Organometallic Compounds of Group 13, 54[◇]

Novel Organoborane Lewis Acids via Selective Boron-Tin Exchange Processes – Steric Constraints to Electrophilic Initiation by the Boron Halide[☆]

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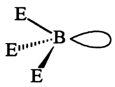
With the purpose of preparing novel mono- and bidentate organoboron Lewis acids, the scope and limitations of synthesizing the requisite organoboranes by the boron-tin exchange between a boron halide and the appropriate organostannane have been examined in detail. The following organotin derivatives have been obtained either from the corresponding RMgBr or RLi reagent and Me_nSnCl_{4-n} or from a Barbier procedure using the organic halide, Me_3SnCl and magnesium metal: 1,2-bis(trimethylstannyl)ethyne, *o*-, *m*-, and *p*-bis(trimethylstannyl)benzenes, α,*o*-bis(trimethylstannyl)toluene, α,α-bis(trimethylstannyl)-*o*-xylene, and 2,2-dimethyl-2-stannaindane. The individual interaction of the 1,2-bis(trimethylstannyl)ethyne and the isomeric bis(trimethylstannyl)benzenes with Et_2BBr produced the corresponding bis(diethylboryl)-derivatives. By contrast, with Et_2BCl the α,*o*-bis(trimethylstannyl)toluene gave only *o*-diethylboryl-α-trimethylstannyltoluene and with BCl_3 the α,α′-bis(trimethylstannyl)-*o*-xylene formed only α,α′-bis(chlorodimethylstannyl)-*o*-xylene. Furthermore, in the attempted double boron-tin exchange between *o*-bis(trimethylstannyl)benzene and BCl_3, an unprecedented rearrangement of the 1-(dichloroboryl)-2-(trimethylstannyl)benzene intermediate into its 1-[chloro(methyl)boryl]-2-(chlorodimethylstannyl) isomer was observed. Likewise, *o*-bis(trimethylstannyl)benzene with $PhBCl_2$ produced by a similar rearrangement 1-[methyl(phenyl)boryl]-2-(chlorodimethylstannyl)benzene. The thermolysis of such boranes led variously to definite dimers or ill-defined oligomers. Preliminary studies of the properties of these organoboranes have identified the heightened Lewis acidity of 1,2-bis(diethylboryl)ethyne and the π-electron delocalization involving the $2p_z$-boron orbitals in the 9,10-dihydro-9,10-diboraanthracene system. Finally, an electronic mechanism for the boron-tin exchange has been developed to account for the selectivity of the boron halide's attack at unsaturated carbon–tin bonds.

As part of an ongoing investigation of Ziegler-Natta olefin-polymerization catalysis the present study has explored the synthesis of novel Group-13 Lewis acids for their potential suitability as cocatalysts with cyclopentadienyl transition metal derivatives in such homogeneous polymerizations.[1][2][3][4] In this contribution the preparation of organoborane Lewis acids bearing substituents of enhanced electron-withdrawing power (**1**) and diminished steric demand (**2**) and possibility multidentate boron centers (**3**) has been the principal focus of research. The electron-withdrawing group E in **1** could favorably be a halide (F > Cl > Br > I) and an organyl group other than alkyl (sp^3) having greater *p*-character, such as aryl (sp^2) or 1-alkynyl (sp). As to steric demands (**2**), smaller groups E (Me versus *t*Bu; 1-alkenyl versus alkyl; and 1-alkynyl versus 1-alkenyl) should engender less B-strain upon the boron center accepting the donor group D and rehybridizing to sp^3. Finally, the coordination of suitably sized donor D (**3**) should be stabilized by chelation, as has been abundantly established by the pioneering researches of Köster and coworkers with *cis*-1,2-diborylalkenes.[5]



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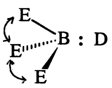

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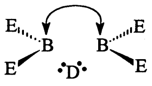
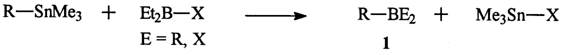


3

In order to synthesize the required organoborane Lewis acids, most of which are mixed or unsymmetrical boranes, such as $PhBCl_2$ or $Et_2B{-}C{\equiv}C{-}BEt_2$, a preparative route occurring under mild conditions is required, so as to minimize any tendency of the desired product E_2BE' to redistribute rapidly into E_3B and E'_3B.[6] For this desideratum it was found that the transmetallation reaction between the appropriate organostannane and a boron halide was generally a feasible route (Eq. 1).[7]



$$R{-}SnMe_3 + \underset{E\,=\,R,\,X}{Et_2B{-}X} \longrightarrow \underset{\mathbf{1}}{R{-}BE_2} + Me_3Sn{-}X \qquad (1)$$

In some situations where such a tin-boron exchange failed to produce the desired borane, it was instead found

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that the analogous tin-lithium exchange is more suitable and that the desired transformation is then attainable by treating the lithium derivative RLi with $E_2B{-}X$ (Eqs. 2, 3).

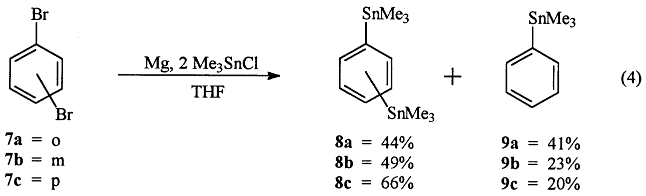
$$\mathrm{R{-}SnMe_3}\ \xrightarrow[\substack{\text{eq. 2}\\ \mathrm{-\ Bu^nSnMe_3}}]{\mathrm{Bu^nLi}}\ \mathrm{R{-}Li}\ \xrightarrow[\substack{\text{eq. 3}\\ \mathrm{-\ LiX}}]{\mathrm{E_2B{-}X}}\ \underset{\mathbf{1}}{\mathrm{R{-}BE_2}}$$

Finally, each of the successes or failures of the tin-boron exchanges in achieving its intended transformation has provided us with valuable insight into the reaction mechanisms of such processes.

Results

Preparation of Organotin Precursors

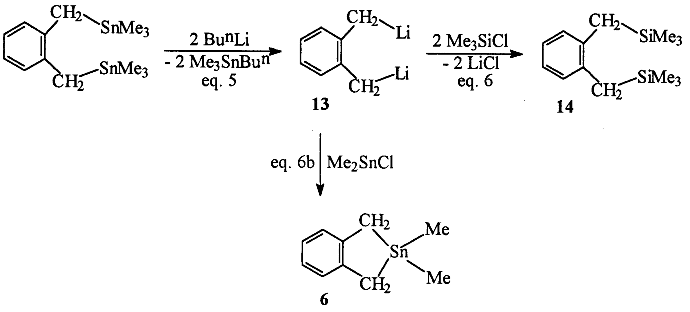
Where successfully applicable, the organotin precursors, such as 1,2-bis(trimethylstannyl)ethyne (**3**), phenyl(trimethyl)tin (**4**), benzyl(trimethyl)tin (**5**), and 2,2-dimethyl-2-stannaindane (**6**) were prepared from the appropriate lithium or magnesium reagent and either Me_3SnCl or Me_2SnCl_2, as required, and were generally attainable according to published procedures[8] or procedures given in this article (cf. infra). The other precursors, containing two trimethylstannyl groups, were individually prepared from the corresponding organyl dibromide or dichloride by preparing the organomagnesium intermediate from magnesium metal in THF in the presence of the organotin chloride reactant (Barbier procedure[9]). Small to moderate amounts of the trimethylstannyl derivative (**9**) were formed as a side product (Eq. 4).



In a similar manner, α,*o*-bis(trimethylstannyl)toluene (**10**) and α,α′-bis(trimethylstannyl)-*o*-xylene (**11**) were prepared from *o*-bromobenzyl bromide in 45% yield and from α,α′-dichloro-*o*-xylene in 85% yield, respectively.

