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# Borabenzene Derivatives. 30. Bis(1-methylboratabenzene) Compounds of Germanium, Tin, and Lead. First Structural Characterization of Facial Bonding of a Boratabenzene to a p-Element and the Structures of $Pb(C_5H_5BMe)_2$ and Its 2,2′-Bipyridine Adduct[†,1]

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Bis(1-methylboratabenzene)lead, $Pb(C_5H_5BMe)_2$ (**1**), was synthesized by the reaction of $Li(C_5H_5BMe)$ with $PbCl_2$ as a low-melting (mp 60 °C) thermochromic yellow crystalline solid (63%). The lighter homologues $Sn(C_5H_5BMe)_2$ (**2**) and $Ge(C_5H_5BMe)_2$ (**3**) were obtained from 1-methyl-2-(trimethylstannyl)-1,2-dihydroborinine, $2\text{-}(Me_3Sn)C_5H_5BMe$, and $SnCl_2$ and $GeI_2$, respectively, as colorless liquids (70%). The plumbocene analogue **1** possesses a monomeric bent-sandwich structure with a bending angle of 135.2(3)°. Compound **1** forms addition compounds with nitrogen bases such as **1**·TMEDA (**6**) and **1**·bipy (**7**). Adduct **7** has a bent-sandwich structure with the 2,2′-bipyridine ligand in the pseudoequatorial plane; the bending angle is 139.1(5)°.

## Introduction

The bis(cyclopentadienyl)element compounds $GeCp_2$,[2] $SnCp_2$,[3] and $PbCp_2$[4] have a long history. The parent compounds and their derivatives have been the subject of several reviews[5,6] and have found renewed interest in recent years.[7] In general, these compounds possess bent-sandwich structures with a 14e valence electron count. However, the lead compound $PbCp_2$ exists as three polymorphs. Two of these are polymers with one side-on bonded $\eta^5$-Cp ligand and one bridging $\mu,\eta^5$: $\eta^5$-Cp ligand.[8,9] The third polymorph is a hexamer with the same bonding characteristics locally.[9] Steric congestion in highly substituted derivatives causes a decrease of the interplanar angle between the two Cp ligands. This effect culminates in decaphenylstannocene, $Sn(C_5Ph_5)_2$, the first stannocene with coplanar ring ligands.[10] Similarly, the plumbocene $Pb(C_5Me_4SiMe_2Bu^t)_2$ is the first plumbocene with coplanar ring ligands.[11]

Boratabenzene ions are more akin to cyclopentadienides than any other anion; they can form metal compounds with metals of all parts of the periodic table.[12] We therefore set out to synthesize and study compounds with group 14 elements. On one hand boratabenzenes act as $\eta^1$-bonded ligands in compounds such as the 1,2-dihydroborinines $2\text{-}(Me_3E)C_5H_5BMe$ with E = Si, Ge, Sn, Pb.[13] On the other hand they can form bent metallocenes with $\eta^6$-bonded ring ligands such as the new compounds $M(C_5H_5BMe)_2$ **1**−**3** (**1**, M = Pb; **2**, M = Sn; **3**, M = Ge), which are the subject of this paper.

## Results and Discussion

**Syntheses.** All three bis($\eta^6$-1-methylboratabenzene)element compounds **1**−**3** can be obtained from a suitable

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[†] Dedicated to Professor Fausto Calderazzo on the occasion of his 70th birthday.

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**Table 1. Proton Chemical Shift Data for Compounds 1−3 (500 MHz, $CD_2Cl_2$)**

| compound | 4-H | 3-/5-H | 2-/6-H | Me |
|---|---|---|---|---|
| **1** | 7.05 | 7.09 | 6.53 | 0.78 |
| **2** | 7.01 | 7.17 | 6.49 | 0.79 |
| **3** | 7.00 | 7.29 | 6.19 | 0.93 |
| **5**[a] | 6.23 | 7.30 | 6.48 | 0.57 |

[a] A minimum amount of DME was added.

metal dihalide ($PbCl_2$, $SnCl_2$, $GeI_2$) and the 1,2-dihydroborinine 2-($Me_3Sn$)$C_5H_5BMe$ (**4**)[13] using pentane or hexane as solvents. The $^1H$ NMR signals of the $Me_3Sn$ groups of the starting material **4** and of the trimethyltin halide formed can be used to monitor the progress of the reaction. Distillative workup of the reaction mixture gave **1** as a thermochromic, low-melting solid that is pale yellow at −196 °C and yellow at ambient temperature and gives a red liquid on melting. The lighter homologues **2** and **3** are obtained as colorless liquids. All three compounds are rather sensitive to air and moisture.

