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The Physical and Chemical Consequences of Cyclic Conjugation in Boracyclopolyenes. The Antiaromatic Character of Pentaarylboroles[1]

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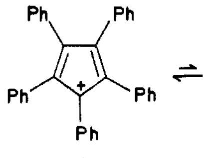
Abstract: Pentasubstituted boroles or boracyclopentadienes have been prepared by two routes: (1) the interaction of an (*E*,*E*)-(1,2,3,4-tetraaryl-1,3-butadien-1,4-ylidene)dilithium in ether solution with an aryl(dihalo)borane to form the borole etherate; and (2) the exchange reaction between a 1,1-dialkyl-2,3,4,5-tetraarylstannole in nondonor media to produce the unsolvated borole. The boroles are unexpectedly strong Lewis acids, complexing with amines and even ethers and nitriles, and very prone to oxidation, solvolytic cleavage, and Diels-Alder reactions. The foregoing chemical behavior, taken together with their unusual nuclear magnetic and electronic spectral properties, can be straightforwardly interpreted in terms of the Hückel antiaromatic character of the 4-π-electron boracyclopentadiene nucleus. By treating such nuclei as perturbed cyclopentadienyl π-systems, a qualitative understanding of both the spectral and chemical properties can be attained. From such considerations, it is evident that the conjugation between the tricoordinate boron's $2p_z$-orbital and the four-carbon butadienylidene array is destabilizing and is the source of the high reactivity of boroles.

An sp^2-hybridized boron atom might be expected to form cyclic conjugated systems with arrays of sp^2-hybridized carbons, because both the covalent radius (0.80 Å) and the Allred-Rochow electronegativity (2.01) of boron are similar to those of carbon (0.77 Å and 2.51).[4] In such conjugated rings the boron center might exert a stabilizing influence if the total number of π electrons would conform to the Hückel $4n + 2$ criterion for aromaticity.[5a] In fact, heterocyclic organoboranes bearing the isoelectronic B=N unit in place of one or more C=C linkages of a benzenoid ring have been shown to possess chemical and physical properties similar to classic aromatic compounds.[5b] Boracyclopolyenes not possessing the appropriate number of π electrons might be destabilized by conjugation and accordingly display unusual reactivity or antiaromaticity.[6] An example of the destabilization of a carbocyclic ring by such antiaromaticity is the instability of the pentaphenylcyclopentadienyl cation (**1**). This deep-blue ion is highly reactive and has a thermally populated triplet (compound **2**). This behavior indicates that the gain in conjugated stabilization attained by placing the four π electrons as pairs in bonding molecular orbitals is not large.



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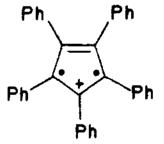

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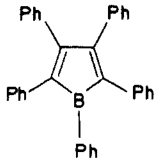

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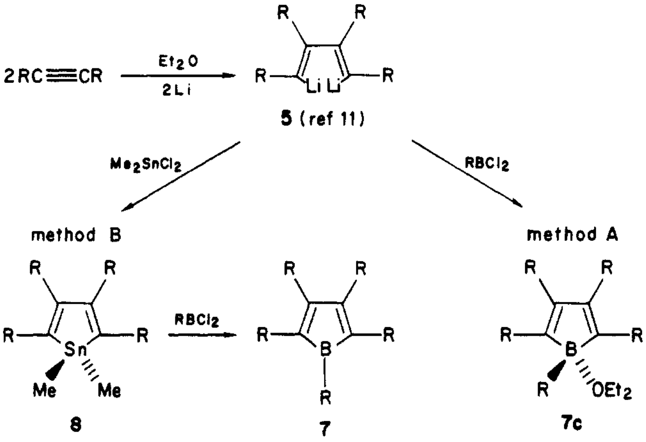
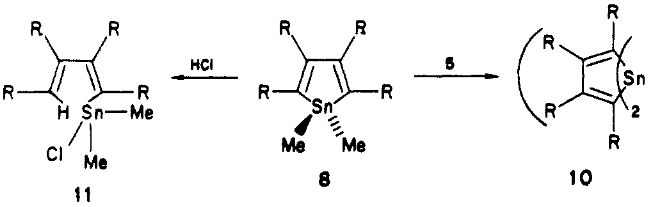
Scheme I



Scheme II



Since pentaphenylborole (**3**) is isoelectric with **1**, we were skeptical of the report that this boron heterocycle could be prepared and isolated as an almost colorless solid, stable both to air and toward ethanol.[7] Our reinvestigation[8] of these incongruous findings demonstrated that authentic pentaphenylborole is actually a deeply colored solid,[9] highly reactive both to air and toward alcohols.[10] The present article offers the results of our detailed examination of the physical and chemical properties of this unusual nucleus and compares its spectral and chemical behavior with the antiaromatic pentaphenylcyclopentadienyl cation. Cogent evidence

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(1) Part 8 in the series, Bora-Aromatic Systems. Part 7: Eisch, J. J.; Shen, F.; Tamao, K. *Heterocycles* **1982**, *18*, 245.

(2) Present address: Research Department, Allied Chemical Corporation, Morristown, NJ 07960.

(3) Present address: Department of Chemistry, College of Liberal Arts and Sciences, Kyoto University, Sakyo-ku, Kyoto 600, Japan.

(4) Eisch, J. J.; Gonsior, L. J. *J. Organomet. Chem.* **1967**, *8*, 53.

(5) (a) Streitwieser, A., Jr. "Molecular Orbital Theory for Organic Chemists"; Wiley: New York, 1961; pp 256-304. (b) Cf. the excellent theoretical and experimental studies of M. J. S. Dewar and co-workers on aromatic boron heterocycles containing the isoelectronic B=N unit in place of the C=C linkage: Dewar, M. J. S. *Prog. Boron Chem.* **1964**, *1*, 235. Gould, R. F. Ed "Boron-Nitrogen Chemistry"; American Chemical Society: Washington, D.C., 1964; Adv. Chem. Ser. No. 42, p 227.

(6) Breslow, R.; Brown, J.; Gajewski, J. J. *J Am. Chem. Soc.* **1967**, *89*, 4383.

(7) Braye, E. H.; Hübel, W.; Caplier, I. *J. Am. Chem. Soc.* **1961**, *83*, 4406.

(8) Eisch, J. J.; Hota, N. K.; Kozima, S. *J. Am. Chem. Soc.* **1969**, *91*, 4575.

(9) Our initial report that **3** appeared to be a deep green solid was based upon its appearance when admixed with Me_2SnCl_2. Subsequent preparations that had been thoroughly washed with toluene appeared deep blue in diffuse light: cf. Eisch, J. J.; Galle, J. E. *J. Am. Chem. Soc.* **1975**, *97*, 4436. The variation in color was not due to oxidation impurities, as implied in ref 14b, but to complexation with Lewis Bases (Cl^- or ethers). Moreover, varying visual perceptions of samples of **3** by workers in our laboratory had led us to characterize samples as dark blue or blue green.

(10) Eisch, J. J.; Shen, F.; Tamao, K. *Heterocycles* **1982**, *18*, 245.

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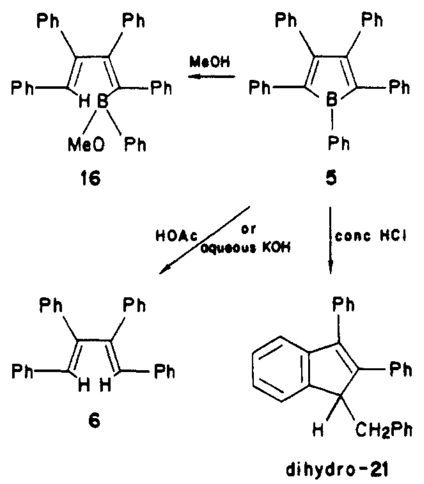
Scheme III



is adduced that conjugation between the boron and the dienylidene system in **3** does indeed destabilize the π-electron system.

