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Articles

Syntheses and Structures of $Mg(C_5H_5BMe)_2$, $Mg(3,5\text{-}Me_2C_5H_3BNMe_2)_2$, the 2,2′-Bipyridine Adduct $Mg(C_5H_5BMe)_2$(bipy), and the N-Bonded Aminoboratabenzene Species $Mg(3,5\text{-}Me_2C_5H_3BNMe_2)_2(THF)_2$[1]

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The donor-free magnesocene analogues bis(1-methylboratabenzene)magnesium (**1**) and bis[3,5-dimethyl-1-(dimethylamino)boratabenzene]magnesium (**2**) are synthesized in good yields by the reactions of dimethylmagnesium with (trimethylstannyl)dihydroborinine precursors **3** and **4**. In the crystalline state, both **1** and **2** possess sandwich structures with η^6-coordinated boratabenzene ligands and display crystallographic centrosymmetry. Compound **1** reacts with the nitrogen donor 2,2′-bipyridine to give the Lewis base adduct (**1**)(bipy) (≡**5**). In the crystal structure of **5**, one boratabenzene ligand is η^6-bonded to the central metal while the other ligand adopts an η^1-bonding mode. Crystallization of compound **2** from THF produces the solvate (**2**)$(THF)_2$ (≡**6**), which exhibits a distorted tetrahedral N_2O_2 coordination environment around the magnesium atom. The average Mg−N bond distance is 2.141(3) Å, and the N−Mg−N angle is 148.0(1)°. The observation of an aminoboratabenzene that is solely σ-bonded to a metal is without precedent.

Introduction

Bis(η^5-cyclopentadienyl)magnesium, or magnesocene,[2] is one of the earliest known metallocenes. The parent magnesocene and its substituted derivatives[3,4] have been widely used as cyclopentadienyl sources in organometallic syntheses.[5] In the solid state, the donor-free magnesocenes [e.g., $Mg(C_5H_5)_2$[2c,h] and $Mg(C_5H_4Bu^t)_2$[4e]] generally possess typical ferrocene-like structures with staggered parallel cyclopentadienyl rings. One exception is bis[1,2,4-tris(trimethylsilyl)cyclopentadienyl]magnesium,[6] in which a slightly bent sandwich structure is adopted, due to the repulsive interactions of bulky trimethylsilyl groups. A polymeric structure was found in the case of bis(indenyl)magnesium.[7] In this compound the structure exhibits two different bonding environments around the central metal; each magnesium atom is coordinated to three indenyl ligands, one facially bonded in an η^5-fashion and the other two bonded with much lower hapticities close to η^1- or η^2-coordination.

Boratabenzene ions can act as facially bonded 6-π-electron ligands, which are closely analogous to cyclopentadienides.

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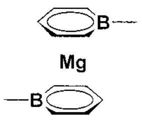
Whereas the previous work in this field has predominantly been devoted to transition metal complexes, the chemistry of the main group metal derivatives has remained relatively undeveloped.[8] Structural data on lithium,[9] sodium,[10] potassium,[11] indium,[12] tin,[13] and lead[14] compounds have appeared only recently. As part of our continuing interest in this area, we report here the syntheses and structural characterizations of two magnesocene analogues, bis(1-methylboratabenzene)magnesium (**1**)[15] and bis[3,5-dimethyl-1-(dimethylamino)boratabenzene]magnesium (**2**), as well as of two Lewis base adducts of these. Our results constitute the first detailed account of boratabenzene derivatives of an alkaline earth metal.



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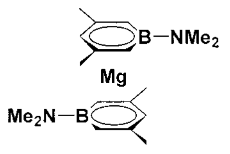
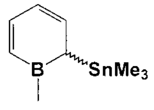


2

Results and Discussion

Dihydroborinines 3 and 4. In previous work we had described the synthesis of 2-(Me_3Sn)C_5H_5BMe (**3**) from lithium 1-methylboratabenzene and Me_3SnCl.[13] Analogously, the reaction of lithium 3,5-dimethyl-1-(dimethylamino)boratabenzene[9c,16] with Me_3SnCl in THF afforded 3,5-dimethyl-1-(dimethylamino)-2-(trimethylstannyl)-1,2-dihydroborinine (**4**) in 91% yield as an air- and moisture-sensitive pale yellow liquid.



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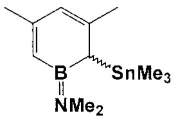

4

The tin compound **4** was characterized by multinuclear NMR spectroscopy. At ambient temperature, **4** displays fluxional behavior due to fast sigmatropic migration[17] of the trimethylstannyl group. This results in effective lateral symmetry in both the ^{1}H and ^{13}C NMR spectra. A $\delta(^{119}\mathrm{Sn})$ chemical shift of 35.8 ppm was observed for **4** in THF-d_8. This value is close to the values observed for **3** (36.9 ppm, in $CDCl_3$)[13] and 5-(Me_3Sn)-C_5H_5 (32.3 ppm, in THF-d_8),[18] thus confirming the expected η^1-bonding situation in **4**.

Variable-temperature ^{1}H and ^{13}C NMR measurements reveal that well-resolved spectra can be recorded at −90 °C which correspond to the two enantiomeric ground states.[13] Upon an increase in temperature, line broadening and coalescence were observed for all the unsymmetrical protons (2-/6-H, 3-/5-Me, 2 NMe) and carbon nuclei (C-3,5, C-2,6, 3-/5-Me, 2 NMe). Rate constants were determined by simulation of the line shapes[19,20] for the ring carbon atoms C-3 and C-5, and an Eyring plot of these data gave as activation parameters $\Delta G_{300}^{\ddagger} = 41.6(5)$ kJ mol^{-1}, $\Delta H^{\ddagger} = 41.2(2)$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -1.4(10)$ J K^{-1} mol^{-1}.