Preparation of Organolithium Precursors

Unusual lithium reagents employed in this study were prepared by the following procedures: a) dilithioethyne (**12**) by either the action of 3 equivalents of *n*-butyllithium on trichloroethylene[10] or the action of 2 equivalents of the lithium reagent on acetylene; b) α,α′-dilithio-*o*-xylene (**13**) from stirring 2.2 equivalents of *n*-butyllithium and 1 equivalent of **11** vigorously for 96 h, whereupon a yellow precipitate of **13** formed; quenching such a reaction mixture with excess Me_3SiCl, hydrolytic work-up and distillation yielded 87% of α,α′-bis(trimethylsilyl)-*o*-xylene (**14**) and 90% of *n*-butyl(trimethyl)tin, indicating that **13** had been formed in at least 90% yield (Eqs. 5−6).



Similarly, the dissolution of **13** in anhydrous diethyl ether and the slow introduction of 1 equivalent of Me_2SnCl_2 led to the isolation of 75% of 2,2-dimethyl-2-stannaindane[11] (**6**) (Eq. 6b).

Preparation of Organoboranes by Boron-Tin Exchange Reactions

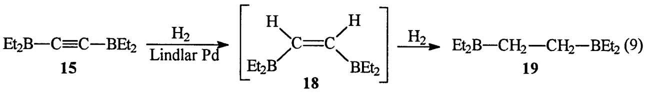
1,2-Bis(diethylboryl)ethyne (**15**): This organoborane could be prepared by the interaction of bromo(diethyl)borane (**16**) with dilithioethyne (**12**), but since the most convenient source of **12** involved the action of *n*-butyllithium on trichloroethylene in THF, **12** was generated as a solid complex with LiCl and 0.5 equiv. of THF. The complexed THF in 12 was then easily cleaved in the reaction of **12** with Et_2BBr, producing also **17** and lowering the yield of **15** (Eq. 7).

$$\underset{\mathbf{12}}{\mathrm{LiC{\equiv}CLi\bullet 0.5\,THF}}\ \xrightarrow[\text{(2.5 equiv.)}]{\mathrm{Et_2BBr_2}}\ \underset{\mathbf{15}\ \ 39\%}{\mathrm{Et_2B{-}C{\equiv}C{-}BEt_2}}\ +\ \underset{\mathbf{17}\ \ 93\%}{\mathrm{Et_2B{-}O{-}(CH_2)_4Br}} \qquad (7)$$

The boron-tin exchange between **16** and 1,2-bis(trimethylstannyl)ethyne (**3**) in pentane precludes this side reaction and permits **15** to be isolated cleanly and in good yield (65%) by distillation. As with all such unsymmetrical boranes, their distillation had to be conducted at as low a temperature (and hence pressure) as possible to minimize redistribution and the formation of triethylborane (cf. infra) (Eq. 8).

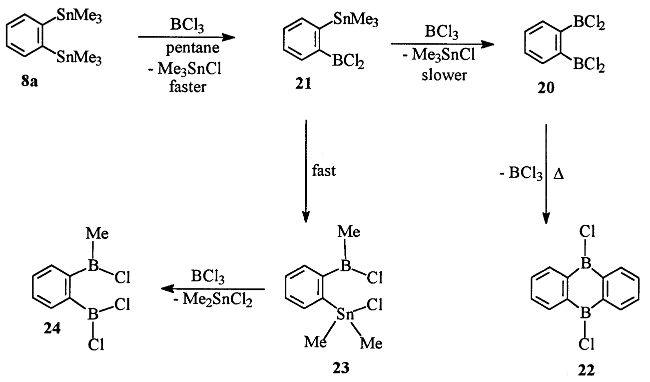
$$\underset{\mathbf{3}}{\mathrm{Me_3Sn{-}C{\equiv}C{-}SnMe_3}}\ \xrightarrow[\mathrm{-\ Me_3SnBr}]{\mathbf{16}}\ \underset{\mathbf{15}}{\mathrm{Et_2B{-}C{\equiv}C{-}BEt_2}}\ \xrightarrow[\Delta]{}\ \mathrm{Et_3B}\uparrow \qquad (8)$$

Attempts were made to reduce **15** selectively to (*Z*)-1,2-bis(diethylboryl)ethene (**18**) with dihydrogen and a Lindlar catalyst, but the hydrogenation could not be halted but proceeded to form 1,2-bis(diethylboryl)ethane (**19**) (Eq. 9). In recording the NMR spectra of **15** and **19** in various solvents, it was discovered that **15**, but not **19**, forms a complex with two equivalents of THF. For example, the ^{11}B signal of **15** in C_6D_6 occurs at $\delta = 72.0$ but in THF is found at $\delta = 36.9$.

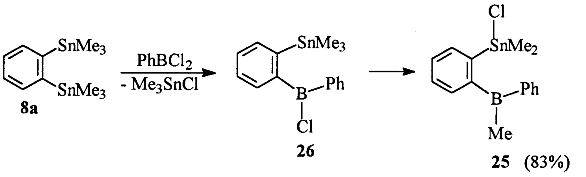


1,2-Bis(dichloroboryl)benzene (**20**): Despite the reported preparation of **20** in 88% yield from the interaction of **8a** with BCl_3 in a 1:3 ratio in CH_2Cl_2 at −78 °C,[12] attempts to reproduce this result in our laboratory under the specified conditions or under a variety of modified procedures did not lead to high yields of isolable **20** but rather to the monomethylated derivative **24** when a large excess of BCl_3 was employed. Other reactions conducted with different ratios of reactants and in different solvents (alkanes, arenes, CH_2Cl_2) gave mixtures of **20–24**. An unmistakable sign that the reaction between **20** and BCl_3 (1:2 ratio) was taking an unexpected course was the isolation of a precipitate composed of 44% of the expected 2 equivalents of Me_3SnCl and 40% of 1 equivalent of the unexpected Me_2SnCl_2. The source of the Me_2SnCl_2 can best be explained by a relatively fast boron-tin exchange leading from **8a** to **21**, which rearranges relatively rapidly to **23** and this undergoes a second boron-tin exchange to produce **24** more rapidly than the diminished concentration of **21** can generate **20**. The small proportion of **22** produced could have arisen from either **20** or **24**.

Scheme 1

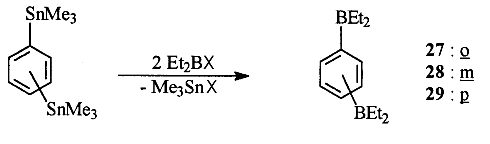


1-[Methyl(phenyl)bory]l-2-(chlorodimethylstannyl)benzene (**25**): Confirmation of the foregoing unusual rearrangement (**21–23**) came from the reaction of **8a** with phenylboron dichloride at −78 °C. The by-product Me_3SnCl was isolated in 78% yield and **25** was isolated by distillation (Eq. 10), a clear indication that **26** is an intermediate in this novel transformation.



(10)

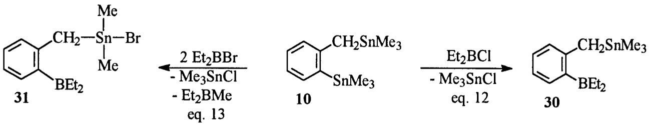
1,2-, 1,3-, and 1,4-Bis(diethylboryl)benzenes (**27–29**): These isomeric diborylbenzenes were readily prepared in high yield (> 80%) by treating the individual bis(trimethylstannyl)benzenes (**8a–8c**) with 2 equivs. of Et_2BBr or Et_2BCl and removing the Me_3SnX under reduced pressure at 50 °C (Eq. 11).



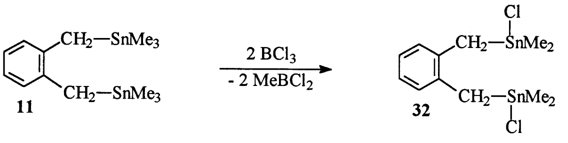
(11)

Diethyl(phenyl)borane could also be prepared similarly from trimethyl(phenyl)tin in 89% yield.

o-(Diethylboryl)-α-(trimethylstannyl)toluene (**30**): The interaction of α,*o*-bis(trimethylstannyl)toluene (**10**) with Et_2BCl (1:2 ratio) at 25 °C led cleanly to 90% of **30** after all volatiles were removed (Eq. 12). When the reaction was conducted with Et_2BBr and with a 4-h heating period, boron-tin exchange had also occurred at tin−methyl bond of **30** as well, forming **31** also in 90% yield (Eq. 13).