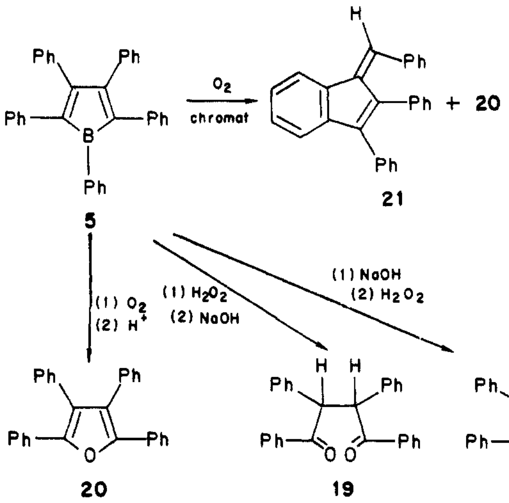
Results

Preparation of Pentaarylboroles. Any practical synthesis of these boroles is ultimately founded on the lithium-metal dimerization product of the corresponding diarylacetylene. The resulting (E,E)-(1,2,3,4-tetraaryl-1,3-butadien-1,4-ylidene)dilithium (**5a**: $R = C_6H_5$; **5b**: $R = p\text{-}CH_3C_6H_4$) can be treated directly in ether solution with an aryl(dihalo)borane (**12**) to form the borole (method A). Alternatively, the lithium reagent **5** can be converted into the analogous stannole **8** by the addition of dichloro(dimethyl)tin (**9**) (method B, Scheme I). Each method has its drawback: method A suffers from the presence of Lewis acids that must either be introduced ($RBCl_2$) or generated (the borole) in an ethereal medium. Not only must the borole etherate (**7c**) be warmed to remove the solvated ether but also there is evidence that, unless the reaction temperature is kept low, the $PhBCl_2$ can promote the isomerization of **5** to the 2,3,4-triphenyl-1-naphthyl group. Thus, the product isolated by Braye and co-workers from **5** and $PhBCl_2$ in ether was, in all likelihood, not pentaphenylborole but actually phenylbis(2,3,4-triphenyl-1-naphthyl)borane (**22**) (cf. Experimental Section).

Following method B successfully entails using almost exactly a 1:1 ratio of **5** and Me_2SnCl_2. An excess of **5** favors the formation of spiro tin compound **10**,[12] while an excess of Me_2SnCl_2 can lead to the generation of HCl, upon hydrolytic workup, and the resultant protodestannation of the stannole to produce the chlorodimethyl-(E,E)-(1,2,3,4-tetraaryl-1,3-butadien-1-yl)tin (**11**, Scheme II).[13] Not only can the formation of **10** and **11** be suppressed by careful observance of 1:1 reaction ratios but also any excess of Me_2SnCl_2 can be removed at 25 °C by extracting the crude product with 95% ethanol before introducing water.

Once the stannole is obtained, its conversion to the borole by the action of $PhBCl_2$ in toluene proceeds smoothly and quantitatively.[14,15] The borole solid can be obtained by simple extraction with toluene to remove Me_2SnCl_2. As will be described below, it forms colorless to pale yellow complexes with a variety of Lewis bases, which are apparently air-stable for some time at 25 °C.

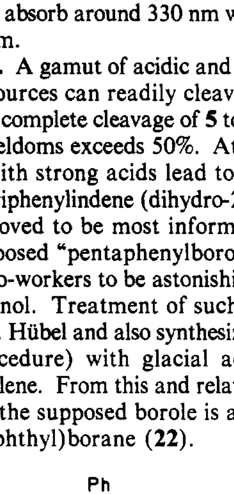
Scheme IV



Chemical Behavior of Boroles. (a) Complexation. As with any triorganoborane, except the most sterically hindered like trimesitylborane,[16] these pentaarylboroles form stable complexes with pyridine. What sets them apart from other R_3B compounds is rather their unusual capability to form stable complexes with weak Lewis bases, such as ethers and even benzonitrile. In all complexation, however, the impact on the visible spectrum is dramatic: the absorption responsible for the blue color of **5**, occurring between 540 and 605 nm, undergoes a pronounced hypsochromic shift, as complexes of **5** absorb around 330 nm with only a shoulder extending over 400 nm.

(b) Protodeboration. A gamut of acidic and neutral proton and even basic hydroxyl sources can readily cleave one ring bond of the borole nucleus, but complete cleavage of **5** to the corresponding tetraarylbutadiene **6** seldoms exceeds 50%. Attempts to enhance such ring cleavages with strong acids lead to the cyclization of **6** into 3-benzyl-1,2,3-triphenylindene (dihydro-**21**) (Scheme III).[17]

Protodeboration proved to be most informative in clarifying the nature of the supposed "pentaphenylborole", which was reported by Braye and co-workers to be astonishingly stable toward both oxygen and ethanol. Treatment of such "borole" samples (kindly provided by Dr. Hübel and also synthesized by us according to the published procedure) with glacial acetic acid yielded 1,2,3-triphenylnaphthalene. From this and related analytical data, we can conclude that the supposed borole is actually phenylbis(2,3,4-triphenyl-1-naphthyl)borane (**22**).



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(c) Oxidation. Direct air oxidation of **5**, followed by column chromatography without intentional hydrolysis, led to the isolation of tetraphenylfuran (**20**) and 3-benzylidene-1,2-diphenylindene (**21**). Air oxidation of various boroles (group on B = C_6H_5, $p\text{-}CH_3C_6H_4$, Cl, Me), followed by hydrolytic workup with 12 N HCl, yielded between 40 and 80% of the tetraarylfuran.

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(11) This compound has been isolated as a yellow solid, which is a dietherate: Eisch, J. J. "Organometallic Syntheses"; Academic Press: New York, 1981; Vol. 2, p 100.

(12) Zavistoski, J. G.; Zuckerman, J. J. *J. Org. Chem.* **1969**, *34*, 4197.

(13) Eisch, J. J. "Organometallic Syntheses"; Academic Press: New York, 1981; Vol. 2, p 177.

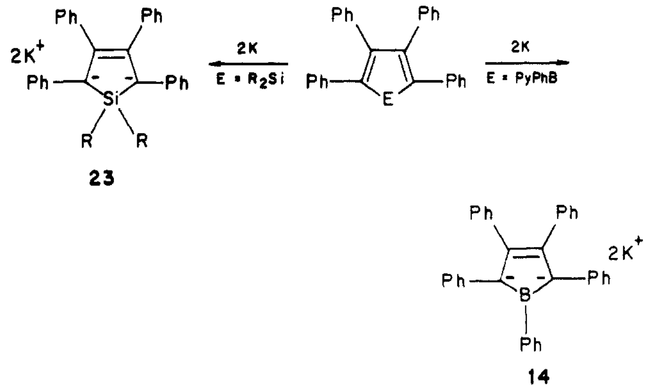
(14) (a) Eisch, J. J. "Organometallic Syntheses"; Academic Press: New York, 1981; Vol. 2, p 131. (b) Herberich, G. E.; Buller, G.; Hessner, B.; Oschmann, W. *J. Organomet. Chem.* **1980**, *195*, 249.