The sizable barrier to sigmatropic automerization of **4** is in sharp contrast to the behavior of the *B*-methyl compound **3**, which shows no tendency toward line broadening, even at a lower temperature of −95 °C.[13] This striking difference can be explained by the different electronic effects of the exocyclic substituents attached to the boron atom. In the case of compound **3** the very low barrier has been attributed to hyperconjugative weakening of the bond between the tin and the boratabenzene ring.[13] In the case of compound **4** the π-interaction between the amino lone pair and the boron atom will reduce this hyperconjugation. Hence, the bond between the tin and carbon C-2 will be stronger, and the barrier to sigmatropic rearrangement is expected to be higher.

Compound **4** displays heteronuclear couplings with all hydrogen nuclei and many carbon nuclei. For compound **3**, the $^{117/119}$Sn satellites could readily be quenched either by using pyridine-d_5 as the solvent or by adding a catalytic amount of DMSO to its THF-d_8 solution. This observation supports a mechanism of intermolecular exchange of $SnMe_3$ groups.[13] However, in the case of compound **4**, such satellite quenching is not observed. Neither the $^{117/119}$Sn satellites nor the chemical shifts are changed in the above-mentioned donor solvent systems. This is in line with the stronger Sn−C interaction in molecule **4** as compared to **3**. On the basis of the structural and NMR characterizations, two limiting bonding descriptions for compound **3** were discussed in our previous work: that of a contact ion pair (Me_3Sn^+, $C_5H_5BMe^-$) with the cation attached to the most electron-rich ring atom C-2 and that of a classical, localized covalent Sn−C bond.[13] We conclude that the localized covalent bonding is more pronounced in compound **4** than in the methyl compound **3**.

Magnesocene Analogues 1 and 2. The tin compounds **3** and **4** were used as precursors to generate the donor-free bis(boratabenzene)magnesium compounds **1** and **2** (Scheme 1). In

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hydrocarbon solvents, the reactions of **3** and **4** with $MgMe_2$,[21] prepared in situ from $HgMe_2$, produced the magnesocene analogues **1** and **2** in 63% and 83% yields, respectively. Both compounds are low-melting colorless crystalline solids (mp: 45−46 °C for **1**; 68−70 °C for **2**). They are highly soluble in hexane and are extremely sensitive to traces of air or humidity.

Scheme 1

$$MgMe_2 + 2\ \underset{\mathbf{3}}{2\text{-}(Me_3Sn)C_5H_5BMe} \rightarrow \underset{\mathbf{1}}{Mg(C_5H_5BMe)_2} + 2SnMe_4$$

$$MgMe_2 + 2\ \underset{\mathbf{4}}{2\text{-}(Me_3Sn)(3,5\text{-}Me_2C_5H_3BNMe_2)} \rightarrow \underset{\mathbf{2}}{Mg(3,5\text{-}Me_2C_5H_3BNMe_2)_2} + 2SnMe_4$$

^{11}B NMR spectroscopy was used to monitor the reactions. At the end of the transformations the signals of the 1,2-dihydroborinines [$\delta(^{11}B)$: 48 ppm for **3**;[13] 38 ppm for **4**] had disappeared completely and new signals with chemical shifts that are characteristic for ionic boratabenzenes [$\delta(^{11}B)$: 37 ppm for **1**; 30 ppm for **2**] were seen. Soon after the addition of the tin compound **3** to $MgMe_2$, a strong signal [$\delta(^{11}B)$ −10 ppm] was detected that gradually weakened and disappeared after 2 h at ambient temperature. This observation reveals that a reversible nucleophilic quaternization at the boron center of **3** was taking place.[22] The role of this borate species has remained unclear. On one hand, it could be the key intermediate which, by way of an intramolecular elimination of $SnMe_4$, would form the product **1**.[23,24] On the other hand, a direct nucleophilic attack of a methylmagnesium species at the tin center of **3** cannot be ruled out. Quite remarkably, no such borate signal could be traced during the preparation of the analogous compound **2**. This is probably due to the particularly effective electronic stabilization of **4** by the exocyclic dimethylamino group at the boron center.[23] As a result, the quaternization of the boron atom is energetically much less favorable.

Another interesting feature of these two reactions is the dramatic difference in the required reaction conditions. The reaction of the methyl compound **3** in pentane solution was completed in 6 h at ambient temperature. For the reaction of the dimethylamino compound **4**, a much higher temperature and a longer reaction time were necessary; heating the reaction mixture to 110 °C for 10 days in toluene was required to complete the transformation. Again, the different reactivities of **3** and **4** can be related to the different bonding situations in these compounds.

Crystal Structures of 1 and 2. Crystals of compounds **1** and **2** suitable for X-ray structure determinations were grown from pentane and hexane, respectively, at −20 °C. In the solid state, both **1** and **2** exhibit typical sandwich structures which possess crystallographic centrosymmetry. The boratabenzene ligands are facially bonded to the magnesium atom. The inversion symmetry implies coplanarity of the ring ligands and antiperiplanar arrangement with respect to the exocyclic substituents (Figures 1 and 2; Table 1).