$$SnCl_2 + 2\ \underset{\textbf{4}}{\text{2-}(Me_3Sn)C_5H_5BMe} \rightarrow \underset{\textbf{2}}{Sn(C_5H_5BMe)_2} + 2\ Me_3SnCl$$

$$GeI_2 + 2\ \underset{\textbf{4}}{\text{2-}(Me_3Sn)C_5H_5BMe} \rightarrow \underset{\textbf{3}}{Ge(C_5H_5BMe)_2} + 2\ Me_3SnI$$

The corresponding bis(cyclopentadienyl)element compounds are usually made more simply from the metal dihalides and LiCp in THF. This method failed in the present case. Although the formation of the compounds **1**−**3** could be observed initially by $^1H$ NMR spectroscopy, the material turned insoluble after some minutes. Later we found that the lead compound can be made using $LiC_5H_5BMe$ (**5**)[14] in diethyl ether as the source of the boratabenzene ring. This alternative synthesis is simpler and gave much better yields.

$$PbCl_2 + 2\ \underset{\textbf{5}}{LiC_5H_5BMe} \rightarrow \underset{\textbf{1}}{Pb(C_5H_5BMe)_2} + 2\ LiCl$$

The compounds **1**−**3** show simple mass spectra with weak parent peaks (1−2%) and sequential loss of the boratabenzene ligands; the most intense peak belongs to the cation $E(C_5H_5BMe)^+$ in all three cases. Proton chemical shifts are collected in Table 1 together with data for **5** for comparison. The chemical shift $\delta(^{207}Pb)$ of −2579 ppm for **1** is at rather high field,[15] but the shielding is less extreme than in $PbCp_2$ [$\delta(^{207}Pb)$ −5030 ppm][16] and $PbCp^*_2$ [$\delta(^{207}Pb)$ −4390 ppm].[16,17] The chemical shift $\delta(^{119}Sn)$ of −1535 ppm for **2** is again at rather high field,[18] and again this effect is less pronounced than for $SnCp_2$ [$\delta(^{119}Sn)$ −2199 ppm],[19a] $Sn(C_5H_4Me)_2$ [$\delta(^{119}Sn)$ −2171.1 ppm],[19b] or $SnCp^*_2$ [$\delta(^{119}Sn)$ −2121 ppm].[17,19c] Following accepted lines of interpretation,[15] we can discuss qualitatively the main effects of going from cyclopentadienide to boratabenzene. The reduced symmetry and the lower donor property of the boratabenzene ligand are expected to result in a decrease of the diamagnetic shielding ($\sigma_{dia}$) of the central metal and a chemical shift to less negative values. Furthermore the HOMO/LUMO separation of the ligand is reduced, and this is expected to result in an increase of the paramagnetic shielding contributions ($\sigma_{para}$) and a further chemical shift to less negative values.

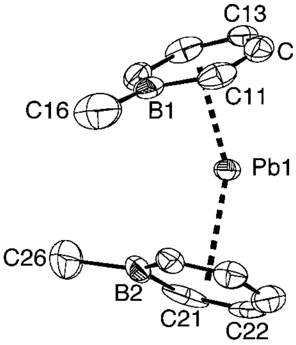

**Figure 1.** PLATON plot[21] of the molecule **1A**. Displacement ellipsoids are scaled to 30% probability.

**Crystal Structure of 1.** Crystals of the lead compound **1** that were of acceptable quality could be obtained by crystallization from pentane. The monoclinic elemental cell contains two independent molecules, **1A** and **1B**, the first one of a well-defined molecular structure and the second one with severe rotational disorder of one boratabenzene ligand. The structure was solved in three steps. The first diffraction data set was collected at −20 °C. It gave an acceptable structure solution[20] but with rather large displacement ellipsoids for the disordered molecule **1B**. A second data set was then collected at −70 °C. On one hand this set allowed the disorder to be resolved; on the other hand it turned out to be of lower quality. In the third step the disorder model so obtained was used to extract an improved solution from the first data set, and this is the solution documented here (Tables 2 and 3, Figures 1 and 2).

Both molecules **1A** and **1B** possess similar bent-sandwich structures with approximately planar boratabenzene ligands and a bending angle of 135.2(3)° for **1A**. In the disordered molecule **1B** the first ring (ring C) is well-defined, while the second ring shows split positions D and E with almost equal occupancies [54(2)/46(2)]. These rings D and E are coplanar, but E is rotated against D by an angle of 20.2°.

There are some remarkably short intermolecular contacts from the Pb atoms to ortho-carbon atoms of neighboring molecules, especially Pb2−C21 [3.356(9) Å] and Pb1−C45a [3.42(2) Å], and these involve, interestingly, the rings B and D that have the longer intramolecular Pb−ring distances. These interactions create a tetrameric packing unit as shown in Figure 2.

