New Alkali Metal Boratabenzenes: Structures of K([18]-Crown-6)(C_5H_5BMe), of the Tetrahydropyran Solvate K(3,5-$Me_2C_5H_3B{-}NMe_2$)$(THP)_2$, and of Two THF Solvates of K[3,5-$Me_2C_5H_3B{-}N(SiMe_3)_2$][‡]

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Keywords: Alkali metal salts / Borabenzene / Boratabenzene / Boron

The potassium salt K(C_5H_5BMe) (**8**) can be obtained from 2-(Me_3Sn)C_5H_5BMe (**7**)/KO*t*Bu in toluene in essentially quantitative yield. Metalation of 1-(dimethylamino)-3-methylene-1,2,3,6-tetrahydroborinine (**9**) with $MN(SiMe_3)_2$ (M = Na, K) in toluene afforded the unsolvated salts M(3,5-$Me_2C_5H_3B$–NMe_2) (M = Na: **11**; M = K: **12**). Morpholino derivatives M(3,5-$Me_2C_5H_3B$–NC_4H_8O) (M = Li: **17**; M = Na: **18**) and the potassium salt K[3,5-$Me_2C_5H_3B$–$N(SiMe_3)_2$] (**19**) were obtained similarly. The unsolvated salts are highly air- and water-sensitive, colorless powders. Crystallization with the help of auxiliary Lewis bases provided crystalline solvates K([18]-crown-6)(C_5H_5BMe) (**20**), K$(THP)_2$(3,5-$Me_2C_5H_3B$–NMe_2) (**21**), and the concomitant pseudopolymorphs K[3,5-$Me_2C_5H_3B$–$N(SiMe_3)_2$]$(THF)_{4/3}$ (α-**22**) and K[3,5-$Me_2C_5H_3B$–$N(SiMe_3)_2$]$(THF)_{3/2}$ (β-**22**), which were characterized structurally. The structures of α-**22** (space group *C*2/*c*) and β-**22** (space group 6_122) display novel chain forms, which have no precedents in boratabenzene and cyclopentadienide chemistry.

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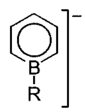
Introduction

The first boratabenzene salts (salts with anions of type **1**[2]) and the first transition metal complexes[3] with boratabenzene ligands were obtained in the very early 1970s. It soon became apparent that boratabenzene ions **1** are similar to the cyclopentadienide ion Cp^- (**2**).[4]



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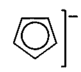

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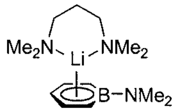
The structural characterization of boratabenzene salts was a relatively late achievement. The first structure determination was published in 1993, and characterized the TMPDA solvate of lithium 1-(dimethylamino)boratabenzene, Li(TMPDA)($C_5H_5B{-}NMe_2$) [TMPDA = Me_2N-$(CH_2)_3NMe_2$] (**3**).[5a] The year 1995 saw the next two structure determinations, that of Li(C_5H_5BH)$(THF)_2$, which was found to possess an ionic structure [Li$(THF)_4$][Li$(C_5H_5BH)_2$] (**4**) with a sandwich-type anion,[5b] similar to the lithocenate ion,[6] and that of the ammonium salt $Me_3PhN(C_5H_5BMe)$ (**5**) with a naked boratabenzene ion.[5c] More recently, the *B*-styryl derivative Na(OEt_2)[(*E*)-$C_5H_5BCH{=}CHPh$] (**6**) was found to be the first example of a zigzag chain structure in a boratabenzene salt.[5d] With the growing number of known structures it is becoming more and more evident that the structural chemistry of the ionic boratabenzenes is closely similar to that of the ionic cyclopentadienides.[7]



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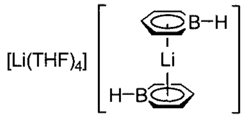

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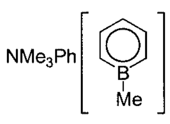

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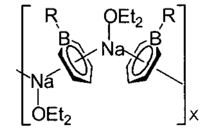

6, R = (*E*)-CH=CHPh

A variety of synthetic approaches to boratabenzene salts are now available. Deprotonation of dihydroborinines was the final step of the "tin route" to borabenzene derivatives in the very first generation of a boratabenzene salt, Li(C_5H_5BPh).[2a] Deprotonation of dihydroborinines has developed into the most versatile method, with a large variety of deprotonation reagents (including Li*t*Bu, LDA, NaH, and NaCp). Methods based on the "cobaltocene route" include the cyanide degradation of the cobalt sandwich

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[‡] Borabenzene Derivatives, 40. Part 39: Ref.[1]

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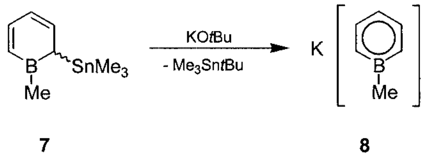
complexes $Co(C_5H_5BR)_2$ to give the first potassium salts $K(C_5H_5BR)$ (R = Me, Ph),[2b] and the reductive degradation of these complexes by elemental lithium, sodium amalgam, and Na/K alloy, which are now of only historical interest.[2d] From 1993 onwards, the renaissance of borabenzene and boratabenzene chemistry was very strongly stimulated by three new and efficient syntheses. The base-induced cyclization of pentadienylboranes,[5a,5c] and the related "dicarbanion route"[8] were based on classical lithiation and kaliation reactions, while a modification of the tin route provided the borabenzene adduct $C_5H_5B-PMe_3$ as a storage form of the borabenzene ring, and subsequent nucleophilic displacement of the Lewis base PMe_3 afforded a large variety of boratabenzene salts with Li, Na, and K counter ions.[5b,9]

In this paper we describe several new alkali metal boratabenzenes. We present four structure determinations, some of which display new structural motifs.

Results and Discussion

A New Synthesis of Potassium 1-Methylboratabenzene

While lithium 1-methylboratabenzene $Li(C_5H_5BMe)$ can readily be prepared in 10−40 g lots,[5c] the higher Na and K homologues have only been obtained in small quantities because of the practical limitations of the cobaltocene route.[2b−2d] In this work we used $2\text{-}(Me_3Sn)C_5H_5BMe$ (**7**),[10] readily available by treatment of $Li(C_5H_5BMe)$ with Me_3SnCl,[10] as precursor for the preparation of the potassium salt $K(C_5H_5BMe)$ (**8**). Treatment of **7** with KO*t*Bu in toluene at ambient temperature slowly (24 h) produced **8** as a microcrystalline precipitate (Scheme 1). Workup by filtration and washing with hexane gave spectroscopically (NMR) pure samples of **8** in essentially quantitative yield. The reaction can by catalyzed by traces of pyridine, as evidenced by the much faster formation of the precipitate **8**. Earlier work had shown that the tin compound **7** displays a heterolytic equilibrium when traces of DMSO or pyridine are present;[10] the formation of $[Me_3Sn(py)_x]^+$ and $C_5H_5BMe^-$ ions is presumably the main cause of the observed catalytic effect.



