926 *Organometallics* **1997,** *16,* 926−931

Borabenzene Derivatives. 24.[1] From Lithium 1-Methylboratabenzene to 2-Mono- and 2,2-Disubstituted 1-Methyl-1,2-dihydroborinines with Me_3Si, Me_3Ge, Me_3Sn, and Me_3Pb Substituents. Degenerate Sigmatropic Rearrangements with Exceptionally Low Barriers and the Structure of 2-(Me_3Sn)C_5H_5BMe

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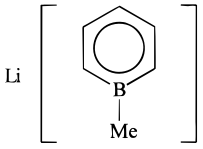
The reaction of Li(C_5H_5BMe) (**1**) with electrophiles Me_3ECl (E = Si, Ge, Sn, Pb) produces 1,2-dihydroborinines 2-(Me_3E)C_5H_5BMe (**2**−**5**). The structure of the Sn compound **4** shows a lengthened Sn−C(ring) bond [228.7(2) pm]. In solution the compounds **2**−**5** are fluxional and show [1,3] sigmatropic migrations of the Me_3E groups from C-2 to C-6. Barriers to the degenerate sigmatropic rearrangements for **2** and **3** have been determined from NMR spectroscopy [for **2** $\Delta G_{300}^{\ddagger} = 58.9(11)$ kJ mol^{-1}, $\Delta H^{\ddagger} = 43.3(6)$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -52(2)$ J K^{-1} mol^{-1}; for **3** $\Delta G_{300}^{\ddagger} = 43.4(9)$ kJ mol^{-1}, $\Delta H^{\ddagger} = 27.8(3)$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -52(2)$ J K^{-1} mol^{-1}] and are lower than those found for previously investigated systems. The Sn and Pb satellites observed for **4** and **5** in THF solutions are quenched by catalytic amounts of DMSO while chemical shifts are not affected even at higher concentrations. The Si compound **2** can be deprotonated to give Li[2-(Me_3Si)C_5H_4BMe] (**6**). Silylation of **6** affords $(Me_3Si)_2C_5H_4$-BMe (**7**) as a slowly interconverting equilibrium mixture of 2,2- and 2,6-isomers whereas stannylation gives the fluxional derivative (Me_3Si)(Me_3Sn)C_5H_4BMe (**8**).

Introduction

Borabenzene chemistry[3] has recently found renewed interest, and new or improved routes to borabenzene neutral Lewis base adducts,[4] boratabenzene salts,[2,5] and transition metal complexes[6] have been published. Our new and efficient synthesis of Li(C_5H_5BMe)[5c] (**1**) allowed us to take up again the study of boratabenzene ion reactivity.

Reactions with main-group electrophiles have not yet been investigated in any detail. Maier et al. have reported trimethylsilylation of Li(C_5H_5BOMe)[7] and an isopropylation of Li(2,4-$Bu^t_2C_5H_3BOMe$).[8] We have now studied reactions of **1** with electrophiles Me_3ECl (E = Si, Ge, Sn, Pb) and report here on the resulting 1-methyl-1,2-dihydroborinines 2-(Me_3E)C_5H_5BMe (**2**−**5**) and some related chemistry.



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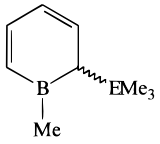

2, E = Si; **3**, E = Ge; **4**, E = Sn; **5**, E = Pb

Results and Discussion

Syntheses of 1-Methyl-1,2-dihydroborinines 2−5. The lithium salt **1** does not react with iodomethane in THF at ambient temperature over a period of several days. This observation demonstrates that boratabenzene ions are not only less basic[9] but also less nucleophilic than the cyclopentadienide ion.[10] When a suspension of **1** in THF is treated with chlorotrimethylsilane and its homologs, a smooth reaction takes place to give the 2-substituted 1-methyl-1,2-dihydroborinines **2**−**5**.

These new 1,2-dihydroborinines are liquids (E = Si, Ge, Sn) or low melting solids (E = Pb) which can be stored for months at ambient temperature. They are sensitive to air and moisture; in addition, the lead compound **5** is decomposed by light.

Crystal Structure of the Tin Compound (4). The structure of the tin compound **4** (Figures 1 and 2, Table 1) was determined by X-ray diffraction. The structure

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[1] Part 23: See ref 2.

[2] Herberich, G. E.; Englert, U.; Schmidt, M. U.; Standt, R. *Organometallics* **1996**, *15*, 2707.

[3] Herberich, G. E.; Ohst, H. *Adv. Organomet. Chem.* **1986**, *25*, 199.

[4] Hoic, D. A.; Wolf, J. R.; Davis, W. M.; Fu, G. C. *Organometallics* **1996**, *15*, 1315.

[5] (a) Qiao, S.; Hoic, D. A.; Fu, G. C. *J. Am. Chem. Soc.* **1990**, *118*, 6329. (b) Hoic, D. A.; Davis, W. M.; Fu, G. C. *J. Am. Chem. Soc.* **1995**, *117*, 8480. (c) Herberich, G. E.; Schmidt, B.; Englert, U. *Organometallics* **1995**, *14*, 471. (d) Herberich, G. E.; Schmidt, B.; Englert, U.; Wagner, T. *Organometallics* **1993**, *12*, 2891.

[6] (a) Herberich, G. E.; Englert, U.; Ganter, B.; Lamertz, C. *Organometallics* **1996**, *15*, 5236. (b) Fu, G. C. *J. Am. Chem. Soc.* **1996**, *118*, 8176. (c) Bazan, G. C.; Rodriguez, G.; Ashe, A. J., III; Al-Ahmad, S.; Müller, C. *J. Am. Chem. Soc.* **1996**, *118*, 2291. (d) Ashe, A. J., III; Kampf, J. W.; Müller, C.; Schneider, M. *Organometallics* **1996**, *15*, 387. (e) Herberich, G. E.; Englert, U.; Pubanz, D. *J. Organomet. Chem.* **1993**, *459*, 1. (f) Herberich, G. E.; Klein, W.; Spaniol, T. P. *Organometallics* **1993**, *12*, 2660.