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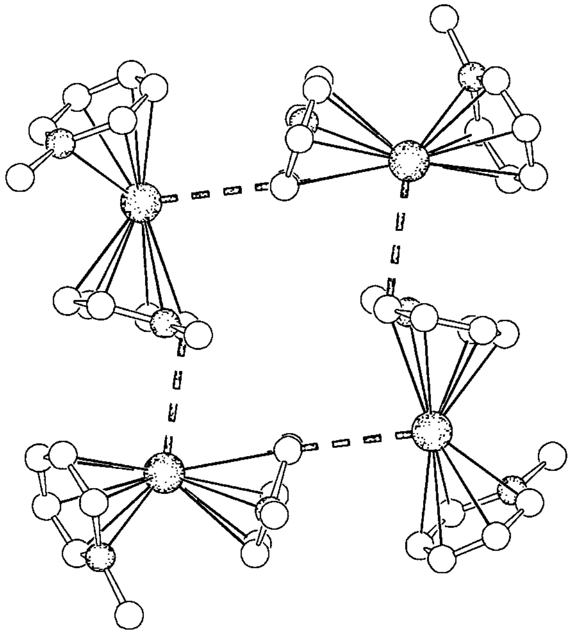

**Figure 2.** SCHAKAL representation[22] of the tetrameric packing unit. The lead and the boron atoms are shaded, and the weak intermolecular contacts are indicated by dotted lines. The tetrameric unit is centrosymmetric with two independent molecules. Ring E of molecule **1B** is omitted for clarity.

**Table 2. Selected Interatomic Distances (Å) for 1**

| | | | |
|---|---|---|---|
| Pb1−C11 | 2.712(9) | Pb1−C21 | 2.929(8) |
| Pb1−C12 | 2.811(9) | Pb1−C22 | 3.037(8) |
| Pb1−C13 | 2.876(9) | Pb1−C23 | 3.032(10) |
| Pb1−C14 | 2.821(9) | Pb1−C24 | 2.887(10) |
| Pb1−C15 | 2.751(9) | Pb1−C25 | 2.795(9) |
| Pb1−B1 | 2.809(10) | Pb1−B2 | 2.858(11) |
| Pb2−C31 | 2.777(8) | Pb2−C34 | 2.851(9) |
| Pb2−C32 | 2.887(9) | Pb2−C35 | 2.748(8) |
| Pb2−C33 | 2.948(9) | Pb2−B3 | 2.804(9) |
| Pb2−C41 | 2.81(2) | Pb2−C51 | 2.73(2) |
| Pb2−C42 | 2.79(2) | Pb2−C52 | 2.80(2) |
| Pb2−C43 | 2.89(2) | Pb2−C53 | 2.94(2) |
| Pb2−C44 | 2.99(2) | Pb2−C54 | 3.01(2) |
| Pb2−C45 | 3.01(2) | Pb2−C55 | 2.94(2) |
| Pb2−B4 | 3.00(3) | Pb2−B5 | 2.86(2) |
| Pb1···C45a | 3.42(2) | Pb2···C21 | 3.356(9) |

The choice of a van der Waals radius for lead is somewhat ambiguous.[23] Batsanov[23a] has recently published values for a large number of elements, among them 2.3 Å for tin and, in agreement with earlier data, 1.7 Å for carbon. On these grounds the above contacts indicate weak intermolecular bonding. We decided to use lattice energy minimizations[24] based on the atom−atom potential approach[25] to judge the extent of bonding within the tetrameric aggregate. In the absence of specific intermolecular forces and for typical molecular crystals these methods reproduce the packing arrangement; at temperatures around 250 K they tend to underestimate the cell constants by about 2−3%.[26] Our calculations showed that both the individual plumbocene molecules and the tetrameric unit may be regarded as van der Waals building blocks of a molecular crystal. Therefore specific interactions are not needed to explain the packing, but also, they are not excluded. Further details concerning the computer modeling of this and related compounds will be the subject of a forthcoming study.

For molecule **1A** the distances of the Pb atom to the best ligand planes are 2.412 and 2.546 Å. For the nondisordered ring ligands A−C the metal−ligand bonding shows slip distortions[27] of 0.14−0.28 Å, which, quite remarkably, are essentially directed toward the boron. This observation is in contrast to the situation in d-metal complexes, where the metal always slips toward carbon C-4 opposite the boron atom.[12b] The distances Pb−C [2.865 Å (av), ranging from 2.712 to 3.037 Å] are larger on average than in monomeric plumbocenes.[7c] The considerable variabilities of the Pb−C distances, of the Pb−B distances, and of the slip distortions indicate that the metal−ligand bond in **1** is mechanically soft. It seems likely that the intermolecular interactions mentioned above contribute to this structural variability.