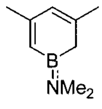
7 **8**

Scheme 1

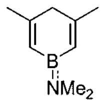
Syntheses of Aminoboratabenzene Salts

The dicarbanion route provides a particularly efficient route to boratabenzene salts. With 2,4-dimethylpentadienes as starting materials, the dicarbanion route affords the 3-methylene-1,2,3,6-tetrahydroborinine **9** as primary product[8] and, after catalyzed isomerization, a mixture of the dihydroborinines **10a** and **10b**[8] in yields of up to 40%.[11] Metalation, with LDA/TMEDA in THF, for example, produces the lithium salt $Li(3,5\text{-}Me_2C_5H_3B-NMe_2)$ as a crystalline TMEDA solvate,[8] and with $LiN(SiMe_3)_2$ in hexane (or other hydrocarbon solvents) the unsolvated salt.[11] In this work we used the bases $NaN(SiMe_3)_2$ and $KN(SiMe_3)_2$ in toluene and obtained the homologous unsolvated salts $Na(3,5\text{-}Me_2C_5H_3B-NMe_2)$ (**11**) and $K(3,5\text{-}Me_2C_5H_3B-NMe_2)$ (**12**) as colorless powders.

9



10a

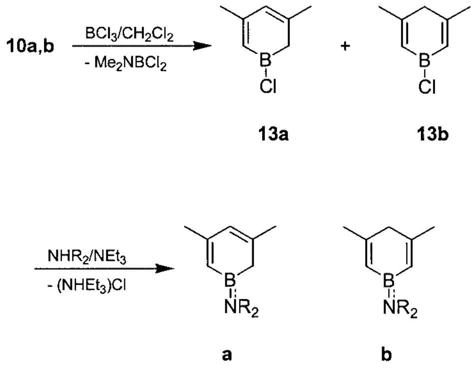


10b

11: $Na(3,5\text{-}Me_2C_5H_3B-NMe_2)$

12: $K(3,5\text{-}Me_2C_5H_3B-NMe_2)$

In many situations it is desirable to replace the *B*-(dimethylamino) substituent by other groups. This may be achieved by a two-step procedure (Scheme 2). Firstly, the dimethylamino compound mixture **10a/10b** is treated with BCl_3 to give the chloro derivatives **13a** and **13b**.[11] In a second step, the new substituent at the boron atom is introduced in many cases by treatment with a secondary amine/NEt_3. In this way we obtained the morpholino derivatives **14a** and **14b**, which after deprotonation by $LiN(SiMe_3)_2$ and $NaN(SiMe_3)_2$ gave the new salts $Li(3,5\text{-}Me_2C_5H_3B-NC_4H_8O)$ (**17**) and $Na(3,5\text{-}Me_2C_5H_3B-NC_4H_8O)$ (**18**) in high yields. Analogously, (*S*)-2-(methoxymethyl)pyrrolidine (SMPH) was used to produce the already published *B*-SMP compounds.[12] With bis(trimethylsilyl)amine, the lithium salt $Li[3,5\text{-}Me_2C_5H_3B-N(SiMe_3)_2]$ had previously been prepared.[11a] Use of $KN(SiMe_3)_2$ in toluene as the base afforded the homologous unsolvated potassium salt $K[3,5\text{-}Me_2C_5H_3B-N(SiMe_3)_2]$ (**19**) as a colorless powder.



14: $NR_2 = N(CH_2CH_2)_2O$

15: NR_2 = SMP

16: $NR_2 = N(SiMe_3)_2$

Scheme 2

17: $Li(3,5\text{-}Me_2C_5H_3B-NC_4H_8O)$

18: $Na(3,5\text{-}Me_2C_5H_3B-NC_4H_8O)$

19: $K(3,5\text{-}Me_2C_5H_3B-N(SiMe_3)_2$

Crystalline Solvates

The new alkali metal boratabenzenes **8**, **11**, **12**, **17**, **18**, and **19** are all microcrystalline powders. Crystallization requires the use of donor solvents and generally produces solvates. Hence, the 1-methylboratabenzene **8** could be dissolved in a warm mixture of toluene/CH_2Cl_2 containing [18]-crown-6 and, when the system had cooled to ambient temperature, gave the solvate K([18]-crown-6)(C_5H_5BMe) (**20**) as crystalline blocks in high yield. Crystallization of the potassium compound **12** from toluene/tetrahydropyran gave the crystalline solvate $K(THP)_2(3,5\text{-}Me_2C_5H_3\text{-}B{-}NMe_2)$ (**21**); the number of tetrahydropyran molecules in this compound was deduced from ^1H NMR spectroscopic data and later confirmed by a structure determination. The bis(trimethylsilyl)amino derivative $K[3,5\text{-}Me_2C_5H_3B{-}N(SiMe_3)_2]$ (**19**) could be crystallized from THF and, unexpectedly, produced a mixture of two concomitant pseudopolymorphs[13] $K[3,5\text{-}Me_2C_5H_3B{-}N(SiMe_3)_2](THF)_x$ with slightly different THF contents: α-**22** with 4/3 mol-equiv. of THF, and β-**22** with 3/2 mol-equiv. THF. The two compounds are not true polymorphs, because their compositions are not fully equal. Note also that two crystalline phases can only be formed in the same system as the result of kinetic control.

20: K([18]-crown-6)(C_5H_5BMe)

21: $K(THP)_2(3,5\text{-}Me_2C_5H_3B{-}NMe_2)$

α-**22**: $K[3,5\text{-}Me_2C_5H_3B{-}N(SiMe_3)_2](THF)_{4/3} \approx [K(THF)]_2[K(THF)_2][3,5\text{-}Me_2C_5H_3B{-}N(SiMe_3)_2]_3$

β-**22**: $K[3,5\text{-}Me_2C_5H_3B{-}N(SiMe_3)_2](THF)_{3/2} \approx [K(THF)]_2[3,5\text{-}Me_2C_5H_3B{-}N(SiMe_3)_2]_2(THF)$

