and $Ni^{2+}$ interact simultaneously with all three phosphate groups.[22,25a] The latter two ions were studied only at pH 8.5–9. At pH ∼7 all four paramagnetic ions bind to the adenine ring of ATP also,[22,25b] the latter three all the time they are bound to the phosphate.[25b]

To resolve apparent disagreement between these conclusions and previous ultraviolet[26] and temperature-jump[27] studies which involved solutions containing only $10^{-4}$ *M* ATP, Sternlicht, *et al.*,[28] performed nmr experiments on $Mn^{2+}$–ATP solutions with only $\approx 5 \times 10^{-4}$ *M* ATP. These authors claim to have shown that at low ATP concentration, $\approx 5 \times 10^{-4}$ *M*, primarily 1:1 complexes are present, but that 1:2 complexes predominate at high ATP concentration, $\approx 0.1$ *M*, *i.e.*, with only $\approx 10^{-4}$ *M* $Mn^{2+}$ in each case. Sternlicht, *et al.*, believe that in the 1:2 complex the $Mn^{2+}$ binds simultaneously to the phosphate of one nucleotide and to the adenine of the second nucleotide, but that the metal is bound only to the phosphate in the 1:1 complex.

Except for the existence of multiple equilibria which depend strongly on solution conditions, there is little reason to expect much similarity between $UO_2^{2+}$–ATP complexes and monatomic cation–ATP complexes in which all three phosphate groups are involved, since ligands attached to the uranyl ion are restricted to positions close to its equatorial plane. On the other hand, one might look for relationships between $UO_2^{2+}$–ATP chelates and those monatomic cation–ATP complexes, like $Cu^{2+}$–ATP, in which only two phosphate groups are involved, but it is apparent that much more extensive and systematic studies, *e.g.*, over wider pH and concentration ranges, are needed for systems containing monatomic cations than are now available. It is of interest to this point that Brintzinger[29] in 1961 claimed that his pH titrations showed involvement of the ribose hydroxyl group in the complexation of $Mn^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Zn^{2+}$, and $Cu^{2+}$ by ATP in basic solution. However, he believed that, unlike the binding in our suggested $UO_2^{2+}$–ATP structures, there was an intervening water molecule attached by its oxygen atom to the metal and by hydrogen bridges to the two ribose hydroxyl oxygens.

(26) P. W. Schneider, H. Brintzinger, and H. Erlenmeyer, *Helv. Chim. Acta*, **47**, 992 (1964).

(27) G. G. Hammes, and S. A. Levison, *Biochemistry*, **3**, 1504 (1964).

(28) H. Sternlicht, D. E. Jones, and K. Kustin, *J. Amer. Chem. Soc.*, **90**, 7110 (1968).

(29) H. Brintzinger, *Helv. Chim. Acta*, **44**, 1199 (1961).

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# Triarylboron Anion Radicals and the Reductive Cleavage of Boron Compounds

**J. E. Leffler,* G. B. Watts, T. Tanigaki, E. Dolan, and D. S. Miller**

*Contribution from the Department of Chemistry, Florida State University, Tallahassee, Florida 32306.* *Received April 9, 1970*

**Abstract:** The boron nuclear spin coupling constant of the triphenylboron anion radical is positive. The assignment of coupling constants to the ortho, meta, and para protons has been confirmed by a study of the tris(*p*-deuteriophenyl)- and tris(3,5-dideuteriophenyl)boron esr spectra. The lines corresponding to $m_B = \pm {}^3/_2$ are selectively broadened either by incomplete averaging of the anisotropic hyperfine coupling or by an unidentified reaction that modulates the boron coupling constant. Prolonged reaction of triphenylboron anion radical with alkali metals in DME degrades it to biphenyl anion radical, *both halves of which come from the same triphenylboron.* The behavior of tris(*p*-chlorophenyl)boron, tris(*p*-methoxyphenyl)boron, tris(*p*-dimethylaminophenyl)boron, tris(*p*-tolyl)boron, several trialkylborons, diphenylboron chloride, and dimesitylboron fluoride with alkali metals is also described.