**Formation of Lewis Base Adducts.** The metallocenes $PbCp_2$ and $SnCp_2$ form weak adducts with nitrogen Lewis bases such as TMEDA and the bipy derivative 4,4′-$Me_2$-2,2′-$(C_5H_3N)_2$.[28] We find that **1** displays the same type of reactivity. Reaction of **1** with TMEDA readily gave a crystalline adduct $Pb(C_5H_5BMe)_2(TMEDA)$ (**6**) as yellow platelets. An attempted structure determination failed because of severe disorder problems. We then turned to 2,2′-bipyridine as Lewis base and readily obtained the orange crystalline adduct $Pb(C_5H_5BMe)_2(bipy)$ (**7**).

**Crystal Structure of 7.** Good crystals of compound **7** were obtained by crystallization from toluene. The overall structure of **7** is that of a bent sandwich with a somewhat distorted 2,2′-bipyridine ligand in the pseudoequatorial plane (Tables 4 and 5, Figure 3) and is rather similar to that of $PbCp_2[4,4'\text{-}Me_2\text{-}2,2'\text{-}(C_5H_3N)_2]$[28b] (≡**8**).

The boratabenzene ligands are essentially planar, and the metallocene bending angle amounts to 139.1(5)° [cf. Cp(centroid)−Pb−Cp(centroid) 139.7° for **8**].[28b] The distances of the Pb atom to the best ligand planes [2.588 and 2.597 Å] are markedly longer than for **1**. This is the expected consequence of the increase in coordination number. What is more surprising are the Pb−N distances [2.666(8) and 2.607(7) Å], which are shorter than for **8** [2.702(5) Å].[28b] Boratabenzenes $(C_5H_5BR)^-$ (R = Me, Ph) have a lower charge density than cyclopentadienide and, hence, are less basic[29] and less nucleophilic than $Cp^-$.[13] Thus we expect a larger positive charge

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**Table 3. Planes and Angles for 1**

(a) Molecule **1A**

plane A ≡ (C11···C15, B1) [with largest vertical displacement: 0.05(1) Å for B1]: distance Pb−plane A 2.412 Å
plane B ≡ (C21···C25, B2) [with largest vertical displacement: 0.02(1) Å for B2]: distance Pb−plane B 2.546 Å
interplanar angle A,B: 44.8(3)°
rotational position A,B:[a] 64.7°

(b) Molecule **1B**

plane C ≡ (C31···C35, B3) [with largest vertical displacement: 0.04(1) Å for B3]: distance Pb−plane C 2.444 Å
plane D ≡ (C41···C45, B4) [with largest vertical displacement: 0.04(2) Å for C41]: distance Pb−plane D 2.530 Å
plane E ≡ (C51···C55, B5) [with largest vertical displacement: 0.02(2) Å for B5]: distance Pb−plane E 2.481 Å
interplanar angle C,D: 44.3(7)°
rotational position C,D:[a] 67.2°
interplanar angle C,E: 41.3(8)°
rotational position C,E:[a] 54.0°

[a] The rotational position X,Y of ring Y relative to ring X is defined as the angle between the projections of the two B−C(Me) bond vectors of ring X and of ring Y onto plane X.

**Table 4. Selected Bond Distances (Å) and Angles (deg) for 7**

| | | | |
|---|---|---|---|
| Bond Distances (Å) | | | |
| Pb−N1 | 2.666(8) | Pb−N2 | 2.607(7) |
| Pb−C11 | 2.861(10) | Pb−C21 | 2.835(12) |
| Pb−C12 | 2.944(10) | Pb−C22 | 2.819(11) |
| Pb−C13 | 3.041(9) | Pb−C23 | 2.937(11) |
| Pb−C14 | 3.034(10) | Pb−C24 | 3.112(11) |
| Pb−C15 | 2.937(12) | Pb−C25 | 3.162(11) |
| Pb−B1 | 2.921(12) | Pb−B2 | 3.040(13) |
| Bond Angles (deg) | | | |
| N1−Pb−N2 | 61.0(2) | N1−C34−C35−N2 | 13(1) |

residing on the lead center of **1** as compared to that of $PbCp_2$ and, consequently, a stronger Pb−N bond for **7**.