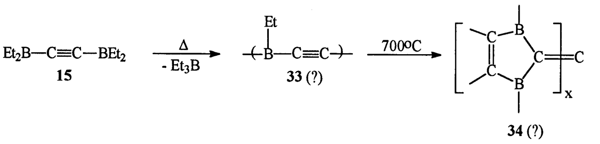
α,α′-Bis(dichloroboryl)-o-xylene (**32**) *(attempted)*: The interaction of α,α′-bis(trimethylstannyl)-*o*-xylene (**11**) with BCl_3 (1:2 ratio) from −50 to 25 °C led to the formation instead of 85% of α,α′-bis(chlorodimethylstannyl)-*o*-xylene (**32**), the product of the boron-tin exchange at the tin−methyl bond (eq. 14).



(14)

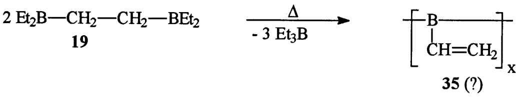
Thermolysis of Organoboranes

1,2-Bis(diethylboryl)ethyne (**15**): A neat sample of **15** was heated to 120 °C and the evolved liquid permitted to reflux for 2 h. Evaporation of the evolved liquid under reduced pressure allowed the condensation of 1.0 equivalent of Et_3B and a red-brown viscous oil remained (**33**). Subsequent heating up to 700 °C in a TGA apparatus left a shiny black residue of empirical formula (by elemental analyses) of $C_3B_2H_{0.14}$ (**34**) (Eq. 15).



(15)

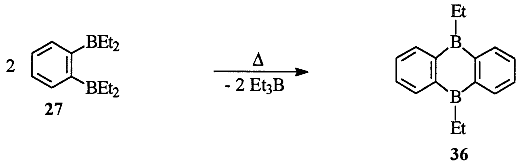
1,2-Bis(diethylboryl)ethane (**19**): Heating **19** to 180 °C for 2 h and subsequent cooling similarly led to the evolution of 1.5 equiv. of Et_3B and a yellow residue (**35**) that lost no further weight up to 350 °C in a TGA apparatus (Eq. 16).



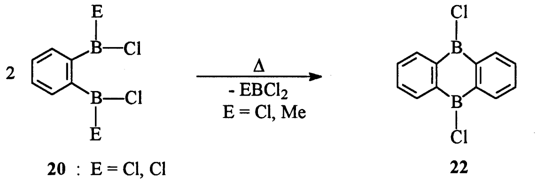
(16)

1,2-Bis(diethylboryl)benzene (**27**): Heating **27** in refluxing heptane for 18 h formed 9,10-diethyl-9,10-dihydro-9,10-diboraanthracene (**36**) almost quantitatively. The triethylborane eliminated was removed with the heptane by evaporation under reduced pressure. Yellow **36** was crystallized from pentane at −78 °C (Eq. 17).

1,2-Bis(dichloroboryl)benzene (**20**) *or 1-(Dichloroboryl)-2-loro(methyl)boryl]benzene* (**24**): Individual samples or


(17)

mixtures of **20** and **24** gradually formed 9,10-dichloro-9,10-dihydro-9,10-diboraanthracene (**22**) when heated at reflux in heptane (Eq. 18). Samples of **22** were purified by sublimation as yellow needles.


(18)

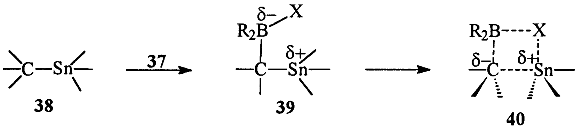
20 : E = Cl, Cl
24 : E = Me, Cl

Discussion

Selectivity of Boron-Tin Exchange

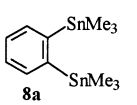
The attack by a boron halide R_2B-X (**37**) on an organotin substrate (**38**) can be viewed as passing through a transition state (**39**) involving electrophilic attack of R_2B-X on the C−Sn bond or one involving concerted electrophilic attack by boron and nucleophilic attack by halide (**40**) (Scheme 2).

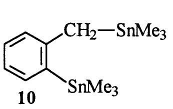
Scheme 2



If the carbon in **38** is involved in π-bonding (sp- or sp^2-hybridized carbon), this situation would explain why transition state **39**, involving principally electrophilic attack by R_2B-X, should be relatively lower in energy and hence rate-determining for the boron-tin exchange. Furthermore, transition state **39** would account readily for the following: 1) the selective borylation of **3** at the acetylenic carbon−tin bonds rather than the methyl carbon−tin bonds; 2) the exclusive borylation of mono- and bis(trimethylstannyl)benzenes, such as **8a**, at the aryl carbon−tin bonds; and 3) the sole monoborylation of **10** at the aryl carbon−tin bond, even when 2 equiv. of the boron halide, Et_2BCl, were employed. Thus, generally when an sp- or sp^2-hybridized carbon−tin bond is pitted against an sp^3-hybridized carbon−tin bond in boron-tin exchange processes, the former carbon centers always react faster (cf. infra for an intramolecular exception to this conclusion.)

$Me_3Sn-C{\equiv}C-SnMe_3$
3


8a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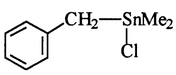
A further interesting structural example of such boron-tin exchanges are the benzylic trimethyltin derivatives, such as benzyltrimethyltin (**5**) and α,α-bis(trimethylstannyl)-*o*-xylene (**11**), which present competing carbon−tin bonds, namely benzylic C−Sn and methyl C−Sn bonds, both formally involving identical sp^3-hybridized carbon centers. When **5** and **11** were individually treated with an excess of BCl_3, they were converted into **41** and **42**, respectively. Thus, exchange took place selectively at the methyl carbon-tin bond. With the absence of any π-electron density at the carbon center, a transition state like **39** would no longer be a low-energy configuration and a bridging transition state resembling **40** may be more accessible. The carbon group bridging between tin and carbon would be more appropriate the smaller its steric requirements would be. Therefore, the greater reactivity of the methyl carbon−tin bond would stem from the methyl group's smaller steric size and better bridging property, compared with the bulkier benzyl group. It should be noted that trimethylaluminum exists as a stable dimer with bridging methyl groups, while tribenzylaluminum is monomeric.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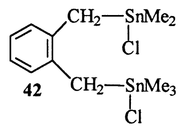
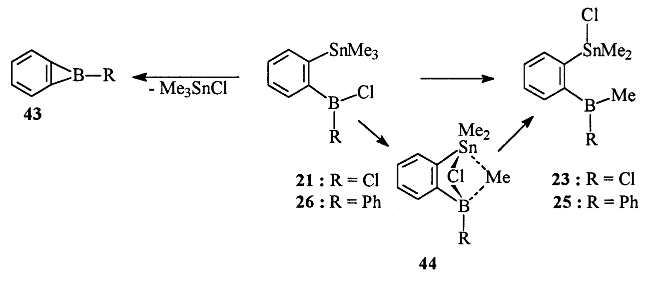

42

The exceptional instance where an sp^3-hybridized carbon−tin bond enters into a boron-tin exchange more readily than an available sp^2-hybridized carbon−tin bond is the facile intramolecular boron-tin exchange first observed in this study (Scheme 1 and Eq. 10) and depicted generally in Scheme 3. Undoubtedly, the failure of **21** or **26** to undergo the boron-tin exchange with the elimination of Me_3SnCl and the formation of benzoborirene **43** stems from the extremely strained transition state of type **39** that would have been required. A four-center transition state involving the methyl groups (**44**), on the other hand, is easily attainable.