Most triarylborons react with alkali metals in DME[1] or other ethers to give anion radicals whose electron spin resonance spectra show quartet splittings due to the predominant $^{11}B$ isotope.[2] These spectra are of theoretical interest because the triarylboron anion radicals are isoelectronic with the corresponding triarylmethyl neutral radicals and triarylaminium cation radicals. One of the properties of interest is the sign of the isotropic coupling constant of the central $^{11}B$, $^{13}C$, or $^{14}N$. The coupling constant is known to be *positive* for $^{13}C$ and $^{14}N$ in the triphenyl compounds,[3,4] but has not been determined with more bulky aryl groups that might be twisted further out of the plane of the central bonds.

At one time the coupling constant for trimesitylboron anion radical was believed to be negative,[2a] but the data have since been reinterpreted.[2d]

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* Address correspondence to this author.

[1] 1,2-Dimethoxyethane.

[2] (a) H. van Willigen, Dissertation, Amsterdam, 1965; (b) S. I. Weissman and H. van Willigen, *J. Amer. Chem. Soc.*, **87**, 2285 (1965); (c) J. E. Leffler, E. Dolan, and T. Tanigaki, *ibid.*, **87**, 927 (1965); (d) H. van Willigen, private communication.

[3] (a) H. van Willigen and S. I. Weissman, *J. Chem. Phys.*, **44**, 420 (1966); (b) F. C. Adam and S. I. Weissman, *J. Amer. Chem. Soc.*, **80**, 2057 (1958).

[4] H. van Willigen, *ibid.*, **89**, 2229 (1967).

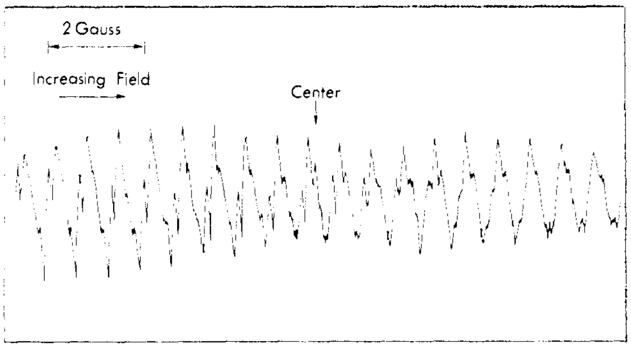

Figure 1. Central portion of $(C_6H_5)_3B\cdot^-$ esr spectrum in DME at room temperature with Na and K gegenions, showing differences in resolution between high and low field.

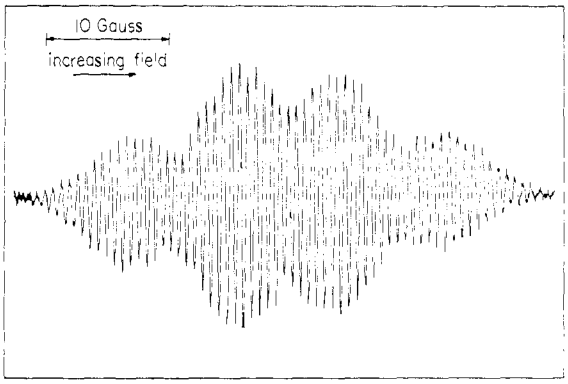

Figure 2. $(C_6H_5)_3B\cdot^-$ in DME at room temperature, Na and K gegenions.

## Triphenylboron Anion Radical

The esr spectrum of the triphenylboron anion radical in DME has broader lines in the high-field half than in the low-field half. This can be seen not only from the greater degree of resolution at low field (Figure 1), but also from the ratios of the derivative amplitudes of the high-field lines to those of corresponding lines in the low-field half of the spectrum (Figure 2).[5] The average ratio (ten spectra) is 0.87, varying only slightly with reaction conditions. A similar difference in derivative intensities can be seen in the spectra of tris(*p*-deuteriophenyl)boron and tris(3,5-dideuteriophenyl) boron anion radicals.