(15) A publication subsequent to our original report in 1969 developed a modified synthesis of borole **3**, which involves the conversion of the dilithium reagent **5** into the 1,1-di-n-butyl-2,3,4,5-tetraphenylstannole by adding (n-Bu)$_2$SnCl$_2$ and the subsequent treatment of the stannole, as in our original method, with $PhBCl_2$.[14b] Although Bu_2SnCl_2 is cheaper than Me_2SnCl_2 and the yield of **3** may be somewhat higher, we find that these factors are not the most crucial points for a high-yield conversion of **5** into **3**. Much more important and sensitive are the lithiation to form **5** and the proper reaction ratio of **5**:Me_2SnCl_2.

(16) Brown, H. C.; Dodson, V. H. *J. Am. Chem. Soc.* **1957**, *79*, 2302.

(17) Richter, W. Ph.D. Dissertation, University of Bochum, 1979, p 71.

Scheme V



The oxidizing action of 30% H_2O_2 in aqueous NaOH solution on borole **5** depends upon the mode of admixing the reagents (Scheme IV). If H_2O_2 is added to **5** before introducing the aqueous NaOH, then both ring bonds are oxidized and the 1,4-diketone **19** is the main product. On the other hand, if the aqueous NaOH is first added to **5**, followed by the H_2O_2, then (*E*)-2,3,4-triphenyl-3-butenophenone (**17**) is the dominant product. In the latter situation, it is apparent that the strong aqueous base hydrolyzes the first ring C–B bond, as depicted in Scheme III.

(d) Addition of Potassium Metal. As previously reported,[15] **5** reacts in THF solution with 2 mol of potassium metal to form a dark-red adduct, $Ph_5C_4BK_2$. However, since other 1,4-diphenyl-1,3-butadienes and metalloles such as siloles **23** also form dimetallo adducts readily,[18] we wished to demonstrate that an available $2p_z$-orbital on boron was involved in the reaction with potassium (Scheme V).

To this end, both the pyridine complex and the 4-(dimethylamino)pyridine complex with pentaphenylborole **5a** were treated with potassium metal in THF solution. In each case, the dipotassium adduct **14** of the borole was formed, devoid of any pyridine base. This observation proves that anionic charge in the borole displaces the coordinated pyridine, in order to utilize the $2p_z$-orbital on boron.

Treatment of the recrystallized dipotassium adduct **14** with a mixture of glacial acetic acid and aqueous 6 *N* HCl produced some dihydrogen, isomeric 1,2,3,4-tetraphenyl-1,3-butadienes, and (*E*)-1,2,3,4-tetraphenyl-1-butene (**15**). These products are ascribable to some protonation at boron, but more at C_1. The final ring disruption seems to occur with allylic rearrangement (Scheme VI).

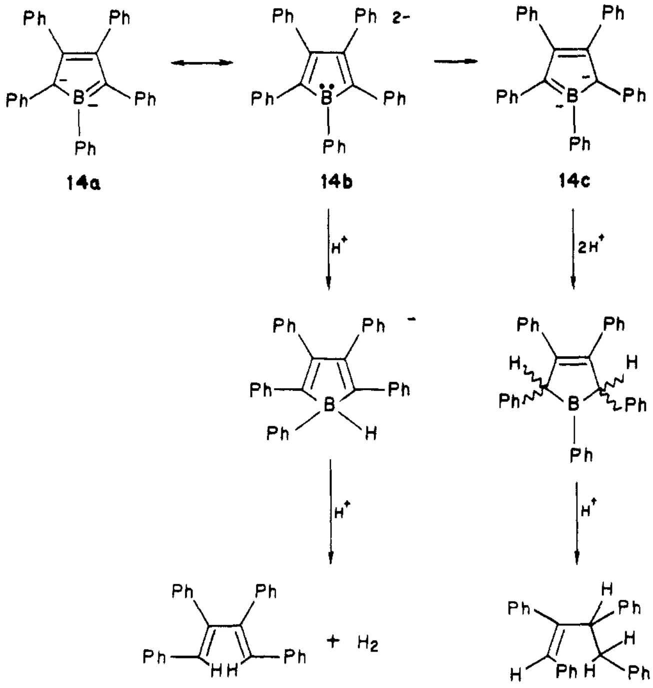
Spectral Properties of the Boroles and Their Adducts. The most striking spectral characteristic is the blue or blue-violet color of the uncompelxed borole (λ_{max} = 540–605 nm) and the pale yellow color of the neutral borole complexes (λ_{max} = 330 nm). The dark red color of the borole dianion (**14**) represents an intermediate electronic spectral shift.

The infrared spectra of the boroles and their adducts also display a sharp band of medium to great intensity in the 1575–1595 cm^{-1} region. This band, which is ascribable to the stretching of the ring C=C bonds conjugated with the phenyl groups, is much weaker in analogous carbocycles like 1,2,3,4-tetraphenylcyclopentadiene and 1-benzylidene-2,3,4,5-tetraphenylcyclopentadiene.

Especially noteworthy is the shift in the C≡N stretching frequency that benzonitrile shows upon complexation with borole **3**, namely from 2300 to 2370 cm^{-1}. Such shifts upon complexation with benzonitrile have been used to assess the Lewis acidity of various organoaluminum compounds.[19] Since the shift observed with borole (**3**, +70 cm^{-1}) is comparable with that reported for the strongest aluminum Lewis acids ($MeAlCl_2$ or $AlCl_3$, +59 cm^{-1}), borole is an unusually strong Lewis acid.

The ^1H, ^{13}C, and ^{11}B NMR spectra of the complexes exhibit absorptions useful in characterizing the borole nucleus and the π-electron density on boron. In the ^1H NMR spectrum of **3**·THF the protons of the B-phenyl group occur at the lowest field (δ 7.3–7.5 ppm), well-separated from the C-phenyl protons. In the ^{13}C NMR spectrum of **3**·THF, however, all the phenyl carbons fall between 125 and 131 ppm. But in the ^{13}C NMR spectrum of the dipotassium adduct of the borole (**14**) the carbons of the B-phenyl group (identified by their relative intensity) are clearly shifted upfield, to 117–121 ppm, while the remaining C-phenyl carbons still resonate between 127 and 136 ppm. Finally, in the ^{11}B NMR spectra of the uncomplexed borole **3** and its pyridine adduct an interesting shift can be discerned. The ^{11}B resonance of **3** at 55 ppm undergoes an upfield shift to 5 ppm upon complexation with pyridine. This shift of 50 ppm is much greater than the shift of 26 ppm reported for the dipotassium complex of **3**.[15]

Scheme VI



Discussion

The difference in chemical and physical properties between the boroles and the borole complexes synthesized in this study proves beyond doubt that the empty $2p_z$-orbital on boron interacts with the π-electrons of the butadienylidene system. Such an electronic interaction provokes a pronounced bathochromic shift in the visible spectrum of the borole **3**, compared with that of its pyridine adduct (yellow → blue). Moreover, the uncomplexes borole is a much more reactive diene partner in the Diels–Alder reaction, reacting even with the usually sluggish dienophile, diphenylacetylene, at 25 °C.[20] Also, in contrast with the moderate stability of the pentaphenylborole–pyridine adduct toward oxygen and protic media, borole **3** reacts rapidly with dioxygen or H_2O_2 to undergo oxidation of both ring C–B bonds. Finally, these boroles are unusual in being extraordinarily strong Lewis acids, forming complexes with even weak donors, such as ethers and nitriles. It should be noted that triphenylborane does not form a complex with benzonitrile. Indeed, the shifts in the C≡N stretch observed when nitriles complex with boroles exceeded those observed with $AlCl_3$.[19] Because the magnitudes of such shifts have been correlated with Lewis acid strength, boroles can, therefore, be ranked among the strongest Lewis acids known.