[7] Boese, R.; Finke, N.; Henkelmann, J.; Maier, G.; Paetzold, P.; Reisenauer, H. P.; Schmid, G. *Chem. Ber.* **1985**, *118*, 1644.

[8] Maier, G.; Wolf, H.-J., Boese, R. *Chem. Ber.* **1990**, *123*, 505.

[9] (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.

[10] Cf. reaction of NaCp/MeI in THF: McLean, S.; Haynes, P. *Tetrahedron* **1965**, *21*, 2313.

[11] Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34; PLATON-94, University of Utrecht, 1994.

S0276-7333(96)00570-5 CCC: $14.00

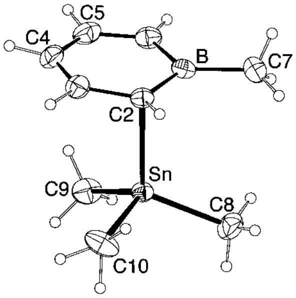

Figure 1. PLATON[11] diagram (at the 30% level, hydrogen atoms with arbitrary displacement parameters) of the molecule **4** with the atom-labeling scheme.

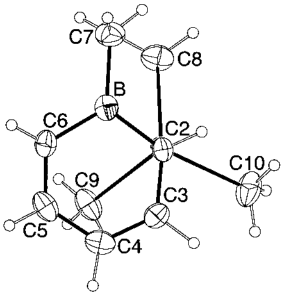

Figure 2. PLATON[11] diagram (at the 30% level, hydrogen atoms with arbitrary displacement parameters) of the molecule **4**, seen along the bond C2−Sn.

Table 1. Selected Interatomic Distances and Angles for 4

(a) Bond Distances (pm)			
Sn−C2	228.7(2)	Sn−C8	212.2(3)
Sn···C3	287.4(2)	Sn−C9	212.8(3)
Sn··B	284.4(3)	Sn−C10	212.0(3)
C2−C3	144.2(3)	C2−B	151.9(4)
C3−C4	135.8(4)	C6−B	153.2(3)
C4−C5	141.2(4)	C7−B	158.1(4)
C5−C6	136.1(4)	C2−H2	93(3)
(b) Bond Angles (deg)			
C2−Sn−C8	114.3(1)	C8−Sn−C9	110.8(2)
C2−Sn−C9	110.5(2)	C8−Sn−C10	110.4(1)
C2−Sn−C10	99.1(1)	C9−Sn−C10	111.2(1)
Sn−C2−C3	98.3(2)	Sn−C2−B	94.6(2)
Sn−C2−H2	92(2)		
C2−C3−C4	120.8(2)	C3−C4−C5	121.5(3)
C4−C5−C6	122.9(3)	C6−B−C2	113.1(2)
C3−C2−B	120.3(3)	C5−C6−B	120.8(2)
C3−C2−H2	119(2)	B−C2−H2	119(2)

solution obtained is of rather good quality allowing us to discuss the data in some detail. Inspection of Figure 1 immediately reveals that the structure is remarkable in several respects.

The molecule of **4** consists of a C_5H_5BMe ring and a $SnMe_3$ group. The $SnMe_3$ group is monohapto-bonded to C2; the distances Sn··B and Sn··C3 are too long for appreciable overlap. A striking feature is the large difference between the lengths of the two types of Sn−C bonds. The Sn−C bond lengths of the $SnMe_3$ group average 212.3 pm and are slightly shorter than in comparable compounds[12] as e.g. $SnMe_4$ [214.4(3) pm, determined by electron diffraction][13a] or $Me_3SnV(CO)_6$ [214.2(6) pm (av)][13b] as well as compared to the sum of the covalent radii (217 pm).[14] On the other hand, the elongation of the Sn−C2 bond to 228.7(2) pm indicates weakened bonding of the $SnMe_3$ group to the borabenzene ring. The $SnMe_3$ group considered alone is very close to perfect C_{3v} symmetry and probably slightly flattened [C−Sn−C 110.8° (av)].

The C_5H_5B ring posseses an approximately planar conformation ressembling a flattened 1,3-cyclohexadiene ring.[15] The carbon atom C2 shows the maximum displacement [5.4(2) pm] from the C_5B best plane, and the boron atom is similarly displaced to the opposite side [−4.6(3) pm]. The bond distances in the ring display a much reduced bond length alternation for the C−C distances. In addition, the C−B bonds in the ring are rather shortened whereas the exocyclic C(Me)−B bond length is normal. The three angles of the C_5H_5B fragment around C2 approach 120° [ranging from 119(2) to 120.3(3)°] while the three angles to the attached Sn atom are small and range from 92(2) to 98.3(2)°. The angle between the C2−Sn vector and the best C_5B amounts to 96.1(1)°; that is, the C2−Sn bond is approaching a perpendicular orientation.

Considering all these structural details we conclude that the bonding situation in **4** is dominated by hyperconjugative weakening of the Sn−C2 bond. One limiting bonding description would be that of a contact ion-pair $\{Me_3Sn^+,C_5H_5BMe^-\}$ with the cationic part of the molecule attached to the most negative ring position C2. The other limiting description would of course be that of a normal, localized covalent Sn−C σ-bond.

The same type of bonding situation is familiar for many cyclopentadienyl compounds of main group elements. The chemistry of these compounds has been reviewed in depth by Jutzi.[16] Most of the older structural work[17] in this area, including e.g. the structures of $CpSnMe_3$[17b] or $SnCp_4$,[17c] is of low accuracy and does not allow meaningful comparisons. However, the structure of $(Me_5C_5)SnI_3$ is similar to that of **4** in that it also shows a long Sn−C bond [224.7(5) pm] and an angle of 98.4(3)° of the Sn−C vector to the best ring plane.[18]

NMR Spectra and Fluxional Behavior. The compounds **2**−**5** were characterized by NMR spectroscopy. In the case of the silicon compound **2** well-resolved spectra were recorded at −50 °C which correspond to the unsymmetrical ground state **2A**,**B** (Chart 1); a ca. 5% admixture of the 4-Me_3Si isomer **2C** can be identified by the signals of its ring protons. When the temperature is raised, line broadening and coalescence is observed e.g. for the ^{13}C signals of the carbon atoms C-3 and C-5 of **2A**,**B**; the signals of **2C** remain sharp and unchanged between −50 and 110 °C. Close to the fast-exchange limit effective lateral symmetry is seen for

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(12) Zubieta, J. A.; Zuckerman, J. J. *Progr. Inorg. Chem.* **1975**, *24*, 251.