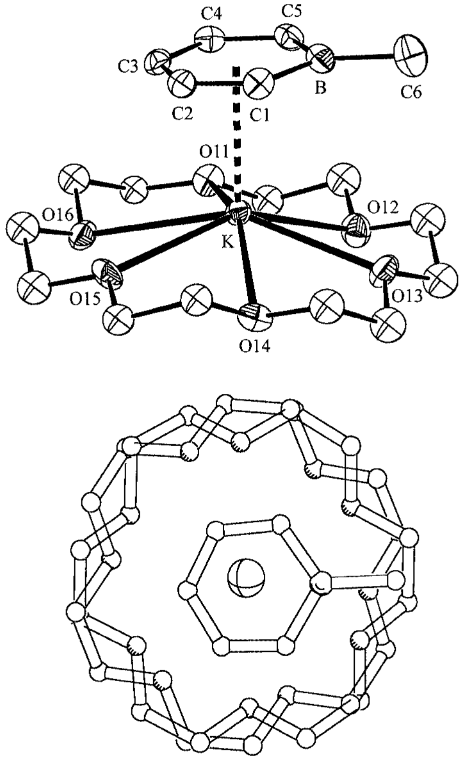


Figure 1. Molecular structure of **20** in the crystal; top: PLATON plot[14] at the 30% probability level; bottom:[15] top view, illustrating the disorder of the [18]-crown-6 ring with an occupancy ratio of 61(1):39(1); selected interatomic distances [Å]: K−C1 3.319(5), K−C2 3.207(5), K−C3 3.089(4), K−C4 3.083(5), K−C5 3.198(5), K−B 3.373(6), K−O11 2.915(5), K−O12 2.892(6), K−O13 2.788(6), K−O14 2.832(5), K−O15 2.848(6), K−O16 3.004(6), K−O21 2.850(8), K−O22 2.863(10), K−O23 2.856(10), K−O24 2.863(10), K−O25 2.794(9), K−O26 2.939(9), C1−B 1.513(7), C1−C2 1.371(7), C2−C3 1.378(7), C3−C4 1.378(7), C4−C5 1.398(7), C5−B 1.507(8)

Crystal Structures

The crown ether adduct **20** crystallizes in the orthorhombic space group $Pna2_1$ as a van der Waals crystal (Figure 1). The molecule is a contact ion pair of the cation [K([18]-crown-6)]$^+$ and the anion $[C_5H_5BMe]^-$. The structural type is therefore the same as that of the known salts K([18]-crown-6)($C_5H_5B{-}NPh_2$) and K([18]-crown-6)($C_5H_5B{-}PPh_2$).[16] The observed rotational disorder of the crown ether ligand could readily be resolved.

The boratabenzene ring is essentially planar, with a maximum perpendicular deviation of 0.011(6) Å for the boron atom. The intra-ring geometry [C−B = 1.510(8) (av), C−C = 1.382(7) Å (av)] does not differ from that of $Me_3PhN(C_5H_5BMe)$ (**5**) [C−B = 1.500(3) (av), C−C = 1.390(3) Å (av)]. The K−C distances average 3.179(5) Å and are significantly shorter than those in K([18]-crown-6)($C_5H_5B{-}NPh_2$) [3.241(7) Å (av)] and K([18]-crown-6)($C_5H_5B{-}PPh_2$) [3.259(5) Å (av)],[16] presumably because of the much smaller *B*-exocyclic substituent in **20**.

The bis(tetrahydropyran) solvate **21** forms monoclinic crystals of space group *C*2/*c* with a zigzag chain structural motif (Figure 2). The potassium atom displays a pseudotetrahedral coordination sphere as previously observed in, for example, the structure of $K(py)_2Cp^*$.[17] The interplanar angle between two neighboring boratabenzene rings is 53.1(1)°, and the metal−boratabenzene distances amount to 2.818(3) and 2.834(3) Å. Since the boratabenzene ring interacts with two potassium cations almost symmetrically, the C_5B moiety is located in a perfect plane [maximum vertical deviation: 0.003(3) Å for C1]. In contrast with this situation, compounds with nonbridging boratabenzene ligands show a folding of the ring, with the boron atom always bending away from the central metal atom. This effect is particularly pronounced for 1-aminoboratabenzenes coordinated to highly charged centers. For instance, in $ScCl(3,5\text{-}Me_2C_5H_3B{-}N\mathit{i}Pr_2)_2$ the folding angle of the C_5 plane against the C_2B plane amounts to 13°.[1]

The THF solvate $K[3,5\text{-}Me_2C_5H_3B{-}N(SiMe_3)_2](THF)_{4/3}$ (α-**22**) crystallizes in the monoclinic space group *C*2/*c*; the asymmetric unit contains two independent THF molecules, 1.5 independent cations K^+, and 1.5 independent anions. The structure of α-**22** (Figures 3 and 4) displays two kinds of potassium atoms − K1 and K2, in a 2:1 ratio − with rather different coordination environments.

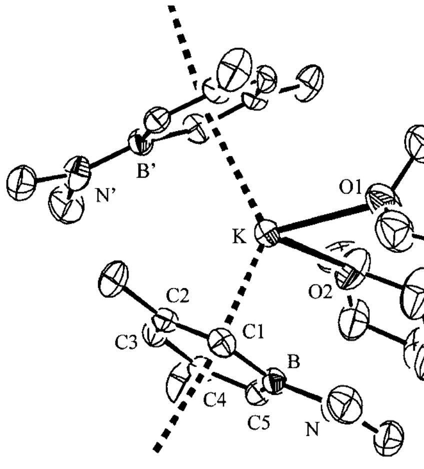


Figure 2. A representative fragment of the structure of **21** in the crystal (asymmetric unit and one anion in addition) (PLATON plot[14] at the 30% probability level); selected interatomic distances [Å]: K−C1 3.282(4), K−C1′ 3.235(4), K−C2 3.139(4), K−C2′ 3.158(4), K−C3 3.021(4), K−C3′ 3.086(5), K−C4 3.055(4),K−C4′ 3.108(4), K−C5 3.188(5), K−C5′ 3.185(4), K−B 3.344(5), K−B′ 3.290(4), K−O1 2.719(3), K−O2 2.757(3), C1−C2 1.383(5), C2−C3, 1.396(4), C3−C4 1.395(4), C4−C5 1.365(5), C1−B,1.501(5), C5−B 1.502(5), N−B 1.468(5)

