].[22] This observation indicates considerable B−N π-interactions which increase with the increasing charge of the central metal and increasing transfer of electron density from the boratabenzene rings to the metal.[7] In benzene, the structure of **14** possesses an effective C_{2v} symmetry, according to NMR spectroscopy, indicating a low barrier to the ring-ring rotation and also to an inversion of the Y(acac) ring in solution.

The nature of the LiCl coordination in **12** and **13** could be clarified by a structure determination of complex **12.** This compound is an approximately centrosymmetric stepped ladder dimer (Figure 2). The new motif of this structure is the internal coordination of a *B*-NMe_2 sidearm of a bent sandwich unit, to a Li^+ of a second bent sandwich, resulting in a central $[YCl_2Li]_2$ unit with a distorted tetrahedral coordination sphere around the Li^+ ions.

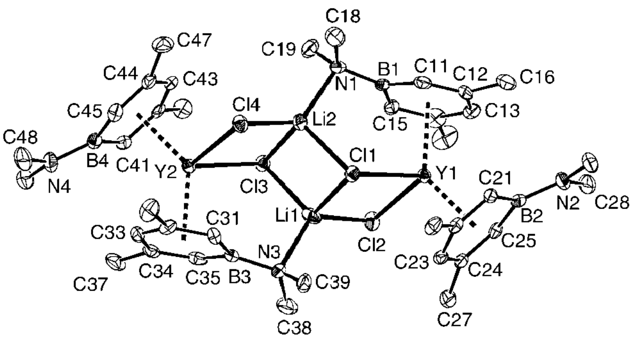


Figure 2. Molecular structure (PLATON plot, see ref.[20], at the 30% probability level) of **12** in the crystal. Selected bond lengths [Å]: Y1−Cl1 2.645(2), Y1−Cl2 2.627(2), Y2−Cl3 2.667(2), Y2−Cl4 2.622(2), Li1−Cl1 2.451(13), Li1−Cl2 2.326(12), Li1−Cl3 2.300(15), Li1−N3 2.093(13), Li2−Cl1 2.345(14), Li2−Cl3 2.400(14), Li2−Cl4 2.336(14), Li2−N1 2.081(14), B1−N1 1.472(10), B2−N2 1.449(9), B3−N3 1.475(10), B4−N4 1.447(9).

The coordination of the *B*-dialkylamino group to a metal center has previously been observed in the chiral (*S*)-2-(methoxymethyl)pyrrolidine derivative $Li(3,5-Mo_2C_5H_3B-SMP)$,[1b] in the Mg compound $Mg(THF)_2(3,5-Me_2C_5H_3BNMe_2)_2$,[7] and in the Sc complex **11**.[3] In all these complexes, the relevant B−N bonds are lengthened because of the polarization exerted by the positive metal center. The same is true for **14**, where the distances B1−N1 and B3−N3 [1.474 Å (av.)] with coordinated N centers are longer than the distances B2−N2 and B4−N4 [1.448 Å (av.)] with free N centers. The Li−N bond lengths [2.087 Å (av.)] and may be compared with those in $[LiCH_2CH_2CH_2NMe_2]_4$ [2.068 Å (av.)].[23] It may be speculated that complex **11** has a different structural type because of the smaller ionic radius of Sc^{3+},[24] suggesting that increased ligand-ligand repulsions disfavor structures with two facially bonded boratabenzene ligands.

The attempted preparation of an analogous, solvent-free Sm complex gave an intractable brown material. The alternative use of THF as the solvent readily gave the Sm complex **15** as large purple crystals that still contained coordinated LiCl and one equivalent of THF. Unfortunately, the quality of these crystals was not satisfactory for single crystal structure analysis. In the related cyclopentadienyl chemistry, complexes of the type $Cp''_2Ln(\mu-Cl)_2Li(OR_2)_2$ with tetrahedrally coordinated lithium, e.g. $(Me_3SiC_5H_4)_2Y(\mu-Cl)_2Li(THF)_2$ [25a] and $Cp^*_2Yb(\mu-Cl)_2Li(OEt_2)_2$,[25b] are common. Therefore, we guessed that the structure of **15** was similar, but with an extra solvate molecule due to the compensating internal coordination of the NMe_2 group. We then prepared the analogous Y complex **16** with a coordinated THP, in the same way as complex **15** using THP as the solvent. Complex **16** can also be prepared by simply dissolving the stepped ladder complex **12** in THP and subsequent crystallization. The pale yellow crystals of complex **16** displays the expected mononuclear structure, with an internally coordinated NMe_2 sidearm to yttrium (Figure 3). The coordination of the two ring ligands to the metal shows marked differences. The first ring [C11..C15,B1] with the coordinated sidearm is planar [largest deviation 0.029 Å at C11], with a small slip distortion of 0.066 Å and a long B1−N1 bond length [1.466(8) Å], while the second ring [C21..C25,B2] shows the usual folding along the line C21,C25 with a folding angle of 13(1)°, a large slip distortion of 0.163 Å and a short B2−N2 bond length [1.429(8) Å]. The central YCl_2Li ring is folded by 51.7(3)° bringing the Li^+ center into the vicinity of N1, however, the resulting bond Li−N1 [2.189(11) Å] remains relatively long.

Metallocenoids with Bulky *B*-(Amino) Substituents

Sterically demanding *N*-substituents were introduced with the aim to prevent the *B*-NMe_2 sidearm from coordinating to the metal centers. Reactions of the bis(trimethylsilyl)amino derivative Li(**4**) in toluene provided the Sc complex **17**,[3] and the Y and Lu complexes **18** and **19** as mononuclear complexes. The new complexes **18** and **19** crystallize from toluene as yellow rods which contain one equivalent of toluene. The molecular structure of **18** (Figure 4) (in the toluene/containing cocrystal) is essentially the same as that of **17**,[3] a two bladed propeller with crystallographic C_2 symmetry and a relatively short Y−Cl bond coinciding with the two fold symmetry axis. The toluene/containing cocrystal of the Lu complex **19** is isomorphous to that of **18**; for selected data see legend of Figure 4. The bending angles are 138.6° for **18** and 140.5° for **19**, and are close to the value of 140.8° observed for the Sc compound

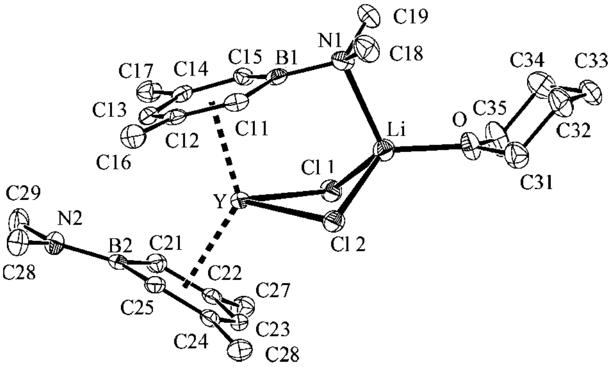


Figure 3. Molecular structure (PLATON plot, see ref.[20], at the 30% probability level) of **16** in the crystal. Selected bond lengths [Å] and bond angles [°]:Y−Cl1 2.6337(17), Y−Cl2 2.6338(17), Y−C1n 2.680(5) for C13 to 2.754(5) for C15, Y−B1 2.832(7), B1−N1 1.466(8), Y−C2n 2.664(5) for C23 to 2.739(5) for C21, Y−B2 2.939(6), B2−N2 1.429(8), Li−Cl1 2.400(10), Li−Cl2 2.371(10), Li−O 1.883(10), Li−N1 2.189(11), Cl1−Y−Cl2 82.00(5), Li−Cl1−Y 80.9(2), Li−Cl2−Y 81.5(2), Cl1−Li−Cl2 92.8(4), angle sum for $BNMe_2$ at N1 344.9° and at N2 360.0°.

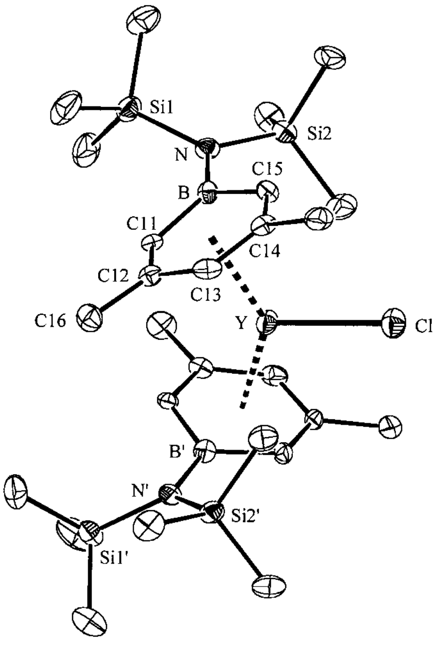


Figure 4. Molecular structure (PLATON plot, see ref.[20], at the 30% probability level) of **18** in the toluene/containing cocrystal and data for **18** and **19**. Selected bond lengths [Å] for **18**: Y−Cl 2.522(2), Y−C1n 2.667(7) for C12 to 2.738(6) for C11, Y−B 2.882(7), B−N 1.493(8), C11−B 1.497(8). C15−B 1.522(9). Selected bond lengths [Å] for **19**: Lu−Cl 2.475(3), Lu−C1n 2.605(9) for C13 to 2.683(8) for C11, Lu−B 2.853(9), B−N 1.464(11), C11−B 1.525(12). C15−B 1.531(11).