(13) (a) Nagashima, M.; Fujii, H.; Kimura, M. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3708. (b) Herberich, G. E.; Wesemann, L.; Englert, U. *Struct. Chem.* **1993**, *4*, 199.

(14) *Tables of Interatomic Distances and Configuration in Molecules and Ions*; Sutton, L., Ed.; The Chemical Society: London, 1958 and 1965; Spec. Publ. Nos. 11 and 18.

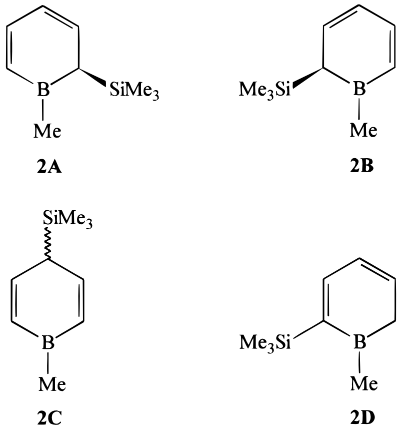
(15) (a) Auf der Heyde, W.; Lüttke, W. *Chem. Ber.* **1979**, *111*, 2384. (b) Oberhammer, H.; Bauer, S. H. *J. Am. Chem. Soc.* **1969**, *91*, 10. (c) Traetteberg, M. *Acta Chem. Scand.* **1968**, *22*, 2305.

(16) Jutzi, P. *Chem. Rev.* **1986**, *86*, 983; *Adv. Organomet. Chem.* **1986**, *26*, 217; *J. Organomet. Chem.* **1990**, *400*, 1.

(17) (a) For a compilation of pertinent older data see: Ustynyuk, Yu. A.; Shestakova, A. K.; Chertkov, V. A.; Zemlyansky, N. N.; Borisova, I. V.; Gusev, A. I.; Tchuklanova, E. B.; Chernyshev, E. A. *J. Organomet. Chem.* **1987**, *335*, 43. (b) Veniaminov, N. N.; Ustynyuk, Y. A.; Alekseev, N. V.; Ronova, I. A.; Struchkov, Y. T. *Doklady Akad. Nauk.* **1971**, *199*, 346. (c) Kulishov, V. I.; Bokii, N. G.; Prikhot'ko, A. F.; Struchkov, Y. T. *Zh. Strukt. Khim.* **1975**, *16*, 252.

(18) Bartlett, R. A.; Cowley, A.; Jutzi, P.; Olmstead, M. M.; Stammler, H.-G. *Organometallics* **1992**, *11*, 2837.

Chart 1



2A,**B**. We note that the coalescence temperatures do not depend on the sample concentration; furthermore, the tin and lead homologs **4** and **5** show heteronuclear couplings. Both observations confirm the intramolecular nature of the observed interconversion of the two enantiomers **2A** and **2B**. On the other hand, all silatropic shifts via C-4 as well as a rearrangement via a π-bonded intermediate[19] can be excluded because isomer **2C** does not participate in the exchange process. We also note that the 6-Me_3Si derivative **2D**, the product of an alternative hydrogen shift, is not seen; this isomer would lack the hyperconjugative stabilization discussed above and hence should be higher in energy.

The heavier congeners **3**−**5** display effective lateral symmetry at room temperature. In the case of the germanium compound **3** the slow-exchange limit could be reached at ca. −95 °C whereas for the tin compound **4** no signs of beginning line broadening could be observed at −95 °C.[20]

Barriers to enantiomerization for **2** and **3** could easily be estimated from the coalescence[21] of the ^{13}C signals of C-3 and C-5 (see Experimental Section). Variable-temperature NMR spectroscopy[21] using an internal temperature calibration[22] and line shape analysis[21,23] was used to obtain more accurate estimates and resulted in $\Delta G_{300}^{\ddagger} = 58.9(11)$ kJ mol^{-1}, $\Delta H^{\ddagger} = 43.3(6)$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -52(2)$ J K^{-1} mol^{-1} for **2** and $\Delta G_{300}^{\ddagger} = 43.4(9)$ kJ mol^{-1}, $\Delta H^{\ddagger} = 27.8(3)$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -52(2)$ J K^{-1} mol^{-1} for **3**. The negative activation entropies are in agreement with the intramolecular nature of the isomerization and indicate a highly ordered transition state.

For the related cyclopentadienyl compounds free energies of activation for migration of the Me_3E group were estimated to be $\Delta G_{300}^{\ddagger} = 63.6$ for E = Si,[24] 55.6 for E = Ge,[25] and 27.6 kJ mol^{-1} for E = Sn.[25] The barriers observed here are lower and, to our knowledge, the lowest barriers known for sigmatropic migrations of trimethylelement groups. We note in this context that [1,3] silatropic rearrangements in allyl silanes require high free energies of activation.[26] Silatropic [1,5] shifts are known for 5-$(Me_3Si)C_5H_5$[27] (and derivatives) and the indenyl compound 1-$(Me_3Si)C_9H_7$;[28] in these situations the rearrangements are symmetry allowed and show relatively low barriers.

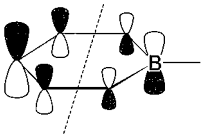


Figure 3.