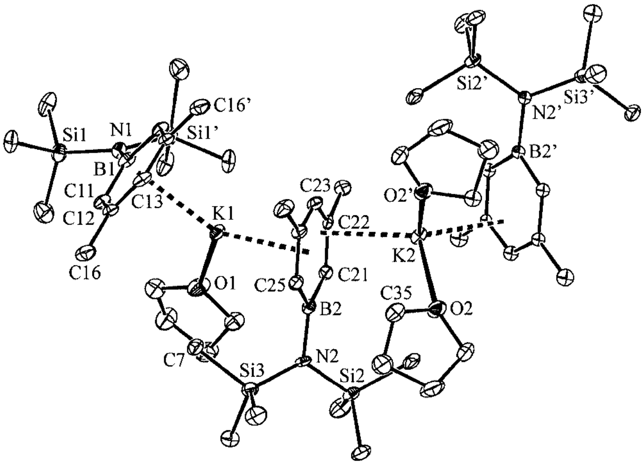


Figure 3. A representative fragment of the structure of α-**22** (PLATON plot[14] at the 30% probability level); the atoms K2, N1, C13, and B1 lie on twofold axes; selected interatomic distances [Å]: K1−C11 3.243(5), K1−C11′ 3.250(4), K1−C12, 3.046(5), K1−C12′ 3.072(4), K1−C13 2.952(3), K1−B1 3.383(5); K1−C21 3.147(5), K2−C21 3.417(5), K1−C22 3.013(3), K2−C22 3.096(5), K1−C23 3.010(5), K2−C23 3.004(5), K1−C24 3.162(5), K2−C24 3.263(5), K1−C25 3.309(5), K2−C25 3.572(5), K1−B2 3.310(5), K2−B2 3.686(6); K1−O1 2.601(4), K2−O2 2.720(3); C11−C12 1.388(6), C12−C13 1.413(6), C11−B1 1.524(6), N1−B1 1.490(9); C21−C22 1.404(6), C22−C23 1.411(6), C23−C24 1.378(7), C24−C25 1.409(6), C25−B2 1.506(7), C21−B2 1.515(7), N2−B2 1.530(6); note also: K1···C7 3.422(5), K2···C35 3.451(6)

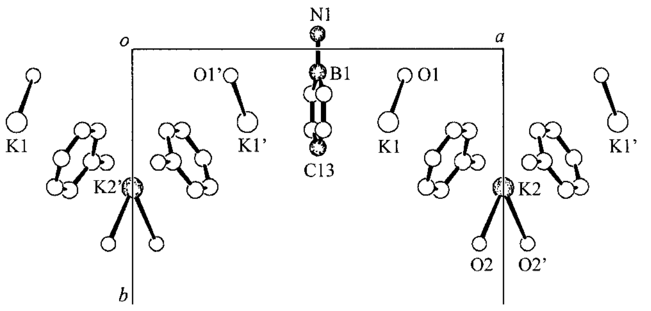


Figure 4. Simplified packing diagram (along *c* axis) of the structure of α-**22**;[15] only the K, O, and $C_5B{-}N$ (boratabenzene) fragments are displayed; the atoms lying on twofold axes (K2, C13, B1, N1) are shown as dotted spheres

The atom K1 is surrounded, essentially in a trigonal mode, by an oxygen atom of a THF ligand and two bridging μ-boratabenzene ligands. Ligand **A** (B1, C11−C13, N1, etc.) occupies a special position, with the B1, C13, and N1 atoms lying on a crystallographic twofold axis, whereas ligand **B** (B2, C21−C25, N2, etc.) is in a general position. Both boratabenzene rings are planar [with vertical displacements of less than 0.007(5) Å] and are facially bonded to K1. The distances between the metal atom and the two C_5B planes are quite small [K1−**A** 2.781(3), K1−**B**: 2.794(3) Å], and the interplanar angle between the two rings is 44.6(2)°.

The potassium atom K2 is located on a twofold axis and exhibits a tetrahedral coordination sphere, being bonded to two THF oxygen atoms and to two boratabenzene ligands **B**. The more crowded geometry around the atom K2 causes the cation to slip away from the boratabenzene ring center, and the lengths K2−C25 [3.572(5) Å] and K2−B2 [3.686(6) Å] adopt rather large values. As expected, both the distance of the metal atom to the boratabenzene plane [2.924(3) Å] and the interplanar angle between the two boratabenzene planes [56.2(2)°] are much larger than the corresponding parameters involving the potassium atom K1. Obviously, the observed soft bonding situation is in line with the essentially electrostatic character of the potassium−boratabenzene interactions.

The packing of α-**22** can be explained with the help of a simplified diagram (Figure 4). It seems somewhat surprising that the one-dimensional polymer develops along the shortest lattice axis *a* [*a* = 14.924(5) Å; cf. *b* = 29.307(5) and *c* = 17.385(4) Å]. More unexpectedly, the polymer is not arranged in a zigzag chain, since the dihedral angle K2,K1,K1′,K2′ is less than 180°, even less than 90°. This novel structural motif has not previously been encountered in cyclopentadienyl chemistry.

Since K^+ is a rather large cation (ionic radius *r* = 1.51 Å for coordination number 8),[18] it tends to have short contacts, as observed in the present case [K1···C7 3.422(5), K2···C35 3.451(6) Å]. Besides packing forces, additional electrostatic interactions may favor the occurrence of short contacts. This is presumably the dominating cause for the short contact K1···C7, which places the negative charge of an *Si*-methyl group close to the cation.

The pseudo-polymorph $K[3,5\text{-}Me_2C_5H_3B{-}N(SiMe_3)_2](THF)_{3/2}$ (β-**22**) crystallizes in the hexagonal space group $P6_122$ with twelve boratabenzene moieties per unit cell (Figures 5 and 6). One molecule of THF per formula unit is coordinated to the cation, while 0.5 mol-equiv. of THF function solely as a space filling building block. The polymer chain extends along the lattice axis *c*, which is much longer than the others [c = 62.2944(17) Å; cf. a = b = 11.9545(2) Å].

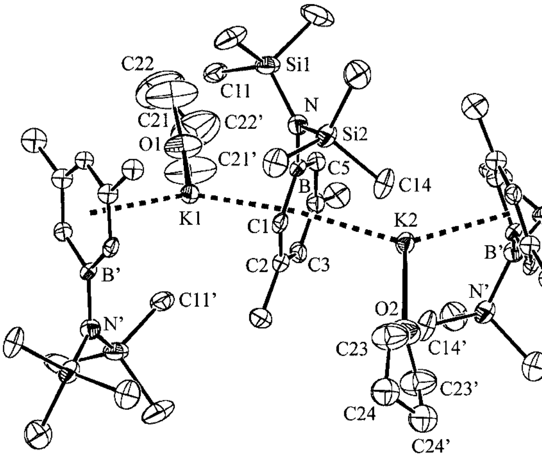


Figure 5. A representative fragment of the structure of β-**22** (PLATON plot[14] at the 30% probability level); the potassium atoms K1 and K2 lie on the twofold axes; selected interatomic distances [Å]: K1−C1 3.169(6), K2−C1 3.209(5), K1−C2 3.079(5), K2−C2 3.093(5), K1−C3 3.053(5), K2−C3 3.021(6), K1−C4 3.139(5), K2−C4 3.070(6), K1−C5 3.236(6), K2−C5 3.166(6), K1−B 3.278(6), K2−B 3.289(6); K1−O1 2.718(7), K2−O2 2.734(8); C1−C2 1.386(8), C2−C3 1.396(8), C3−C4 1.399(9), C4−C5 1.391(9), C1−B 1.508(8), C5−B 1.509(9), N−B 1.502(8); note also: K1···C11 3.328(6), K2···C14 3.311(6), K1···K2 5.599(2)