Scheme 3



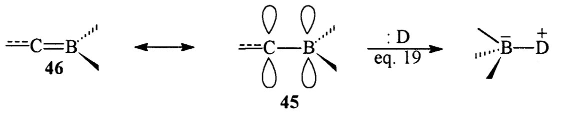
Thermal Redistribution of Unsymmetrical Organoboranes

The unsymmetrical organoboranes synthesized in this study uniformly underwent a redistribution of groups upon heating over 100°C. With diethylboryl derivatives the amount of evolved triethylborane corresponded rather well with the selective formation of defined oligomers or polymers. The formation of the dihydro-9,10-diboraanthracene (**36**, Eq. 17) from the 1,2-diborylbenzene **27** and the production of some polymeric structure of the $Et-B-C{\equiv}C-$ unit (**33**, Eq. 15) are illustrative. If such thermolyses are continued up to 700°C, there are indications that boron carbides of unusual stoichiometry may result. Such thermolysis of diborylacetylene **15** yields a glistening black solid of approximate composition C_3B_2. Further work is required to learn whether this solid **34** (Eq. 15) is a novel boron carbide or a mixture of B_4C and carbon.[13]

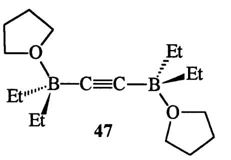
Unusual Properties of Unsymmetrical Organoboranes

An exploration of the boron-tin exchange route to organoboranes has been undertaken, in order to prepare such boranes that might exhibit novel properties, such as enhanced Lewis acidity and unusual spectral properties.[14] Both kinds of properties would involve the ability of the $2p_z$-orbital on tricoordinate boron to accept electron density, either intermolecularily from a Lewis base (Eq. 19) or from an adjacent π-electron cloud (resonance structure **45** and **46**, Scheme 4).

Scheme 4



Although the study of the properties of such boranes has just begun, two observations are already noteworthy: 1) 1,2-bis(diethylboryl)ethyne (**15**) readily forms a stable bis-complex with THF (**47**), whereas the structurally similar 1,2-bis(diethylboryl)ethane (**19**) does not complex with THF at all nor do Et_3B, $PhBEt_2$, or the dihydro-9,10-diboraanthracene **36**; and 2) both the known 9,10-dichloro- (**22**) and the novel 9,10-diethyl- (**36**) -9,10-dihydro-9,10-diboraanthracenes absorb in the visible spectrum (yellow) and exhibit their ^{11}B-NMR signals shifted considerably upfield ($\delta < 70$), that is, attributable to a more shielded boron nucleus, than those of $PhBEt_2$ or o-$(Et_2B)_2C_6H_4$ (**27**), whose ^{11}B signals occurs at $\delta = 78-80$. Both the electronic and the ^{11}B-NMR spectral data are consistent with the interaction of the $2p_z$-orbitals of boron in **22** and **36** with the adjacent π clouds (**48**).



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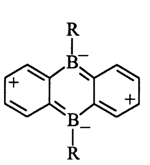

48 : R = Cl, Et

As to the enhanced Lewis acidity of **15** over **19**, it is to be expected that the steric F-strain generated in complex **47** by the neighboring C≡C group would be somewhat smaller than that of an adjacent CH_2-CH_2 group in such a complex formed by **19** and two THF units. But such steric factors alone seem inadequate in explaining the enhanced acidity of **15**. Therefore, we propose that the enhanced electronegativity of the sp-hybridized carbon centers in **15** withdraws electron density more effectively along the σ C−B bond, thereby enhancing the Lewis acidity of boron.

Our continuing studies will investigate the significance and consequences of π-electron interactions between boron and unsaturated carbon.[15]

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Experimental Section

General Techniques: All preparations and purification procedures involving manipulations with oxygen- and moisture-sensitive reagents were carried out under an anhydrous, oxygen-free argon or nitrogen atmosphere employing Schlenk techniques.[16] Those procedures which did not require a protective atmosphere but involved working with toxic chemicals (such as boron and tin compounds) were carried out in an exhaust hood evacuating air at 100 ft/min. For the operations under reduced pressure the required vacuum was provided either by a rotary vacuum oil pump (down to 0.1 Torr) or by a water pump (down to 10 Torr) and toxic volatiles were condensed in cold baths.

In instances when acetylene and hydrogen were used, tanks were connected through purification columns directly to the one of the manifold's outlets. Acetylene was purified by passing through a bubbler with concentrated sulfuric acid and a 25-cm column filled with activated charcoal and 4-Å molecular sieves. Hydrogen was delivered to the system after passing through a similar column filled only with 4-Å molecular sieves. When a volume of hydrogen needed to be measured, a calibrated gas buret was used.

Commercially available solvents of reagent grade were purified according to the recommended methods.[16] Solvents used in reactions were always freshly distilled under argon or nitrogen from the appropriate drying agents: aliphatic hydrocarbons from $LiAlH_4$; toluene from sodium; dichloromethane from CaH_2; and ethers from sodium/benzophenone combination. Deuteriated solvents (Cambridge Scientific) for NMR measurements of oxygen- and moisture-sensitive substance were vacuum-transferred to the Schlenk glass vessels and stored over 4-Å molecular sieves under argon. − Nuclear magnetic resonance (NMR) spectra were recorded with Bruker AM 360 (^1H: 360.0 MHz, ^{11}B: 115.5 MHz, ^{13}C: 90.5 MHz, ^{27}Al: 93.8 MHz, ^{119}Sn: 134.2 MHz) or Bruker-IBM AM 300 (^1H: 299.9 MHz, ^{11}B: 96.2 MHz, ^{13}C NMR: 75.4 MHz, ^{27}Al: 78.2 MHz, ^{119}Sn: 111.8 MHz) instruments. $[D_6]$Benzene, [D]chloroform, or 95% tetrachloromethane and 5% $[D_6]$benzene mixture were used as solvents. The chemical shifts are reported on a δ scale in parts per million (ppm) from the reference signals set as $\delta = 0$. The following substances served as references: ^1H and ^{13}C NMR: tetramethylsilane (TMS), internal; ^{11}B NMR: boron trifluoride−diethyl ether ($BF_3 \cdot Et_2O$), external; ^{119}Sn NMR: tetramethyltin (Me_4Sn), external. − Gas chromatographic analysis (GC) was performed with a Hewlett-Packard Chromatograph, model 5880A, with helium as the carrier gas.

Lithium Compounds

Dilithioethyne (**12**). − *Method 1:*[10] A flask was charged with a solution of *n*-butyllithium (231 ml of 2.0 M pentane solution, 0.462 mol) and then the pentane was removed under vacuum. With cooling a mixture of freshly distilled THF (50 ml) and Et_2O (50 ml) was slowly added to the residue. The resulted solution was cooled to −78 °C and stirred for 0.5 h. Then a solution of trichloroethylene (20.2 g, 0.154 mol) in 50 ml of Et_2O was added dropwise. After completion of the addition the resulting clear yellow solution was stirred for 2 h at −78 °C and then allowed to warm up to ambient temperature. A white precipitate gradually began to fill the flask and at approximately 0 °C the flask was full of solid. The solvents were removed partly by filtration and partly in vacuum. The yellow solid was washed with pentane (2 × 100 ml), filtered, and dried under vacuum (0.5 Torr, 40°C). Analysis of the resulting powder (20.4 g) allowed an estimation of its composition as $Li_2C_2 \cdot LiCl \cdot 0.5$ THF with 29.8% content of dilithioethyne (6.07 g, 96%).[17]

Method 2: A solution of *n*-butyllithium (70 ml of 2.5 M in hexane, 0.175 mol) was diluted with freshly distilled hexane (100 ml) and cooled to −15°C. With vigorous stirring acetylene was then passed through the solution at a rate maintaining the reaction temperature below −10°C. After approximately 15 min, a white precipitate started to form. When gas evolution was evident (bubbling through the check valve) a slow delivery of acetylene was continued for 0.5 h and then stopped. The reaction mixture was allowed to warm up to room temperature and then was heated at reflux for 2 h to expel all dissolved gas. The solvent was removed partly by filtration and partly by evaporation in vacuum. The remaining white solid residue was washed with hexane (2 × 100 ml), filtered and dried in vacuum (0.5 Torr, 60°C). The resulting fine, white powder (3.40 g) was analyzed and found to have 92% of dilithioethyne (**12**) (3.13 g, 82%).