17.[3] As discussed recently, the B−N bond length in 1-(dimethylamino)boratabenzene complexes strongly depends on the polarizing influence of the central metal (i.e. primarily on the formal charge of the central metal).[7] The B−N bond lengths in ligand **4** are always relatively long [1.493(8) for **18**, 1.46(1) for **19**, and 1.471(3) Å for **17**]. This indicates weakened B−N π-interactions due to the polarizing influence of the positive Si centers, and presumably also because of the steric repulsion between the borabenzene ring and the close *Si*−Me groups. The large interplanar angles between the C_5B and NSi_2 planes [41.3° for **18**, and 42.2° for **19**] also suggest a rather soft torsional mode around the B−N bond. The fact that even the Y complex **18** is a monomer suggests that ligand **4** provides a more efficient steric protection than the Cp* ligand.

In the following experiments we reduced the size of the substituent at boron and treated $ScCl_3$ with Li(**3**) in a toluene suspension. Thus, we obtained the Sc complex **20** as red crystals. The crystal structure determination of **20** was complicated due to the existence of two modifications. The data of the high-temperature modification **α-20** (Figure 5a and 5b) were collected at −40 °C. The space group of **α-20** was found to be *C*2/*c*; the molecule of **20** possesses crystallographic C_2 symmetry (as in **17**−**19**), but an unusual anisotropic displacement parameter for the Cl atom (perpendicular to the Sc−Cl vector and mainly in the pseudoequatorial plane). This indicates some disorder. This disorder could be due to a large-amplitude vibration for the Sc−Cl bending, or could be a positional disorder of the chlorine atom.

As the temperature is reduced, a reversible phase transition and the formation of twinned crystals of the low-temperature modification **β-20** are observed. The data were collected at −73 °C. The crystal symmetry is now $P\bar{1}$, and the molecular symmetry is reduced to C_1 (Figure 6). The solved structure is less accurate for the low-temperature modification because of the twinning problem. The resulting molecular structure is closely related to those of **18** and **19**.

Attempts to prepare a Y complex analogous to **20** using toluene as the solvent were unsuccessful, only oily materials were obtained. When THF was used as the solvent, complex **21** was readily isolated as yellow crystals, and analogous Sm complex **22** was obtained as purple crystals. The crystals of **21** were of suitable quality to allow a structure determination. The molecular structure of **21** (Figure 7) is related to that of **16**. Since internal coordination of the B−N*i*Pr₂ group is now unfavorable because of the larger size of the dialkylamino group, a second donor molecule is added to the coordination sphere of Li instead, and the central Y(μ-Cl)₂Li core is planar.

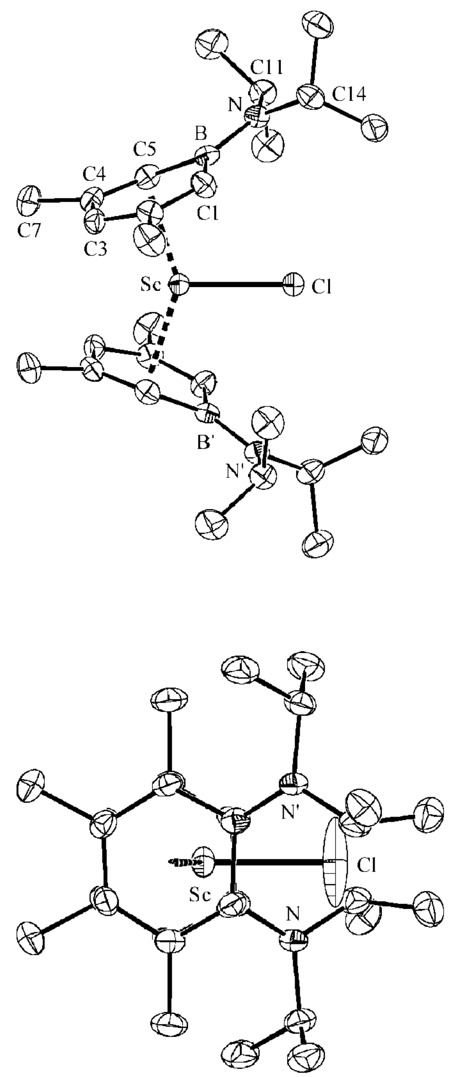


Figure 5. Left: Side-view of the molecular structure (PLATON plot, see ref.[20], at the 30% probability level) of **α-20** in the crystal. Right: Top-view showing the unusual displacement ellipsoid of the Cl atom in the high temperature α-modification. Selected bond lengths [Å] for **α-20**: Sc−Cl 2.377(2), Sc−Cn 2.463(3) for C3 to 2.571(3) for C1, Sc−B 2.756(3), B−N 1.412(4), C1−B 1.542(4). C5−B 1.539(4).

A *B,B′*-Bridged ansa Complex

Finally, we treated $LuCl_3$ with the bis(boratabenzene) salt Li_2(**5**) in THF and obtained the complex (**5**)Lu(μ-Cl)₂Li(THF)₂ (**23**). Crystallization from toluene gave large yellow rods, which according to NMR spectroscopy contained half an equivalent of toluene. The crystals readily lost toluene on standing, thus precluding the characterization by elemental analysis and also the determination of the crystal structure. A completely analogous preparation in THP as the solvent gave the solvate (**5**)Lu(μ-Cl)₂Li(THP)₂ (**24**), this time without the incorporation of toluene. The crystal structure determination proves the presence of an ansa-bridge that contains two nitrogen stereocenters in an approximate C_2-symmetry (Figure 8). In other words, we find the exclusive formation of the racemic form. We also note that the steric constraints of the ansa-bridge do not permit a perfectly eclipsed arrangement of the two boratabenzene rings. The compounds **23** and **24** are the first examples of group 3 ansa complexes with boratabenzene ligands. In group 4 a number of ansa complexes have been synthesized,[8a,8f,8g] and Ashe III et al. have

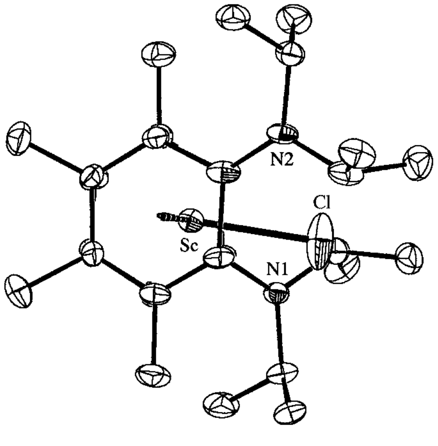


Figure 6. Top-view of the molecule (PLATON plot, see ref.[20], at the 30% probability level) of **β-20** in the crystal. Sc−Cl 2.385(3) Å.