The foregoing array of properties amply justifies the conclusion that the π-electron delocalization in boroles is destabilizing and produces a 4-π-electron antiaromatic system. The antiaromaticity is evidenced by the rapidity of reactions that remove the $2p_z$-orbital on boron from conjugation (Lewis complexation) or disrupt the

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(18) Janzen, E. G.; Harrison, W. B.; Dubose, C. M. *J. Organomet. Chem.* **1972**, *40*, 281.

(19) Starowieyski, S.; Pasynkiewicz, S. *Rocz. Chem.* **1964**, *38*, 331.

(20) Eisch, J. J.; Galle, J. E. *J. Am. Chem. Soc.* **1975**, *97*, 4436.

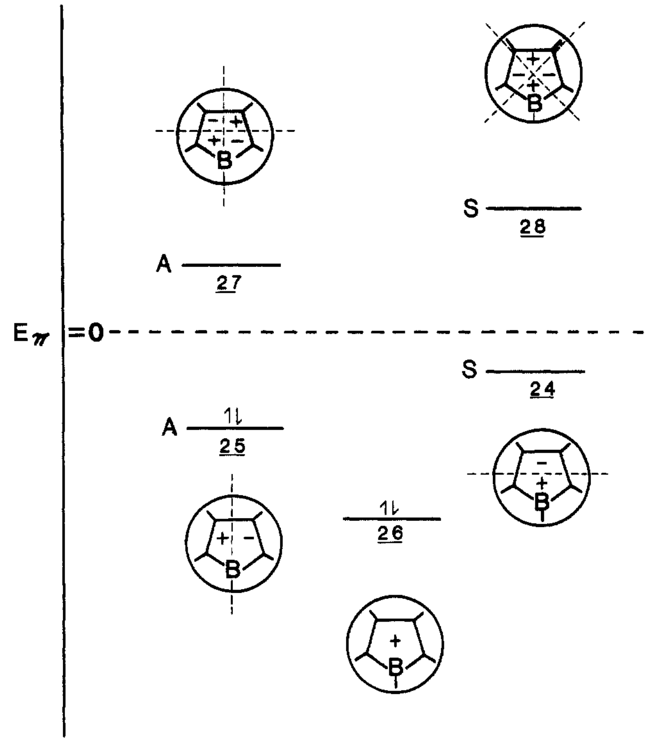


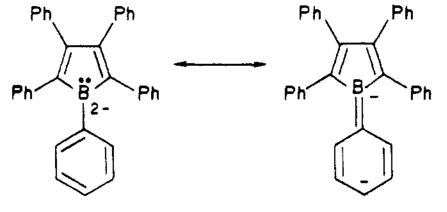
Figure 1. Qualitative ordering of the energies for the π-electron molecular orbitals of the boracyclopentadiene (borole) system.

borole ring system altogether (Diels–Alder adduction, oxidation, or protodeboration).

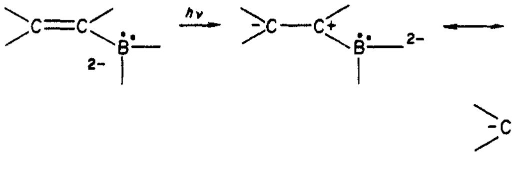
The borole ring system can be considered as a perturbed cyclopentadienyl system and the relative energies of the π-electron orbitals can be calculated by the Hückel MO or the extended Hückel MO approximations.[21a,c] Introduction of the boron atom raises the degeneracy of the HOMO pair in the C_5H_5 system by increasing the energy of the symmetric MO (**24**, nodal planes shown by dashed lines). The lesser electronegativity of boron in a nonnodal position would be expected to be destabilizing. This perturbation makes the antisymmetric MO (**25**) lower in energy, and hence, it serves as the highest occupied MO (Figure 1). It is worthy to note that a similar perturbation comes into play in calculating the electronic ground state of cyclobutadiene, where simple Hückel molecular orbital theory predicts a square-planar structure and a triplet ground state. More elaborate calculations favor a distortion to a rectangular shape and hence a singlet ground state.[21b]

This qualitative MO analysis suffices to reconcile many of the observed chemical and spectral properties of boroles. Firstly, the diamagnetic character of boroles, contrasting with the biradical character of the isoelectronic pentaphenylcyclopentadienyl cation,[22] is in accord with a considerable energy gap between **24** and **25**. Our recent extended Hückel MO calculations suggest an energy gap of 2 eV (46 kcal) between the HOMO and LUMO levels.[21c] The four π-electrons can thus be preferentially ensconced in the two MO of lowest energy, namely **25** and **26**. Secondly, the low-energy (48 kcal), long-wavelength absorption of boroles at about 600 nm can be ascribed principally to the π → π* transition between HOMO **25** and LUMO **24**. When the boron atom is coordinated with pyridine, the only possible π → π* transition would be from **25** to an antibonding 1,3-butadiene-like orbital **27** (Figure 1), involving an energy increase of 66 kcal. Even the smaller shifts in the visible spectrum, which are observed by changing the substituents on the borole ring, can be understood from this MO scheme. The 20 to 35 nm bathochromic shift observed between 1-chloro- or 1-phenyltetraphenylborole and the analogous 1-chloro- or 1-phenyltetra-*p*-tolylborole can be ascribed to the electron-donating tolyl group raising the energy of **25** (tolyls at nonnodal sites) and thus reducing the HOMO–LUMO gap. On the other hand, if the phenyl group on boron in borole **3** is replaced by a methyl group, a hypsochromic shift of 25 nm is observed. Here, the electron release of the methyl toward boron raises the energy of LUMO **24** and thus increases the HOMO–LUMO gap. Thirdly, since **24** is a bonding orbital, it would be expected to add up to 2 electrons and form the dianion of the borole. Such 1- or 2-electron additions to **3** are exactly what Herberich and co-workers have observed.[14b] The red color of dianion **14**, intermediate between the blue color of borole **3** and the yellow of borole complexes, is understandable in terms of the intermediate amount of energy required for the π → π* transition between **24** and **27**.

We have examined the formation, properties, and reactions of this dianion and are able to comment on its similarity to the isoelectronic pentaphenylcyclopentadienyl anion.[23] As is shown in Scheme V, the driving force for borole dianion formation is much greater than that of the analogous silole and requires an available $2p_z$-orbital. Any firmly complexed pyridine on the boron center is readily displaced during dianion formation. Furthermore, once formed, dianion **14** has much of the negative charge on boron and the boron–phenyl system, rather than on C_2 and C_5 as in the silole anion **23**. This conclusion is based upon the ^{13}C NMR spectrum of **14**, in which the carbons of the B-phenyl group are shifted to higher magnetic fields (125 → 117–121 ppm) from their position in the borole–THF adduct. This shift is consonant with the greater importance of resonance structures **14b** and **14d** over contributors **14a** and **14c**. [Some support for high electron density on boron **14b** is seen in the evolution of H_2 when **14** is protonated in strong acid (Scheme VI).] In addition, the C=C stretch ascribable to the ring C=C group conjugated with a phenyl becomes extraordinarily intense when **3** is converted into **14**. We ascribe this intensity increase to the greater change in dipole for a C=C stretch in **14**.



14b **14d**



Finally, as already observed,[14b] the ^{11}B signal in **14** is shifted upfield from that of borole by 26 ppm, a further sign of the importance of resonance structure **14b**.

In conclusion, therefore, the heightened reactivity of the borole ring system, be it toward Lewis bases, dienophiles, mucleophiles, protolyzing agents, or oxidants, can be umabiguously attributed to the available $2p_z$-orbital on the tricoordinate boron. Once the antiaromaticity of the borole ring has been lifted, either by complexation or ring cleavage, the resulting organoborane displays only the low reactivity of a typical, sterically hindered arylborane. The unusually stable phenylbis-(2,3,4-triphenyl-1-naphthyl)borane, synthesized by Braye and co-workers and thought to be pentaphenylborole, illustrates the unusual inertness of this type of borane.