## Conclusion

This paper presents work on compounds of the p-block metals with facial (or $\eta^6$) bonding of boratabenzene ligands. The structure determinations of **1** and **7** represent the first structural characterizations of this bonding mode for p-block metals. We note that a facial and bridging (or $\mu$-$\eta^6$:$\eta^6$) bonding mode have been assumed for thallium boratabenzenes $Tl(C_5H_5BR)$ (R = Me, Ph)[30] by mere analogy with the bonding situation in TlCp; we have never been able to grow crystals of these thallium compounds for a crystal structure determination. A third and more localized (or $\eta^1$) bonding mode is that found in the 1,2-dihydroborinines 2-($Me_3E$)-$C_5H_5BMe$ (E = Si, Ge, Sn, Pb)[13] and $InMe(C_5H_5BMe)_2$,[31] which are all fluxional with very low barriers to [1,3]-sigmatropic automerization. Much more work will be needed in the future to fully unfold these facets of boratabenzene chemistry.

## Experimental Section

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

NMR spectra were recorded on a Varian Unity 500 ($^1$H, 500 MHz; $^{13}$C, 125.7 MHz; $^{11}$B, 160.4 MHz; $^{119}$Sn, 186.5 MHz; $^{207}$Pb, 104.6 MHz), a Varian VXR 300 ($^1$H, 300 MHz; $^{13}$C, 75.4 MHz), and a PMR Firenze spectrometer ($^{11}$B, 27.9 MHz). Chemical shifts are given in ppm and are relative to TMS for $^1$H and $^{13}$C, to $BF_3.OEt_2$ for $^{11}$B, to $SnMe_4$ for $^{119}$Sn, and to $PbMe_4$ for $^{207}$Pb; in the case of $^{207}$Pb a 17% solution of $PbEt_4$ in $CD_2Cl_2$ was used as external standard.[32] Mass spectra were recorded on a Finnigan MAT-95 at a nominal electron energy of 70 eV.

**Synthesis of Bis(1-methylboratabenzene)lead (1).** $LiC_5H_5BMe$ (1.35 g, 13.8 mmol) in $Et_2O$ (20 mL) was added dropwise to a suspension of $PbCl_2$ (1.89 g, 6.80 mmol) in $Et_2O$ (10 mL) at 0 °C. The temperature was allowed to rise to ambient temperature, and stirring was continued for 6 h. A yellow slurry formed. The solvent was completely removed under vacuum, pentane (30 mL) was added to the residue, and a precipitate of LiCl was filtered off. The filtrate was concentrated and cooled to −20 °C to give **1** as a yellow crystalline solid. Concentrating the mother liquor and cooling afforded a second crop of **1** (total yield 1.67 g, 63%): sensitive to heat, air, and moisture, mp 60 °C, soluble in pentane, and very soluble in toluene and $CH_2Cl_2$.

**Data for 1**: $^1$H NMR (500 MHz, $CD_2Cl_2$) $\delta$ 7.29 (dd, $J$ = 10.1, 7.0 Hz, 3-/5-H), 7.00 (tt, $J$ = 7.0, 1.2 Hz, 4-H), 6.20 (dd, $J$ = 10.1, 1.2 Hz, 2-/6-H), 0.92 (s, BMe); $^{13}$C NMR (126 MHz, $CD_2Cl_2$) $\delta$ 137.6 (C-3,5; $^{207}$Pb satellites with $^1J$ = 78.7 Hz), 134.9 (br, C-2,6), 116.7 (C-4), 2.6 (br, BMe); $^{11}$B NMR (160 MHz, $CD_2Cl_2$, $BF_3\cdot OEt_2$ external) $\delta$ 36.1; $^{207}$Pb NMR (105 MHz, $CD_2Cl_2$, $PbEt_4$ external) $\delta$ −2584, relative to $PbMe_4$;[27] MS (EI) $m/z$ ($I_{rel}$) 390 (>1, $M^+$), 299 (100, $M^+ - C_5H_5BMe$), 208 (30, $Pb^+$), 91 (40, $C_5H_5BMe^+$). Anal. Calcd for $C_{12}H_{16}B_2Pb$: C, 37.04; H, 4.14. Found: C, 37.31; H, 4.19.

**Synthesis of Bis(1-methylboratabenzene)tin (2).** 1-Methyl-2-(trimethylstannyl)-1,2-dihydroborinine[13] (**4**) (2.4 g, 9.4 mmol) was added to a suspension of $SnCl_2$ (2.0 g, 10.5 mmol) in pentane. The reaction mixture was stirred overnight. Then the excess $SnCl_2$ was filtered off, and all volatiles, including the $Me_3SnCl$ formed, were completely removed from the filtrate under reduced pressure. The residue was then heated to ca. 70 °C in a vacuum ($10^{-6}$ bar), and **2** (2.2 g, 70%) was collected by condensation as a very moisture-sensitive colorless liquid.