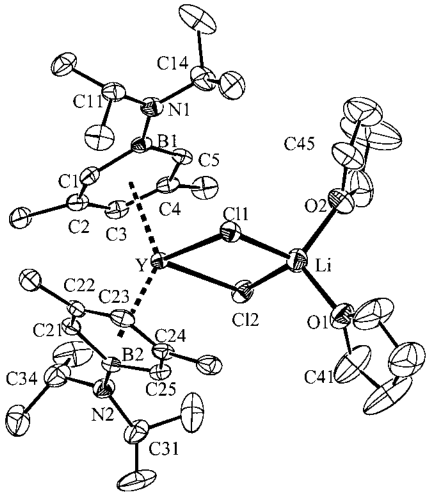


Figure 7. Molecular structure (PLATON plot, see ref.[20], at the 30% probability level) of **21** in the crystal. Selected bond lengths [Å] and bond angles [°]:Y−Cl1 2.628(2), Y−Cl2 2.624(2), Y−Cn 2.683(5) for C3 to 2.782(5) for C5, Y−B1 2.938(5), B1−N1 1.437(6), Y−C2n 2.686(5) for C23 to 2.794(5) for C25, Y−B2 2.912(5), B2−N2 1.445(7), Li−Cl1 2.346(10), Li−Cl2 2.333(11), Li−O1 1.901(11), Li−O2 1.913(11), Cl1−Y−Cl2 84.65(5), Cl1−Li−Cl2 98.2(4), Y−Cl1−Li 88.4(3), Y−Cl2−Li 88.7(3), O1−Li−O2 108.0(5), Cl1−Li−O1 116.5(5), Cl1−Li−O2 110.6(5), Cl2−Li−O1 110.7(5), Cl2−Li−O2 112.9(5).

shown that the exclusive formation of a related *rac*-stereomer is the result of thermodynamic control.[8a]

Conclusions

In this paper we have extended our earlier work on bis(boratabenzene)scandium complexes and have developed a chapter on the systematic synthetic and structural chemistry of 1-aminoboratabenzene complexes of scandium group metals. The ability of the *B*-dimethylamino group to coordinate to Li^+ centers gives rise to unusual structures such as the stepped ladder structures of **12** and **13**, and to the mononuclear complexes **15** and **16**. With larger substituents at boron this ability is suppressed. Both the 1-diisopropylamino ligand **3** and the 1-bis(trimethylsilyl)amino ligand **4** stabilize the coordinatively highly unsaturated mononuclear complexes **17−20**, and both these ligands seem to be more effective in this respect than the pentamethylcyclopentadienyl ligand Cp*. We have also prepared the first group 3 ansa-bridged complexes **23** and **24**.

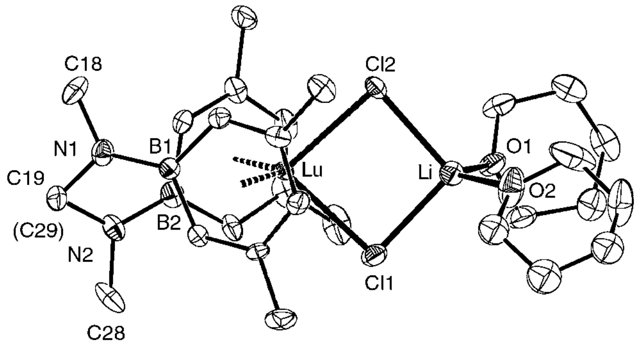


Figure 8. Top-view of the molecular structure (PLATON plot, see ref.[20], at the 30% probability level) of **24** in the crystal. Selected bond lengths [Å] and bond angles [°]:Lu−Cl1 2.579(3), Lu−Cl2 2.583(3), Lu−C1n 2.673(8) for C12 to 2.709(11) for C14, Lu−B1 2.873(12), B1−N1 1.440(15), Lu−C2n 2.671(9) for C23 to 2.702(11) for C21 and C25, Lu−B2 2.857(12), B2−N2 1.424(15), Li−Cl1 2.34(2), Li−Cl2 2.41(2), Li−O1 1.91(2), Li−O2 1.88(3), Cl1−Y−Cl2 85.4(1), Cl1−Li−Cl2 95.0(7), Lu−Cl1−Li 90.6(5), Lu−Cl2−Li 88.7(5), O1−Li−O2 112.5(11), Cl1−Li−O1 111.9(11), Cl1−Li−O2 110.1(9), Cl2−Li−O1 111.9(9), Cl2−Li−O2 114.2(11). The dihedral angle N1−C19−C29−N2 is 73.0(9)°.

In most structures a strong preference for the eclipsed ring-ring conformations with 60° and 180° torsional angles is seen, which is enforced by transannular repulsions between the ring substituents in the 1,3,5-positions. In solution, all molecules are dynamic and display the highest possible effective symmetries in their NMR spectra.

Finally, we note that we still do not have boratabenzene complexes of the larger central metals, such as the early lanthanides, the divalent lanthanides, as well as of Th and U. Furthermore, the reaction chemistry of the bonds in the mouth of the bent sandwich molecules remains essentially untouched. We hope that this paper will stimulate other chemists to pursue these open aspects in the future.

Experimental Section

General: All manipulations were carried out under an inert atmosphere of nitrogen by means of standard Schlenk techniques. Hexane was distilled from Na/K alloy and toluene from sodium; Et_2O, THF, and THP were distilled from sodium benzophenone ketyl. Anhydrous lanthanide trichlorides were purchased from commercial sources and used as received. Elemental analyses were performed by Analytische Laboratorien, D-51779 Lindlar, Germany.

NMR spectra were recorded on a Varian Unity 500 (^1H, 499.6 MHz. ^{13}C, 125.6 MHz; ^{11}B, 160.3 MHz; ^7Li, 194.2 MHz) at ambient temperature. Chemical shifts are given in ppm; they are relative to internal TMS for ^1H and ^{13}C, to external $BF{\cdot}OEt_2$ for ^{11}B, and to external $LiBr/D_2O$ for ^7Li. Electron-impact mass spectra were recorded on a Finnigan MAT-95 at a nominal electron energy of 70 eV.

1-(Diisopropylamino)-5-methyl-3-methylene-1,2,3,6-tetrahydroborinine (7b): A solution of LiBu in hexane (1.6 M, 281 mL, 0.45 mol) was added to a suspension of KOBu*t* (50.5 g, 0.45 mol) in hexane at 0 °C. After the mixture was stirred at room temperature for 3 h, 2,4-dimethylpenta-1,3-diene[26] (21.6 g, 0.225 mol) in hexane (100 mL) was added and the reaction system was heated under reflux for 20 h. A precipitate of the dipotassio- compound was filtered off and washed thoroughly with hot hexane (3 × 500 mL). The solid was then suspended in hexane (250 mL) and was slowly added to a solution of BCl_2NiPr_2 [27] (40.3 g, 0.222 mol) in hexane/THF (4:1, 560 mL) at 0 °C. The mixture was stirred overnight and a white precipitate of KCl was removed by filtration. After removal of all volatiles, **7b** was collected by condensation (80 °C, 10^{-2} mbar) as a colorless liquid (30.3 g, containing 90% **7b**, 0.133 mol, 60%). On standing at room temperature overnight, **7b** solidified to form large needles, which afforded a spectroscopically pure sample of **7b**.

Data for 7b: ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.55$ (br. s, 2 H, 6-H), 1.81 (s, 5-Me), 2.07 (br. s, 2 H, 2-H), 4.63 (m, 1 H, $CH_2=$), 4.66 (m, 1 H, $CH_2=$), 6.01 (m, 4-H), N*i*Pr_2: 1.12 (d, $J = 7.0$ Hz, 2 Me), 1.23 (d, $J = 7.0$ Hz, 2 Me), 3.54 (m, NCH), 3.73 (m, NCH). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): $\delta = 24.0$ and 27.3 (C-2,6), 26.6 (5-Me), 107.9 ($CH_2=$), 126.6 (C-4), 139.9 (C-5), 146.8 (C-3), N*i*Pr_2: 22.5 (Me), 24.0 (Me), 45.7 (NCH), 48.0 (NCH). ^{11}B NMR (160 MHz, $CDCl_3$): $\delta = 44.6$. MS (70 eV): *m/z* (%) = 206 (87) [$M^+ + H$], 190 (100) [$M^+ - Me$], 105 (10) [$M^+ - NiPr_2$], 100 (12) [$NiPr_2^+$]. $C_{13}H_{24}BN$ (205.2): calcd. C 76.11, H 11.79, N 6.83; found C 76.28, H 11.99, N 7.56.

1-[Bis(trimethylsilyl)amino]-5-methyl-3-methylene-1,2,3,6-tetrahydroborinine (7c): A crop of the dipotassio- compound, prepared from KOBu*t* (42.1 g, 0.37 mol), LiBu (1.6 M in hexane, 238 mL, 0.38 mol), and 2,4-dimethylpenta-1,3-diene (17.3 g, 0.18 mol), was suspended in hexane (250 mL). The suspension was added to a solution of $BCl_2N(SiMe_3)_2$ [28] (42.1 g, 0.17 mol) in hexane/THF (4:1, 450 mL) at 0 °C. Workup as described for **7b** gave, after condensation (140 °C, 10^{-2} mbar), a colorless liquid of **7c** together with some impurities (12.1 g, containing ca. 82% **7c**, 0.037 mol, 22%).

Data for 7c: ^1H NMR (500 MHz, $CDCl_3$): $\delta = 0.25$ (s, 2 $SiMe_3$), 1.82 (s, 5-Me), 1.65 (br. s, 2 H, 6-H), 2.06 (br. s, 2 H, 2-H), 4.60 (m, 1 H, $CH_2=$), 4.70 (m, 1 H, $CH_2=$), 6.00 (m, 4-H) − $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): $\delta = 4.4$ ($SiMe_3$), 26.6 (5-Me), 30.7 and 33.8 (C-2,6), 108.7 ($CH_2=$), 126.9 (C-4), 138.7 (C-5), 146.2 (C-3). ^{11}B NMR (160 MHz, $CDCl_3$): $\delta = 57.9$. MS (70 eV): *m/z* (%) = 265 (47) [M^+], 250 (100) [$M^+ - Me$], 146 (40) [$Si_2Me_6^+$], 73 (79) [$SiMe_3^+$].