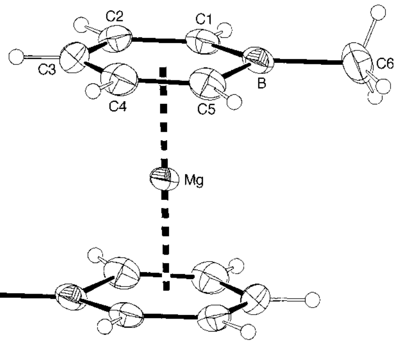

Figure 1. Platon plot[25] of molecule **1**. Displacement ellipsoids are scaled to 30% probability.

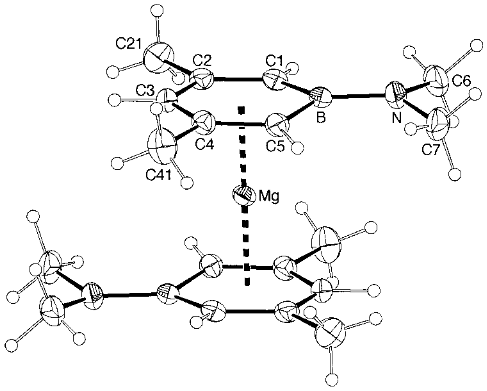

Figure 2. Platon plot[25] of molecule **2**. Displacement ellipsoids are scaled to 30% probability.

Table 1. Selected Bond Distances (Å) for **1** and **2**

	1	2		1	2
Mg−C1	2.359(2)	2.350(1)	C2−C3	1.390(3)	1.406(2)
Mg−C2	2.422(2)	2.409(1)	C3−C4	1.385(3)	1.404(2)
Mg−C3	2.453(2)	2.429(2)	C4−C5	1.398(2)	1.405(2)
Mg−C4	2.420(2)	2.411(2)	C1−B	1.520(2)	1.537(2)
Mg−C5	2.361(2)	2.356(1)	C5−B	1.508(3)	1.532(2)
Mg−B	2.436(2)	2.458(1)	X−B[a]	1.586(2)	1.431(2)
C1−C2	1.394(2)	1.404(2)			

[a] X = C6 for **1** and X = N for **2**.

The good quality of the diffraction data for **1** and **2** allows us to discuss the molecular geometries in some detail. The boratabenzene ligands of both molecules are planar in their C_5 moieties [maximum deviations from the best planes: 0.002(2) Å for C3 in **1**; 0.003(1) Å for C3 in **2**]. In the case of molecule **1**, the boron atom is bent away from the magnesium atom with a folding angle of 5.7(9)° and a vertical displacement of 0.083(2) Å. For compound **2**, the deviation of the boron from the best ligand plane is slightly more pronounced; the folding angle is 8.0(5)°, and the vertical displacement of the boron atom is 0.118(1) Å. The Mg−C distances in **1** [2.403 Å (average), ranging from 2.359(2) to 2.453(2) Å; Mg−C_5 plane distance 1.920(1) Å] and **2** [2.391 Å (average), ranging from 2.350(1) to 2.429(2) Å; Mg−C_5 plane distance 1.896(1) Å] are slightly longer than those in the magnesocenes (2.28−2.35 Å).[2−4] This difference may be understood as the consequence of the lower charge density of the six-membered boratabenzene ring com-

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[23] For the generation of boratabenzene species through borate intermediates, see: Herberich, G. E.; Schmidt, B.; Englert, U. *Organometallics* **1995**, *14*, 471.

[24] Recent work on nucleophilic substitution reactions of the neutral borabenzene Lewis base adducts also reveals quaternization of the boron center. See: (a) Qiao, S.; Hoic, D. A.; Fu, G. C. *J. Am. Chem. Soc.* **1996**, *118*, 6329. (b) Putzer, M. A.; Rogers, J. S.; Bazan, G. C. *J. Am. Chem. Soc.* **1999**, *121*, 8112.

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Table 2. Structural Comparison of Nitrogen−Boron π-Interactions in Aminoboratabenzene Complexes

compound	N−B, Å	B−C(average), Å	C−C(average), Å	ref
$[Li(C_5H_5BNMe_2)](TMPTA)$	1.442(2)	1.515(2)	1.384(3)	9a
$Mg(3,5\text{-}Me_2C_5H_3BNMe_2)_2$ (**2**)	1.431(2)	1.534(2)	1.405(2)	this work
$[ScCl(3,5\text{-}Me_2C_5H_3BNMe_2)_2]_2$[a]	1.417(3)	1.537(3)	1.402(3)	16
$ZrCl_2(C_5H_5BNPr^i_2)_2$	1.396(6)	1.552(7)	1.391(7)	27c

[a] Only the geometry of the η^6-coordinated boratabenzene ligand was considered; the other ligand, coordinated in η^3-fashion, was ignored because of the bonding between the Sc atom and the exocyclic N atom.

pared to the five-membered cyclopentadienide ring. The Mg−B distances of 2.436(2) Å for **1** and 2.458(1) Å for **2** confirm that the boratabenzene ligands are η^6-coordinated to the metal.