1,4-Dilithiobenzene: The reaction of 1,4-bis(trimethylstannyl)-benzene (0.86 g, 2.1 mmol) with *n*-butyllithium (2.8 ml of 1.6 M hexanes solution, 4.3 mmol) in pentane/diethyl ether (1:1 v/v, 10 ml) after stirring for 2 d gave 0.75 g of colorless precipitate. The precipitate was derivatized with methyl iodide to give 92% of *p*-xylene. *n*-Butyl(trimethyl)tin was formed in 95% yield.[11]

1,4-Bis(trimethylsilyl)benzene: To a similarly prepared suspension of 1,4-dilithiobenzene was added 2.1 equiv. of chlorotrimethylsilane. Usual work-up provided crude solid 1,4-bis(trimethylsilyl)-benzene, which was washed with cold pentane (90%; recrystallized from hexane, mp 92−93°C).

α,α′-Dilithio-o-xylene (**13**): The reaction of α,α′-bis(trimethylstannyl)-*o*-xylene (0.80 g, 1.85 mmol with *n*-butyllithium (2.4 ml of 1.6 M hexanes solution, 3.8 mmol) in pentane/diethyl ether (1:1 v/v, 10 ml) after stirring for 2 d gave 0.62 g of a bright yellow precipitate. The precipitate was derivatized with methyl iodide to give 90% of 1,2-diethylbenzene. *n*-Butyl(trimethyl)tin was formed in 89% yield.

Tin Compounds

1,2-Bis(trimethylstannyl)ethyne (**3**): To a stirred suspension of dilithioethyne (1.22 g, 32.2 mmol) in 100 ml of dry pentane at −25°C was added dropwise over 40 min a solution of trimethyltin chloride (12.94 g, 65.0 mmol) in 100 ml of pentane. The reaction was then warmed to room temperature and heated at reflux for 1 h. The lithium chloride was filtered off and the filtrate upon concentration deposited pale yellow crystals. The crude product was recrystalized from pentane at −78°C and dried under vacuum (40°C, 5 Torr) to give off-white crystals of 1,2-bis(trimethylstannyl-ethyne) (8.56 g, 76%); mp 57−59°C (mp 58−60°C). − ^{1}H NMR (C_6D_6): δ = 0.15 (s, 18 H, $J_{\text{Sn-H}}$ = 58 Hz). − ^{13}C NMR (C_6D_6): δ = 8.0 (Sn-*C*H$_3$, $J_{\text{Sn-C}}$ = 400 Hz), 115.8 (Sn−*C*≡*C*−Sn). − ^{119}Sn NMR (C_6D_6) δ = 80.9. − A corresponding reaction with trimethyltin bromide yielded 64% of the product.

1,2-Bis(trimethylstannyl)benzene (**8a**): Magnesium turnings (3.16 g, 130 mmol) in 20 ml of THF were activated with 0.3 ml of ethylene bromide. A fresh 50-ml portion of THF was then added and 0.2 ml more of ethylene bromide was injected. The mixture was heated at reflux until gas evolution stopped. At reflux a solution of 1,2-dibromobenzene (5.89 g, 25 mmol) in 30 ml of THF and trimethyltin chloride (50 ml of 1.0 M THF solution, 50 mmol) was added dropwise. As the reaction progressed, a green-brown solution developed. After the addition the reaction mixture was heated at reflux for 6 h, poured into 150 ml of a cold, saturated aqueous solution of ammonium chloride and then extracted with two 75-ml portions of ethyl ether. The extracts were washed with water, dried with anhydrous Na_2SO_4, and then concentrated under reduced pressure. Vacuum distillation of the remaining residue gave 1,2-bis(trimethylstannyl)benzene (**8a**) as a colorless, viscous liquid (4.46 g, 44%); bp 90−94°C/0.1 Torr (bp 92−94°C/0.145 Torr). − ^{1}H NMR (C_6D_6): δ = 0.28 (s, 18 H, $J_{\text{Sn-H}}$ = 52 Hz), 7.15 (dd, *J* = 5.3, 3.5 Hz, 2 H), 7.52 (dd, *J* = 5.3, 3.5 Hz, 2 H). − ^{13}C NMR (C_6D_6) δ = −7.2 (Sn-*C*H$_3$), 127.4, 137.3, 151.6 (*C*$_{\text{ar}}$-Sn). − ^{119}Sn NMR (C_6D_6): δ = 34.1. − *Trimethyl(phenyl)tin* (**9**) (2.46 g, 41%) was isolated as a major by-product; bp 65−68°C/0.1 Torr). − ^{1}H NMR (C_6D_6): δ = 0.20 (s, 9 H, $J_{\text{Sn-H}}$ = 54 Hz), 7.20 (m, 3 H), 7.43 (dd, 2 H). − ^{13}C NMR (C_6D_6) δ = −9.9 (Sn-*C*H$_3$), 128.5, 136.1, 142.0 (*C*$_{\text{ar}}$-Sn). − ^{119}Sn NMR (C_6D_6): δ = 29.9. − The following bis(trimethylstannyl) derivatives were also prepared analogously.

1,3-Bis(trimethylstannyl)benzene (**8b**): This compound was prepared from 1,3-dibromobenzene (5.89 g, 25 mmol) and trimethyltin chloride (50 ml of 1.0 M THF solution, 50 mmol). Vacuum distillation yielded trimethyl(phenyl)tin (**9**) (1.37 g, 23%) and the desired compound as a colorless liquid (4.93 g, 49%); bp 92−95°C/0.1 Torr. − ^{1}H NMR (C_6D_6): δ = 0.24 (s, 18 H, $J_{\text{Sn-H}}$ = 54 Hz), 7.27 (t, *J* = 7 Hz, 1 H, $J_{\text{Sn-H}}$ = 10 Hz), 7.44 (d, *J* = 7 Hz, 2 H, $J_{\text{Sn-H}}$ = 46 Hz), 7.79 (s, 1 H, $J_{\text{Sn-H}}$ = 42 Hz). − ^{13}C NMR (C_6D_6): δ = −9.7 (Sn-*C*H$_3$), 128.5, 136.2, 142.0, 143.3. − ^{119}Sn NMR (C_6D_6): δ = 30.4.

1,4-Bis(trimethylstannyl)benzene (**8c**): This compound was prepared from 1,4-dibromobenzene (6.63 g, 28 mmol) and trimethyltin chloride (56 ml of 1.0 M THF solution, 56 mmol). The crude product was recrystallized from pentane at −78°C to give 1,4-bis(trimethylstannyl)benzene as short, white needles (7.44 g, 66%); mp 125−127°C (mp 124°C).[18] − ^{1}H NMR (C_6D_6): δ = 0.24 (s, 18 H, $J_{\text{Sn-H}}$ = 54 Hz), 7.49 (s, 4 H). − ^{13}C NMR (C_6D_6) δ = −9.9 (Sn-*C*H$_3$), 136.0, 142.1 (*C*$_{\text{ar}}$-Sn). − ^{119}Sn NMR (C_6D_6): δ = 30.8.

α,o-Bis(trimethylstannyl)toluene (**10**): This compound was prepared from 2-bromobenzyl bromide (5.61 g, 22.5 mmol) and trimethyltin chloride (50 ml of 1.0 M THF solution, 50 mmol). Vacuum distillation of the crude product yielded the compound as a colorless, viscous liquid (4.21 g, 45%); bp 89−92°C/0.1 Torr. − ^{1}H NMR (C_6D_6): δ = 0.03 (s, 9 H, $J_{\text{Sn-H}}$ = 52 Hz), 0.28 (s, 9 H, $J_{\text{Sn-H}}$ = 52 Hz), 2.38 (s, 2 H, $J_{\text{Sn-H}}$ = 62 Hz), 6.97−7.00 (m, 2 H), 7.12 (d, *J* = 7 Hz, 1 H), 7.38 (d, *J* = 7 Hz, 1 H). − ^{13}C NMR (C_6D_6): δ = −9.6 (CH$_2$-Sn-*C*H$_3$), −8.2 (*C*$_{\text{ar}}$-Sn-*C*H$_3$), 24.2 (Sn-*C*H$_2$), 123.6, 126.8, 129.1, 136.7, 138.7, 149.9. − ^{119}Sn NMR (C_6D_6): δ = 36.6 [Ph-*Sn*-(CH$_3$)$_3$], −0.8 [Ph-CH$_2$-*Sn*-(Me$_3$)$_3$].