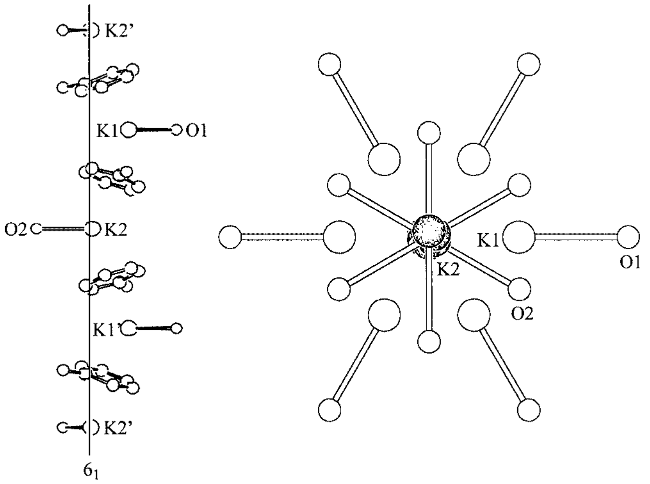


Figure 6. Simplified packing diagrams of the structure of β-**22**;[15] (a) left: view perpendicular to the sixfold screw axis 6_1 (direction [110]); only the K, O, and C$_5$B−N (boratabenzene) fragments are displayed; (b) right: view along the screw axis (direction [001]), showing only the K and O atoms

The K1−O1 and K2−O2 vectors coincide with twofold axes, and so the two potassium atoms possess trigonal coordination spheres. The distances from K1 and K2 to the best boratabenzene C$_5$B plane are 2.809(3) and 2.788(3) Å, respectively, and the bending angles of the sandwich units around K1 and K2 correspond to 133.3(2) and 140.5(2)°. The bridging boratabenzene ring is again planar [with a maximum vertical deviation of 0.007(6) Å for C5] and its intra-ring geometry is quite similar to that in α-**22**. We also again note the occurrence of short contacts between *Si*-methyl groups and the cations [K1···C11 3.328(6), K2···C14 3.311(6) Å].

As shown in Figure 6 (a), the distance of K1 from the 6_1 axis (2.22 Å) is much larger than that of K2 (0.15 Å). As a consequence, the hexagonal helix of the symmetry-related cations K2 nearly coincide with the 6_1 axis whereas the cations K1 form an alternating outer hexagonal screw.

Conclusion

The structures of boratabenzene salts now known are collected in Table 1. They belong to one of four types: structures with naked anions (type A), contact ion pair structures (type B), structures with sandwich-type anions (type C), and chain structures with side-on-coordinated donor

Table 1. Crystal structures of boratabenzene salts

No.	Formula	Type	Ref.
1	Me$_3$PhN(C$_5$H$_5$BMe) (**5**)	A	[5c]
2	[Na(dibenzo-[18]-crown-6)(THF)$_2$](C$_5$H$_5$B−CH=CHPh)[a]	A	[5d]
3	[Na(dibenzo-[18]-crown-6)(THF)$_2$]$_2$(C$_5$H$_5$B−CH=CH-1,4-C$_6$H$_4$-CH=CH−BC$_5$H$_5$)[a]	A	[19]
4	Li(TMPDA)(C$_5$H$_5$B−NMe$_2$) (**3**)[b]	B	[5a]
5	Li(TMEDA)(5-*t*Bu-3-MeC$_5$H$_3$B−NMe$_2$)	B	[8]
6	K([18]-crown-6)(C$_5$H$_5$B−NPh$_2$)	B	[15]
7	K([18]-crown-6)(C$_5$H$_5$B−PPh$_2$)(PhMe)$_{0.5}$	B	[15]
8	Li(TMEDA)(6-MePBb−NMe$_2$)[c]	B	[20]
9	Li(TMEDA)(6-MePBbMe)[c]	B	[21]
10	[Na(THF)$_3$]$_2$(C$_5$H$_5$B−CH=CH-1,4-C$_6$H$_4$-CH=CH−BC$_5$H$_5$)[a]	B	[19]
11	K([18]-crown-6)(C$_5$H$_5$BMe) (**20**)	B	this work
12	[Li(THF)$_4$][Li(C$_5$H$_5$BH)$_2$] (**4**)	C	[5b,9]
13	Li(3,5-Me$_2$C$_5$H$_3$B−SMP)[d] [e]	C	[12]
14	Na(OEt$_2$)(C$_5$H$_5$B−CH=CHPh) (**6**)[a]	D	[5d]
15	K(THP)$_2$(3,5-Me$_2$C$_5$H$_3$B−NMe$_2$) (**21**)	D	this work
16	[K(THF)]$_2$[K(THF)$_2$](3,5-Me$_2$C$_5$H$_3$B−N(SiMe$_3$)$_2$]$_3$ (α-**22**)	D	this work
17	[K(THF)]$_2$[3,5-Me$_2$C$_5$H$_3$B−N(SiMe$_3$)$_2$]$_2$(THF) (β-**22**)	D	this work

[a] With (*E*)-CH=CH units. [b] TMPDA = Me$_2$N(CH$_2$)$_3$NMe$_2$. [c] PBb = a pinene-fused, enantiomerically pure borabenzene moiety C$_{12}$H$_{15}$B. [d] SMP = (*S*)-2-(methoxymethyl)pyrrolidin-1-yl. [e] Polymer with alternating LiN$_2$O$_2$ and Li(C$_5$H$_5$B)$_2$ units.

molecules (type D). We note that the disorder found in the structure of **20** may be understood as the consequence of the shape of the auxiliary base present. Simple crown ethers should be much more prone to disorder than the dibenzo crown ethers used in some of the previously studied compounds. Chain structures may be simple zigzag chains as in **6** and **21** but, as this work shows, may also be of much more complex types. Finally, we note that the structure elucidation of the simple, unsolvated alkali metal cyclopentadienides MCp (M = Li, Na, K) belongs to the milestones of cyclopentadienide chemistry.[22] The analogous structures of the most simple, unsolvated alkali metal boratabenzenes [M(C_5H_5BR), for instance with M = Li, K and R = H, Me, Ph] still wait to be resolved, however.