Lithium 1-(Diisopropylamino)-3,5-dimethylboratabenzene [Li(3)]: A solution of $LiN(SiMe_3)_2$ in hexane (1.0 M, 20 mL, 20 mmol) was added dropwise to a solution of 1-(diisopropylamino)-5-methyl-3-methylene-1,2,3,6-tetrahydroborinine (**7b**) (4.10 g, 20 mmol) in ether (35 mL) at −78 °C. The mixture was kept at this temperature for 2 h, and was then allowed to warm to ambient temperature. A fine white precipitate gradually formed in the reaction system. After the suspension was stirred for 7 days, the solid was collected by filtration through a frit, washed with hexane (3 ′ 20 mL), and dried overnight under high vacuum to give Li(**3**) as an air- and moisture-sensitive, white powder (3.21 g, 76%).

Data for Li(3): ^1H NMR (500 MHz, [D_8]THF): $\delta = 2.03$ (s, 6 H, 3-/5-Me), 5.15 (s, 4-H), 5.30 (s, 2-/6-H), N*i*Pr_2: 1.15 (d, $J = 7.0$ Hz, 4 Me), 3.66 (sept, $J = 7.0$ Hz, 2 NCH). $^{13}C\{^1H\}$ NMR (126 MHz, [D_8]THF): $\delta = 26.0$ (3-/5-Me), 100.2 (C-4), 110.9 (br, C-2,6), 142.3 (C-3,5), N*i*Pr_2: 23.2 (Me), 46.1 (NCH). ^{11}B NMR (160 MHz, [D_8]THF): $\delta = 30.5$.

TMEDA Solvate Li(TMEDA)(3): The lithium salt Li(**3**) (0.59 g, 2.80 mmol) was added to a solution of TMEDA (0.32 g, 2.80 mmol) in hexane (30 mL). The solution was filtered through a frit to remove some insoluble material and kept at −30 °C overnight to give Li(TMEDA)(**3**) (0.80 g, 87%) as moisture- and air-sensitive colorless rods.

Data for Li(TMEDA)(3): ^1H NMR (500 MHz, C_6D_6): $\delta = 2.34$ (s, 3-/5-Me), 5.53 (s, 4-H), 5.81 (s, 2-/6-H), N*i*Pr_2: 1.46 (d, $J = 6.7$ Hz, 4 Me), 3.93 (sept, $J = 6.7$ Hz, 2 NCH), TMEDA: 1.45 (s, 2 NCH_2), 1.73 (s, 2 NMe_2). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): $\delta = 26.5$ (3-/5-Me), 100.4 (C-4), 110.9 (br, C-2,6), 142.4 (C-3,5), N*i*Pr_2: 23.4 (Me), 46.2 (NCH), TMEDA: 45.1 (NMe_2), 55.8 (NCH_2). ^{11}B NMR (160 MHz, C_6D_6): $\delta = 31.4$. $C_{19}H_{39}BLiN_3$ (327.3): calcd. C 69.73, H 12.01, N 12.84; found C 69.73, H 11.86, N 13.03.

1,1′-(*N,N*′-Dimethylethylenediamino)bis(3,5-dimethyldihydroborinines) 10: A mixture of *N,N*′-dimethylethylenediamine (0.99 g, 11.2 mmol) and triethylamine (2.28 g, 22.5 mmol) was added dropwise to a solution of 1-chloro-3,5-dimethyldihydroborinines[3] (3.15 g, 22.4 mmol) in hexane (25 mL) at 0 °C. The reaction mixture was stirred at ambient temperature for 6 h. A white precipitate, presumed to be $NHEt_3Cl$, was removed by filtration and washed with hexane (3 × 20 mL). The combined filtrate was evaporated to dryness under vacuum to give a pale yellow solid of **10** (2.19 g, 66%) as a mixture of isomers.

Lithium 1,1′-(*N,N*′-Dimethylethylenediamino)bis(3,5-dimethylboratabenzene) [Li_2(5)]: A solution of $LiN(SiMe_3)_2$ in hexane (1.0 M, 14.2 mL, 14.2 mmol) was added dropwise to a solution of the dihydroborinines **10** (2.10 g, 7.09 mmol) in ether (10 mL) at −78 °C. The mixture was allowed to warm to ambient temperature and a white precipitate formed. After the suspension was stirred for 1 day, the solid was collected by filtration through a frit, washed with hexane (3 ′ 10 mL), and dried overnight under high vacuum to give Li_2(**5**) as an extremely air- and moisture- sensitive white powder (1.90 g, 87%).

Data for Li_2(5): ^1H NMR (500 MHz, [D_6]DMSO): $\delta = 1.93$ (s, 3-/3′-/5-/5′-Me), 2.66 (s, 2 NMe), 2.90 (s, 2 NCH_2), 4.89 (s, 4-/4′-H), 4.94 (s, 2-/2′-/6-/6′-H). $^{13}C\{^1H\}$ NMR (126 MHz, [D_6]DMSO): $\delta =$ 26.5 (3-/3′-/5-/5′-Me), 37.9 (NMe), 50.7 (NCH_2), 102.7 (C-4,4′), 108.7 (br, C-2,2′,6,6′), 139.4 (C-3,3′,5,5′). ^{11}B NMR (160 MHz, [D_6]DMSO): $\delta = 32.4$.

Complex [$(3,5\text{-}Me_2C_5H_3BNMe_2)_2Y(\mu\text{-}Cl)_2Li]_2$ (12): A suspension of YCl_3 (2.52 g, 12.9 mmol) and $Li(3,5\text{-}Me_2C_5H_3BNMe_2)$ [Li(**2**)] (4.13 g, 26.6 mmol) in toluene (60 mL) was stirred at 110 °C for 3 days. An insoluble material, presumed to be LiCl, was filtered off and washed with toluene (20 mL). The combined yellow filtrate was concentrated to ca. 10 mL and kept at room temperature overnight to give **12** as air- and moisture-sensitive, pale yellow platelets. Crystallization of the concentrated mother liquor afforded a second crop of **12** (total: 3.44 g, 64%).

Data for 12: ^1H NMR (500 MHz, C_6D_6): $\delta = 2.24$ (s, 3-/5-Me), 2.79 (s, NMe_2), 5.76 (s, 2-/6-H), 5.85 (s, 4-H). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): $\delta = 26.9$ (3-/5-Me), 40.1 (NMe_2), 107.9 (C-4), 115.5 (br, C-2,6), 153.7 (C-3,5). ^{11}B NMR (160 MHz, C_6D_6): $\delta = 37.3$. ^7Li NMR (194 MHz, C_6D_6): $\delta = 0.22$. $C_{36}H_{60}B_4Cl_4Li_2N_4Y_2$ (925.7): calcd. C 46.71, H 6.53, N 6.05; found C 47.41, H 6.61, N 6.27.

Complex [$(3,5\text{-}Me_2C_5H_3BNMe_2)_2Lu(\mu\text{-}Cl)_2Li]_2$ (13): Treatment of $LuCl_3$ (465 mg, 1.65 mmol) with $Li(3,5\text{-}Me_2C_5H_3BNMe_2)$ [Li(**2**)] (531 mg, 3.42 mmol), as described for **12,** produced **13**. After crystallization from toluene (ca. 5 mL) at ambient temperature, air- and moisture-sensitive, pale yellow platelets were obtained (770 mg, 85%).

Data for 13: ^{1}H NMR (500 MHz, C_6D_6): δ = 2.29 (s, 3-/5-Me), 2.77 (s, NMe_2), 5.67 (s, 2-/6-H), 5.85 (s, 4-H). $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): δ = 27.0 (3-/5-Me), 40.0 (NMe_2), 107.2 (C-4), 113.8 (br, C-2,6), 153.6 (C-3,5). ^{11}B NMR (160 MHz, C_6D_6): δ = 37.0. ^{7}Li NMR (194 MHz, C_6D_6): δ = 0.19. $C_{36}H_{60}B_4Cl_4Li_2Lu_2N_4$ (1097.8): calcd. C 39.39, H 5.51, N 5.10; found C 39.62, H 5.55, N 5.28.