**Data for 2**: $^1$H NMR (300 MHz, $CD_2Cl_2$) $\delta$ 7.18 (dd, $J$ = 10.0, 7.0 Hz, 3-/5-H), 7.05 (tt, $J$ = 7.0, 1.3 Hz, 4-H), 6.51 (dd, $J$ = 10.0, 1.3 Hz, 2-/6-H), 0.79 (s, BMe); $^{13}$C NMR (75 MHz, $CD_2Cl_2$) $\delta$ 137.5 (C-3,5; $^{117/119}$Sn satellites with $^1J$ = 37.9 Hz), 134.0 (br, C-2,6), 116.8 (C-4), 3.0 (br, BMe); $^{11}$B NMR (28 MHz,

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(29) (a) 1-Phenyl-1,4-dihydroborinine can be deprotonated by NaCp in THF: Sandford, H. F., Ph.D. Thesis, University of Michigan, 1979. (b) Gas-phase acidities: Sullivan, S. A.; Sandford, H.; Beauchamp, J. L.; Ashe, A. J., III. *J. Am. Chem. Soc.* **1978**, *100*, 3737.

(30) Herberich, G. E.; Becker, H. J.; Engelke, C. *J. Organomet. Chem.* **1978**, *153*, 265.

(31) Englert, U.; Herberich, G. E.; Rosenplänter, J. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1098.

(32) For $PbEt_4$ (17% in $CH_2Cl_2$) $\delta$($^{207}$Pb) +74.8(1) ppm: Kennnedy, J. D.; McFarlane, W.; Pyne, G. S. *J. Chem. Soc., Dalton Trans.* **1977**, 2332.

**Table 5. Planes and Angles for 7**

plane A ≡ (C11···C15, B1) [with largest vertical displacement: 0.03(1) Å for B1]: distance Pb−plane A 2.588 Å and slip distortion[a] 0.21 Å
plane B ≡ (C21···C25, B2) [with largest vertical displacement: 0.02(1) Å for B2]: distance Pb−plane B 2.597 Å and slip distortion[a] 0.38 Å
plane C ≡ (Pb, N1, N2)
plane D ≡ (C30···C34, N1) [with largest vertical displacement: 0.027(9) Å for C34]
plane E ≡ (C35···C39, N2) [with largest vertical displacement: 0.016(9) Å for C35]
interplanar angle A,B: 40.9(5)°
interplanar angle A,C: 20.9(6)°
interplanar angle B,C: 20,8(8)°
centroid(A)−Pb−centroid(B): 135.9°
rotational position A:[b] 27.3°
rotational position B:[b] 136.0°
interplanar angle D,E: 15.4(10)°

[a] For definition see ref 27. [b] The rotational position is defined as the angle between the bisector of the two Pb−N bonds and the projection of the B−C(Me) bond vector onto plane C.

**Table 6. Crystal Data, Data Collection Parameters, and Convergence Results for 1 and 7**

| | 1 | | 7 |
|---|---|---|---|
| formula | $C_{12}H_{16}B_2Pb$ | | $C_{22}H_{24}B_2N_2Pb$ |
| fw | 389.07 | | 545.26 |
| cryst syst | monoclinic | | orthorhombic |
| space group (no.) | *P*2₁/*c* (14) | | *Pbca* (61) |
| *a*, Å | 14.032(1) | 13.956(1) | 13.630(7) |
| *b*, Å | 10.735(1) | 10.696(2) | 16.855(6) |
| *c*, Å | 18.479(3) | 18.391(6) | 18.556(5) |
| $\beta$, deg | 108.06(1) | 107.88(2) | |
| cell volume, Å$^3$ | 2646.7(5) | 2613(1) | 4263(5) |
| *Z* | 8 | | 8 |
| *F*(000) | 1440 | | 2096 |
| temperature, K | 253 | 203 | 218 |
| $d_{calcd}$, g cm$^{-3}$ | 1.953 | 1.978 | 1.699 |
| $\mu$, cm$^{-1}$ | 128.1 | 129.8 | 79.8 |
| $\theta_{max}$, deg | 26.0 | 28.0 | 27.0 |
| scan mode | $\omega$ | $\omega-2\theta$ | $\omega-2\theta$ |
| cryst dimens, mm$^3$ | 0.65 × 0.16 × 0.08 | 0.26 × 0.18 × 0.12 | 0.42 × 0.21 × 0.16 |
| no. of rflns | 5018 | 25625 | 11769 |
| no. of indep rflns | 3866 | 6285 | 4633 |
| no. of indep obsd rflns | 2872 ($I > 2\sigma(I)$) | 2608 ($I > 2\sigma(I)$) | 3229 ($I > 1\sigma(I)$) |
| no. of variables | 270 | 270 | 244 |
| *R*,[a] obsd (all data) | 0.031 (0.060) | 0.041 (0.13) | 0.053 |
| $R_w$[b] | | | 0.045 |
| wR2,[c] obsd (all data) | 0.069 (0.074) | 0.076 (0.092) | |
| GOF, obsd (all data) | 1.056 (0.969) | 0.938 (0.713) | 1.109 |
| max resid density, e Å$^{-3}$ | 1.50 | 1.65 | 1.84 |