Experimental Section

General: All manipulations were carried out under nitrogen by use of standard Schlenk techniques. Et_2O, THF, and THP were distilled from sodium benzophenone ketyl. Hexane was distilled from Na/K alloy, toluene from sodium, and CH_2Cl_2 from CaH_2. Elemental analyses were performed at the Analytische Laboratorien, 51779 Lindlar, Germany. NMR spectra were recorded with a Varian Unity 500 (^1H, 500 MHz; ^{13}C, 125.7 MHz; ^{11}B, 160.4 MHz). Chemical shifts are given in ppm; they are referenced to TMS for ^1H and ^{13}C, and to $BF_3{\cdot}OEt_2$ for ^{11}B. Electron-impact mass spectra were recorded with a Finnigan MAT-95 at a nominal electron energy of 70 eV.

Potassium 1-Methylboratabenzene (8) and Its [18]-Crown-6 Solvate (20): 1-Methyl-2-(trimethylstannyl)-1,2-dihydroborinine (1.02 g, 4.00 mmol) was added to a solution of KO*t*Bu (0.44 g, 3.92 mmol) in toluene (20 mL). The reaction mixture was stirred at room temperature for 24 h, and a fine white precipitate formed during this time. The precipitate was collected by filtration through a frit, washed with hexane (3 × 10 mL), and dried under high vacuum to afford **8** (0.50 g, 98%) as a moisture- and air-sensitive, white powder. The potassium salt **8** (0.286 g, 2.20 mmol) and [18]-crown-6 (0.607 g, 2.30 mmol) were dissolved at 50 °C in a mixture of toluene and CH_2Cl_2 (8:1, 45 mL). The solution was stored overnight at ambient temperature to give the solvate **8**·([18]-crown-6) (≡ **20**) (0.711 g, 82%) as large, colorless, crystalline blocks.

Data for 8: ^1H NMR (500 MHz, [D_8]THF, 20 °C): $\delta = 0.44$ (s, BMe), 5.91 (tt, $J = 6.9$, 0.9 Hz, 4-H), 6.23 (dd, $J = 9.4$, 0.9 Hz, 2-/6-H), 7.01 (dd, $J = 9.4$, 6.9 Hz, 2 H, 3-/5-H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, [D_8]THF, 20 °C): $\delta = 4.6$ (br., BMe), 109.1 (C-4), 127.6 (br., C-2,6), 133.3 (C-3,5) ppm. $^{11}B\{^1H\}$ NMR (160 MHz, [D_8]THF, external $BF_3{\cdot}OEt_2$, 20 °C): $\delta = 35.4$ ppm.

Data for 20: ^1H NMR (500 MHz, CD_2Cl_2, 20 °C): $\delta = 0.54$ (s, BMe), 3.56 (s, 12 OCH_2), 5.32 (tt, $J = 7.0$, 1.2 Hz, 4-H), 6.29 (dd, $J = 9.8$, 1.2 Hz, 2-/6-H), 7.14 (dd, $J = 9.8$, 7.0 Hz, 2 H, 3-/5-H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 20 °C): $\delta = 4.6$ (br., BMe), 70.4 (OCH_2), 108.8 (C-4), 126.8 (br., C-2,6), 133.4 (C-3,5) ppm. $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, external $BF_3{\cdot}OEt_2$, 20 °C): $\delta = 35.3$ ppm. $C_{18}H_{32}BKO_6$ (394.36): calcd. C 54.82, H 8.17; found C 54.95, H 7.80.

Sodium 1-(Dimethylamino)-3,5-dimethylboratabenzene (11): Sodium bis(trimethylsilyl)amide in toluene (0.6 M, 27.5 mL, 16.5 mmol) was added dropwise at −78 °C to a solution of 1-(dimethylamino)-5-methyl-3-methylene-1,2,3,6-tetrahydroborinine (**9**, 2.50 g, 16.5 mmol) in toluene (15 mL). The reaction mixture was kept at −78 °C for 1 h and was then warmed to ambient temperature. Stirring was continued for an additional 5 d, and a white precipitate gradually formed. The precipitate was collected by filtration through a frit, washed with toluene (3 × 10 mL), and dried under high vacuum to give **11** (1.75 g, 62%) as a moisture- and air-sensitive, white powder.

Data for 11: ^1H NMR (500 MHz, [D_8]THF, 20 °C): $\delta = 2.08$ (s, 3-/5-Me), 2.66 (s, NMe_2), 5.16 (s, 4-H), 5.24 (s, 2-/6-H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, [D_8]THF, 20 °C): $\delta = 26.0$ (3-/5-Me), 39.8 (NMe_2), 102.8 (C-4), 107.6 (br., C-2,6), 142.5 (C-3,5) ppm. $^{11}B\{^1H\}$ NMR (160 MHz, [D_8]THF, external $BF_3{\cdot}OEt_2$, 20 °C): $\delta = 32.0$ ppm.

Potassium 1-(Dimethylamino)-3,5-dimethylboratabenzene (12) and Its THP Solvate 21: Potassium bis(trimethylsilyl)amide in toluene (0.5 M, 27 mL, 13.5 mmol) was added dropwise at −78 °C to a solution of 1-(dimethylamino)-5-methyl-3-methylene-1,2,3,6-tetrahydroborinine (**9**, 2.04 g, 13.7 mmol) in toluene (10 mL). The reaction mixture was kept at −78 °C for 1 h and was then warmed to ambient temperature. Stirring was continued for an additional 5 d and a white precipitate gradually formed. The precipitate was collected by filtration through a frit, washed with toluene (3 × 10 mL), and dried under high vacuum to give **12** (1.64 g, 64%) as a moisture- and air-sensitive, white powder. Crystallization of **12** (0.27 g) from a mixture of THP and toluene (1:1, 8 mL) at −30 °C overnight afforded **12**·$(THP)_2$ (≡ **21**) as colorless prisms. The ratio of THP to **12** in **21** was established by NMR spectroscopy and X-ray diffraction methods.

Data for 12: ^1H NMR (500 MHz, [D_8]THF, 20 °C): $\delta = 2.04$ (s, 3-/5-Me), 2.64 (s, NMe_2), 5.13 (s, 4-H), 5.15 (s, 2-/6-H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, [D_8]THF, 20 °C): $\delta = 25.9$ (3-/5-Me), 39.8 (NMe_2), 103.8 (C-4), 109.0 (br., C-2,6), 142.9 (C-3,5) ppm. $^{11}B\{^1H\}$ NMR (160 MHz, [D_8]THF, external $BF_3{\cdot}OEt_2$, 20 °C): $\delta = 33.0$ ppm.