The boron isotropic splitting constant in these unhindered boron anion radicals is therefore positive, like those of the central atoms of the trityl and triphenylaminium radicals.[6]

Besides the difference in line width between the high- and low-field halves of the spectrum, there is a difference in width between lines corresponding to different values for the square of the boron nuclear spin quantum number. The $^{11}B$ quartet splitting causes the envelope of the first-derivative lines in the triphenylboron anion radical spectrum (Figure 2) to have four maxima, corresponding to $m_B = -^3/_2, -^1/_2, +^1/_2$, and $+^3/_2$. The lines in the outer two groups have conspicuously smaller derivative amplitudes than those of the inner two groups, the average ratio being 0.44 for a set of ten spectra. Part of this difference is due merely to the fact that the lines are degenerate and the central groups receive intensity from two neighbors while the other groups receive contributions from only one neighbor. Using our coupling constants the ratio due to this trivial cause is about 0.8, a value close to that found by us and by van Willigen[2a] for trimesitylboron, but about twice the value observed for triphenylboron. We conclude that the lines of $m_B = \pm ^3/_2$ are in fact wider than those of $m_B = \pm ^1/_2$ in the triphenylboron anion radical spectrum.

Line widths can depend on the square of a nuclear spin quantum number either because the averaging of the anisotropic hyperfine interaction by tumbling is incomplete, or because the coupling constant is being modulated by some reaction that changes the magnetic environment, or both. There are several possible explanations for the fact that the dependence of the line width on $m^2$ is large in the case of the triphenylboron anion radical, but negligible in the case of the trimesitylboron anion radical. First of all, processes involving rotation about the aryl-to-carbon bond axis[7,8] or processes involving coordination at the central boron are prevented by steric hindrance in the trimesitylboron anion radical but not in the triphenylboron. We note, for example, that triphenylboron readily forms complexes with anions whereas trimesitylboron does not.

If the $m^2$-dependent line-width variation is caused by incomplete averaging of the anisotropic hyperfine interaction, the correlation time for the rotation of the trimesitylboron anion radical must be shorter than that of the triphenylboron anion radical. According to the Debye equation, $\tau_c$ should be larger for the mesityl compound because trimesitylboron anion radical is the larger molecule. On the other hand, it is also more nearly spherical, as can be seen readily from models, and spherical molecules conform very poorly to the Debye equation. For example, *tert*-butyl chloride rotates with a very low energy of activation even in solid *tert*-butyl chloride.[9,10] Incomplete averaging of the hyperfine interaction by tumbling may therefore be a sufficient explanation for the line-width variation.

In an attempt to learn more about the process causing the $m^2$-dependent line widths, we observed the spectra of triphenylboron, tris(*p*-deuteriophenyl)boron, and tris(3,5-dideuteriophenyl)boron anion radicals in DME over a range of temperatures from −45 to +45° (Figures 3 and 4). This was not very successful, because lowering the temperature drastically decreases the amplitude of the derivative signal. The low-temperature spectra, like those reported by van Willigen[2a] for the trimesitylboron anion radical, appear to consist of four broad lines with the resolved spectrum superimposed upon them. At still lower temperatures, the

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(5) For lines of the same actual intensity and shape the amplitudes in a first-derivative spectrum are inversely proportional to the square of the line widths.

(6) We assume that the magnetogyric ratio component $\gamma_\perp$ is less than $\gamma_\parallel$. This has been shown experimentally only for the case of planar aromatic hydrocarbon anion radicals. However, the same assumption was made with regard to the $^{13}C$ and $^{14}N$ radicals.[3,4]

(7) H. C. Brown and S. Sujishi, *J. Amer. Chem. Soc.*, **70**, 2793 (1948).

(8) T. J. Weismann and J. C. Schug, *J. Chem. Phys.*, **40**, 956 (1964).

(9) C. P. Smyth, *J. Phys. Chem.*, **58**, 580 (1954).

(10) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 101.

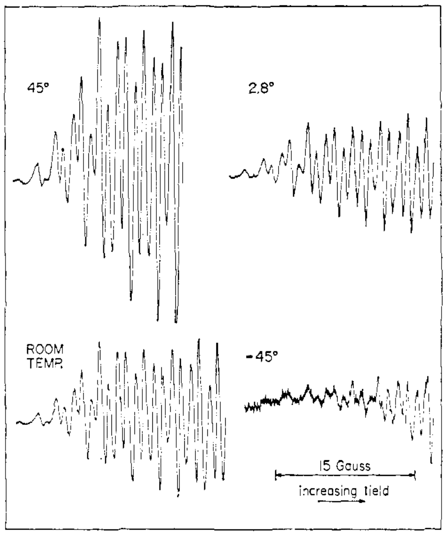

Figure 3. Tris(3,5-dideuteriophenyl)boron anion radical in DME, Li gegenion.