Both structures show a marked slip distortion (the distance between the projection of the Mg atom onto the C_5 plane and the geometric mean of the projections of the C_5B ring onto the C_5 plane, amounting to 0.12 Å for **1** and 0.11 Å for **2**) which shifts the magnesium atom toward (!) the boron atom. A similar situation was previously noted for $Pb(C_5H_5BMe)_2$[14] but is in sharp contrast to the behavior of d metal complexes which generally display slip distortions away from the boron.[8c] The slip distortion in combination with the ligand folding results in particularly pronounced bonding interactions between the Mg atom and the α-carbon atoms. A simple electrostatic bonding model provides a qualitative explanation for the underlying bonding situation. The π-electrons of the boratabenzene rings concentrate negative charge on the carbon atoms in α- and γ-positions of the ring. Within the σ-skeleton, the B−C bond polarity places more negative charge on the α-carbon atoms. For the case of an Mg^{2+} ion and two boratabenzene ions, the cation will interact most strongly with the α-carbons. This will result in particularly short distances to the α-carbon atoms and will induce the ligand folding observed experimentally. A detailed all-electron density functional study on the bonding in **1** and **2** will be presented in a forthcoming paper.[26]

The π-interaction between the exocyclic nitrogen atom and the boron of aminoboratabenzene compounds has attracted much research interest.[23,27] The structural characterization of the bis(aminoboratabenzene)magnesium complex **2** completes a series of structures of group 1 to group 4 compounds (Table 2). The structural data show a clear trend. On going from Li(I) to Zr(IV), the exocyclic N−B distances shrink, thus showing the increasing importance of the B−N π-interactions. Simultaneously, the average intra-ring C−B distances increase, in agreement with the notion that the B−N π-interactions are antibonding with respect to the B−C π-interactions. We may also say that the aminoboratabenzenes become increasingly similar to the open pentadienyl ligands.

Formation of the Lewis Base Adducts. It is well-known that magnesocenes form Lewis base adducts with N or O donors.[28] Recently the structures of THF adducts of several *ansa*-magnesocenes,[29] and the structure of an adduct of decamethylmagnesocene, $Mg(C_5Me_5)_2$, with a stable carbene have been described.[30] We found that compounds **1** and **2** display the same type of reactivity, and we give a detailed description of two examples. Adding a stoichiometric amount of 2,2′-bipyridine to a solution of **1** in toluene readily afforded $Mg(C_5H_5BMe)_2(bipy)$ (**5**) as an orange-brown powder in almost quantitative yield. Crystallization of **2** from THF produced large colorless crystals of $Mg(THF)_2(3,5\text{-}Me_2C_5H_3BNMe_2)_2$ (**6**). Both **5** and **6** are very sensitive to air and moisture. While the THF solvate **6** is quite soluble in hydrocarbon solvents such as hexane, the 2,2′-bipyridine adduct **5** is only sparingly soluble in THF, and moderately soluble in hot toluene.

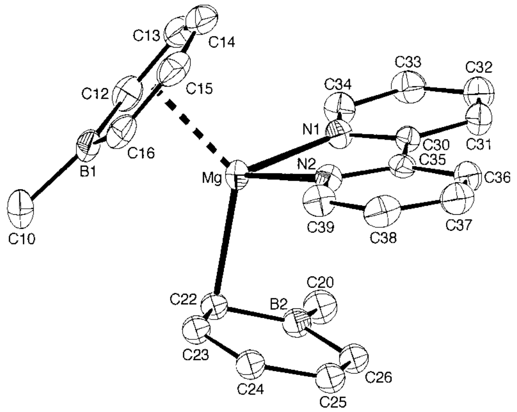

Figure 3. Platon plot[25] of molecule **5**. The disordered boratabenzene ring with minor occupancy (ring C) has been omitted for clarity. Displacement ellipsoids are scaled to 30% probability. Selected distances (Å) and bond angles (deg) are as follows. For the bipy ligand: Mg−N1 2.139(2), Mg−N2 2.117(2), N1−Mg−N2 77.22(8). For ring A: Mg−C12 2.504(3), Mg−C13 2.657(3), Mg−C14 2.743(3), Mg−C15 2.651(3), Mg−C16 2.504(3), Mg−B 2.549(3). For ring B: Mg−C22 2.313(7), Mg···C23 2.770(7), Mg···B2 2.913(8). For ring C: Mg−C42 2.403(10), Mg···C43 2.704(10), Mg···B3 2.976(11).

Crystal Structure of 5. We knew from preliminary work that the addition of a Lewis base to **1** induces profound changes in the bonding situation.[8b] Therefore we proceeded to investigate the crystal structures of **5** and **6**.

Crystals of **5**, suitable for an X-ray diffraction study, were grown by slowly cooling a saturated toluene solution of **5** from 100 °C to ambient temperature. The molecule of **5** contains two boratabenzene rings (Figure 3). The first one (ring A) is well defined, while the second one suffers from a rotational disorder which can be described by two split positions. The split positions (rings B and C) are essentially coplanar [interplanar angle 6(2)°] and are rotated with respect to each other by an angle of 154° approximately around the axis defined by the magnesium and the mid point between C22 and C42. In the structural model, these two sites were refined with a 60%:40% occupancy ratio.