It is clear from qualitative MO considerations and has been confirmed by several theoretical studies[29] that the HOMO (the π_3 orbital) of the boratabenzene ion is of lateral symmetry and displays a nodal plane across the bonds C-2, C-3 and C-5, C-6. This suggests that a [1,3] silatropic migration across the boron [similar to the [1,5] shift in 5-$(Me_3Si)C_5H_5$[16,27]] is an allowed process and is in fact operating here. We note that the distance Si··B will be decreasing during the migration and then increasing again. It remains an open question whether the closest approach corresponds to a transition state or a high-energy intermediate. In the latter case the [1,3] shift would be composed of two sequential [1,6] shifts.

Hyperconjugative bond weakening will facilitate sigmatropic rearrangements involving the weakened bond. Since 1-methylboratabenzene ion is less basic and less nucleophilic than cyclopentadienide ion, the resulting lowering of the barrier should be more pronounced for the compounds **2**−**5** than for the corresponding cyclopentadienyl derivatives, in agreement with the experimental situation.

The boron chemical shifts range from $\delta(^{11}B) = 65$ for the silicon compound **2** to $\delta(^{11}B) = 40$ for the lead compound **5**. These values may be compared with $\delta(^{11}B) = 70$ for the parent 1-methyl-1,2-dihydroborinine and $\delta(^{11}B) = 36$ for the salt **1**.[5c] We believe to see here again the effect of the hyperconjugative interaction discussed above; this effect is small in **2** and becomes increasingly more important as we go down to the heavy congeners.

Compound **4** shows $^{117/119}Sn$ satellites for all protons except those in the 3,5-positions and for all carbon atoms. When a catalytically small amount of DMSO is added to a solution of **4** in d_8-THF all satellites between the Sn nuclei and the atoms of the boratabenzene moiety are quenched. The chemical shifts of all signals remain essentially unchanged, even with higher admixtures of DMSO. Solutions of **4** in d_5-pyridine also show no satellites for the Sn−Me groups. The situation for **5** is analogous.

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(19) (a) Trong Anh, N.; Elian, M.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 110. (b) Schoeller, W. W. *Z. Naturforsch.* **1984**, *39B*, 1767.

(20) At lower temperature the solubility is insufficient. The more soluble Et_3Sn derivative gave two-phase systems with CCl_2F_2.

(21) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1984.

(22) Van Geet, A. L. *Anal. Chem.* **1980**, *42*, 679.

(23) Haegele, G.; Lenzen, T.; Fuhler, R. *Comput. Chem.* **1995**, *19*, 277.

(24) Sergeyev, N. M.; Avramenko, G. I.; Kisin, A. V.; Korenevsky, V. A.; Ustynyuk, Yu. A. *J. Organomet. Chem.* **1971**, *32*, 55.

(25) Kisin, A. V.; Korenevsky, V. A.; Sergeyev, N. M.; Ustynyuk, Yu. A. *J. Organomet. Chem.* **1972**, *34*, 93.

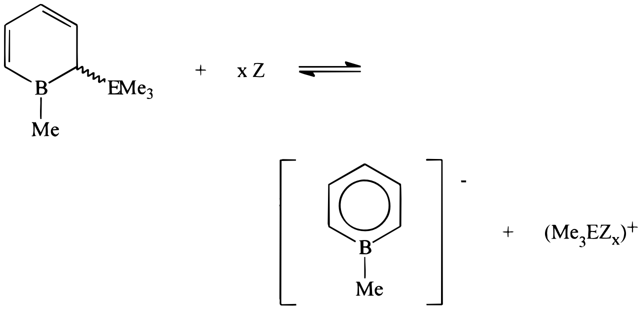
(26) Kwart, H.; Slutsky, J. *J. Am. Chem. Soc.* **1972**, *94*, 2515; *J. Am. Chem. Soc.* **1973**, *95*, 8678. Wilson, S. R.; Phillips, L. R.; Natalie, K. J. *J. Am. Chem. Soc.* **1979**, *101*, 3340.

(27) (a) Fritz, H. P.; Kreiter, C. G. *J. Organomet. Chem.* **1965**, *4*, 313. (b) Ashe, A. J., III. *J. Am. Chem. Soc.* **1970**, *92*, 1233. (c) Eggert, K. W.; James, T. L. *J. Organomet. Chem.* **1971**, *26*, 335.

(28) (a) Larrabee, R. B.; Dowden, B. F. *Tetrahedron Lett.* **1970**, 915. (b) Ashe, A. J., III. *Tetrahedron Lett.* **1970**, 2105. (c) Rakita, P. E.; Taylor, G. A. *Inorg. Chem.* **1972**, *11*, 2136.

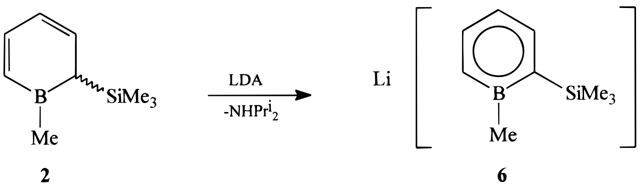
(29) See literature quoted in ref 3 and also: (a) Cioslowski, J.; Hay, P. J. *J. Am. Chem. Soc.* **1990**, *112*, 1707. (b) Schulman, J. M.; Disch, R. L. *Organometallics* **1989**, *8*, 733. (c) Raabe, G.; Schleker, W.; Heyne, E.; Fleischhauer. J. *Z. Naturforsch.* **1987**, *42B*, 352.