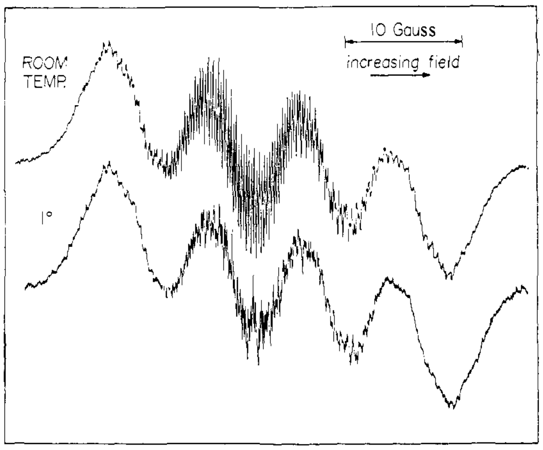

Figure 4. Tris($p$-deuteriophenyl)boron anion radical in DME, Li gegenion.

resolved spectrum vanishes and only the four-line background is seen. This has been interpreted in terms of a temperature-sensitive cluster formation, only the monomeric radical component of the equilibrium mixture giving the resolved spectrum.[2a] Although it is difficult to be sure, it appears from our spectra that the derivative amplitudes for the $m_B = \pm {}^1/_2$ and $m_B = \pm {}^3/_2$ lines of the resolved component of the mixture become more nearly equal as the temperature is lowered. The $m_B{}^2$ dependence of the line width caused by insufficiently rapid tumbling should be greater at lower temperatures. On the other hand, a temperature dependence of an effect due to a fast chemical equilibrium which modulated the coupling constant could have either sign.

**Coupling Constants.** Coupling Constants were assigned by fitting the calculated[11,12] esr spectra to the experimentally observed spectra for triphenylboron,

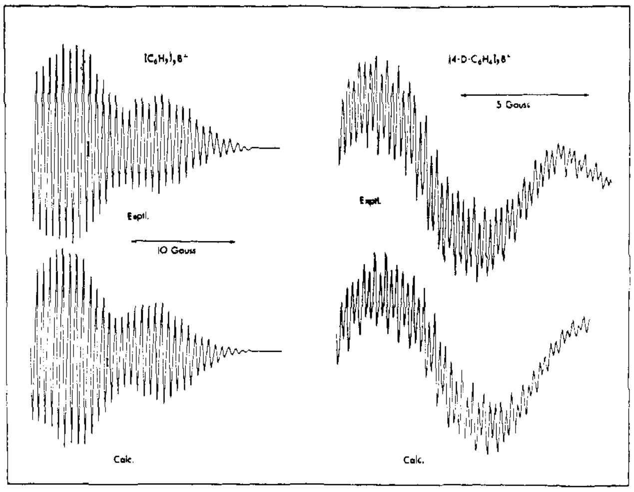

Figure 5. Triphenylboron and tris($p$-deuteriophenyl)boron anion radical spectra, calculated and experimental.

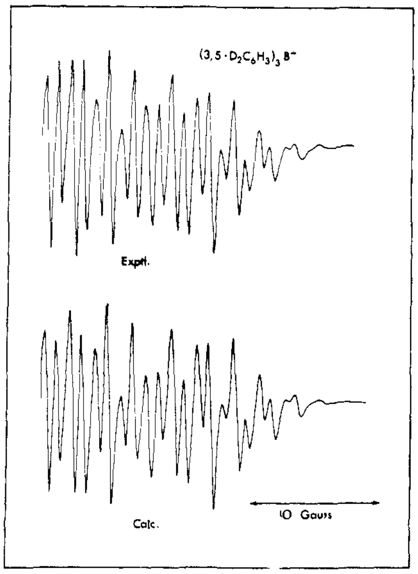

Figure 6. Tris(3,5-dideuteriophenyl)boron anion radical experimental and calculated spectra.

tris($p$-deuteriophenyl)boron, and tris(3,5-dideuteriophenyl)boron anion radicals (Figures 5 and 6). All of the experimental spectra were in DME with Li or Na–K as the metal used to reduce the triarylboron to the radical. The metal has no effect on the hyperfine splittings. Dilution of the tris($p$-deuteriophenyl)boron anion radical removes the broad four-line background signal, leaving the fine structure apparently unchanged in coupling constants or in line width. The coupling constants and line widths used to approximate the experimental spectra are summarized in Table I. Figures 5 and 6 show the fit achieved with these parameters.