The overall structure of **5** is that of a pseudo-piano-stool molecule. The addition of 2,2′-bipyridine to the donor-free compound **1** causes a dramatic structural change. The comparatively strong Mg−N bonds [2.139(2) and 2.117(2) Å]

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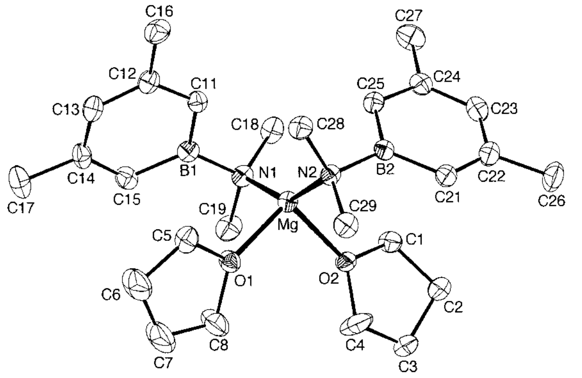

Figure 4. Platon plot[25] of molecule **6**. Displacement ellipsoids are scaled to 30% probability. Selected distances (Å) and bond angles (deg) are as follows. For the Mg center: Mg−O1 2.035(2), Mg−O2 2.052(2), Mg−N1 2.140(3), Mg−N2 2.142(3), Mg···B1 2.700(4), Mg···B2 2.657(4), O1−Mg−O2 98.2(1), N1−Mg−N2 148.0(1), O1−Mg−N1 98.5(1), O1−Mg−N2 103.7(1), O2−Mg−N1 103.3(1), O2−Mg−N2 96.2(1). For the first ring: N1−B1 1.539(4), C11−C12 1.402(4), C12−C13 1.399(5), C13−C14 1.400(6), C14−C15 1.386(5), C11−B1 1.517(5), C15−B1 1.497(5). For the second ring: N2−B2 1.537(5), C21−C22 1.374(5), C22−C23 1.400(6), C23−C24 1.394(5), C24−C25 1.403(5), C21−B2 1.506(5), C25−B2 1.489(6).

partially quench the positive charge residing on the magnesium atom. In addition to the expected elongation of the metal−boratabenzene ligand bonds, a steric constraint in the coordination environment is seen. One ring remains facially bonded to the magnesium atom while the hapticity of the second ring is reduced and only one of the α-carbon atoms remains within bonding distance of the central metal.

The C_5 fragment of ring A is planar, and the boron atom is bent away from the metal with a vertical distance of 0.115(3) Å and a folding angle of 8(1)°. The Mg−C distances in **5** [2.618 Å (average), ranging from 2.504(3) to 2.743(3) Å; distance of the metal to best C_5 plane 2.137(1) Å] are much longer than those in **1**, and again, the metal-to-ring bonding pattern is characterized by a large slip distortion of 0.31 Å toward the boron [cf. the distances Mg−B1 of 2.549(3) and Mg−C14 of 2.743(3) Å]. The disordered ring (rings B and C) is also planar in its C_5 part but is much less tightly bonded. The only appreciable bonding interaction is between the magnesium atom and the coordinated α-carbon [distances Mg−C22 of 2.313(7) (ring B) and Mg−C42 of 2.403(10) Å (ring C)]. We note in passing that monohapto coordination is still quite rare in boratabenzene chemistry and has only been structurally characterized in the more covalent compounds $InMe(C_5H_5BMe)_2$[12] and $2\text{-}(Me_3Sn)C_5H_5BMe$[13] of p-block metals in their high valence state.

Crystal Structure of 6. A totally unexpected coordination mode was found in the crystal structure of the THF adduct **6** (Figure 4). The closest interatomic distances of the central metal to the boratabenzene ring atoms are 2.700(4) Å for Mg···B1 and 2.657(4) Å for Mg···B2. These distances rule out any direct bonding between the magnesium atom and the boratabenzene rings. Instead, the Mg atom is tetrahedrally coordinated by two nitrogen atoms of the exocyclic dimethylamino groups and two THF molecules. The Mg−N bond distances [2.140(3) and 2.142(3) Å] are quite close to those of the bipyridine adduct **5** and slightly longer than the Mg−O distances [2.035(2) and 2.052(2) Å]. The N−Mg−N bond angle is remarkably large [148.0(1)°], while the other angles around the magnesium center are less than the ideal tetrahedral value (ranging from 96.2 to 103.7°). The coordination of the nitrogen atoms is accompanied by pyramidalization of the dimethylamino group. This bonding situation greatly diminishes the π-interaction between the amino group and boron atom, which is so characteristic for aminoboratabenzene complexes. As a result, a less perturbed or, in other words, a more delocalized aromatic boratabenzene system is seen in the structure with much longer exocyclic B−N bond distances [1.538(5) Å (average)] and more even intra-ring distances. A similar coordination of a pyramidalized exocyclic dialkylamino group was previously described for the aminoborol dianion in $[Li_2(C_4H_4BNEt_2)(TMEDA)]_2$.[31]

Overall, the molecular geometry of **6** can be described as a tetrahedron that is strongly distorted owing to the electrostatic repulsion between the two negatively charged boratabenzene rings. Two limiting descriptions may shed additional light on the bonding situation. One description would be that of a THF-solvated contact ion triple; there is a similarity to solvent-separated ion pairs, and the N-coordinated amino groups would play the role of a tertiary amine. The other description, which is perhaps more extreme, would consider **6** as a borabenzene adduct[32] (rather than a boratabenzene derivative) of a magnesium amide, $Mg(NMe_2)_2(THF)_2$.