Scheme 1



E = Sn, Pb
Z = Me_2SO, C_5H_5N

Scheme 2



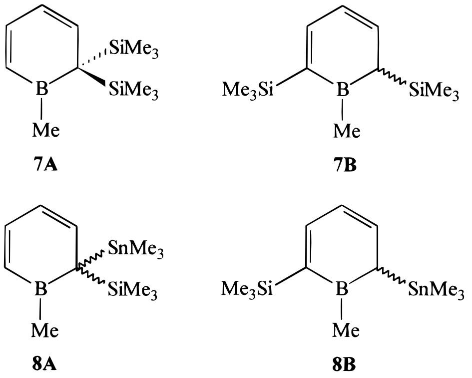
These observations indicate a much reduced Lewis acidity for **4** and **5**. They also hint to a heterolytic cleavage equilibrium (Scheme 1) as observed in earlier work on 5-(Me_3Sn)C_5H_5.[30] While the cleavage does only take place to a small extent, too small to be seen in terms of chemical shifts,[31] it provides a mechanism for *intermolecular* exchange of the Me_3Sn and Me_3Pb groups and consequent quenching of the couplings. In line with this interpretation **4** can be used as a mild, nonbasic source of 1-methylboratabenzene ion in many preparations.[32]

Metalation of the Trimethylsilyl Compound 2. We had hoped that a combination of metalation and trimethylsilylation steps could be used to synthesize polysilylated boratabenzene species. Several problems were encountered. It was already noted above that trimethylsilylation may occur to some extent at C-4. We also found that proton and trimethylsilyl transfer reactions become more noticeable with the more highly substituted systems. As a consequence, we could not obtain the polysubstituted compounds in pure form.

Metalation of **2** with LDA in THF at 20 °C gave a lithium salt **6** as a white solid in high yield (80−90%) (Scheme 2). When NaCp in d_8-THF was used as the base, desilylation took place to some extent and the product was contaminated by Na(C_5H_5BMe).

The 2-(trimethylsilyl)boratabenzene salt **6** was again treated with Me_3SiCl. When this reaction was run in THF, a mixture of the monosilylated compound **2**, the expected bis(trimethylsilyl) derivatives **7A**,**B** (Chart 2), and more highly silylated species was formed. This undesirable result was presumably caused by protolysis reactions between the various boratabenzene ions and dihydroborinines involved. When pentane was used as the reaction medium, the chemoselectivity was much improved.[33] The product obtained (after workup) was essentially an equilibrium mixture of the two isomers **7A**,**B** in a 4/3 ratio with an admixtures of **2** (10−20%). The ^1H and ^{13}C NMR spectra of **7** corresponded to a slow-exchange situation and showed no line broadening for the two isomers **7A**,**B**; however, NOE experiments confirmed that the two isomers were exchanging indeed. In the cyclopentadienyl series the second trimethylsilylation gives a product that is essentially the 5,5-disubstituted isomer (95%)[34] corresponding to the predominating isomer **7A**; **7B** has no analog in cyclopentadiene chemistry.

Chart 2



Analogous stannylation of **6** with Me_3SnCl in pentane gave a silylstannyl derivative **8**. The NMR spectra of **8** are in agreement with a fluxional structure with two interconverting isomers **8A**,**B**. Other conceivable isomers should give rise to separate spectra as the migration of hydrogen and of Me_3Si groups would be slow on the NMR time scale at −50 °C.

Concluding Remarks. This paper presents a systematic development of the chemistry of 2-substituted 1,2-dihydroborinines. The structure of the Sn compound **4** demonstrates the presence of a hyperconjugative stabilization of the 1,2-dihydroborinine ring and a weakening of the Sn−C(ring) bond. Strong donors are able to induce heterolysis of the Sn− and Pb−C(ring) bonds as evidenced by the quenching of the magnetic couplings between the Me_3E group (E = Sn, Pb) and the ring atoms. That the Sn compound **4** and to a lesser extent also the Si compound **2** can be used to transfer boratabenzene ions to many other metals will be the subject of forthcoming papers.

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, and THF was distilled from sodium benzophenone ketyl.

NMR spectra were recorded on a Varian Unity 500 spectrometer (^1H, 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 (^1H, 300 MHz; ^{13}C, 75.4 MHz), and a Varian EM 390A (^{11}B, 28 MHz). Chemical shifts are relative to TMS for ^1H and ^{13}C, 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

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[30] Boche, G.; Heidenhain, F.; Staudigl, B. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 218.

[31] Note that the protons in the 2,6-positions would show the largest shifts if ionization took place to an appreciable extent.

[32] Herberich, G. E.; Rosenplänter, J.; Schmitz, A. Unpublished work.

[33] The salt **7** is slightly soluble. The unsubstituted salt **6** does not react with Me_3SiCl in pentane.

[34] Ustynyuk, Yu. A.; Kisin, A. V.; Pribytkova, I. M.; Zenkin, A. A.; Antonova, N. D. *J. Organomet. Chem.* **1972**, *42*, 47.

standard;[35] the coupling constants for **4** and **5** are from simulations. Mass spectra were recorded on a Varian MAT CH-5 and Finnigan MAT-95 spectrometer.

1-Methyl-2-(trimethylsilyl)-1,2-dihydroborinine (2). Me_3SiCl (26.4 g, 0.243 mol) was added to a suspension of $Li(C_5H_5BMe)$ (**1**) (12.0 g, 0.123 mol) in THF (5 mL). After the reaction mixture was stirred for 30 min, the volatiles were removed under vacuum. Pentane was added to the residue, and a precipitate of LiCl was filtered off. After removal of the solvent under reduced pressure, the residue was heated under vacuum (10^{-4} bar) to 60 °C and **2** (10 g, 50%) was collected by condensation as a colorless liquid.

2A,**B**: ^1H NMR (500 MHz, $CDCl_3$, −50 °C) δ 7.30 (ddd, J = 11.6, 5.8, 0.9 Hz, 1H, 5-H), 6.81 (dd, J = 8.8, 5.5 Hz, 1H, 3-H), 6.53 (d, J = 11.6 Hz, 1H, 6-H), 6.44 (dd, J = 8.9, 5.8 Hz, 1H, 4-H), 3.68 (d, J = 5.5 Hz, 1H, 2-H), 0.73 (s, 3H, BMe), −0.06 (s, 9H, $SiMe_3$); ^1H NMR (500 MHz, $C_2D_2Cl_4$, 110 °C) δ 7.18 ("t", J = 7.6 Hz, 2H, 3-/5-H), 6.50 (t, J = 7.6 Hz, 1H, 4-H), 5.1 (br, 2H, 2-/6-H), 0.87 (s, 3H, BMe), 0.01 (s, 9H, $SiMe_3$); ^{13}C NMR (126 MHz, $CDCl_3$, −50 °C) δ 145.9 and 143.5 (C-3,5), 135.1 (br, C-6), 123.0 (C-4), 56.1 (br, C-2), 10 (br, BMe), −0.3 ($SiMe_3$); ^{13}C NMR (126 MHz, $C_2D_2Cl_4$, 110 °C) δ 144.4 (C-3,5), 123.3 (C-4), C-2,6 not observed, 9.6 (br, MBe), −0.3 ($SiMe_3$); $\Delta\nu$ = 52 Hz (for C-3 and C-5 at −40 °C), T_c = 280 K, $\Delta G_{280}^{\ddagger}$ = 57(2) kJ mol^{-1}; ^{11}B NMR (32 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$ external) δ 65; MS (70 eV) m/z (I_{rel}) 164 (7, M^+), 149 (4, $M^+ - Me$), 73 (100, $SiMe_3^+$).