## Reductive Cleavage of Triarylborons

On prolonged contact with alkali metal in ethers some triarylborons are not cleaved at all, some are

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(11) Using the SESRS program for first-order spectra: E. W. Stone and A. H. Maki, *J. Chem. Phys.*, 38, 1999 (1963).

(12) All calculated spectra include a contribution from the $^{10}B$ species.

**Table I.** Triphenylboron

| | Coupling constants, G | | | | Line widths, G[a] | |
|---|---|---|---|---|---|---|
| Substituent | $^{11}B$ | Para | Ortho | Meta | $m_B$ = $^1/_2$ | $m_B$ = $^3/_2$ |
| None | 7.84 | 2.73 | 1.99 | 0.670 | 0.30 | 0.33 |
| Tris(4-*d*) | 7.84 | 0.44 | 1.96 | 0.670 | 0.28 | 0.33 |
| Tris(3,5-$d_2$) | 7.84 | 2.73 | 1.96 | 0.104 | 0.30 | 0.33 |

[a] The $m_B$ = $^1/_2$ line width was also used for the central three lines of the $^{10}B$ septet species, while the $m_B$ = $^3/_2$ line width was used for the outer four lines.

cleaved to the arene (eq 1), and some are cleaved to the biaryl (eq 2). Trimesitylboron and tris(2,4-dimethylphenyl)boron[2a,13] are examples of compounds not cleaved at all, while tris($\alpha$-naphthyl)boron and tris(*o*-phenylphenyl)boron react as indicated in eq 1.[2a]

$$Ar_3B\cdot^- + M \longrightarrow ArH\cdot^- \tag{1}$$

$$Ar_3B\cdot^- + M \longrightarrow ArAr\cdot^- \tag{2}$$

We find that tris(2,4,6-trimethyl-3,5-dinitrophenyl)boron[14,15] gives the dinitromesitylene anion radical quite readily, which suggests that bulky ortho substituents interfere with both reaction 1 and reaction 2, while electron-withdrawing substituents counteract this effect at least for reaction 1.

Triphenylboron anion radical in DME is stable for weeks, but prolonged contact with alkali metal causes the $(C_6H_5)_3B\cdot^-$ esr spectrum to be replaced by that of *biphenyl* anion radical. Analysis of the reaction product reveals some benzene, but in less than 2% yield, so reaction 1 is only a minor process. Tris(*p*-tolyl)boron gives *p,p'*-ditolyl, and tris(*p*-deuteriophenyl)boron and tris(3,5-dideuteriophenyl) boron give the corresponding deuterated biphenyls. The boron-containing products are presumed to be derivatives of phenylboronic acid.[16] The presence of the biphenyls as impurities in the rereagents was excluded by analysis with thin-layer chromatography and by oxidizing a sample of the triphenylboron and then testing for biphenyl by means of the reaction with alkali metal to give biphenyl anion radical.

*Reaction 2 was shown to be intramolecular, both moieties of the biphenyl coming from the same parent triphenylboron,* by means of a deuterium-labeling experiment. When a mixture of equal amounts of tris(*p*-deuteriophenyl)boron and tris(3,5-dideuteriophenyl)boron is treated with Li in DME the product contains only the two symmetrically labeled biphenyls. This was demonstrated by matching the experimental esr spectrum with one computed for the mixture of the symmetrical products, using experimentally determined coupling constants.[17] The test is a good one for the unsymmetrical biphenyl because that species should have several peaks in a region relatively free from interference from the two symmetrical biphenyls.

There are two precedents for the intramolecular formation of biaryls from arylboron compounds. One is the formation of di-$\alpha$-naphthyl in good yield from the photolysis of tris($\alpha$-naphthyl)boron in $CCl_4$.[18a,b] Experiments with bis($\alpha$-naphthoyl) peroxide have shown that free $\alpha$-naphthyl radicals are largely converted to $\alpha$-chloronaphthalene, and hence cannot be intermediates in the formation of binaphthyl.[18c] The other example is the exclusive formation of symmetrical biphenyl by the electrode oxidation of a mixture of labeled and unlabeled tetraphenylborate ion.[19]