3,5-Dimethyl-1-morpholinodihydroborinines (14a, 14b): A mixture of morpholine (1.95 g, 22.4 mmol) and triethylamine (2.33 g, 23.0 mmol) in hexane (10 mL) was added dropwise at 0 °C to the 1-chloro-3,5-dimethyldihydroborines **13a** and **13b** (3.15 g, 22.4 mmol) in hexane (30 mL). A white precipitate of Et_3NHCl formed immediately. After the reaction mixture had been stirred at room temperature for 5 h, the solid was removed by filtration and washed with hexane (3 × 20 mL). The combined filtrates were concentrated to dryness under reduced pressure to afford **14a** and **14b** (3.87 g, 90%, **a**/**b** = 2:3) as a pale yellow solid, moderately sensitive to air and moisture.

Data for 14a and 14b: ^1H NMR (500 MHz, $CDCl_3$, 20 °C): **14a**: $\delta = 1.64$ (s, 2 H, 2-CH_2), 1.98, 1.89 (s, 3-/5-Me), 2.89, 3.37 (t, $J = 4.5$ Hz, 4 H, 2 NCH_2), 3.60 (m, 4 H, 2 OCH_2), 5.66 (s, 1 H, 6-H), 5.76 (m, 1 H, 4-H); **14b**: $\delta = 1.96$ (s, 6 H, 3-/5-Me), 2.81 (s, 2 H, 4-CH_2), 3.42 (t, $J = 4.6$ Hz, 4 H, 2 NCH_2), 3.63 (t, $J = 4.6$ Hz, 4 H, OCH_2), 5.90 (s, 2 H, 2-/6-H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 20 °C): **14a**: $\delta = 24.1$ (br., C-2), 26.1, 26.6 (3-/5-Me), 42.6, 47.0 (2 NCH_2), 68.4 (2 OCH_2), 119.1 (br., C-6), 124.9 (C-4), 143.7 (C-3), 155.4 (C-5); **14b**: $\delta = 26.5$ (3-/5-Me), 42.6 (C-4), 47.5 (2 NCH_2), 68.9 (2 OCH_2), 123.2 (br., C-2,6), 156.4 (C-3,5) ppm. $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$, external $BF_3{\cdot}OEt_2$, 20 °C): **14a**: $\delta = 39.8$ ppm; **14b**: $\delta = 32.6$ ppm. MS (EI): *m*/*z* (%) = 191 (100) [M^+], 176 (26) [$M^+ - Me$], 162 (5) [$M^+ - 2\ Me$], 105 (14) [$Me_2C_5H_4B^+$], 91 (10) [$MeC_5H_4B^+$]. $C_{11}H_{18}B{-}NO$ (191.08): calcd. C 69.14, H 9.50, N 7.33; found C 69.05, H 9.57, N 7.45.

Lithium 3,5-Dimethyl-1-morpholinoboratabenzene (17): Lithium bis(trimethylsilyl)amide in hexane (1.0 M, 5.4 mL, 5.4 mmol) was added dropwise at −78 °C to a solution 3,5-dimethyl-1-(morpholino)-dihydroborinines (**14a/14b**, 1.03 g, 5.4 mmol) in diethyl ether (10 mL). The reaction mixture was kept at −78 °C for 1 h and was then warmed to ambient temperature. Stirring was continued for an additional 24 h and a white precipitate formed. The precipitate was collected by filtration through a frit, washed with hexane (3 × 10 mL), and dried under high vacuum to give **17** (1.04 g, 98%) as a moisture- and air-sensitive, white powder.

Data for 17: ^{1}H NMR (500 MHz, [D$_8$]THF, 20 °C): δ = 1.99 (s, 3-/5-Me), 3.06 (t, J = 4.5 Hz, 2 NCH$_2$), 3.46 (t, J = 4.5 Hz, 2 OCH$_2$), 5.08 (s, 4-H), 5.09 (s, 2-/6-H) ppm. ^{13}C{^{1}H} NMR (126 MHz, [D$_8$]THF, 20 °C): δ = 25.7 (3-/5-Me), 48.0 (2 NCH$_2$), 69.3 (2 OCH$_2$), 103.0 (C-4), 107.1 (br., C-2,6), 142.7 (C-3,5) ppm. ^{11}B{^{1}H} NMR (160 MHz, [D$_8$]THF, external BF$_3$·OEt$_2$, 20 °C): δ = 31.2 ppm. $C_{11}H_{17}BLiNO$ (197.01): calcd. C 67.06, H 8.70, N 7.11; found C 66.90, H 8.74, N 6.89.

Sodium 3,5-Dimethyl-1-morpholinoboratabenzene (18): Sodium bis(trimethylsilyl)amide in toluene (0.6 M, 9.5 mL, 5.70 mmol) was added dropwise at −78 °C to a solution of 3,5-dimethyl-1-(morpholino)dihydroborinines (**14a/14b**, 1.09 g, 5.70 mmol) in toluene (10 mL). The reaction system was kept at −78 °C for 1 h and was then warmed to ambient temperature. The mixture was stirred for 24 h and a white precipitate formed. The precipitate was collected by filtration, washed with toluene (3 × 10 mL), and dried under high vacuum to afford **18** as a moisture- and air-sensitive, white powder (1.09 g, 90%).

Data for 18: ^{1}H NMR (500 MHz, [D$_8$]THF, 20 °C): δ = 2.08 (s, 3-/5-Me), 3.07 (t, J = 4.7 Hz, 2 NCH$_2$), 3.43 (t, J = 4.7 Hz, 2 OCH$_2$), 5.21 (s, 4-H), 5.24 (s, 2-/6-H) ppm. ^{13}C{^{1}H} NMR (126 MHz, [D$_8$]THF, 20 °C): δ = 26.0 (3-/5-Me), 48.2 (2 NCH$_2$), 69.3 (2 OCH$_2$), 103.7 (C-4), 107.6 (br., C-2,6), 142.7 (C-3,5) ppm. ^{11}B{^{1}H} NMR (160 MHz, [D$_8$]THF, external BF$_3$·OEt$_2$, 20 °C): δ = 32.0 ppm. $C_{11}H_{17}B{-}NNaO$ (213.06): calcd. C 62.01, H 8.04, N 6.57; found C 61.76, H 7.87, N 6.68.