Complex $Y(acac)(3,5\text{-}Me_2C_5H_3BNMe_2)_2$ (14): Sodium acetylacetonate[29] (114 mg, 0.94 mmol) was added to a yellow solution of $[(3,5\text{-}Me_2C_5H_3BNMe_2)_2YCl(LiCl)]_2$ (**12**) (423 mg, 0.46 mmol) in toluene (15 mL). The reaction mixture was stirred at ambient temperature overnight. An insoluble material, presumed to be a mixture of LiCl and NaCl, was removed by filtration and washed with toluene (5 mL). The combined filtrate was concentrated to ca. 5 mL under vacuum. Large yellow crystals of **14** formed after the liquid was stored at −30 °C for 2 days. Crystallization of the concentrated mother liquor afforded a second crop of **14** (total: 282 mg, 64%), as air- and water-sensitive crystals.

Data for 14: ^{1}H NMR (500 MHz, C_6D_6): δ = 2.05 (s, 2 3-/5-Me), 2.92 (s, 2 NMe_2), 5.52 (t, *J* = 1.8 Hz, 2 4-H), 5.67 (d, *J* = 1.8 Hz, 2 2-/6-H), acac: 1.67 (s, 2 Me), 5.15 (s, CH). $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): δ = 25.8 (3-/5-Me), 39.1 (NMe_2), 105.1 (C-4), 112.3 (br, C-2,6), 152.0 (C-3,5), acac: 27.2 (C-1,5), 102.2 (C-3), 191.1 (C-2,4). ^{11}B NMR (160 MHz, C_6D_6): δ = 33.4. MS (70 eV): *m/z* (%) = 484 (8) [M^+], 385 (<1) [M^+ − acac], 336 (37) [M^+ − $Me_2C_5H_3BNMe_2$], 149 (100) [$Me_2C_5H_3BNMe_2^+$], 134 (28) [149^+ − Me]. $C_{23}H_{37}B_2N_2O_2Y$ (485.1): calcd. C 57.07, H 7.70, N 5.79; found C 56.69, H 8.08, N 5.78.

Complex $(3,5\text{-}Me_2C_5H_3BNMe_2)_2Sm(\mu\text{-}Cl)_2Li(THF)$ (15): $SmCl_3$ (277 mg, 1.08 mmol) was added, with stirring, to a solution of $Li(3,5\text{-}Me_2C_5H_3BNMe_2)$ [Li(**2**)] (343 mg, 2.21 mmol) in THF (20 mL). The reaction mixture was stirred at ambient temperature for 8 h to give a purple solution. The THF was evaporated under reduced pressure, and toluene (10 mL) was then added to the residue. The resulting mixture was stirred vigorously for 1 h. An insoluble material was removed by filtration and washed with toluene (5 mL). The combined filtrate was concentrated to ca. 5 mL and stored at 4 °C to give **15** as moisture-sensitive, purple crystals (397 mg, 62%).

Data for 15: ^{1}H NMR (500 MHz, C_6D_6): δ = 0.61 (br. s, 12 H, 3-/5-Me), 3.68 (br. s, 2 NMe_2), 6.50 (br. s, 2 2-/6-H), 15.84 (br. s, 2 4-H), THF: 1.64 (br, CH_2CH_2), 4.28 (br, 2 OCH_2). $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): δ = 27.1 (3-/5-Me), 41.0 (NMe_2), 99.3 (br, C-4), 103.8 (br, C-2,6), 159.2 (C-3,5), THF: 25.6 (CH_2CH_2), 69.4 (OCH_2). ^{11}B NMR (160 MHz): δ = 46.2. ^{7}Li NMR (194 MHz, C_6D_6): δ = 6.51. $C_{22}H_{38}B_2Cl_2LiN_2OSm$ (596.4): calcd. C 44.30, H 6.42; found C 44.20, H 6.05.

Complex $(3,5\text{-}Me_2C_5H_3BNMe_2)_2Y(\mu\text{-}Cl)_2Li(THP)$ (16). − Method 1: Treatment of YCl_3 (239 mg, 1.23 mmol) with $Li(3,5\text{-}Me_2C_5H_3BNMe_2)$ [Li(**2**)] (384 mg, 2.48 mmol) in THP (20 mL), as described for **15**, gave **16**. After crystallization from toluene (ca. 5 mL) at ambient temperature, air- and moisture-sensitive, pale yellow crystals were obtained (371 mg, 55%). **Method 2:** Crystallization of $[(3,5\text{-}Me_2C_5H_3BNMe_2)_2YCl(LiCl)]_2$ (**12**) (565 mg, 0.61 mmol) from THP (8 mL) at ambient temperature gave **16** as pale yellow crystals (556 mg, 83%).

Data for 16: ^{1}H NMR (500 MHz, C_6D_6): δ = 2.31 (s, 2 3-/5-Me), 2.81 (s, 2 NMe_2), 5.86 (s, 2 2-/6-H), 6.06 (s, 2 4-H), THP: 1.08 (br, 2 H, $OCH_2CH_2\mathit{CH_2}$), 1.18 (br, 4 H, $OCH_2\mathit{CH_2}$), 3.42 (t, 4 H, OCH_2). $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): δ = 26.7 (3-/5-Me), 39.5 (NMe_2), 108.5 (C-4), 117.1 (br, C-2,6), 151.6 (C-3,5), THP: 22.8 ($OCH_2CH_2\mathit{CH_2}$), 26.0 ($OCH_2\mathit{CH_2}$), 69.5 ($O\mathit{CH_2}$). ^{11}B NMR (160 MHz, C_6D_6): δ = 34.9. ^{7}Li NMR (194 MHz, C_6D_6): δ = −0.20. $C_{18}H_{30}B_2Cl_2LiN_2Y(C_5H_{10}O)_{0.8}$ (531.7): calcd. C 49.69, H 7.20, N 5.27; found C 49.73, H 7.15, N 5.31.

Complex $YCl[3,5\text{-}Me_2C_5H_3BN(SiMe_3)_2]_2$ (18): Treatment of YCl_3 (218 mg, 1.12 mmol) with $Li[3,5\text{-}Me_2C_5H_3BN(SiMe_3)_2]$ [Li(**4**)] (613 mg, 2.26 mmol) in toluene (15 mL), as described for **12**, gave **18**·(PhMe). After crystallization at −30 °C, air- and moisture-sensitive, yellow crystals were obtained (571 mg, 78%), which seem to easily lose part of the cocrystallized toluene.

Data for 18: ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 0.19 [s, $N(SiMe_3)_2$], 2.36 (s, 3-/5-Me), 5.82 (br, 4-H), 6.06 (d, *J* = 1.2 Hz, 2-/6-H). $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2): δ = 4.4 ($SiMe_3$), 27.1 (3-/5-Me), 112.1 (C-4), 129.3 (br, C-2,6), 154.1 (C-3,5). $^{11}B\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2): δ = 39.2. $C_{26}H_{54}B_2ClN_2Si_4Y(C_7H_8)_{0.5}$ (699.1): calcd. C 50.68, H 8.36, N 4.01; found C 50.30, H 8.11, N 3.81.

Complex $LuCl[3,5\text{-}Me_2C_5H_3BN(SiMe_3)_2]_2$ (19): Treatment of $LuCl_3$ (364 mg, 1.29 mmol) with $Li[3,5\text{-}Me_2C_5H_3BN(SiMe_3)_2]$ [Li(**4**)] (729 mg, 2.69 mmol) in toluene (20 mL), as described for **12**, afforded **19**·(PhMe). After crystallization at −30 °C, air- and moisture-sensitive, yellow rods were obtained (686 mg, 72%), which seem to easily lose part of the cocrystallized toluene.

Data for 19: ^{1}H NMR (500 MHz, C_6D_6): δ = 0.37 [s, $N(SiMe_3)_2$], 2.33 (s, 3-/5-Me), 5.52 (br, 4-H), 6.19 (br, 2-/6-H). $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): δ = 4.6 ($SiMe_3$), 27.1 (3-/5-Me), 108.6 (C-4), 110.4 (br, C-2,6), 157.0 (C-3,5). ^{11}B NMR (160 MHz, C_6D_6): δ = 38.9. $C_{26}H_{54}B_2ClLuN_2Si_4\ (C_7H_8)_{0.5}$ (785.2): calcd. C 45.13, H 7.45, N 3.57; found C 44.87, H 7.30, N 3.76.

Complex $ScCl(3,5\text{-}Me_2C_5H_3BN\mathit{i}Pr_2)_2$ (20): Treatment of $ScCl_3$ (192 mg, 1.27 mmol) with $Li(3,5\text{-}Me_2C_5H_3BN\mathit{i}Pr_2)$ [Li(**3**)] (543 mg, 2.57 mmol) in toluene (20 mL), as described for **12,** afforded **20**. After crystallization at −30 °C, air- and moisture-sensitive, red crystals were obtained (391 mg, 63%).