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F_o)$. [c] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

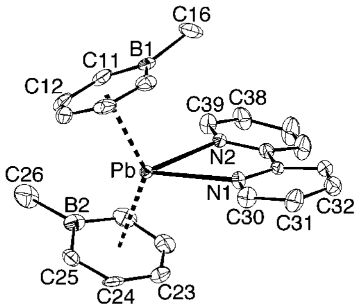

**Figure 3.** PLATON plot[21] of the molecule **7**. Displacement ellipsoids are scaled to 30% probability.

$CD_2Cl_2$, $BF_3.OEt_2$ external) $\delta$ 38; $^{119}$Sn NMR (186 MHz, $CD_2Cl_2$, $SnMe_4$ external) $\delta$ −1535; MS (EI) *m*/*z* ($I_{rel}$) 302 (2, $M^+$), 211 (100, $M^+ - C_5H_5BMe$), 120 (25, $Sn^+$), 91 (40, $C_5H_5BMe^+$). Anal. Calcd for $C_{12}H_{16}B_2Sn$: C, 47.95; H, 5.36. Found: C, 47.54; H, 5.28.

**Synthesis of Bis(1-methylboratabenzene)germanium (3).** 1-Methyl-2-(trimethylstannyl)-1,2-dihydroborinine[13] (**4**) (1.4 g, 5.5 mmol) was added to a suspension of $GeI_2$ (2.0 g, 6.1 mmol) in pentane (5 mL). Workup and condensation (ca. 40 °C, $10^{-6}$ bar) as described for **2** afforded **3** (1.0 g, 70%) as a highly moisture-sensitive colorless liquid.

**Data for 3**: $^1$H NMR (500 MHz, $CD_2Cl_2$) $\delta$ 7.09 (dd, *J* = 9.8, 7.0 Hz, 3-/5-H), 7.05 (tt, *J* = 7.0, 1.5 Hz, 4-H), 6.53 (dd, *J* = 9.8, 1.5 Hz, 2-/6-H), 0.78 (s, BMe); $^{13}$C NMR (75 MHz, $CD_2Cl_2$) $\delta$ 137.5 (C-3,5), 134.3 (br, C-2,6), 119.5 (C-4), 3.0 (br, BMe); $^{11}$B NMR (28 MHz, $CD_2Cl_2$, $BF_3{\cdot}OEt_2$ external) $\delta$ 41; MS (EI) *m*/*z* ($I_{rel}$) 256 (1, $M^+$), 165 (100, $M^+ - C_5H_5BMe$), 91 (25, $C_5H_5BMe^+$). Because of the high sensitivity of **3**, a satisfactory elemental analysis was not obtained. Anal. Calcd for $C_{12}H_{16}B_2Ge$: C, 56.64; H, 6.34. Found: C, 54.18; H, 6.50.

**Synthesis of the TMEDA Adduct of 1 (6).** TMEDA (0.15 g, 1.29 mmol) was injected into a solution of **1** (0.48 g, 1.23 mmol) in toluene (10 mL). The mixture was stirred for 10 min and was then filtered. The filtrate was concentrated to ca. 5 mL and stored at 4 °C to give **6** (0.43 g, 69%) as moisture-sensitive yellow platelets, mp 124−128 °C (dec).

**Data for 6**: $^1$H NMR (500 MHz, $CD_2Cl_2$, 20 °C) $\delta$ 7.23 (dd, *J* = 9.5, 7.0 Hz, 3-/5-H), 6.94 (t, *J* = 7.0 Hz, 4-H), 6.21 (d, *J* = 9.5 Hz, 2-/6-H), 0.87 (s, BMe); for TMEDA, 2.36 (s, 2 $NCH_2$), 2.22 (s, 2 $NMe_2$); cooling of solutions in $CD_2Cl_2$ or toluene-$d_6$ resulted only in some line broadening. $^{13}$C NMR (126 MHz, $CD_2Cl_2$): $\delta$ 137.2 (C-3,5), 134.8 (br, C-2,6), 115.7 (C-4), 2.4 (br, BMe); for TMEDA, 57.9 (2 $NCH_2$), 46.1 (2 $NMe_2$). $^{11}$B NMR (160 MHz, $CD_2Cl_2$, $BF_3{\cdot}OEt_2$ external): $\delta$ 36.1. Anal. Calcd for $C_{18}H_{32}B_2N_2Pb$: C, 42.79; H, 6.38; N, 5.54. Found: C, 42.90; H, 6.00; N, 5.83.