α,α′-Bis(trimethylstannyl)-o-xylene (**11**): This compound was prepared from α,α′-dichloro-*o*-xylene (4.34 g, 24.6 mmol) and trimethyltin chloride (50 ml of 1.0 M THF solution, 50 mmol). The crude product was distilled under vacuum to yield the pure derivative as a colorless, viscous liquid (9.14 g, 85%); bp 92−95°C/0.05 Torr. − ^{1}H NMR (C_6D_6): δ = 0.04 (s, 18 H, $J_{\text{Sn-H}}$ = 54 Hz), 2.16 (s, 4 H, $J_{\text{Sn-H}}$ = 62 Hz), 6.93 (s, 4 H). − ^{13}C NMR (C_6D_6): δ = −9.5 (Sn-*C*H$_2$), 124.3, 128.3, 138.4 (*C*$_{\text{ar}}$-Sn). − ^{119}Sn NMR (C_6D_6): δ = 2.7.

α-(Trimethylstannyl)-o-xylene was formed as a reaction by-product (0.51 g, 7%). − ^{1}H NMR (C_6D_6) δ = −0.02 (s, $J_{\text{Sn-H}}$ = 50 Hz, 9 H), 2.05 (s, 2 H), 6.90 (m, 2 H), 6.92 (m, 2 H), 7.04 (d, 1 H). − ^{13}C NMR (C_6D_6): δ = −9.7 (Sn-*C*H$_3$), 18.2 (Sn-*C*H$_2$), 124.0, 126.4, 127.6, 130.3, 133.3, 141.5 (*C*$_{\text{ar}}$-Sn). − ^{119}Sn NMR (C_6D_6): δ = 2.4.

α,α′−Bis(chlorodimethylstannyl)-o-xylene (**32**): To a stirred solution of α,α′-bis(trimethylstannyl)-*o*-xylene (4.78 g, 11 mmol) in dry pentane (50 ml) at −50°C was added 22 ml of a 1.0 M hexane solution of boron trichloride in portions of 0.5 ml over 1.5 h. During the addition a white precipitate formed. After the addition the reaction was stirred at −50°C for 2 h and then allowed to reach ambient temperature. Upon warming the initially formed precipitate redissolved. When the reaction mixture reached room temperature, a new precipitate formed. The reaction mixture was stirred for 12 h at room temperature and the precipitate was then filtered off, washed twice with two 20-ml portions of dry pentane and dried under vacuum (1 Torr, room temp.) to give the desired derivative as a white, moisture-sensitive powder (4.04 g, 85%). − ^{1}H NMR (C_6D_6): δ = 0.27 (s, 12 H, $J_{\text{Sn-H}}$ = 56 Hz), 2.48 (s, 4 H, $J_{\text{Sn-H}}$ = 70 Hz), 6.90 (m, 4 H). − ^{13}C NMR (C_6D_6): δ = −2.0 (Sn-CH_3), 25.3 (Sn-CH_2), 125.7, 129.1, 135.8. − ^{119}Sn NMR (C_6D_6): δ = 2.44.

2,2-Dimethyl-2-stannaindane (**6**): A suspension of 10 mmol of α,α′-dilithio-*o*-xylene was prepared from 11 mmol of α,α′-bis(trimethylstannyl)-*o*-xylene and 22 mmol of *n*-butyllithium according to the aforementioned procedure. After dilution with dry diethyl ether, the lithium reagent was treated at 0°C with an ether solution of 10 mmol of dimethyltin dichloride. The reaction was stirred at reflux for 2 h and then poured into a solution of aqueous NH_4Cl. Usual work-up gave an orange-yellow oil with the desired stannaindane as the major component by NMR criteria. Distillation under reduced pressure gave an 85% yield of colorless product. − ^{1}H NMR (C_6D_6): δ = 0.09 (s, $J_{\text{Sn-H}}$ = 55 Hz, 6 H), 2.20 (s, $J_{\text{Sn-H}}$ = 41 Hz, 4 H), 7.03 (dd, *J* = 5.3, 3.5 Hz, 2 H), 7.03 (dd, *J* = 4.5, 3.5 Hz, 2 H). − ^{13}C NMR (C_6D_6): δ = −10.1 (Sn-CH_3), 17.95 (Sn-CH_2), 125.4, 131.2, 143.6 (C_{ar}-Sn).

Boron Compounds

1,2-Bis(diethylboryl)ethyne (**15**). − *Method A:* In this method the active dilithioethyne was prepared from trichloroethylene and *n*-butyllithium (cf. supra). The composition of solids from this reaction varied and the actual proportions of Li_2C_2, LiCl, and THF had to be analyzed after each preparation. The quantity of the dilithioethane used in the preparation described here refers to 14.7 g of a solid of the composition 33% Li_2C_2, 37% LiCl, and 30% THF by weight. An excess of Et_2BBr was used to allow for the formation of diethyl[(4-bromo)butoxy]borane ($Et_2B-O-[CH_2]_4Br$), a side-product formed from a THF ring cleavage reaction by Et_2BBr even at low temperatures.

A solution of diethylboron bromide (47.2 g, 0.317 mol) in 100 ml of dry pentane was added to a stirred suspension of the dilithioethyne (4.85 g, 0.128 mol) in 100 ml of pentane at such a rate as to maintain the temperature below 40°C. After the addition, the reaction mixture had turned red-brown. Lithium bromide was filtered off and the pentane was removed from the filtrate under reduced pressure. The residue was then distilled at 0.3 Torr to yield 1,2-bis(diethylboryl)ethyne as a colorless liquid (8.1 g, 39%); bp 40−50°C/0.3 Torr. − ^{1}H NMR (C_6D_6): δ = 1.08 (t, *J* = 7 Hz, 12 H), 1.19 (q, *J* = 7 Hz, 8 H). − ^{13}C NMR (C_6D_6): δ = 9.4 (CH_2-CH_3), 20.6 (br., CH_2-CH_3), 137.2 (br., B-$C{\equiv}C$-B). − ^{11}B NMR (C_6D_6): δ = 72.

Diethyl(4-bromobutoxy)borane was formed as a reaction byproduct (12.52 g, 93%); recovered as a distillation residue. − ^{1}H NMR (C_6D_6): δ = 0.76 (q, *J* = 7 Hz, 4 H), 0.93 (t, *J* = 7 Hz, 6 H), 1.04 (m, 2 H), 1.62 (m, 2 H), 3.01 (t, *J* = 7 Hz, 2 H), 3.50 (t, *J* = 6 Hz, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 8.0 (CH_2-CH_3), 12.1 (br., B-CH_2), 29.7, 30.3, 33.4, 64.2 (O-CH_2). − ^{11}B NMR (C_6D_6) δ = 53.2.

Method B: To a stirred solution of diethylboron bromide (0.68 g, 4.6 mmol) in 10 ml of dry pentane at −30°C was added a solution of bis(trimethylstannyl)ethyne (0.80 g, 2.3 mmol) in 20 ml of dry pentane. After the addition, the reaction mixture was stirred for 1 h at 25°C and then cooled to −78°C, upon which white trimethyltin bromide precipitated. After this solid was filtered off at −78°C, pentane was partly removed from the cold filtrate under reduced pressure and the residue was allowed to warm up to ambient temperature. A fresh 10-ml portion of dry pentane was added to the residue and the solution again cooled to −78°C whereupon further precipitate was filtered off. The pentane was partly removed from the filtrate in vacuo and the remaining residue distilled under vacuum to give 1,2-bis(diethylboryl)ethyne (0.24 g, 65%) containing less than 2 mol-% of trimethyltin bromide.