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(21) (a) Van der Kerk, S. M. *J. Organomet. Chem.* **1981**, *215*, 315. (b) C.f.: Dewar, M. J. S.; Gleicher, G. J. *J. Am. Chem. Soc.* **1965**, *87*, 3255. (c) Unpublished studies of J. J. Eisch, in collaboration with R. Hoffmann, Cornell University, 1985.

(22) Breslow, R.; Chang, H. W. *J. Am. Chem. Soc.* **1961**, *83*, 3728; **1963**, *85*, 2033.

(23) Zhang, R.; Tsutsui, M.; Bergbreiter, D. *J. Organomet. Chem.* **1982**, *229*, 109.

Experimental Section

General Procedure and Measurements. All operations involved in the preparation, transfer, and analyses of organometallic compounds were conducted under an atmosphere of pure, anhydrous nitrogen or argon.[24a] Likewise, all the solvents employed in such procedures were purified and distilled under an atmosphere of nitrogen from the following drying agents: $LiAlH_4$ for ethers and hydrocarbons and BaO for pyridine and benzonitrile.[24b]

The spectral samples were prepared by published techniques,[24c] and the spectra were measured with the following instruments: ^1H NMR spectra with a Varian A-60 or EM-360 spectrophotometer and ^{13}C NMR spectra with a Varian FT-80 spectrometer; mass spectra at the Mass Spectral Facility at Cornell University, where a Perkin-Elmer Model 270, an AEI-902, or a CEC-21-103A instrument was employed; IR spectra with a Perkin-Elmer Model 270; and electronic spectra with a Cary Instrument Model 14.

Chromatographic analyses were performed with an F&M, dual-column, programmed-temperature gas chromatograph, Model 720. Elemental analyses were carried out by Galbraith Laboratories, Knoxville, TN.

Starting Materials and Reagents. Dichloro(dimethyl)tin was purchased from Alfa (Ventron). Dichloro(phenyl)borane was either purchased from Alfa or synthesized from BCl_3 and tetraphenyltin.[24d] Diphenylacetylene, free of stilbenes, was prepared from benzil and triethyl phosphite.[25]

(*E*,*E*)-(1,2,3,4-Tetraphenyl-1,3-butadien-1,4-ylidene)dilithium (5).[24e] The interaction of diphenylacetylene with lithium can lead to a variety of lithium derivatives, depending upon the solvent, temperature, and contact time: (*Z*,*Z*)-(1,2-diphenyl-1,2-ethenylidene)dilithium,[26] **5**,[24e] or 2,3,4-triphenyl-1-naphthyllithium.[27] The successful preparation of **5** is no routine matter, so the following procedure should be reproduced carefully and the resulting product analyzed. Either a solid sample of **5** or a solution aliquot should be hydrolyzed under nitrogen and the organic products analyzed by combined gas chromatography and spectroscopy. By NMR and IR spectroscopy the presence of (*E*,*E*)-1,2,3,4-tetraphenyl-1,3-butadiene (**6**), the 1,2-diphenylethenes, and 1,2,3-triphenylnaphthalene can readily be ascertained. If only **6** is detected upon hydrolysis, then a further tared solid or solution sample can be hydrolyzed and the total alkali titrated with standard acid. It is known that **5** exists principally as a dietherate and can be stored unchanged for several months at 0 °C or below.

Solid samples of **5** can be prepared in the following manner. A *magnetically stirred solution of 17.8 g (0.1 mol) of pure diphenyl*acetylene (free of *trans*-stilbene) in 90 mL of anhydrous ethyl ether was admixed with 0.455 g (6.55 mol) of lithium metal (wire pieces previously hammered into foil strips), and the suspension was stirred for 3.5 h. After the stirrer was stopped, the large remaining lithium pieces were removed from the yellow suspension with long forceps (recovered lithium being retared). The reaction mixture was then stirred an additional 15 h at 20–25 °C to remove any remaining specks of lithium. The yellow precipitate was filtered off on a coarse glass frit under nitrogen and then washed with anhydrous, deoxygenated ether, in order to remove any soluble red impurities and remaining diphenylacetylene. After drying under vacuum the bright yellow solid **5** amounted to 9–12 g (55–75%). Hydrolysis of a tared sample and titration with standard acid gave an apparent equivalent weight of 250 ± 5. The calculated equivalent weight of $\mathbf{5}\cdot 2(C_2H_5)O$ is 259.

A solution of **5** can be obtained by following the foregoing procedure through the point at which the residual lithium pieces were removed. Thereupon the red-yellow suspension of **5** was diluted with 175 mL of anhydrous, deoxygenated tetrahydrofuran to produce a green solution. Aliquots of such a solution could be hydrolyzed and titrated with standard acid.

1,1-Dimethyl-2,3,4,5-tetraphenylstannole (8a). The synthesis of this compound in high yield posed no difficulty, if a stoichiometric amount of **5** was added to the dichloro(dimethyl)tin (**9**). Thus, a stirred solution of 25.3 g (0.115 mol) of **9** in 100 mL of anhydrous THF was treated with 0.230 mol of **5** in 750 mL of a 1:2 (v/v) ethyl ether–THF mixture over a period of 30 min. Slight coloration from the lithium reagent remaining in the reaction mixture was decharged by adding small amounts of **9** (<1.0 g). The solvent was then evaporated in vacuo, and the solid residue was washed several times at room temperature with 95% ethanol to remove the lithium salts and any residual tin halides. Recrystallization of the extracted residue from a CH_2Cl_2–95% ethanol pair gave almost colorless needles, mp 185–187 °C (lit.[28] 192 °C) (95% based on lithium metal consumed in preparing **5** or 80% based on the diphenylacetylene employed): ^1H NMR ($CDCl_3$) δ 0.60 (s, 6 H) and 6.7–7.2 (m, 20 H).

If inadvertently an excess of the dilithium reagent **5** were employed, the spirostannole, bis(1,2,3,4-tetraphenyl-1,3-butadien-1,4-ylidene)tin (**10**), could be isolated, mp 275–277 °C, from CH_2Cl_2–95% EtOH (lit.[13]). When 0.150 mol of **5** in 900 mL of ethyl ether–THF solution (1:2 v/v) was *treated at* 0 °C *with* 30.0 g (0.14 *mol*) *of* **9** *in* THF *over* 10 *min* and the reaction allowed to continue for 30 min at 25 °C, the usual workup and recrystallization yielded 37 g of **10** (64%).

On the other hand, if an excess of the dichloro(dimethyl)tin were present, and if the crude stannole were recrystallized directly from a CH_2Cl_2–95% EtOH, *without prior washing with 95% EtOH at 25 °C*, the stannole ring was completely cleaved by the HCl generated by the ethanolysis of **9**. When 1.01 g (1.0 mmol) of **8a**, 0.24 g (1.1 mmol) of **9**, 10 mL of 95% EtOH, and 10 mL of CH_2Cl_2 were heated at reflux for 15 min, and the CH_2Cl_2 was then evaporated off, colorless crystals of chlorodimethyl(*E*,*E*)-(1,2,3,4-tetraphenyl-1,3-butadien-1-yl)tin (**11a**) precipitated, 0.91 g (84%), mp 189–191 °C (lit.[12]), which was identified by its ^1H NMR spectrum.