**Synthesis of the 2,2′-Bipyridine Adduct of 1 (7).** Bipy (94 mg, 0.60 mmol) was added to a solution of 1 (0.23 g, 0.59 mmol) in toluene (8 mL). Workup as described for **6** gave **7** (0.24 g, 75%) as moisture-sensitive orange crystalline blocks, mp 169−172 °C (dec).

**Data for 7**: $^1$H NMR (500 MHz, $CD_2Cl_2$) $\delta$ 7.13 (dd, $J$ = 9.9, 6.8 Hz, 4H, 3-/5-H), 6.87 (t, $J$ = 6.8 Hz, 2H, 4-H), 6.08 (d, $J$ = 9.9 Hz, 4H, 2-/6-H), 0.70 (s, 2 BMe); for bipy, 8.65 (ddd, $J$ = 4.9, 1.8, 0.9 Hz, 2H, 6-H), 8.26 (ddd, $J$ = 8.1, 1.2, 0.9 Hz, 2H, 3-H), 7.92 (ddd, $J$ = 8.1, 7.5, 1.8 Hz, 2H, 4-H), 7.47 (ddd, $J$ = 7.5, 4.9, 1.2 Hz, 2H, 5-H); $^{13}$C NMR (126 MHz, $CD_2Cl_2$) $\delta$ 137.0 (C-3,5), 134.1 (br, C-2,6), 115.2 (C-4), 2.9 (br, BMe); for bipy, 155.3 (C-2), 148.9 (C-6), 138.0 (C-4), 125.0 (C-5), 121.8 (C-3); $^{11}$B NMR (160 MHz, $CD_2Cl_2$, $BF_3{\cdot}OEt_2$ external) $\delta$ 36.0. Anal. Calcd for $C_{22}H_{24}B_2N_2Pb$: C, 48.46; H, 4.44; N, 5.14. Found: C, 48.67; H, 4.46; N, 5.37.

**Crystal Structure Determinations.** The data collections were performed on an ENRAF-Nonius CAD4 diffractometer with Mo Kα radiation (graphite monochromator, $\lambda$ = 0.7107 Å). Crystal data, data collection parameters, and convergence results are given in Table 6. Empirical absorption corrections on the basis of azimuthal scans[33] were applied to the data sets before merging symmetry-related reflections.

The structure of **1** was solved by conventional heavy atom methods followed by Fourier difference syntheses and refined on $F^2$ with the SHELX-93 program.[34] The unit cell contains two independent molecules; one of the four boratabenzene ligands suffers from rotational disorder. The disorder model was established with the help of a second data set collected at lower temperature (see below). Two almost equally occupied orientations (ligand D, C41⋯C46,B4; ligand E, C51⋯C56,B5) are coplanar within the limit of this structure determination and are related to each other by an angle of ca. 20°. The boron and carbon atoms of the disordered ligand were refined isotropically, and seven restraints were applied to set the corresponding bond distances of these atoms between two sites within a standard deviation of 0.02 Å (refinement without restraints gave an average difference of 0.05 Å for these bonds and a largest difference of 0.15 Å between C43−C44 and C53−C54). All other non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were included as riding with fixed displacement parameters [C−H = 0.98 Å, $U_{iso}$(H) = 1.3 $U_{eq}$(C)] in the final full-matrix least-squares refinement of the structure model.

An additional data set was collected on a second crystal at lower temperature (cf. Table 6). The slightly smaller displacement parameters [$U_{iso}$(−70 °C) = 0.050 Å$^2$ (av), $U_{iso}$(−20 °C) = 0.066 Å$^2$ (av) for the disordered non-hydrogen atoms] and the higher resolution limit were of help in deconvoluting the disorder. However, the overall quality of this second data set was lower, as evidenced by the higher estimated standard deviations and agreement factors.

The structure of **7** was solved by conventional heavy atom methods followed by Fourier difference syntheses and refined on structure factors with the SDP program system.[35] All non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were included as riding with fixed displacement parameters [C−H = 0.98 Å, $U_{iso}$(H) = 1.3 $U_{eq}$(C)] in the refinement of the structure model.

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**Supporting Information Available:** Tables of bond distances and angles, anisotropic displacement parameters, and positional coordinates for **1** and **7**.[36] This material is available free of charge via the Internet at http://pubs.acs.org.

OM990547Q

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[36] Further details of the crystal structure determinations are available from the Cambridge Crystallographic Data Center, on quoting the depository numbers CCDC-133684 for **1** and CCDC-133685 for **7**.