1,2-Bis(diethylboryl)ethane (**19**): The modified Lindlar catalyst used here refers to the commercial product $Pd/CaCO_3$. In the original Lindlar procedure the catalyst, $Pd/CaCO_3$, was partly deactivated by addition of quinoline. Since quinoline forms a pale yellow complex with bis(diethylboryl)ethyne and the hydrogenation then does not proceed at all, the palladium catalyst used in these experiments was not poisoned with quinoline. A suspension of the modified Lindlar catalyst (0.16 g) in 5 ml of cyclohexane was stirred at room temperature under a slow flow of hydrogen gas for 1 h. Thereafter a solution of bis(diethylboryl)ethyne (1.31 g, 8.1 mmol) in 10 ml of cyclohexane was introduced and the hydrogen flow was stopped. From there the reaction was carried out by admission of hydrogen gas from a calibrated gas burette. The reaction was stopped when the hydrogen consumption had ceased. Hydrogen was purged by a stream of argon passing through the flask. The cyclohexane was removed under reduced pressure and the residue distilled under vacuum to yield pure 1,2-bis(diethylboryl)ethane (1.2 g, 85%). bp 30−34°C/2 Torr. − ^{1}H NMR (C_6D_6): δ = 1.0−1.3 (m), no signals at δ = 2.0−10.0. − ^{13}C NMR (C_6D_6): signals at δ = 10−30, no signals at δ = 40−150. − ^{11}B NMR (C_6D_6): δ = 75.

Pyrolysis of 1,2-Bis(diethylboryl)ethyne (**15**): This compound (1.45 g, 9 mmol) was slowly heated under argon at about 100°C, whereupon a colorless liquid began to distill. The heating was continued until the internal temperature reached 120°C. Further gentle reflux was maintained for 2 more hours after which the reaction mixture was cooled to room temperature and the volatiles removed under vacuum. The distillate consisted of triethylborane (0.99 g, 10 mmol). The red-brown residue (0.45 g) was then heated to 350°C under vacuum to give a viscous dark oil and then up to 700°C in a TGA apparatus to yield a glistening black solid which contained 55.13% C, 38.12% B, and 2.68% H, approximating an empirical formula of $C_3H_2H_{0.14}$.

Pyrolysis of 1,2-bis(diethylboryl)ethane (**19**): 1,2-Bis(diethylboryl)ethane (**19**) (0.64 g, 3.9 mmol) was slowly heated under argon to 120°C where triethylborane started to distill. Further heating in a TGA apparatus was continued until the internal temperature reached approximately 350°C and the evolution of volatiles had stopped. The reaction was cooled to room temperature and volatile substances removed under vacuum, which proved to be triethylborane (0.59 g, 6.0 mmol). The composition of the yellow residue (0.03 g) was not determined.

1,2-Bis(dichloroboryl)benzene (**20**) *and 1-Dichloro-2-[chloro(methyl)boryl]benzene* (**24**): To a stirred solution of 1,2-bis(trimethylstannyl)benzene (**8a**) (2.31 g, 5.7 mmol) in 20 ml of dry pentane was added a solution of boron trichloride (11.4 ml of 1.0 M hexanes solution, 11.4 mmol) at −40°C. During the addition a white precipitate formed gradually. The precipitate was separated from the solution at −40°C and dried under vacuum to give 1.51 g of white solid identified as a mixture of trimethyltin chloride (5.0 mmol, 44%) and dimethyltin dichloride (2.3 mmol, 40%). From the solution the solvents were removed in vacuo to give 1.23 g of a yellow oil. Since the separation of the substances present in the residue was unsuccessful, the components were identified spectroscopically.

1-Dichloroboryl-2-[chloro(methyl)boryl]benzene (40 mol-%) (**24**): ^{1}H NMR (C_6D_6): δ = 1.21 (s, 3 H), 7.19 (dd, *J* = 5.5, 3.3 Hz, 2 H), 8.18 (dd, *J* = 5.5, 3.3 Hz, 2 H). − ^{13}C NMR (C_6D_6): δ = 9.5, 133.9, 136.4. − ^{11}B (C_6H_6): δ = 33. − *1-[Chloro(methyl)boryl]-2-(chlorodimethylstannyl)benzene* (65 mol-%) (**23**): ^{1}H NMR (C_6D_6): δ = 0.24 (s, 6 H), 1.21 (s, 3 H), 7.42 (d, 1 H) 7.86 (td, 1 H), 7.92 (d, 1 H) 8.36 (td, 1 H). − ^{13}C NMR (C_6D_6): δ = −0.3 (Sn-*C*H_3), 10.0 (B-CH_3), 132.8, 133.8, 135.8, 136.4. − ^{11}B (C_6H_6): δ = 38.7. − ^{119}Sn (C_6H_6): δ = 172.1. − *9,10-Dichloro-9,10-Dihydro-9,10-diboraanthracene* (**22**)[19] (ca. 10 mol-%). − ^{1}H NMR (C_6D_6): δ = 7.27 (dd, *J* = 5.55, 3.5 Hz, 4 H), 7.68 (dd, J = 5.5, 3.5 Hz, 4 H). − ^{13}C NMR (C_6D_6): δ = 132.9, 137.1.

When the reaction was repeated by employing 6.0 mmol of 1,2-bis(trimethylstannyl)benzene and 24.0 mmol of boron trichloride, Me_3SnCl and Me_2SnCl_2 were filtered off from the chilled reaction solution (−40°C), the filtrate freed of volatiles and the residue distilled under vacuum to yield 80% of **24**.

Diethyl(phenyl)borane: A solution of trimethyl(phenyl)tin (2.65 g, 11 mmol) in 10 ml of dry pentane was added dropwise to a stirred solution of diethylboron bromide (1.80 g, 12 mmol) in 10 ml of pentane at room temperature. The reaction mixture was heated under atmospheric pressure until pentane started to distill. When distillation stopped, the reaction was heated and stirred at 70°C for 3 h. The volatiles were removed under vacuum to give a clear, brownish liquid which was identified as nearly pure diethyl(phenyl)borane (1.43 g, 89%). − ^{1}H NMR (C_6D_6): δ = 1.01 (t, *J* = 7.8 Hz, 6 H), 1.54 (q, *J* = 7.8 Hz, 4 H), 7.25 (m, 3 H), 7.75 (d, *J* = 6.5 Hz, 2 H). − ^{13}C NMR (C_6D_6): δ = 8.8 (-*C*H_3), 16.0 (br., B-*C*H_2), 128.2, 132.1, 134.5, 139.3 (C_{ar}-B). − ^{11}B NMR (C_6D_6): δ = 78.1.

1,2-Bis(diethylboryl)benzene (**27**): A solution of 1,2-bis(trimethylstannyl)benzene (1.81 g, 4.5 mmol) in 5 ml of dry pentane was added dropwise to a refluxing solution of diethylboron bromide (1.78 g, 12 mmol) in 10 ml of pentane. After the addition, the reaction mixture was heated at reflux for 1 h. The pentane and unreacted Et_2BBr were removed under reduced pressure and a fresh 10-ml portion of dry pentane was added to the yellow residue and the solution was cooled to −78°C. Upon cooling a precipitate was formed and was filtered off at −78°C. The pentane was removed from the filtrate under vacuum to give a crude product as a lemon-colored oil (1.16 g). Distillation of the crude product yielded **27** as a yellowish, viscous liquid (0.81 g, 84%). During distillation partial decomposition with the evolution of some triethylborane was observed. − ^{1}H NMR (C_6D_6): δ = 1.00 (t, *J* = 8 Hz, 12 H), 1.35 (q, *J* = 8 Hz, 8 H), 7.24 (dd, *J* = 5.0, 3.0 Hz, 2 H), 7.35 (dd, *J* = 5.0, 3.0 Hz, 2 H). − ^{13}C NMR (C_6D_6): δ = 8.2 (CH_2-*C*H_3), 21.6 (br., B-*C*H_2-CH_3), 128.6, 130.3, 139.7 (C_{ar}-B). − ^{11}B NMR (C_6D_6): δ = 80.8.