Data for 20: ^{1}H NMR (500 MHz, $C_6D_5CD_3$): δ = 1.95 (s, 3-/5-Me), 5.56 (br. s, 2-/6-H), 5.61 (t, *J* = 1.7 Hz, 4-H), $N\mathit{i}Pr_2$: 1.26 (br, 4 Me), 3.78 (br, 2 NCH). $^{13}C\{^{1}H\}$ NMR (126 MHz, $C_6D_5CD_3$): δ = 26.5 (3-/5-Me), 109.1 (C-4), 117.7 (br, C-2,6), 152.4 (C-3,5), $N\mathit{i}Pr_2$: 23.2 (Me), 46.5 (NCH). ^{11}B NMR (160 MHz, $C_6D_5CD_3$): δ = 34.7. MS (70 eV): *m/z* (%) = 488 (3) [M^+], 473 (4) [M^+ − Me], 453 (<1) [M^+ − Cl], 284 (3) [M^+ − $Me_2C_5H_3BN\mathit{i}Pr_2$], 205 (25) [$C_{13}H_{24}BN^+$], 190 (100) [$C_{13}H_{24}BN^+$ − Me]. $C_{26}H_{46}B_2ClN_2Sc$ (488.7): calcd. C 63.90, H 9.49, N 5.73; found C 63.65, H 9.66, N 5.66.

Complex $(3,5\text{-}Me_2C_5H_3BN\mathit{i}Pr_2)_2Y(\mu\text{-}Cl)_2Li(THF)_2$ (21): Treatment of YCl_3 (206 mg, 1.05 mmol) with $Li(3,5\text{-}Me_2C_5H_3BN\mathit{i}Pr_2)$ [Li(**3**)] (452 mg, 2.14 mmol) in THF (20 mL), as described for **15**, afforded **21**. After crystallization at −30 °C, air- and moisture-sensitive, yellow rods were obtained (399 mg, 64%).

Data for 21: ^{1}H NMR (500 MHz, C_6D_6): δ = 2.40 (s, 2 3-/5-Me), 5.74 (s, 2 4-H), 5.92 (s, 2 2-/6-H), $N\mathit{i}Pr_2$: 1.43 (d, 8 Me), 3.94 (br, 4 NCH), THF: 1.34 (br, 2 CH_2CH_2), 3.58 (br, 4 OCH_2). $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): δ = 27.4 (3-/5-Me), 104.5 (C-4), 117.5 (br, C-2,6), 151.7 (C-3,5), $N\mathit{i}Pr_2$: 23.4 (*i*Pr-Me), 46.4 (NCH), THF: 25.4 (CH_2CH_2), 68.4 (OCH_2). ^{11}B NMR (160 MHz, C_6D_6): δ = 34.0. ^{7}Li NMR (194 MHz, C_6D_6): δ = −0.33. $C_{34}H_{62}B_2Cl_2Li$-

N_2O_2Y (719.3): calcd. C 56.78, H 8.69, N 3.90; found C 57.14, H 8.91, N 3.95.

Complex ($3,5$-$Me_2C_5H_3BN$*i*Pr_2)$_2$Sm(μ-Cl)$_2$Li(THF)$_2$ (22): Treatment of $SmCl_3$ (286 mg, 1.11 mmol) with Li($3,5$-$Me_2C_5H_3BN$*i*Pr_2) [Li(**3**)] (490 mg, 2.32 mmol) in THF (20 mL), as described for **15**, afforded **22**. After crystallization at 4 °C, air- and moisture-sensitive, purple rods were obtained (428 mg, 65%).

Data for 22: ^{1}H NMR (500 MHz, C_6D_6): δ = 2.35 (br. s, 2 3-/5-Me), 7.06 (br. s, 2 2-/6-H), 12.09 (br. s, 2 4-H), N*i*Pr_2: 1.0(br, 8 Me), 3.71 (br. s, 4 NCH), THF: 1.57 (br, 2 CH_2CH_2), 3.89 (br, 4 OCH_2). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ = 29.1 (3-/5-Me), 96.0 (C-4), 106.6 (br, C-2,6), 159.1 (C-3,5), N*i*Pr_2: 22.8 (Me), 46.5 (NCH), THF: 25.6 (CH_2CH_2), 68.72 (OCH_2). ^{11}B NMR (160 MHz, C_6D_6): δ = 37.8. ^{7}Li NMR (194 MHz, C_6D_6): δ = 1.59. $C_{26}H_{46}B_2Cl_2LiN_2Sm(C_4H_8O)_{1.5}$ (744.7): calcd. C 51.61, H 7.85, N 3.76; found C 51.70, H 7.66, N 4.60.

Complex [($3,5$-$Me_2C_5H_3BNMeCH_2$)$_2$]Lu(μ-Cl)$_2$Li(THF)$_2$ (23): Treatment of $LuCl_3$ (437 mg, 1.54 mmol) with Li_2[($3,5$-$Me_2C_5H_3BNMeCH_2$)$_2$] [Li_2(**5**)] (510 mg, 1.66 mmol) in THF (20 mL), as described for **15**, afforded **23**. After crystallization at ambient temperature, air- and moisture-sensitive, large yellow rods were obtained (689 mg, 65%).

Data for 23: ^{1}H NMR (500 MHz, C_6D_6): δ = 2.45 and 2.48 (s, 2 3-/5-Me), 5.19, 5.78, 6.02 (s, 2H each, 2-/4-/6-H), ansa-bridge: 2.76 and 4.18 (m, 2H each, NCH_2CH_2N), 3.08 (s, 2 NMe), THF: 1.32 (br, 2 CH_2CH_2), 3.52 (br, 4 OCH_2). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ = 27.3 and 27.8 (3-/5-Me), 107.9 (C-4), 104.8 and 112.6 (br, C-2,6), 150.8 and 155.7 (C-3,5), ansa-bridge: 37.7 (NMe), 50.7 (NCH_2), THF: 25.4 (CH_2CH_2), 68.4 (OCH_2). ^{11}B NMR (160 MHz, C_6D_6): δ = 34.8. ^{7}Li NMR (194 MHz, C_6D_6): δ = −0.43.

Complex [($3,5$-$Me_2C_5H_3BNMeCH_2$)$_2$]Lu(μ-Cl)$_2$Li(THP)$_2$ (24): Treatment of $LuCl_3$ (266 mg, 0.95 mmol) with Li_2[($3,5$-$Me_2C_5H_3BNMeCH_2$)$_2$] [Li_2(**5**)] (307 mg, 1.00 mmol) in THP (15 mL) afforded large yellow rods of **24** (478 mg, 70%).

Data for 24: ^{1}H NMR (500 MHz, C_6D_6): δ = 2.45 and 2.52 (s, 2 3-/5-Me), 5.20, 5.84, 6.02 (s, 2H each, 2-/4-/6-H), ansa-bridge: 2.75 and 4.18 (m, 2 H each, NCH_2CH_2N), 3.09 (s, 2 NMe), THP: 1.23 (br, 2 $OCH_2CH_2CH_2$), 1.24 (br, 4 OCH_2CH_2), 3.47 (br, 4 OCH_2). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ = 27.3 and 27.9 (3-/5-Me), 107.9 (C-4), 104.8 and 112.5 (br, C-2,6), 150.8 and 155.9 (C-3,5), ansa-bridge: 37.7 (NMe), 50.7 (NCH_2), THP: 23.1 ($OCH_2CH_2CH_2$), 26.3 (OCH_2CH_2), 69.0 (OCH_2). ^{11}B NMR (160 MHz, C_6D_6): δ = 34.8. ^{7}Li NMR (194 MHz, C_6D_6): δ = −0.62. $C_{28}H_{48}B_2Cl_2LiLuN_2O_2$ (719.1): calcd. C 46.77, H 6.73, N 3.90; found C 46.73, H 6.84, N 4.05.