Biphenyl has also been observed as a product of the reduction of triphenylamine[20] and triphenylphosphine,[21] and in the mass spectra of triarylcarbinols.[22a] Substituent effects in the latter reaction suggested an attack by a radical site on one aryl group on the polarizable $\pi$ electrons of the other aryl group, with elimination of the bridging moiety. Oxidation of triphenylmethane dyes gives benzidines by a reaction that has been shown to be intramolecular.[22b]

## Reactions of Other Trisubstituted Borons with Alkali Metals

Triethylboron and tri-*n*-propylboron failed to give esr signals on treatment with Na–K in DME although the metal was consumed. Tribenzylboron[23] reacted with Na–K in DME to give a dark green solution whose esr signal consisted of a single line about 30 G wide. Tris(cyclohexyl)boron gave only a very weak and unstable signal.

Tris(*p*-chlorophenyl)boron, on treatment with Na–K in DME, gave a signal completely identical with that of the unsubstituted triphenylboron anion radical. This result means that the replacement of chlorine atoms by hydrogen is much faster than either of the triarylboron cleavage reactions, 1 or 2. The final spectrum was again that of diphenyl anion radical, the main cleavage product of triphenylboron. However, *p,p'*-dichlorobiphenyl is rapidly reduced to biphenyl under the same conditions.[24]

The reaction of tris(*p*-methoxyphenyl)boron[23,25] with

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(13) The report in ref 2c that trimesitylboron is cleaved under these conditions should be disregarded. Dimesitylboron fluoride and trimesitylboron react with alkali metal to give identical esr spectra, but the spectrum is that of trimesitylboron anion radical rather than a cleavage product.

(14) R. T. Hawkins, W. J. Lennarz, and H. R. Snyder, *J. Amer. Chem. Soc.*, **82**, 3053 (1960).

(15) The first signal consists of three broad lines separated by about 20 G, the center one more intense than the others. On further reaction the signal becomes identical with that from an authentic sample of dinitromesitylene.

(16) A nearly quantitative yield of phenylboronic anhydride was obtained from an experiment with diphenylboron chloride and Na–K in DME. Diphenylboron chloride in DME disproportionates and gives the $Ph_3B\cdot^-$ esr signal followed by a $Ph_2\cdot^-$ esr signal.

(17) T. W. Lapp, J. G. Burr, and R. B. Ingalls, *J. Chem. Phys.*, **43**, 4183 (1965).

(18) (a) B. G. Ramsey, Dissertation, Florida State University, 1962; (b) J. L. R. Williams, P. J. Grisdale, and J. C. Doty, *J. Amer. Chem. Soc.*, **89**, 4538 (1967); (c) J. E. Leffler and R. Zepp, *ibid.*, **92**, 3713 (1970).

(19) D. H. Geske, *J. Phys. Chem.*, **66**, 1743 (1962).

(20) (a) M. Iwaizumi and T. Isobe, *Bull. Chem. Soc. Jap.*, **38**, 501 (1965); (b) A. D. Britt, M. M. Urberg, and E. T. Kaiser, *J. Org. Chem.*, **31**, 1661 (1966).

(21) (a) A. D. Britt and E. T. Kaiser, *J. Phys. Chem.*, **69**, 2775 (1965); (b) K. S. V. Santhanam and A. J. Bard, *J. Amer. Chem. Soc.*, **90**, 1118 (1968).

(22) (a) F. W. McLafferty, G. E. van Lear, and R. Kornfeld, *ibid.*, **90**, 6240 (1968); (b) Z. Galus and R. N. Adams, *ibid.*, **86**, 1666 (1964); V. Hanousek and M. Matrka, *Collect. Czech. Chem. Commun.*, **24**, 16 (1959).

(23) E. Krause and P. Nobbe, *Chem. Ber.*, **63**, 934 (1930).

(24) R. E. Schwerzel, this laboratory.

(25) D. S. Miller, Thesis, Florida State University, 1969.

Li in DME gave an esr signal attributable to the para-substituted triphenylboron anion radical, since it resembles that obtained from tris(*p*-deuteriophenyl)boron. The spectrum consists of four broad lines at about 8-G separation, with partly resolved fine structure superimposed. The fine structure has a spacing of about 0.75 G and is much more nearly resolved in the $m_B = \pm {}^1/_2$ group than in the $m_B = \pm {}^3/_2$ groups.