Recent work by Fu et al. described a similar bonding duality for *B*-(diphenylphosphido)boratabenzene (DPB). This anion is isoelectronic with triphenylphosphine and is intrinsically pyramidal at the phosphorus. Its potassium salt $[K(DPB)(18\text{-crown-}6)](toluene)_{1/2}$ displays the expected ion-pair coordination of $[K(18\text{-crown-}6)]^+$ to its boratabenzene ring.[11] On the other hand, if bonded to transition metals, it tends to be σ-coordinated through its phosphorus atom.[33]

Concluding Remarks. Work presented in this paper provides a convenient preparative route to donor-free bis(boratabenzene)magnesium complexes, which could serve as hydrocarbon-soluble boratabenzene sources in organometallic syntheses. The addition of Lewis bases such as 2,2′-bipyridine and THF to these magnesocene analogues induces dramatic structural changes. The nature of the bonding between the magnesium atom and the cyclopentadienyl rings has drawn much theoretical argument[2,34,35] ever since the discovery of the parent magnesocene, $Mg(C_5H_5)_2$. The structures presented here and especially our observation of considerable charge separation in the THF adduct **6** are in line with a highly ionic bonding interaction between the magnesium atom and the boratabenzene ligands.

Experimental Section

General Procedures. Reactions were carried out under an atmosphere of dinitrogen by means of conventional Schlenk techniques. Pentane and hexane were distilled from an Na/K alloy, toluene was distilled from sodium, and Et_2O and THF were distilled from sodium benzophenone ketyl. Melting points were determined in sealed capillaries on a Büchi 510 melting point apparatus and are uncorrected. Elemental analyses were performed at Analytische Laboratorien, 51779 Lindlar, Germany.

NMR spectra were recorded on a Varian Unity 500 (^1H, 500 MHz; ^{13}C, 125.7 MHz; ^{11}B, 160.4 MHz; ^{119}Sn, 186.5 MHz) spectrometer. Chemical shifts are given in ppm and are referenced to TMS for ^1H and ^{13}C, to $BF_3{\cdot}OEt_2$ for ^{11}B, and to $SnMe_4$ for ^{119}Sn NMR. Mass

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Table 3. Crystal Data, Data Collection Parameters, and Convergence Results for **1**, **2**, **5**, and **6**

	1	**2**	**5**	**6**
empirical formula	$C_{12}H_{16}B_2Mg$	$C_{18}H_{30}B_2N_2Mg$	$C_{22}H_{24}B_2N_2Mg$	$C_{26}H_{46}B_2N_2O_2Mg$
fw	206.20	320.39	362.38	464.60
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	6.7311(7)	8.056(2)	10.4664(9)	10.097(6)
b, Å	8.363(2)	10.884(3)	13.776(2)	15.740(2)
c, Å	11.622(2)	11.606(3)	14.236(2)	18.151(5)
β, deg	103.80(1)	101.81(2)	98.962(9)	105.74(3)
V, Å^3	635.3(2)	997.2(9)	2027.5(5)	2777(3)
Z	2	2	4	4
T, K	203	193	228	233
λ, Å	0.7107	1.5418	1.5418	0.7107
ρ_{calcd}, g cm^{-3}	1.079	1.067	1.187	1.111
μ, cm^{-1}	0.98	7.21	7.75	0.83
R^a	0.051	0.059	0.063	0.093
$R_w{}^b$	0.051	0.058	0.068	0.069

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F_o)$.

spectra were recorded on a Finnigan MAT-95 at a nominal electron energy of 70 eV.

3,5-Dimethyl-1-(dimethylamino)-2-(trimethylstannyl)-1,2-dihydroborinine (4). Me_3SnCl (4.42 g, 22.2 mmol) in THF (10 mL) was added dropwise to a suspension of lithium 3,5-dimethyl-1-(dimethylamino)boratabenzene[9c,16] (3.27 g, 21.1 mmol) in THF (10 mL) at −78 °C. The system was allowed to warm to ambient temperature, and stirring was continued for 2 h. The volatiles were completely removed under vacuum. Pentane (40 mL) was then added to the residue, and a white precipitate of LiCl was filtered off. After removal of the solvent under reduced pressure, the residue was heated to 60 °C in a high vacuum (10^{-5} bar) and **4** (6.02 g, 91%) was collected by condensation as an air- and moisture-sensitive pale yellow liquid.

Data for 4. ^{1}H NMR (500 MHz, THF-d_8, 20 °C): δ 5.62 [br s, $J(^{117/119}Sn-^1H) = 24$ Hz, 4-H], 4.34 [br s, $J(^{117/119}Sn-^1H) = 45$ Hz, 2-/6-H], 2.70 [s, $J(^{117/119}Sn-^1H) = 7$ Hz, NMe_2], 1.93 [s, $J(^{117/119}Sn-^1H) = 6$ Hz, 3-/5-Me], 0.03 [s, $J(^{117}Sn-^1H) = 51$ Hz, $J(^{119}Sn-^1H) = 53$ Hz, $SnMe_3$]. ^{1}H NMR (500 MHz, THF-d_8, −90 °C): δ 5.72 (br s, 6-H), 5.62 (br s, 4-H), 3.12 [br s, $J(^{117/119}Sn-^1H) = 88$ Hz, 2-H], 2.77 (br s, 3H, NMe), 2.61 (br s, 3H, NMe), 1.97 (br s, 3H, Me), 1.90 (br s, 3H, Me), 0.03 [s, $J(^{117/119}Sn-^1H) = 51$ Hz, 9H, $SnMe_3$]. ^{13}C NMR (126 MHz, THF-d_8, 20 °C): δ 120.2 [$J(^{117/119}Sn-^{13}C) = 36$ Hz, C-3,5], 119.9 [$J(^{117/119}Sn-^{13}C) = 43$ Hz, C-4], 82.3 (br, C-2,6), 38.5 (NMe_2), 25.9 (3-/5-Me), −7.2 [s, $J(^{117}Sn-^{13}C) = 302$ Hz, $J(^{119}Sn-^{13}C) = 317$ Hz, $SnMe_3$]. ^{13}C NMR (126 MHz, THF-d_8, −90 °C): δ 153.0 (C-5), 147.6 [$J(^{117/119}Sn-^{13}C) = 56$ Hz, C-3], 121.2 (C-6), 119.2 [$J(^{117/119}Sn-^{13}C) = 41$ Hz, C-4], 43.4 (C-2), 38.8 and 38.1 (NMe_2), 26.7 (5-Me), 25.6 (3-Me), −7.5 [$J(^{117}Sn-^{13}C) = 306$ Hz, $J(^{119}Sn-^{13}C) = 320$ Hz, $SnMe_3$]. ^{11}B NMR (160 MHz, THF-d_8, $BF_3{\cdot}Et_2O$ external, 20 °C): δ 38.1. ^{119}Sn NMR (186 MHz, THF-d_8, $SnMe_4$ external, 20 °C): δ 35.8. MS (70 eV): m/z (I_{rel}) 313 (39, M$^+$), 298 (24, M$^+$ − Me), 165 (100, $SnMe_3{}^+$), 148 (66, M$^+$ − $SnMe_3$), 135 (10, $SnMe^+$), 120 (3, Sn^+). Anal. Calcd for $C_{12}H_{24}BNSn$: C, 46.22; H, 7.76; N, 4.49. Found: C, 45.98; H, 7.71; N, 4.50.