2C: ^1H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, slightly broadened, ^3J = 11.5 Hz, 2H, 3-/5-H), 6.75 (d, ^3J = 11.5 Hz, 2H, 2-/6-H), 3.64 (s, slightly broadened, 1H, 4-H), 0.79 (s, 3H, BMe), 0.00 (s, 9H, $SiMe_3$).

1-Methyl-2-(trimethylgermyl)-1,2-dihydroborinine (3). Reaction of Me_3GeCl (2.3 g, 0.015 mol) with $Li(C_5H_5BMe)$ (**1**) (1.5 g, 0.015 mol) in THF (5 mL), workup, and condensation (3 mbar, 60 °C) as described for **2** gave **3** (2.2 g, 70%) as a colorless liquid.

3: ^1H NMR (500 MHz, $CDCl_3$, 20 °C) δ 7.11 (dd, J = 7.9, 7.3 Hz, 2H, 3-/5-H), 6.44 (tt, J = 7.3, 0.6 Hz, 1H, 4-H), 5.22 (d, br, J = 7.9 Hz, 2H, 2-/6-H), 0.73 (s, 3H, BMe), 0.19 (s, 9H, $GeMe_3$); ^{13}C NMR (126 MHz, $CDCl_3$, 20 °C) δ 144.4 (C-3,5), 122.5 (C-4), 96.7 (C-2,6), 8.6 (br, BMe), −0.4 ($GeMe_3$); ^{13}C NMR (126 MHz, CD_2Cl_2, −95 °C) δ 146.4 and 145.1 (C-3,5), 136.5 (br, C-6), 123.4 (C-4), 60.0 (br, C-2), 9.8 (BMe), 1.0 ($GeMe_3$); $\Delta\nu$ = 165 Hz (for C-3 and C-5 at −95 °C), T_c = 197 K, $\Delta G_{197}^{\ddagger}$ = 37.8(3) kJ mol^{-1}; ^{11}B NMR (160 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$ external) δ 60; MS (70 eV) m/z (I_{rel}) 210 (10, M^+), 119 (100, $GeMe_3^+$).

1-Methyl-2-(trimethylstannyl)-1,2-dihydroborinine (4). Me_3SnCl (25.0 g, 0.126 mol) in THF (10 mL) was added to a suspension of $Li(C_5H_5BMe)$ (**1**) (12.0 g, 0.123 mol) in THF (5 mL). Workup and condensation (10^{-3} bar, 25 °C) as described for **2** gave **4** (22.8 g, 73%) as a yellow liquid which crystallizes at low temperature; mp ca. −10 °C. Crystals suitable for the X-ray diffraction work were grown from pentane at temperatures between −70 and −80 °C.

4: ^1H NMR (500 MHz, $CDCl_3$, 20 °C) δ 7.26 (ddm, J = 9.20, 7.35, 1.7, 0.1 Hz, 2H, 3-/5-H), 6.54 [tt, J = 7.35, 1.1 Hz, $J(^{117/119}Sn{-}^1H) \approx 15$ Hz, 1H, 4-H], 5.82 [ddm, J = 9.2, 1.2, 1.1, 0.1 Hz, $J(^{117/119}Sn{-}^1H \approx 39$ Hz, 2H, 2-/6-H], 0.66 [s, $J(^{117/119}Sn{-}^1H) \approx$ 15 Hz, 3H, BMe], 0.12 [s, $J(^{117/119}Sn{-}^1H) \approx 54$ Hz, 9H, $SnMe_3$]; ^{13}C NMR (126 MHz, $CDCl_3$, 20 °C) δ 141.9 [C-3,5, $J(^{117/119}Sn{-}^{13}C) \approx 24$ Hz], 121.5 [C-4, $J(^{117/119}Sn{-}^{13}C) \approx 24$ Hz], 105.4 (br, C-2,6), 5.9 (br, BMe), −5.1 [$SnMe_3$, $J(^{119}Sn{-}^{13}C)$ = 340, $J(^{117}Sn{-}^{13}C)$ = 325 Hz]; ^{11}B NMR (160 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$ external) δ 48; ^{119}Sn NMR (186 MHz, $CDCl_3$, $SnMe_4$ external) δ 36.9; MS (70 eV) m/z (I_{rel}) 256 (15, M^+), 165 (100, $SnMe_3^+$).

1-Methyl-2-(trimethylplumbyl)-1,2-dihydroborinine (5). Me_3PbCl (10.0 g, 0.035 mol) in THF (20 mL) was added to a suspension of $Li(C_5H_5BMe)$ (**1**) (3.4 g, 0.0.035 mol) in THF (2 mL). Workup as described for **2** and condensation (10^{-3} mbar, 60 °C) gave **5** (7.2 g, 60%, with a <7% admixture of $PtMe_4$) as a yellow to orange liquid which crystallizes below room temperature; mp 21 °C.