X-ray Crystal Structure Determinations: Diffraction intensity data were collected on ENRAF-Nonius CAD4 diffractometers equipped with graphite monochromators. Crystal data, data collec-

Table 2. Crystal data, data collection parameters, and convergence results for **12**, **14**, **16**, **18**·(PhMe) and **19**·(PhMe)

	12	**14**	**16**	**18**·PhMe	**19**·PhMe
Empirical formula	$C_{36}H_{60}B_4Cl_4Li_2N_4Y_2$	$C_{23}H_{37}B_2N_2O_2Y$	$C_{23}H_{40}B_2Cl_2LiN_2OY$	$C_{33}H_{62}B_2ClN_2Si_4Y$	$C_{33}H_{62}B_2ClLuN_2Si_4$
Molecular mass	925.65	484.09	548.96	745.20	831.25
Crystal system	Triclinic	triclinic	triclinic	orthorhombic	orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_12_12$	$P2_12_12$
Radiation (λ [Å])	Mo-K_α (0.71073)	Mo-K_α (0.71073)	Mo-K_α (0.71073)	Mo-K_α (0.71073)	Mo-K_α (0.71073)
a [Å]	12.149(2)	8.6551(5)	8.139(2)	13.042(2)	12.999(5)
b [Å]	13.526(2)	10.603(4)	11.013(3)	18.451(6)	18.468(7)
c [Å]	14.736(8)	14.21(1)	15.890(5)	8.548(3)	8.550(4)
α [deg]	101.56(2)	84.93(6)	77.80(2)		
β [deg]	90.44(2)	81.08(6)	83.70(3)		
γ [deg]	107.82(1)	78.45(4)	80.97(2)		
V [Å^3]	2252(2)	1260(2)	1370.5(8)	2057(2)	2052.5(15)
Z	2	2	2	2.00	2.00
$d_{calcd.}$ [g/cm^3]	1.36	1.28	1.33	1.20	1.35
F(000)	952	508	572	792	856
μ [cm^{-1}]	28.47	23.47	23.53	16.28	26.15
Absorption correction	Numerical	empirical	empirical	numerical	numerical
Max./min. transmission	0.609/0.409	0.999/0.749	0.999/0.599	0.556/0.410	0.565/0.413
θ range [deg]	3.2−27.0	3.0−26.0	3.0−27.0	3.1−27.0	3.1−25.5
Temperature [K]	213	223	213	213	223
Scan mode	ω−2θ	ω	ω−2θ	ω−2θ	ω
Crystal size [mm]	0.34 × 0.30 × 0.18	0.30 × 0.25 × 0.20	0.64 × 0.47 × 0.45	0.56 × 0.24 × 0.22	0.61 × 0.49 × 0.29
Reflections collected	18652	5390	9507	6957	4843
Reflections unique	9811	4929	5957	4482	3803
Reflections observed	3695	2551	3720	2007	2640
Criterion for observation	$I > 2\ \sigma(I)$	$I > 2\ \sigma(I)$	$I > 2\ \sigma(I)$	$I > 2\ \sigma(I)$	$I > 2\ \sigma(I)$
Variables	485	281	297	206	206
R_1 [a], observed (all data)	0.064 (0.190)	0.079 (0.179)	0.067(0.118)	0.070 (0.182)	0.046 (0.079)
wR_2[b], observed (all data)	0.093 (0.115)	0.129 (0.152)	0.136(0.148)	0.082 (0.102)	0.090 (0.100)
GOF[c]	0.771	0.914	0.967	0.844	0.987
Max. resd. density [e/Å^3]	0.73	0.52	1.16	0.33	0.97

[a] $R_1 = \|F_o| - |F_c\|/|F_o|$. − [b] $wR_2 = [w(F_o^2 - F_c^2)^2/w(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2]$ and $P = [\max(F_o^2,0) + 2F_c^2]/3$. − [c] GOF = $[w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$.

Table 3. Crystal data, data collection parameters, and convergence results for **α-20**, **β-20**, **21**, and **24**

	α-20	**β-20**	**21**	**24**
Empirical formula	$C_{26}H_{46}B_2ClN_2Sc$	$C_{26}H_{46}B_2ClN_2Sc$	$C_{34}H_{62}B_2Cl_2LiN_2O_2Y$	$C_{28}H_{48}B_2Cl_2LiLuN_2O_2$
Molecular mass	488.70	488.70	719.26	719.11
Crystal system	Monoclinic	triclinic	triclinic	orthorhombic
Space group	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$
Radiation (λ [Å])	Mo-K_α (0.71073)	Cu-K_α (1.54056)	Mo-K_α (0.71073)	Mo-K_α (0.71073)
a [Å]	10.247(1)	8.264(2)	11.784(5)	9.353(3)
b [Å]	13.083(3)	8.308(2)	13.481(2)	12.582(7)
c [Å]	21.883(5)	21.83(1)	15.312(3)	27.855(6)
α [deg]		96.78(4)	64.34(2)	
β [deg]	102.91(1)	98.83(5)	88.79(2)	
γ [deg]		103.62(2)	68.13(2)	
V [Å^3]	2859(2)	1421(1)	2006.0(10)	3278(2)
Z	4	2	2	4.00
$d_{\text{calcd.}}$ [g/cm^3]	1.13	1.14	1.19	1.46
F(000)	1056	528	764	1456
μ [cm^{-1}]	3.65	32.30	16.24	32.01
Absorption correction	not applied	empirical	empirical	numerical
Max./min. transmission		0.998/0.919	0.999/0.739	0.379/0.282
θ range [deg]	3.1−27.0	4.1−74.8	3.1−26.0	3.1−27.0
Temperature [K]	233	200	213	223
Scan mode	ω−2θ	ω	ω−2θ	ω−2θ
Crystal size [mm]	0.50 × 0.45 × 0.40	0.35 × 0.30 × 0.20	0.62 × 0.30 × 0.23	0.49 × 0.42 × 0.41
Reflections collected	10680	10125	11051	10006
Reflections unique	3123	5854	7851	6896
Reflections observed	1293	2126	4729	5590
Criterion for observation	$I > 2\,\sigma(I)$	$I > 2\,\sigma(I)$	$I > 2\,\sigma(I)$	$I > 2\,\sigma(I)$
Variables	238	299	409	342
R_1 [a], observed (all data)	0.051 (0.137)	0.140 (0.226)	0.067 (0.128)	0.051 (0.075)
wR_2 [b], observed (all data)	0.092 (0.105)	0.312 (0.354)	0.137 (0.154)	0.120 (0.131)
GOF[c]	0.746	0.907	0.926	1.056
Max. resd. density [e/Å^3]	0.60	1.89	0.61	1.62

[a] $R_1 = \|F_o| - |F_c\|/|F_o|$. − [b] $wR_2 = [w(F_o^2 - F_c^2)^2/w(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2]$ and $P = [\max(F_o^2,0) + 2F_c^2]/3$. − [c] GOF = $[w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$.

tion parameters, and convergence results are listed in Tables 2 and 3. Before averaging over symmetry-related reflections, numerical[30] or empirical absorption[31] corrections were applied to the data sets with absorption coefficients (μ) larger than 10 cm^{-1}. Structures were solved by direct methods with the help of the SHELXS-97 program[32] and refined on reflection intensities (F^2) using the SHELXL-97 program.[33] In the final least-squares refinements, all non-hydrogen atoms were assigned anisotropic displacement parameters. In the case of **α-20**, the hydrogen atoms were refined isotropically. For all other structures, hydrogen atoms were included as riding with fixed displacement parameters [C−H = 0.98 Å, U_{iso}(H) = 1.3 U_{eq}(C)].

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-166215 (**12**), CCDC-166216 (**14**), CCDC-166217 (**16**), CCDC-166218 (**18**·PhMe), CCDC-166219 (**19**·PhMe), CCDC-166220 (**α-20**), CCDC-166221 (**β-20**), CCDC-166222 (**21**), and CCDC-166223 (**24**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44 (0)1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We thank Dr. A. Fischer and Dr. J. Ni for helpful advice regarding the synthesis of Li_2(**5**) and Dr. U. Englert concerning the X-ray structure determinations. This work was generously supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

---

[1] [1a] X. Zheng, G. E. Herberich, *Eur. J. Inorg. Chem.* **2001**, 3013−3019; [1b] X. Zheng, G. E. Herberich, *Organometallics*, **2001**, *20*, 3097−3100.

[2] [2a] G. C. Fu, *Adv. Organomet. Chem.* **2001**, *47*, 101−119; [2b] A. J. Ashe III, S. Al-Ahmad, X. Fang, *J. Organomet. Chem.* **1999**, *581*, 92−97; [2c] G. E. Herberich, *Boratabenzene Chemistry Revisited*, in *Advances in Boron Chemistry* (Ed.: W. Siebert), The Royal Society of Chemistry: Cambridge, U. K., **1997**; Special Publication No. 201, p. 211−223; [2d] G. E. Herberich in *Comprehensive Organometallic Chemistry II* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon Press, Oxford, **1995**, Vol. 1 (Volume ed.: C. E. Housecraft), p. 197−216; [2e] G. E. Herberich, H. Ohst, *Adv. Organomet. Chem.* **1986**, *25*, 199−236.

[3] G. E. Herberich, U. Englert, A. Fischer, J. Ni, A. Schmitz, *Organometallics* **1999**, *18*, 5496−5501.

[4] [4a] S. Qiao, D. A. Hoic, G. C. Fu, *J. Am. Chem. Soc.* **1996**,

118, 6329−6330; [4b] D. A. Hoic, J. R. Wolf, W. M. Davis, G. C. Fu, *Organometallics* **1996**, *15*, 1315−1318.