Pentaphenylborole (7a). (a) Reaction of (*E*,*E*)-(1,2,3,4-Tetraphenyl-1,3-butadien-1,4-ylidene)dilithium (5) with Dichloro(phenyl)borane. (12). A 5.18-g (10 mmol) sample of **5** was suspended in 25 mL of anhydrous ethyl ether at −78 °C, and then 1.57 g (9.9 mmol) of **12** was added. After the stirred reaction mixture was brought to 20 °C, reaction commenced exothermically, and an olive-green color developed. The mixture stood for 2 h at 20–25 °C and then the ether was removed in vacuo. Addition of 5–40-mL portions of anhydrous, deoxygenated toluene, with through shaking at 60–70 °C for each portion, brought about the extraction of the blue borole from the insoluble lithium salts. Cooling the separated toluene extracts deposited 3.5 g (80%) of the deep-blue, microcrystalline borole **7a**, mp >240 °C dec.

Anal. Calcd for $C_{34}H_{25}B$: 91.90; H, 5.67; B, 2.43. Found: C, 91.75; H, 5.80; B, 2.30.

(b) Reaction of 1,1-Dimethyl-2,3,4,5-tetraphenylstannole (8a) with Dichloro(phenyl)borane (12). A 100-mL, two-necked flask, whose necks were respectively provided with a rubber septum and a three-way stopcock, was evacuated while warm and refilled with pure, dry argon. Then 10.08 g (20 mmol) of the powdered and dried stannole and 40 mL of anhydrous, deoxygenated toluene were placed in the flask and the flushing with argon gas repeated. Then the stirred suspension was treated with 2.65 mL (20 mmol) or dichloro(phenyl)borane by means of an argon-flushed airtight syringe. During a stirring period of 3 h at 25 °C the reaction mixture turned rapidly from yellow to dark green to blue. The toluene was siphoned off by immersion filter (a siphon whose one leg is fused to a coarse filter), and the blue residue was washed 3 times, with agitation, with 15-mL portions of toluene. The deep blue borole **8a** residue amounted to 6.6 g (74%). Cooling and concentrating the toluene extracts and filtrates could yield another 10–15% of the borole.

Alternatively, the toluene extracts were treated with 7.9 g (0.10 mol) of anhydrous pyridine to yield the pyridine complexes of the borole and *dichlorodimethyltin. The toluene was evaporated in vacuo, and the* residue was extracted with warm benzene to leave an insoluble residue and $Me_2SnCl_2\cdot 2C_5H_5N$. By adding petroleum ether to the warm benzene extracts until turbidity appeared and then cooling, the pale yellow pentaphenylborole–pyridine complex (**7a·Py**), mp 180–182 °C, was obtained.

Mass spectrum (50 °C at inlet, 70 eV), *m*/*e* (relative intensity) 523 (M^+, weak), 445 (~20% of 444 peak), and 444 ($M^+ - 79$, 100), 79 and 52; ^1H NMR (CS_2) 6.5 (m, 7 H), 6.81 (s, 10 H), 7.15 (m, 10 H), 7.70 (d, 1 H, γ-pyridyl H), and 8.6 (d, 2 H, α-pyridyl H); ^{11}B NMR (C_6H_6, relative to BF_3–OEt_2) 5.1. Anal. Calcd for $C_{39}H_{30}BN$: C, 89.48; H, 5.73; B, 2.70; N, 2.67. Found: C, 89.44; H, 5.65; B, 2.32; N, 2.58.

Treatment of this borole–pyridine complex with an ethanolic picric acid solution promptly deposits pyridine picrate, mp 166–167 °C.

1,1-Dimethyl-2,3,4,5-tetra-*p*-tolylstannole (8a). A solution of 51.5 g (0.250 mol) of di-*p*-tolylacetylene and 5.0 mL of THF in 225 mL of ethyl ether was stirred for 3 h with 1.40 g (0.200 mol) of lithium wire pieces that had been hammered into foil. The remaining lithium pieces (0.7 g) were removed, the solution was cooled to −78 °C, and 21.9 g (0.10 mol) of the dichloro(dimethyl)tin was added in one portion. After slow warming to 25 °C, *the reaction mixture was freed of volatile components* in vacuo, and the resultant solid residue was washed with 95% EtOH *without warming*. Recrystallization of the residue from a warm

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CH_2Cl_2–95% EtOH pair gave 28.5 g (51%) of pale yellow stannole **8b**, mp 202–204 °C. An analytical sample from the same solvent melted at 203–205 °C.

^{1}H NMR ($CDCl_3$) δ 0.55 (s, 6 H), 2.11 (s, 6 H), 2.17 (s, 6 H), and 6.2–7.2 (m, 16 H). Anal. Calcd for $C_{34}H_{34}Sn$: C, 72.75; H, 6.11. Found: C, 72.88; H, 6.35.

If the crude stannole was not washed with 95% EtOH at 25 °C but was directly heated with CH_2Cl_2 and 95% EtOH for recrystallization, then most of the stannole was cleaved by HCl (from Me_2SnCl_2 and EtOH) to produce chlorodimethyl-(*E,E*)-(1,2,3,4-tetra-*p*-tolyl-1,3-butadien-1-yl)tin (**11b**), mp 178.5–181 °C (from CH_2Cl_2–95% EtOH).

^{1}H NMR ($CDCl_3$) δ 0.63 (s, 6 H), 2.03 (s, 3 H), 2.18 (s, 3 H), 2.23 (s, 2 H), 2.28 (s, 3 H), and 6.5–7.4 (m, 17 H). Anal. Calcd for $C_{34}H_{35}ClSn$: C, 68.31; H, 5.90. Found: C, 68.09; H, 5.85.

Stannole **8b** (1.12 g, 2.0 mmol) was heated at reflux in 15 mL of glacial acetic acid for 30 min. Dilution with water precipitated a colorless solid, which was recrystallized from a $CHCl_3$–EtOH pair to yield 0.80 g (97%) of (*E,E*)-1,2,3,4-tetra-*p*-tolyl-1,3-butadiene, mp 259–262 °C.

Anal. Calcd for $C_{28}H_{30}$: C, 91.75; H, 8.25. Found: C, 91.53; H, 8.20.

1-Phenyl-2,3,4,5-tetra-*p*-tolylborole (7b). A solution of 0.603 g (1.07 mmol) of stannole **8b** in pure, deoxygenated CCl_4 was treated with 0.175 g (1.1 mmol) of dichloro(phenyl)borane. The deep blue color appeared and was monitored by ^{1}H NMR spectroscopy, and the signal of the Me_2Sn group of the stannole was rapidly replaced by that of Me_2SnCl_2. Concurrently, the tolyl Me groups were shifted downfield by 5 Hz and were two singlets barely separated by 2 Hz. The whole exchange was complete in 15 min.

In a similar experiment done in toluene on a 10-millimolar scale, the deep blue borole intermediate was treated with dry O_2 for 60 min at 25–75 °C. The resulting red-orange mixture was freed of volatiles in vacuo, and the residue was heated for 15 h at reflux with 15 mL of aqueous 12 N HCl and 125 mL of 95% EtOH. Again, volatiles were removed in vacuo, and the residue was extracted with CH_2Cl_2. After the extracts were filtered and dried (anhydrous $MgSO_4$), the CH_2Cl_2 was evaporated, and the residue was then dissolved in hot 95% EtOH. The cooled solution deposited 2.8 g (65%) of tetra-*p*-tolylfuran (**13**), mp 180–183 °C. Column chromatography on silica gel with a benzene–petroleum ether eluant and final recrystallization from a CH_2Cl_2–EtOH pair gave the pure sample, mp 187–188.5 °C.

Anal. Calcd for $C_{32}H_{28}O$: C, 89.67; H, 6.58. Found: C, 89.66; H, 6.65.

Physical Measurements on Pentaphenylborole (7a). The borole is only sparingly soluble in toluene and in methylene chloride, but it can be recrystallized from warm toluene (1 g per 30 mL). It forms colorless to pale yellow adducts with tetrahydrofuran, pyridine, or benzonitrile.