5: ^1H NMR (500 MHz, $CDCl_3$, 20 °C) δ 7.25 (ddm, J = 9.6, 7.4, 1.0, 0.1 Hz, 2H, 3-/5-H), 6.54 [tt, J = 7.4, 1.1 Hz, $J(^{207}Pb{-}^1H)$ = 28.7 Hz, 1H, 4-H), 6.12 [ddm, J = 9.6, 1.7, 1.1, 0.1 Hz, $J(^{207}Pb{-}^1H)$ = 35.2 Hz, 2H, 2-/6-H], 0.95 [s, $J(^{207}Pb{-}^1H)$ = 56.8 Hz, 9H, $PbMe_3$], 0.69 [s, $J(^{207}Pb{-}^1H)$ = 24.1 Hz, 3H, BMe]; ^{13}C NMR (126 MHz, $CDCl_3$, 20 °C) δ 139.7 [C-3,5, $J(^{207}Pb{-}^{13}C)$ = 34.9 Hz], 121.7 [C-4, $J(^{207}Pb{-}^{13}C)$ = 53.5 Hz], 114.0 (br, C-2,6), 9.3 [$PbMe_3$, $J(^{207}Pb{-}^{13}C)$ = 204.6 Hz], 4.5 (br, BMe); ^{11}B NMR (160 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$ external) δ 40; ^{207}Pb NMR (104.5 MHz, $CDCl_3$, $PbEt_4$ external) δ 173.9; MS (70 eV) m/z (I_{rel}) 344 (3, M^+), 299 (30, $M^+ - 3Me$), 253 (100, $PbMe_3^+$), 238 (20, $PbMe_2^+$), 223 (60, $PbMe^+$), 208 (100, Pb^+), 91 (70, $M^+ - PbMe_3$).

Lithium 1-Methyl-2-(trimethylsilyl)boratabenzene (6). A mixture of **2** (2.0 g, 12 mmol) and LDA (1.3 g, 12 mmol) in THF (5 mL) was stirred for 1 h. The volatiles were carefully removed under vacuum. After addition of pentane the solid residue was collected on a frit, washed with a small volume of pentane, and dried under vacuum to give **6** (1.9 g, 92%) as a white solid.

6: ^1H NMR (500 MHz, d_8-THF) δ 7.24 (dd, J = 6.9, 1.5 Hz, 1H, 3-H), 7.04 (ddd, J = 10.1, 6.7, 1.5 Hz, 1H, 5-H), 6.14 (dd, J = 10.1, 1.2 Hz, 1H, 6-H), 5.98 (td, J = 6.9, 1.2 Hz, 1H, 4-H), 0.60 (s, 3H, BMe), 0.12 (s, 9H, $SiMe_3$); ^{13}C NMR (126 MHz, d_8-THF) δ 137.9 and 134.1 (C-3,5), 128.6 (br, C-2), 126.6 (br, C-6), 109.1 (C-4), 6.4 (br, BMe), 1.4 ($SiMe_3$); ^{11}B NMR (160 MHz, d_8-THF, $BF_3{\cdot}OEt_2$ external) δ 38.

1-Methyl-2,2-bis(trimethylsilyl)-1,2-dihydroborinine (7). Me_3SiCl (2.5 g, 23 mmol) was added to the salt **6** (1.9 g, 11 mmol) in pentane. Workup as described for **2** and condensation (10^{-3} mbar, 50 °C) gave **7** (1.9 g, 72%, with a 12% impurity of **2**) as a colorless liquid. MS (70 eV): m/z (I_{rel}) 236 (10, M^+), 73 (100, $SiMe_3^+$). ^1H NMR assignments of the ring protons can be made unambiguously on the basis of multiplicities and coupling constants. The C(sp^2)-bonded 6-Me_3Si group of **7B** is at lower field than other Me_3Si groups. Assignments of the ring carbon atoms are largely based on HETCOR spectra. The ^1H and ^{13}C assignments for the 2-Me_3Si group of **7B** are tentative.

7A: ^1H NMR (500 MHz, $CDCl_3$, 20 °C) δ 7.32 (ddd, J = 11.4, 5.8, 1.2 Hz, 1H, 5-H), 6.79 (dd, J = 8.8, 1.2 Hz, 1H, 3-H), 6.68 (ddd, J = 8.8, 5.8, 0.9 Hz, 1H, 4-H), 6.55 (dd, J = 11.4, 0.9 Hz, 1H, 6-H), 0.93 (s, 3H, BMe), 0.024 (s, 18H, $SiMe_3$); ^{13}C NMR (126 MHz, $CDCl_3$, 20 °C) δ 145.7 (C-5), 144.7 (C-3), 136 (br, C-6), 126.0 (C-4), 56 (br, C-2), 11.8 (br, BMe), 0.9 ($SiMe_3$); ^{11}B NMR (160 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$ external) δ 65.

7B: ^1H NMR (500 MHz, $CDCl_3$, 20 °C) δ 7.53 (dd, J = 5.7, 1.2 Hz, 1H, 5-H), 6.84 (ddd, J = 8.7, 5.2, 1.2 Hz, 1H, 3-H), 6.46 (dd, J = 8.7, 5.7 Hz, 1H, 4-H), 3.60 (d, J = 5.2 Hz, 1H, 2-H), 0.88 (s, 3H, BMe), 0.16 (s, 9H, 6-$SiMe_3$), −0.02 (s, 9H, 2-$SiMe_3$); ^{13}C NMR (126 MHz, $CDCl_3$, 20 °C) δ 152.5 (C-5), 144.5 (C-3), 136 (br, C-6), 123.7 (C-4), 58 (br, C-2), 11.8 (br, BMe), −0.13 (6-$SiMe_3$), −0.07 (2-$SiMe_3$); ^{11}B NMR (160 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$ external) δ 65.

1-Methyl-2-(trimethylsilyl)-2-(trimethylstannyl)-1,2-dihydroborinine (8). Me_3SnCl (3.50 g, 17.6 mmol) in pentane was added to a suspension of **6** (3.0 g, 17.6 mmol) in pentane. Workup as described for **2** and condensation (10^{-6} mbar, 40 °C) gave **8** (4.6 g, 80%) as a yellow liquid which crystallizes at low temperature; mp −2 °C.