Variable-Temperature NMR Studies of 4. ^{1}H and $^{13}C\{^1H\}$ NMR spectra of a solution of **4** in THF-d_8 were recorded on the Varian Unity 500 spectrometer. The temperature was varied in 10 K intervals over the range from +20 to −90 °C; to achieve thermal equilibrium, the sample was kept at the chosen temperature for 20 min. The shapes of the signals for C-3 and C-5 of the borinine ring were simulated with the help of the program DNMR−SIM[20] to obtain the rate constants. In the subsequent calculation of activation parameters, the transmission coefficient of the Eyring equation was set to 1.[19] $T_c = 228$ K, $\Delta\nu = 680$ s^{-1} (for the ^{13}C chemical shifts between C-3 and C-5 at −90 °C), and $\Delta G_{228}{}^{\ddagger} = 41.5(5)$ kJ mol^{-1}.

Bis(1-methylboratabenzene)magnesium (1). $MgMe_2$[21] was prepared in situ from $HgMe_2$ (1.63 g, 7.06 mmol) and magnesium turnings (0.35 g, 14.4 mmol). A solution of 1-methyl-2-(trimethylstannyl)-1,2-dihydroborinine[13] (3.66 g, 14.36 mmol) in pentane (10 mL) was then added, and the reaction mixture was stirred at room temperature for 6 h. After complete removal of the solvent and $SnMe_4$ under vacuum, pentane (20 mL) was added to the residue and excess magnesium was filtered off. The filtrate was concentrated to ca. 5 mL and cooled to −20 °C to give **1** as a colorless crystalline solid; concentrating and cooling the mother liquor afforded a second crop (total yield of 1.21 g, 83%). The crystals were extremely sensitive to air and moisture and very soluble in pentane, toluene, and CH_2Cl_2; mp 45−46 °C.

Data for 1. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.61 (dd, $J = 10.4$, 7.0 Hz, 3-/5-H), 6.69 (dd, $J = 10.4$, 1.5 Hz, 2-/6-H), 6.42 (tt, $J = 7.0$, 1.5 Hz, 4-H), 0.57 (s, BMe). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 137.7 (C-3,5), 127.7 (br, C-2,6), 111.4 (C-4), 2.8 (BMe). ^{11}B NMR (160 MHz, C_6D_6, $BF_3{\cdot}Et_2O$ external): δ 37.2. MS (EI, 70 eV): m/z (I_{rel}) 206 (6, M$^+$), 115 (10, M$^+$ − C_5H_5BMe), 91 (100, $C_5H_5BMe^+$). Anal. Calcd for $C_{12}H_{16}B_2Mg$: C, 69.90; H, 7.82. Found: C, 69.63; H, 7.73.

Bis[3,5-dimethyl-1-(dimethylamino)boratabenzene]magnesium (2). $MgMe_2$[21] was prepared in situ from $HgMe_2$ (1.85 g, 8.02 mmol) and magnesium turnings (0.39 g, 16.5 mmol). A solution of 3,5-dimethyl-1-(dimethylamino)-2-(trimethylstannyl)-1,2-dihydroborinine (3.66 g, 14.36 mmol) in toluene (15 mL) was then added, and the mixture was stirred at 110 °C for 10 days. After removal of the volatiles under vacuum, hexane (20 mL) was added and excess magnesium was filtered off. The filtrate was then concentrated to ca. 5 mL. Cooling to −20 °C gave **2** (1.62 g, 63%) as large colorless prisms, extremely sensitive to air and moisture and very soluble in hexane, toluene, and CH_2Cl_2; mp 68−70 °C.