9,10-Diethyl-9,10-dihydro-9,10-diboraanthracene (**36**): A solution of 1,2-bis(diethylboryl)benzene (**27**) (0.98 g, 4.6 mmol) in dry heptane (10 ml) was heated under reflux for 12 h. The solvent was then gradually distilled off as the reaction temperature rose to 140°C. The residue was stirred at 140−150°C for 6 h and the volatiles then were removed under vacuum. The oily, yellow residue (0.63 g) contained (**36**) and unreacted (**27**) in an approximate molar ratio of 1.0:0.3. Freshly distilled pentane (10 ml) was added to the residue and the resulting solution was cooled to −78°C, whereupon a fine, pale yellow precipitate settled out. The colorless supernatant solution was decanted and the precipitate dried under vacuum. The precipitate was identified by spectral data as pure **36** (0.12 g, 23%). − ^{1}H NMR (C_6H_6): δ = 1.09 (t, *J* = 8.2 Hz, 6 H), 1.89 (q, *J* = 8.2 Hz, 4 H), 7.33 (dd, *J* = 5.4, 3.2 Hz, 4 H), 8.01 (dd, *J* = 5.3, 3.4 Hz, 4 H). − ^{13}C NMR (C_6H_6): δ = 10.3 (*C*H_3), 12.4 (br., B-*C*H_2), 132.7, 136.0, 145.6 (br., C_{ar}-B). − ^{11}B NMR (C_6H_6): δ = 67.5.

1,3-Bis(diethylboryl)benzene (**28**): A solution of 1,3-bis(trimethylstannyl)benzene (1.46 g, 3.6 mmol) in 3 ml of dry pentane and diethylboron chloride (0.85 g, 8.1 mmol) were stirred at room temperature for 1 h. Thereupon the reaction mixture was heated under atmospheric pressure until the pentane started to distill. Then, the reaction mixture was stirred and heated to 70°C for 3 h. Volatiles were removed under vacuum to leave a yellowish, oily residue that was identified as essentially pure 1,3-bis(diethylboryl)benzene (0.67 g, 87%). − ^{1}H NMR (C_6D_6): δ = 1.07 (t, *J* = 7.9 Hz, 12 H), 1.62 (q, *J* = 7.8 Hz, 8 H), 7.35 (t, *J* = 7.5 Hz, 1 H), 7.87 (d, *J* = 7.3 Hz, 2 H), 8.45 (s, 1 H). − ^{13}C NMR (C_6D_6): δ = 8.8 (*C*H_3), 17.3 (br., B-*C*H_2), 127.7, 137.8, 139.4, 140.3. − ^{11}B NMR (C_6D_6): δ = 78.5. − Attempts to further purify the crude product by distillation failed and resulted in its significant decomposition with the liberation of triethylborane.

A parallel procedure was conducted with 1,4-bis(trimethylstannyl)benzene (**8**) and diethylboron chloride to provide a 90% yield of 1,4-bis(diethylboryl)benzene (**29**) at the stage where volatiles had been removed from the reaction mixture. Attempted distillation again led to the evolution of triethylborane.

2-(Diethylboryl)-α-(trimethylstannyl)toluene (**30**): At room temperature a solution of α,2-bis(trimethylstannyl)toluene (1.71 g, 4 mmol) in 3 ml of dry pentane was added dropwise to a neat sample of diethylboron chloride (0.85 g, 8 mmol). The reaction mixture was stirred at room temperature for 1 h and then heated gradually until pentane started to distill. The reaction mixture then was stirred and heated at 70°C for 3 h. After that, volatiles were removed under reduced pressure to leave a pale yellow, oily mixture of **30** and unreacted tin derivative in approximately a 1:1 molar ratio. The residue was then allowed to react further with an excess of Et_2BCl (1.0 g, 10 mmol). After stirring the mixture at 60°C for 12 h, the volatiles were removed in vacuo. The clear yellow oil was identified by spectral data as 2-(diethylboryl)-α-(trimethylstannyl)-toluene. Further purification of the crude product by distillation resulted in its partial decomposition. − ^{1}H NMR (C_6D_6): δ = 0.03 (s, $J_{\text{Sn-H}}$ = 52 Hz, 9 H), 1.03 (t, *J* = 7.6 Hz, 6 H), 1.49 (q, *J* = 7.6 Hz, 4 H), 2.20 (s, 2 H, $J_{\text{Sn-H}}$ = 72 Hz), 6.93 (t, *J* = 7.5 Hz, 1 H), 6.94 (d, *J* = 6.2 Hz, 1 H), 7.00 (t, *J* = 7.4 Hz, 1 H), 7.12 (td, *J* = 7.4, 1.2 Hz, 1 H). − ^{13}C NMR (C_6D_6): δ = −9.5 (Sn-*C*H_3, *J* = 324, 308 Hz), 8.95 (B-CH_2-*C*H_3), 21.6 (Sn-*C*H_2, *J* = 300, 244 Hz), 22.0 (br., *C*H_2), 123.1, 127.6, 128.36, 128.42, 143.1 (*C*H_{ar}-B). − ^{11}B NMR (C_6D_6): δ = 85.3. − ^{119}Sn NMR (C_6D_6): δ = 3.7.

2-(Diethylboryl)-α-(bromodimethylstannyl)toluene (**31**): A solution of α,2-bis(trimethylstannyl)toluene (2.11 g, 5 mmol) in 5 ml of dry pentane was added to a solution of diethylboron bromide (1.78 g, 12 mmol) in 5 ml of pentane at room temperature. The reaction mixture was heated at reflux for 3 h and then the pentane was partly distilled off under atmospheric pressure. The residue was further heated at 70°C for 4 h. The volatiles were removed under vacuum to leave a colorless oil of almost pure **31** (1.75 g, 90%). − ^{1}H NMR (C_6D_6): δ = 0.31 (s, $J_{\text{Sn-H}}$ = 55 Hz, 6 H), 0.97 (t, *J* = 7.5 Hz, 6 H), 1.44 (q, *J* = 7.5 Hz, 4 H), 2.58 (s, 2 H, $J_{\text{Sn-H}}$ = 68 Hz); 6.85−7.05 (m, 4 H). − ^{13}C NMR (C_6D_6): δ = −2.6 (Sn-*C*H_3), 8.9 (B-CH_2-*C*H_3), 22.1 (br., B-*C*H_2), 27.9 (Sn-*C*H_2), 124.3, 127.9, 128.6, 128.7, 139.1 (C_{ar}-Sn). − ^{11}B NMR (C_6D_6): $\delta = 84.9$. − ^{119}Sn NMR (C_6D_6): $\delta = 3.6$.

1-[Methyl(phenyl)boryl]-2-(chlorodimethylstannyl)benzene (**25**): A solution of 1,2-bis(trimethylstannyl)benzene (1.85 g, 4.6 mmol) in 10 ml of pentane was added dropwise to a refluxing solution of dichloro(phenyl)borane (0.73 g, 4.6 mmol) in 10 ml of pentane. The reaction mixture was then heated at reflux for 1 h and thereafter cooled to −78 °C. The precipitate of trimethyltin chloride (0.71 g, 78%) was filtered off at −78 °C and the volatiles were removed from the filtrate under reduced pressure. The light yellow oil (1.69 g) was further distilled under vacuum (0.1 Torr, 60 °C) to give partly decomposed **25** (1.03 g, 61%). − ^{1}H NMR (C_6D_6): $\delta = 0.16$ (s, 6 H, $J_{\text{Sn-H}} = 56$ Hz), 1.26 (s, 3 H), 7.01 (t, $J = 7.2$ Hz, 2 H), 7.09 (d, $J = 7.2$ Hz, 1 H), 7.20−7.29 (m, 2 H), 7.42 (m, 2 H), 8.07 (d, 1 H). − ^{13}C NMR (C_6D_6): $\delta = 0.5$ (Sn-CH_3), 12.5 (br., B-CH_3), 128.5, 128.7, 129.6, 132.4 (B-C_{ar}), 132.8, 133.1, 136.2, 137.2 (B-C_{ar}), 137.7, 147.0 (Sn-C_{ar}).

☆ Dedicated to Professor *Heinrich Nöth* on the occasion of his 70th birthday.

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