Further reaction of the tris(*p*-methoxyphenyl)boron anion radical destroyed the boron anion radical signal but did not give a biphenyl anion radical signal.[26] Since control experiments show that *both p,p'*-dimethoxybiphenyl and anisole give strong signals characteristic of the unsubstituted biphenyl anion radical,[24,27] we conclude that the reaction responsible for the destruction of the boron signal is neither eq 1 nor eq 2.

The reaction of tris(*p*-dimethylaminophenyl)boron with Li in DME gave only the four-line signal, separation about 8.3 G, and no resolved proton or nitrogen hyperfine structure. This signal gradually decayed on prolonged reaction with Li, but without producing a biphenyl signal.[26] The reaction of tris(*p*-dimethylaminophenyl)boron with Na–K in DME again gives the four-line signal, but further brief shaking with the Na–K converts this into a seven-line signal with 3.1-G intervals and relative derivative intensities of 1:2:3:4:3:2:1,[28] which slowly decays back to the four-line signal on standing out of contact with the metal. The four line to seven line to four line cycle can be repeated for several days before all signals disappear.[26] Again, no biphenyl anion radical signal is seen, though a control experiment shows that *p,p'*-bis(dimethylamino)biphenyl gives a strong unsubstituted biphenyl anion radical signal on reaction with Na–K in DME.[24] The species responsible for the seven-line signal could be a cleavage product $Ar_2B{-}BAr_2\cdot^-$ which slowly regenerates triarylboron.[29] This would be consistent with the results of some of our experiments with diarylboron halides, to be described next.

**Reactions of Diarylboron Halides.** The first observable signal from the reaction of dimesitylboron fluoride with Na–K in DME is that of the trimesitylboron anion radical which then persists unchanged on further exposure to the alkali metal.[13]

The behavior of diphenylboron chloride is somewhat variable and dependent on the reaction conditions. In DME with Na–K the $(C_6H_5)_3B\cdot^-$ esr spectrum is observed, followed on prolonged reaction by that of the biphenyl anion radical. However, in one experiment with perdeuteriodiphenylboron chloride and Na–K in DME, a poorly resolved seven-line signal with about a 3-G splitting was obtained. Prolonged reaction of diphenylboron chloride in benzene or cyclohexane with Na–K gives a pyrophoric black solid. Brief reaction of perdeuteriodiphenylboron chloride with Na–K in benzene gave a waxy solid which on further reaction with Na–K in DME showed an esr signal consisting of seven broad lines with relative intensities fitting the two-boron model and a splitting constant of 2.9 G. Further reaction with Na–K caused this signal to be replaced by one like that of triphenylboron anion radical. The final signal appeared to correspond to a 2:1 mixture of perdeuteriobiphenyl and biphenyl. However, an attempted repetition of this experiment with ordinary diphenylboron chloride and perdeuteriobenzene failed to give any signal that could be attributed to a two-boron species, and ultimately gave an ordinary biphenyl anion radical unaccompanied by deuterated biphenyls.

## Experimental Section

**Diphenylboron Chloride.** $BCl_3$ (70 g) at −80° is added to $(C_6H_5)_4Sn$ (70 g) and the mixture allowed to come to room temperature under a −80° reflux condenser and an atmosphere of dry $N_2$. The reflux rate gradually increases and the $(C_6H_5)_4Sn$ goes into solution, after which refluxing is continued for 1 hr. $SnCl_4$ and some $C_6H_5SnCl_3$ are then removed by distillation through a short column (glass helices). The residue, consisting of crude $C_6H_5BCl_2$, is then refluxed under $N_2$ with an additional 65 g of $(C_6H_5)_4Sn$ for 2 hr, after which $SnCl_4$ is again removed at 1 atm. The crude product, consisting of $(C_6H_5)_2BCl$ and $(C_6H_5)_3B$, is then distilled *in vacuo* and a center fraction, bp 83–85° (0.05 mm), is recrystallized from *n*-pentane at −6° under argon. The recrystallized $(C_6H_5)_2BCl$ is again distilled and a center fraction is used for the esr experiments. $(C_6H_5)_2BCl$ was also prepared *via* 2-aminoethyl diphenylborinate[30] and diphenylborinic anhydride.[31]