Data for 2. ^{1}H NMR (500 MHz, C_6D_6): δ 5.54 (d, $J = 1.5$ Hz, 2-/6-H), 5.32 (br s, 4-H), 2.73 (s, NMe_2), 2.10 (s, 3-/5-Me). ^{13}C NMR (126 MHz, C_6D_6): δ 149.8 (C-3,5) 105.2 (br, C-2,6), 103.2 (br, C-4), 38.9 (NMe_2), 25.0 (3-/5-Me). ^{11}B NMR (160 MHz, C_6D_6, $BF_3{\cdot}Et_2O$ external): δ 30.2. MS (EI, 70 eV): m/z (I_{rel}) 320 (38, M$^+$), 171 (51, M$^+$ − $Me_2C_5H_3BNMe_2$), 149 (100, $Me_2C_5H_3BNMe_2{}^+$). Anal. Calcd for $C_{18}H_{30}B_2MgN_2$: C, 67.48; H, 9.44; N, 8.74. Found: C, 67.03; H, 9.10; N, 9.12.

2,2′-Bipyridine Adduct 5. 2,2′-Bipyridine (0.13 g, 0.83 mmol) was added to a solution of $Mg(C_5H_5BMe)_2$ (**1**) (0.17 g, 0.82 mmol) in toluene (10 mL). An orange-brown precipitate formed immediately, which was collected by filtration and washed with toluene (3 × 5 mL). The solid so obtained was dried under high vacuum to afford **5** (0.29 g, 97%) as a powder, sensitive to air and moisture and moderately soluble in hot toluene but almost insoluble at ambient temperature; mp 198−200 °C.

Data for 5. ^{1}H NMR (500 MHz, C_6D_6): δ 7.48 (dd, $J = 10.1$, 7.0 Hz, 3-/5-H), 6.61 (dd, $J = 10.1$, 7.0 Hz, 2-/6-H), 6.43 (tt, $J = 7.0$, 1.2 Hz, 4-H), 0.79 (s, BMe); for bipy δ 8.03 (ddd, $J = 5.2$, 1.8, 0.9 Hz, 6-H), 6.83 (ddd, $J = 8.0$, 7.5, 1.8 Hz, 4-H), 6.75 (ddd, $J = 8.0$, 1.0, 0.9 Hz, 3-H), 6.51 (ddd, $J = 7.5$, 5.2, 1.0 Hz, 5-H). ^{13}C NMR (126 MHz, C_6D_6): δ 137.7 (C-3,5), 125 (br, C-2,6), 113.1 (C-4), 2 (br, BMe); for bipy δ 149.3 (C-2), 149.0 (C-6), 139.0 (C-4), 124.6 (C-5), 120.1 (C-3). ^{11}B NMR (160 MHz, C_6D_6, $BF_3{\cdot}Et_2O$ external): δ 37.5. MS (EI, 70 eV): m/z (I_{rel}) 271 (1, M$^+$ − C_5H_5BMe), 206 (40, M$^+$ − bipy), 156 (100, bipy), 115 [75, $Mg(C_5H_5BMe)^+$], 91 (26, $C_5H_5BMe^+$). Anal. Calcd for $C_{22}H_{44}B_2N_2Mg$: C, 72.79; H, 6.68. Found: C, 72.26; H, 7.09.

THF Solvate 6. A solution of $Mg(Me_2C_5H_3BNMe_2)_2$ (**2**) (0.28 g, 0.87 mmol) in THF (2 mL) was stored overnight at 4 °C to afford **6**

(0.25 g, 62%) as large colorless crystals, sensitive to air and moisture and soluble in benzene and CH_2Cl_2.

Data for 6. ^{1}H NMR (500 MHz, C_6D_6): δ 5.58 (s, 2-/6-H), 5.51 (br s, 4-H), 2.69 (s, NMe_2), 2.18 (s, 3-/5-Me); for THF δ 3.45 (m, OCH_2), 1.37 (m, CCH_2CH_2C). ^{13}C NMR (126 MHz, C_6D_6): δ 149.5 (C-3,5), 105 (br, C-2,4,6), 39.0 (NMe_2), 25.3 (3-/5-Me); for THF δ 68.0 (OCH_2), 25.6 (CH_2). ^{11}B NMR (160 MHz, C_6D_6, $BF_3{\cdot}Et_2O$ external): δ 31.4. Anal. Calcd for $C_{26}H_{46}B_2N_2O_2Mg$: C, 67.22; H, 9.98; N, 6.03. Found: C, 66.70; H, 9.09; N, 6.58.

Crystal Structure Determinations of 1, 2, 5, and 6. Data collections were performed on ENRAF-Nonius CAD4 diffractometers, each equipped with a graphite monochromator. Crystal data, data collection parameters, and convergence results are listed in Table 3. Before averaging was performed over symmetry-related reflections, absorption corrections[36,37] were applied to the data sets collected with Cu Kα radiation. All four structures were solved by direct methods with the help of the SHELXS-86 program[38] and refined on structure factors with the local version of the SDP program system.[39]

All hydrogen atoms were isotropically refined in the structures of **1** and **2**. For the crystal of **5**, one boratabenzene ligand suffers from a rotational disorder. Two essentially coplanar sites (rings B and C), which are related to each other by an angle of 154°, were refined with a 60%: 40% occupancy ratio in the disorder model. These atoms were assigned with isotropic displacement parameters. The hydrogen atoms of the well-defined fragments were refined isotropically while the remaining ones were treated as riding [C−H = 0.98 Å, $U_{iso}(H) = 1.3U_{eq}(C)$]. In the case of **6**, the hydrogen atoms of the boratabenzene moieties were refined on positional parameters with fixed displacement parameters [$U_{iso}(H) = 1.3\ U_{iso}(C)$] and the H atoms of the THF ligands were included as riding with fixed displacement parameters [C−H = 0.98 Å, $U_{iso}(H) = 1.3U_{eq}(C)$] in structure factor calculations.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determinations of **1**, **2**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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