8: ^1H NMR (300 MHz, $CDCl_3$, 20 °C) δ 7.50 (dd, J = 6.7, 0.6 Hz, 1H, 3-H), 7.20 ["t"d, J = 7.8, 1.0 Hz, $J(^{117/119}Sn{-}^1H) \approx 7.6$ Hz, 1H, 5-H], 6.60 ["t"d, J = 7.3, 1 Hz, 1H, 4-H], 5.28 [d, J = 7.9 Hz, $J(^{117/119}Sn{-}^1H) \approx 56.5$ Hz, 1H, 6-H], 0.77 [s, $J(^{117/119}Sn{-}^1H) \approx 15.0$ Hz, 3H, BMe], 0.18 (s, 9H, $SiMe_3$), 0.10 [d, J = 0.6 Hz, $J(^{117/119}Sn{-}^1H) \approx 52.5$ Hz, 9H, $SnMe_3$]; numbering as in formula **8A**. ^1H NMR assignments of the ring protons can be made on the basis of multiplicities and coupling constants;

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[35] Kennedy, J. D.; McFarlane, W.; Pyne, G. S. *J. Chem. Soc., Dalton Trans.* **1978**, 960.

6-H is at highest field and displays tin satellites with large coupling constants; cf. formula **8B**. ^{13}C NMR (75 MHz, $CDCl_3$, 20 °C): δ 147.8 (C-3), 142.6 [$J(^{117/119}Sn-^{13}C) \approx 33$ Hz, C-5], 130.6 (br, C-2), only observed at low temperature (−50 °C), 122.3 (C-4), 88 (br, C-6), 7.5 br, (BMe), 0.4 ($SiMe_3$), −5.3 [$J(^{117/119}Sn-^{13}C) = 330$ Hz, $SnMe_3$]. Assignments of the ring carbon atoms are largely based on HMQC spectra. ^{11}B NMR (28 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$ external): δ 55. MS (70 eV): m/z (I_{rel}) 328 (1, M^+), 165 (80, $SnMe_3^+$), 163 (65, $M^+ - SnMe_3$), 89 (100, $C_6H_6B^+$).

Variable-Temperature NMR Studies of 2 and 3. $^{13}C\{^1H\}$ NMR spectra were recorded in 5 mm sample tubes with an inner reference tube. The reference tube was filled with a solution of hydrogen chloride [aqueous HCl(conc), 0.030% by volume] in methanol. During the recording of the ^{13}C spectrum the temperature of the sample increased by ≤2 °C. The instrument was then switched to protons (≤1 s), and the methanol signals were recorded (≤4 s). Temperatures were calculated from the ^1H chemical shifts of the methanol signals on the basis of the calibration by Van Geet.[22] The line shapes of the signals for C-3 and C-5 of the borinine ring were simulated with the help of program DNMR-SIM to give rate constants;[23] in the subsequent calculation of activation parameters the transmission coefficient of the Eyring equation was set to 1.[23]

Crystal Structure Determination of 4. The data collection was performed on an ENRAF-Nonius CAD4 diffractometer with Mo Kα radiation (graphite monochromator). Crystal data, data collection parameters, and refinement parameters are given in Table 2.

Due to the low melting point of the compound a relatively large, almost isometric crystal fragment with an average diameter of 0.8 mm was choosen for intensity data collection. No significant variation in intensities of three standard reflections was obtained. To account for both slight aberrations from spherical shape and a systematic θ dependence of absorption, a redundant data set was collected and an empirical correction on the basis of azimuthal scans[36] (minimum transmission 0.872, maximum transmission 0.995) and a spherical correction[37] were applied to the data set before merging symmetry-related reflections. The structure was solved by conventional heavy atom methods followed by Fourier difference syntheses and refined on structure factors with the SDP program system.[38] In the final full-matrix least-squares refinement, a correction for secondary extinction was applied to the calculated structure factors.[39] All non-hydrogen atoms were refined with anisotropic displacement parameters; the hydrogen atoms of the ring and of the *B*-methyl group were refined isotropically whereas the hydrogen atoms of the $SnMe_3$ group were treated as riding on their carbon atoms. Refinement converged with 133 parameters using a statistical weighting scheme $w = 1/[\sigma^2(F_o)]$ at values of $R = 0.033$ and $R_w = 0.041$ with a goodness of fit of 1.275.[40]

Table 2. Crystallographic Data, Data Collection Parameters, and Refinement Parameters for 4

formula	$C_9H_{17}BSn$
fw	254.74
cryst system	orthorhombic
space group	*Pbca* (No. 61)
a, pm	1260.8(3)
b, pm	1233.1(3)
c, pm	1446.6(6)
V, nm^3	2.249(1)
d_{calc}, g cm^{-3}	1.505
Z	8
F(000), electrons	1008
μ, cm^{-1}	22.26
radiation (λ, pm)	Mo Kα (71.073)
T, K	203
scan mode (θ range, deg)	ω (3−29)
tot, data	6699
unique data	3351
unique obsd data	2692 ($I > \sigma(I)$)
sec extinction coeff	6.24×10^{-7}
no. of variables	133
R, R^{w}[a]	0.033, 0.041
max resid dens, 10^{-6} e pm^{-3}	1.9 at 20 pm from Sn

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

Acknowledgment. We thank Dr. A. Dölle for advice with the temperature control in the variable-temperature NMR measurements. This work was generously supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Supporting Information Available: Tables[40] of fractional coordinates and U values of all atoms, anisotropic displacement parameters, and bond distances and angles for **4** and NMR spectra for **2**−**8** (23 pages). Ordering information is given on any current masthead page.

OM9605701

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(36) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.

(37) *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Press: Dordrecht, The Netherlands, 1995; Vol. C, Table 6.3.3.3.

(38) ENRAF-Nonius, SDP Version 5.0, Delft, The Netherlands, 1989.

(39) Zachariasen, W. H. *Acta Crystallogr.* **1963**, *16*, 1139.

(40) Further details of the crystal structure analysis are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-406458 for **4**, the names of the authors, and this journal citation.