Potassium 1-[Bis(trimethylsilyl)amino]-3,5-dimethylboratabenzene (19) and Its THF Solvates (α- and β-22): Potassium bis(trimethylsilyl)amide in toluene (0.5 M, 9 mL, 4.5 mmol) was added dropwise at −78 °C to a solution of 1-bis(trimethylsilyl)amino-3,5-dimethyl-dihydroborinines (**16a/16b**, 1.2 g, 4.5 mmol) in toluene (10 mL). The system was kept at −78 °C for 1 h and was then warmed to ambient temperature. Stirring was continued for 24 h, and a fine white precipitate formed. The precipitate was collected by filtration through a frit, washed with toluene (3 × 10 mL), and dried under high vacuum to give **19** (1.25 g, 91%) as a moisture- and air-sensitive, white powder. Crystallization of **19** (0.25 g) from THF (5 mL) at −4 °C for a week afforded large, colorless crystals possessing ca. 1.4 equiv. of THF per unit **19** (^{1}H NMR). The concomitant presence of the two pseudo-polymorphs α-**22** and β-**22** was established by X-ray diffraction methods.

Data for 19: ^{1}H NMR (500 MHz, [D$_8$]THF, 20 °C): δ = 0.06 (s, 2 SiMe$_3$), 2.08 (s, 3-/5-Me), 5.43 (t, J = 1.5 Hz, 4-H), 5.52 (d, J = 1.5 Hz, 2-/6-H) ppm. ^{13}C{^{1}H} NMR (126 MHz, [D$_8$]THF, 20 °C): δ = 4.9 (2 SiMe$_3$), 25.7 (3-/5-Me), 107.9 (C-4), 121.9 (br., C-2,6), 141.5 (C-3,5) ppm. ^{11}B{^{1}H} NMR (160 MHz, [D$_8$]THF, external

Table 2. Crystal data, data collection parameters, and convergence results for **20**, **21**, α-**22**, and β-**22**

	20	**21**	α-**22**	β-**22**
Empirical formula	$C_{18}H_{32}BKO_6$	$C_{19}H_{35}BKNO_2$	$C_{13}H_{27}BKNSi_2\cdot(C_4H_8O)_{4/3}$	$C_{13}H_{27}BKNSi_2\cdot(C_4H_8O)_{3/2}$
Formula mass	394.37	359.41	399.60	411.60
Crystal system	orthorhombic	monoclinic	monoclinic	hexagonal
Space group	$Pna2_1$	$C2/c$	$C2/c$	$P6_122$
Radiation (λ [Å])	Cu-K_α (1.54184)	Mo-K_α (0.71073)	Cu-K_α (1.54184)	Mo-K_α (0.71073)
a [Å]	19.659(9)	18.062(7)	14.924(5)	11.9545(2)
b [Å]	9.921(4)	10.280(5)	29.307(5)	
c [Å]	11.114(3)	24.379(6)	17.385(4)	62.294(2)
β [°]		100.52(2)	106.07(3)	
V [Å^3]	2168(2)	4450(5)	7306(3)	7709.8(3)
Z	4	8	12	12
$d_{\text{calcd.}}$ [g/cm^3]	1.21	1.07	1.09	1.06
F(000)	848	1568	2608	2688
μ [cm^{-1}]	23.93	2.45	29.39	3.09
Absorption correction	empirical	not applied	empirical	not applied
Max./min. transmission	0.999/0.732		1.000/0.563	
θ range [°]	4.5−75.1	3.1−26.0	4.0−68.0	2.0−24.4
Temperature [K]	200	218	150	173
Scan mode	ω	ω−2θ	ω−2θ	ω
Crystal size [mm]	0.7 × 0.6 × 0.4	0.4 × 0.4 × 0.3	0.6 × 0.4 × 0.4	0.55 × 0.35 × 0.3
Reflections collected	9540	9581	13237	31996
Reflections unique	4466	4355	6655	4077
Reflections observed	3687	1370	3411	3512
Criterion for observation	$I > 2\,\sigma(I)$	$I > 2\,\sigma(I)$	$I > 2\,\sigma(I)$	$I > 2\,\sigma(I)$
Variables	299	363	346	216
R_1,[a] observed (all data)	0.074 (0.086)	0.056 (0.213)	0.070 (0.128)	0.080 (0.093)
wR_2,[b] observed (all data)	0.192 (0.201)	0.067 (0.087)	0.142 (0.160)	0.205 (0.213)
GOF[c]	1.103	0.702	0.839	1.172
Max. resd. density [e/Å^3]	0.48	0.18	0.56	0.53

[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 $= [w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$.

$BF_3\cdot OEt_2$, 20 °C): $\delta = 35.5$ ppm. $C_{13}H_{27}BKNSi_2$ (303.45): calcd. C 51.46, H 8.97, N 4.62; found C 51.41, H 8.90, N 4.73.

X-ray Crystal Structure Determinations: Data collections for the compounds **20**, **21**, and α-**22** were performed with ENRAF-Nonius CAD4 diffractometers (Mo- or Cu-K_α radiation with graphite monochromators). The reflection data set for β-**22** was collected with a Bruker Apex X-ray diffractometer (Mo-K_α radiation with a graphite monochromator) equipped with a CCD area detector.[23] Crystal data, data collection parameters, and convergence results are listed in Table 2. Before symmetry-related reflections were merged, empirical absorption corrections on the basis of azimuthal scans[24] were applied to the data sets collected with the Cu-K_α radiation. All structures were solved by direct methods with the help of the SHELXS-97 program[25a] and refined on reflection intensities (F^2) by use of the SHELXL-97 program.[25b] The [18]-crown-6 ligand in the structure **20** suffers from rotational disorder. The two orientations, with an occupancy ratio of 61(1)/39(1), are related to each other by a rotational angle of ca. 20.5°. In the case of **21**, one of the two THP ligands displays flapping disorder (O2, C15−C19/C25−C29); the oxygen atom is well defined whereas all the other atoms split into two sites with an occupancy ratio of 64(1):36(1). Two types of THF are present in the structure of β-**22**; one serves as a ligand to the potassium atom, while the other acts solely as a space-filling molecule. The latter type of THF is disordered into two sites with the oxygen atom (O3) residing on a twofold crystallographic axis. Several restrains were applied in the disordered structural models to set the C−C and C−O distances, respectively, to be equal with a standard deviation of 0.03 Å. In the final structural refinements, non-hydrogen atoms other than disordered ones were assigned with anisotropic displacement parameters. Hydrogen atoms were either refined isotropically or included as riding with fixed displacement parameters [C−H = 0.98 Å, $U_{\text{iso}}(\text{H}) = 1.3\,U_{\text{eq}}(\text{C})$].[26]

Acknowledgments

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[26] 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-202182 (**20**), -202183 (**21**), -202184 (α-**22**), and -202185 (β-**22**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U. K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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