**Triphenylboron.** Instead of isolating the $(C_6H_5)_2BCl$ made from $(C_6H_5)_4Sn$, an additional 64 g of $(C_6H_5)_4Sn$ is added and the mixture refluxed under $N_2$ for 3 hr. A fraction, bp 80–112° (0.05 mm), is discarded and the crude $(C_6H_5)_3B$, 86 g, collected at 144–151° (0.05 mm). The material used in the esr experiments was crystallized three times from dry ether at −6° under argon, yielding white crystals, mp 148°. Triphenylboron was also made by a Grignard synthesis from bromobenzene.[32,33]

**Tris(*p*-chlorophenyl)boron.** This compound was prepared from *p*-chlorophenylmagnesium bromide and boron trifluoride etherate. The yellow solid remaining after removal of the ether by distillation is distilled *in vacuo*. The crude product, bp 208–213° (0.01 mm), is recrystallized from hot benzene under argon, mp 197–202° (*in vacuo*). *Anal.*[34] Calcd for $C_{18}H_{12}Cl_3B$: B, 3.14. Found: B, 3.17. The uv spectrum has the characteristic triphenylboron band at 2871 Å in cyclohexane.

**Deuterium-Substituted Triphenylborons.** These compounds were made from the corresponding deuterated bromobenzenes[35] *via* the Grignard reaction with boron trifluoride etherate.

**Perdeuteriodiphenylboron Chloride.** This compound was made *via* 2-aminoethyl perdeuteriodiphenylborinate and the borinic anhydride.[31]

**Trimesitylboron and Dimesitylboron Fluoride.** These were made by the method of Brown and Dodson.[32]

**Tris(4-*N*,*N*-dimethylaminophenyl)boron.** This compound was made by the reaction of *p*-dimethylaminophenyllithium with boron trifluoride etherate.[36]

**1,2-Dimethoxyethane.** DME solvent for the esr experiments was refluxed over Na for several hours and then distilled through a column packed with glass helices. It was further distilled from $LiAlH_4$ under argon just prior to use.

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(26) A precipitate is formed.

(27) J. K. Brown, D. R. Burnham, and N. A. J. Rojers, *J. Chem. Soc. B*, 1149 (1969).

(28) An unresolved biphenyl anion radical signal has nine lines at 2.76-G intervals. The seven-line signal was strong enough so that two additional lines in the wings would have been easily detected.

(29) The corresponding reaction is known *not* to occur in the case of triphenylboron and Li because it would lead to mixing of aryl groups from differently deuterated triphenylborons.

(30) R. L. Letsinger and I. Skoog, *J. Amer. Chem. Soc.*, 77, 2491 (1955).

(31) E. W. Abel, *J. Chem. Soc.*, 4697 (1956).

(32) H. C. Brown and V. H. Dodson, *J. Amer. Chem. Soc.*, **79**, 2302 (1957).

(33) E. Krause and R. Nitsche, *Ber.*, **55**, 1261 (1922).

(34) Boron analyses were by the procedure of G. B. Watts, Dissertation, London, 1967.

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**Preparation of the Esr Samples.** Solutions of the radicals were prepared in separate glass manifolds each having an esr tube, a frit for filtering the solution, a solvent bulb, a side bulb for the alkali metal, and a connection to the vacuum line that could be sealed off after degassing. Reagents were loaded into the manifold in an inert-atmosphere box. In a typical experiment, about 5 mg of triarylboron was washed into the solvent bulb by about 20 ml of DME and a small amount of alkali metal was placed in the side bulb. The manifold was then stoppered, removed from the inert-atmosphere box, and connected to the vacuum line *via* a vessel containing $LiAlH_4$. After freezing the solution and evacuating to $10^{-6}$ mm, the solvent was distilled onto the $LiAlH_4$ and then back onto the $Ar_3B$ to remove any last traces of water. It was then degassed by freeze–thaw cycles and the sealed manifold removed from the vacuum line. The $Ar_3B$ solution could be brought in or out of contact with the alkali metal by tilting the apparatus. Tilting the apparatus in a different direction caused the solution to flow through the frit and into the esr tube.

**Experiments with Pyridine.** Attempts to trap organoboron intermediates of the cleavage reaction as pyridine or perdeuteriopyridine complexes[37] gave only dipyridyl esr signals.

**Esr Spectra.** The esr spectra were run on Varian E-3 and V4500-10A spectrometers, both using the 9-GHz band.

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