Visible spectrum of the uncomplex borole(toluene): λ_{max} 567 nm. IR (mineral oil): 700 vs, 730 s, 740 (sh) s, 768 s, 775 s, 797 s, 918 s, 1024 s, 1072 s, 1215 s, 1595 s, 1675 m.

Nuclear magnetic spectra of 1:1 borole–tetrahydrofuran adduct: ^{1}H NMR (CCl_4) δ 1.66 (m, 4 H), 4.05 (m, 4 H), 6.7–7.0 (br s, 11 H), 7.1 (s, 10 H), and 7.3–7.5 (m, 4 H); ^{13}C (THF-d_8, vs Me_4Si (intensity)) 124.84 (*26*), 125.96 (*30*), 126.51 (*14*), 127.66 (*100*), 127.84 (*5*), 127.89 (*4*), 128.53 (*6*), 128.83 (*9*), 129.69 (*52*), 129.82 (*9*), 129.93 (*4*), 130.87 (*7*), 130.99 (*56*), 131.89 (*3*), 132.14 (*4*), 133.04 (*26*), 140.41 (*3*), 143.78 (*4*).

UV spectrum of the borole–pyridine adduct: (*n*-heptane, λ_{max} (log ϵ)) 209 (peak 4.072), 231 (sh 3.850), 259 (sh 3.659), and 332 (sh 3.193); IR (mineral oil) 695 s, 722 m, 735 m, 1025 m, 1095 m, 1225 m, 1295 m, 1590 m, 1595 m, 1620 w.

^{11}B NMR spectrum (CH_2Cl_2, vs. $BF_3 \cdot OEt_2$): +5.1. IR spectrum of the borole–benzonitrile adduct (mineral oil) benzonitrile IR band at 2300 cm^{-1} replaced by an intense band at 2370 cm^{-1}.

Physical Measurements on the 2:1 Adduct (14) Resulting from Potassium Metal and Pentaphenylborole (7a). By following published directions,[14b] this potassium adduct was prepared from potassium metal and borole **7a** in THF and then recrystallized from a 1:5 THF–Et_2O pair. The dark red solid was obtained in 91% yield.

Spectral data: IR (mineral oil) 702 vs, 730 m, 765 m, 770 m, 795 w, 890 m, 900 m, 990 m, 1050 s, 1150 w, 1175 m, 1575 vs; nuclear magnetic spectra in THF-d_8, ^{1}H NMR 6.2–7.7 (m, with main peak centered at 6.65 and approximately a four-proton shoulder centered at 7.1 ppm); ^{13}C NMR (vs. Me_4Si (intensity) 117 (39), 119.87 (5), 120.12 (38), 121.33 (20), 125.73 (8), 126.49 (54), 126.66 (100), 126.88 (90), 127.96 (6), 128.03 (6), 130.81 (76), 132.52 (79), and 136.10 (37).

Protodeboronation of the 2:1 Adduct (14) of Potassium Metal wtih Borole (7a). Heating 2.6 g (5.0 mmol) of **14** in 20 mL of toluene with 2 mL of glacial acetic acid and 10 mL of aqueous 6 N HCl for 20 h at reflux gave a modest amount of H_2 evolution. Usual workup and isolation of the organic layer, followed by thin-layer chromatography, showed the presence of small amounts of (*E,E*)-1,2,3,4-tetraphenyl-1,3-butadiene (**6**) and its (*E,Z*)- and (*Z,Z*)-isomers. Also, a large amount of an ether-like oil, possibly a polymer from THF, was present. Finally, 0.45 g of (*E*)-1,2,3,4-tetraphenyl-1-butene (**15**), mp 147–149.5 °C, was isolated by column chromatography.

Since a sample of this hydrocarbon was recovered unchanged after a 3-h heating period at 80 °C in glacial acetic acid containing some concentrated H_2SO_4, it was concluded that **15** has the *E*-configuration.

Other fractions from the attempted chromatographic separation contained OH groups (IR) and phenyl and vinylic protons (NMR).

Generation of Various Boroles from Stannoles and Boron Halides. (a) Spectral Measurements in Situ. Visible spectra were recorded in toluene solution by admixing, under argon, 0.01 M solutions of stannole **7a** with, in turn, equimolar amounts of $PhBCl_2$, BCl_3, and $MeBCl_2$. The respective λ_{max} appeared at 567, 560, and 542 nm. Similar visible spectra resulting from the tetra-*p*-tolylstannole **7b**, and $PhBCl_2$, and BCl_3 displayed λ_{max} at 602 and 580, respectively.

Similarly, ^{1}H NMR spectra in CCl_4 were generated from stannole **7a** and $MeBBr_2$ or BCl_3: the spectrum of 1-methyl-2,3,4-tetraphenylborole had its Me–B at 1.5 and its aromatic protons in three multiplets centered at 6.97 (10 H), 7.25 (6 H), and 7.55 (4 H) ppm; the spectrum of 1-chloro-2,3,4,5-tetraphenylborole had a broad, complex aromatic multiplet between 6.6 and 7.3 ppm. The tetra-*p*-tolylstannole with BCl_3 and $PhBCl_3$ yielded the spectra of 1-chloro-2,3,4,5-tetra-*p*-tolylborole (2.18, s, 12 H and 6.45–7.2 m, 16 H) and of 1-phenyl-2,3,4,5-tetra-*p*-tolylborole (2.12 and 2.15, merged singlets, 12 H, and 6.3–7.4, three merged multiplets, 21 H), respectively.

Although the foregoing stannole–boron halide exchanges proceeded rapidly to completion, it is noteworthy that the reaction between stannole **7a** and diiodo(mesityl)borane did not occur. Monitoring of the components by ^{1}H NMR spectroscopy showed that no new products were formed. The interaction of stannole **7a** with dichloro(cyclohexyl)borane in toluene at 25 °C led to the development of a rose-colored solution. In CCl_4 a bright purple color developed, but the color faded in seconds to a rose color.

(b) *Oxidative Degradation of the Boroles in Situ.* In a manner analogous to the air oxidation of 1-phenyl-2,3,4,5-tetra-*p*-tolylborole (cf. supra), each of the borole solutions in the foregoing section was oxidized by dry air, and the corresponding tetraarylfuran was isolated in yields ranging from 40 to 80%.

Reactions of Pentaphenylborole (7a) Protodeboronation. Heating 1.0 g (2.2 mmol) of borole **7a** with 5.0 mL of glacial acetic acid in 30 mL of refluxing toluene for 24 h gave, upon column chromatographic separation of the neutralized and dried toluene extract, 0.20 g (25%) of (*E,E*)-1,2,3,4-tetraphenyl-1,3-butadiene (**6**), mp 182–183 °C, and other hydrocarbon oils. Stronger acids, such as HCl–HOAc mixtures, could not be employed to cleave **7a**, for these conditions isomerize **6** into 3-benzyl-1,2,3-triphenylidene.[17]

Likewise, heating **7a** with concentrated aqueous KOH in toluene emulsion for 24 h led only to a 45% yield of **6**.

However, one carbon–boron bond in **7a** can be quantitatively cleaved, even in the much more stable pyridine adduct. Dissolving the borole–pyridine complex in refluxing methanol and concentrating the solution deposited 75% of methoxy(phenyl)(*E,E*-(1,2,3,4-tetraphenyl-1,3-butadien-1-yl)borane (**16**) as colorless crystals, mp 104.5–105 °C.