[5] M. A. Putzer, J. S. Rogers, G. C. Bazan, *J. Am. Chem. Soc.* **1999**, *121*, 8112−8113.

[6] X. Zheng, B. Wang, U. Englert, G. E. Herberich, *Inorg. Chem.* **2001**, *40*, 3117−3123.

[7] X. Zheng, U. Englert, G. E. Herberich, J. Rosenplänter, *Inorg. Chem.* **2000**, *39*, 5579−5585.

[8] [8a] A. J. Ashe III, S. Al-Ahmad, X. Fang, J. W. Kampf, *Organometallics* **2001**, *20*, 468−473; [8b] G. E. Herberich, U. Englert, B. Ganter, M. Pons, *Eur. J. Inorg. Chem.* **2000**, 979−986; [8c] G. C. Bazan, W. D. Cotter, Z. J. A. Komon, R. A. Lee, R. J. Lachicotte, *J. Am. Chem. Soc.* **2000**, *122*, 1371−1380; [8d] A. J. Ashe, III, S. Al-Ahmad, J. W. Kampf, *Organometallics* **1999**, *18*, 4234−4236; [8e] A. J. Ashe III, X. Fang, J. W. Kampf, *Organometallics* **1999**, *18*, 1363−1365; [8f] J. S. Rogers, R. J. Lachicotte, G. C. Bazan, *J. Am. Chem. Soc.* **1999**, *121*, 1288−1298; [8g] A. J. Ashe III, S. Al-Ahmad, X. Fang, J. W. Kampf, *Organometallics* **1998**, *17*, 3883−3888; [8h] R. W. Barnhart, G. C. Bazan, T. Mourey, *J. Am. Chem. Soc.* **1998**, *120*, 1082−1083; [8i] J. S. Rogers, G. C. Bazan, C. K. Sperry, *J. Am. Chem. Soc.* **1997**, *119*, 9305−9306; [8j] A. J. Ashe III, S. Al-Ahmad, J. W. Kampf, V. G. Young, Jr., *Angew. Chem.* **1997**, *109*, 2104−2106; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2014−2016; [8k] G. E. Herberich, U. Englert, A. Schmitz, *Organometallics* **1997**, *16*, 3751−3757; [8l] G. C. Bazan, G. Rodriguez, A. J. Ashe III, S. Al-Ahmad, J. W. Kampf, *Organometallics* **1997**, *16*, 2492−2494; [8m] G. C. Bazan, G. Rodriguez, A. J. Ashe III, S. Al-Ahmad, C. Müller, *J. Am. Chem. Soc.* **1996**, *118*, 2291−2292.

[9] [9a] F. T. Edelmann in *Metallocenes* (Eds.: A. Togni, R. L. Halterman), Wiley-VCH, Weinheim, Germany, **1998**, Vol. 1, p. 55−110; [9b] P. J. Chirik, J. E. Bercaw, in *Metallocenes* (Eds.: A. Togni, R. L. Halterman), Wiley-VCH, Weinheim, Germany, **1998**, Vol. 1, p. 111−152; [9c] G. Bombieri, G. Paolucci, *Organometallic p Complexes of f-elements*, in *Handbook on the Physics and Chemistry of Rare Earths* (Eds.: K. A. Gschneidner, Jr., L. Eyring), Elsevier Science, Amsterdam, The Netherlands, **1998**, Vol. 25, p. 265−413; [9d] H. Schumann, J. A. Meese-Marktscheffel, L. Esser, *Chem. Rev.* **1995**, *95*, 865−986.

[10] A. J. Ashe III, P. Shu, *J. Am. Chem. Soc.* **1971**, *93*, 1804−1805.

[11] [11a] G. E. Herberich, B. Schmidt, U. Englert, *Organometallics* **1995**, *14*, 471−480; [11b] G. E. Herberich, B. Schmidt, U. Englert, T. Wagner, *Organometallics* **1993**, *12*, 2891−2893.

[12] D. A. Hoic, M. DiMare, G. C. Fu, *J. Am. Chem. Soc.* **1997**, *119*, 7155−7156.

[13] G. E. Herberich, U. Englert, M. U. Schmidt, R. Standt, *Organometallics* **1996**, *15*, 2707−2712.

[14] B. Wang, Dissertation, Technische Hochschule Aachen, Aachen, Germany, **2001**.

[15] G. E. Herberich, U. Englert, B. Ganter, M. Pons, R. Wang, *Organometallics* **1999**, *18*, 3406−3413.

[16] [16a] J. L. Atwood, K. D. Smith, *J. Chem. Soc., Dalton Trans.* **1973**, 2487−2490; [16b] E. C. Baker, L. D. Brown, K. N. Raymond, *Inorg. Chem.* **1975**, *14*, 1376−1379.

[17] M. E. Thompson, S. M. Baxter, A. R. Bulls, B. J. Burger, M. C. Nolan, B. D. Santarsiero, W. P. Schaefer, J. E. Bercaw, *J. Am. Chem. Soc.* **1987**, *109*, 203−219.

[18] [18a] W. J. Evans, T. T. Peterson, M. D. Rausch, W. E. Hunter, H. Zhang, J. L. Atwood, *Organometallics* **1985**, *4*, 554−559; [18b] W. J. Evans, D. K. Drummond, J. W. Grate, H. Zhang, J. L. Atwood, *J. Am. Chem. Soc.* **1987**, *109*, 3928−3936.

[19] [19a] F. Bottomley, D. E. Paez, P. S. White, *J. Organomet. Chem.* **1985**, *291*, 35−41; [19b] W. Lamberts, H. Lueken, *Inorg. Chim. Acta* **1987**, *132*, 119−122; [19c] W. Lamberts, B. Hessner, H. Lueken, *Inorg. Chim. Acta* **1987**, *139*, 215−217; [19d] W. J. Evans, D. K. Drummond, *Organometallics* **1988**, *7*, 797−802.

[20] A. L. Spek, *Acta Crystallogr., Sect. C* **1990**, *46*, 34.

[21] The slip distortion is defined as the distance between the geometric mean of the C5B plane and the projection of the central metal onto this plane.

[22] P. Paetzold, *Adv. Inorg. Chem.* **1987**, *31*, 123−170.

[23] G. W. Klumpp, M. Vos, F. J. J. de Kanter, C. Slob, H. Krabbendam, A. L. Spek, *J. Am. Chem. Soc.* **1985**, *107*, 8292−8294.

[24] [24a] R. D. Shannon, *Acta Crystallogr., Sect. A* **1976**, *32*, 751−767; [24b] Y. Q. Jia, *J. Solid State Chem.* **1991**, *95*, 184−187.

[25] [25a] J. L. Atwood, W. E. Hunter, R. D. Rogers, J. Holton, J. McMeeking, R. Pearce, M. F. Lappert, *J. Chem. Soc., Chem. Commun.* **1978**, 140−142; [25b] P. L. Watson, J. F. Whitney, R. L. Harlow, *Inorg. Chem.* **1981**, *20*, 3271−3278.

[26] The isomer mixture of 2,4-dimethylpentadienes was prepared from a MeMgI Grignard reagent and mesityloxide, followed by dehydration at the distillation temperature: [26a] O. N. Jitkow, M. T. Bogert, *J. Am. Chem. Soc.* **1941**, *63*, 1979−1984; [26b] R. G. Kelso, K. W. Greenlee, J. M. Derfer, C. E. Boord, *J. Am. Chem. Soc.* **1955**, *77*, 1751−1755.

[27] W. Gerrard, H. R. Hudson, E. F. Mooney, *J. Chem. Soc.* **1960**, 5168−5172.

[28] P. Geymayer, E. G. Rochow, U. Wannagat, *Angew. Chem.* **1964**, *74*, 499−500; *Angew. Chem. Int. Ed. Engl.* **1964**, *3*, 633−634.

[29] R. S. P. Coutts, P. C. Wailes, *J. Organomet. Chem.* **1970**, *25*, 117−122.

[30] P. Coppens, L. Leiserowitz, D. Rabinovich, *Acta Crystallogr.* **1965**, *18*, 1035−1038.

[31] A. C. T. North, D. C. Phillips, F. S. Mathews, *Acta Crystallogr., Sect. A* **1968**, *24*, 351−359.

[32] G. M. Sheldrick, *SHELXS-97*, *Program for Structure Solution*, University of Göttingen, Göttingen, Germany, **1997**.

[33] G. M. Sheldrick, *SHELXL-97*, *Program for Structure Refinement*, University of Göttingen, Göttingen, Germany, **1997**.

Received June 29, 2001
[I01240]