Mass spectrum, *m/e* M$^+$, 476; ^{1}H NMR ($CDCl_3$) 3.72 (s, 3 H), 6.5–7.4 (m, 24 H, 8.0 (7, 2 H). Anal. Calcd for $C_{35}H_{29}BO$: C, 88.23; H, 6.14. Found: C, 88.10; H, 6.01.

(c) Oxidation with Alkaline Hydrogen Peroxide. An ethereal solution of borole **7a**, which was prepared from **8a** with dibromo(phenyl)borane, was divided into portions.

A solution of 4.0 mmol of **7a** in 20 mL of ether was concentrated under nitrogen, and the residue was treated with 400 mg of NaOH dissolved in 20 mL of 95% ethanol. After a few minutes, 3 mL of 30% H_2O_2 was added, and a prompt exothermic reaction took place. After 2 h, the mixture was diluted with water, and the precipitated solids were collected (1.51 g). Recrystallization from CCl_4–MeOH gave 0.82 g (49%) of colorless needles, mp 176–177.5 °C. On the basis of its UV spectrum (λ_{max} 248 nm), IR spectrum (1680 cm^{-1}), and ^{1}H NMR signals (singlets at 5.81 and 6.51 ppm) this compound was identified as *cis*-2,3,4-triphenyl-3-butenophenone (**17**). Heating **17** with 10 drops of 12 N HCl in ethanol yielded isomer **18**, which was identified as *trans*-2,3,4-triphenyl-2-butenophenone, mp 136–137 °C: IR 1650 cm^{-1}; ^{1}H NMR 3.92 ppm (s, H).[29]

If in oxidizing an aliquot of **7a** in ether the 3.0 mL of 30% H_2O_2 was added first and then the ethanolic NaOH solution was added later, the usual workup gave, as the main product, 1,2,3,4-tetraphenylbutane-1,4-dione (**19**), mp 254–256 °C. Heating this compound in ethanolic HCl

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[29] Boykin, D. W., Jr.; Lutz, R. E. *J. Am. Chem. Soc.* **1964**, *86*, 5046.

gave principally tetraphenylfuran (**20**), mp 185–186 °C.[30]

Direct air oxidation of an aliquot of **7a** in ether, evaporation of solvent, and direct column chromatography, without intentional hydrolysis, of the residue leads to the isolation of tetraphenylfuran and 3-benzylidene-1,2-diphenylindene.

Nature of the "Pentaphenylborole" Reported by Braye, Hübel, and Caplier. From the foregoing reactions of authentic pentaphenylborole with oxygen and protolyzing agents, it is clear that the boron compound isolated by Braye, Hübel, and Caplier and recrystallized in air from ethanol could not have been the borole. The following repetition of their procedure in our laboratory has clarified the nature of their product.

After conducting the reaction of **5** with dichloro(phenyl)borane in ethyl ether, exactly as published, the dried benzene extract was freed of solvent and chromatographed on silica gel. The sample was introduced onto the column in 4 mL of benzene and eluted with petroleum ether (bp 30–60 °C)–benzene–ethanol gradient. The main fraction, 1.6 g of yellow solid, was recrystallized from a benzene–ethanol pair to give 250 mg of pale yellow crystals, mp 182–184 °C dec, which displayed only one spot on TLC developed with benzene–petroleum ether. A second crop, mp 189–193 °C dec, was completely different by TLC and IR spectroscopy (the latter had an OH band).

The main compound had the following spectral characteristics: IR (mineral oil) no OH or B–O absorptions, but C_6H_5–B bond at 1250 cm^{-1}; ^1H NMR ($CDCl_3$) br merged peaks at 6.83, 7.0, and 7.33 ppm; UV (95% EtOH) 205, 240, 293, and 366 (sh) nm; mass spectrum m/e 814 (M^+ + 0), 799, 798; mol wt by ^1H NMR vs. $(Me_2SiO_3)_3$ 880.

Heating a sample of this compound in glacial HOAc for 50 h, dilution with water, collection of the precipitated product, and recrystallization from MeOH gave a colorless solid, mp 147.5–149 °C, that was identified as 1,2,3-triphenylnaphthalene.

On the basis of the foregoing, the boron compound melting at 182–184 °C dec is concluded to be phenylbis(2,3,4-triphenyl-1-naphthyl)borane (**22**). A sample of Braye, Hübel, and Caplier's compound, kindly provided by Dr. Hübel, was compared with our sample by TLC, NMR, and IR techniques. The two compounds were almost identical by these criteria, except that the BHC sample showed two minor contaminants by TLC. The published elemental analyses (C, 92.16; H, 6.04; B, 2–3) compare reasonably with those calculated for **22** (C, 93.22; H, 5.42; and B, 1.35). The small amount of oxygen contaminants in the BHC sample, as revealed by IR, MS, and TLC techniques, explains the low carbon and hydrogen values.

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Carbon–Oxygen Bond Cleavage of Esters Promoted by Hydrido and Alkylcobalt(I) Complexes Having Triphenylphosphine Ligands. Isolation of an Insertion Intermediate and Molecular Structure of Phenoxotris(triphenylphosphine)cobalt(I)

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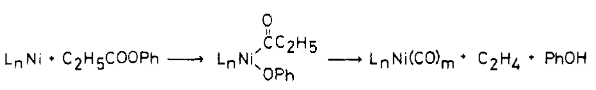
Abstract: Carbon–oxygen bonds in aryl and alkyl carboxylates (R′COOR) are selectively cleaved by $CoH(N_2)(PPh_3)_3$, and carboxylic esters $R'COOCH_2R'$ are formed by a Tischchenko type dimerization of aldehyde R′CHO, whereas the reaction of $CoMe(PPh_3)_3$ with the esters yields ketones R′COMe. The reaction products are accounted for by assuming insertion of the ester C=O double bond into the Co–H or Co–Me bond, followed by abstraction of the β-alkoxo group by cobalt. The intermediate (β-(ethoxy)alkoxo)cobalt(I) complex $Co(OCH(CF_3)OEt)(PPh_3)_3$ has been isolated in the reaction of $CoH(N_2)(PPh_3)_3$ with ethyl trifluoroacetate as well as by alcoholysis of $CoH(N_2)(PPh_3)_3$ with $CF_3CH(OEt)OH$. Treatment of $CoH(N_2)(PPh_3)_3$ with phenyl acetate affords a tetrahedral phenoxocobalt(I) complex, $Co(OPh)(PPh_3)_3$. Crystals of the complex are monoclinic, space group $P2_1/c$, with a = 13.142 (2) Å, b = 19.661 (3) Å, c = 18.714 (3) Å, and β = 91.49 (3)°. Block-diagonal least-squares refinement leads to R = 0.075 and R_w = 0.081 for 2966 reflections. The molecular structure of the complex consists of a tetrahedron with an O-bonded phenoxo group and three PPh_3 ligands: the average Co–P distance is 2.320 (4) Å and Co–O 1.900 (9) Å, and the average P–Co–P angle is 109.9 (1)°, P–Co–O 109.1 (4)°, and Co–O–C 138.2 (9)°, respectively.

Synthetic methods utilizing selective cleavage of C–O bonds in allyl carboxylates promoted by palladium complexes have been well developed.[1] However, studies on selective cleavage of C–O bonds in carboxylic esters and anhydrides promoted by other transition-metal complexes are limited.[2] Previously we have demonstrated that aryl esters undergo acyl–O bond cleavage and subsequent reactions on interaction with Ni(0) complexes.[3]



$$L_nNi + C_2H_5COOPh \longrightarrow L_nNi(C(=O)C_2H_5)(OPh) \longrightarrow L_nNi(CO)_m + C_2H_4 + PhOH \quad (1)$$

In contrast to the reaction of esters with the Ni(O) complexes, transition-metal hydrides are anticipated to behave somewhat

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