The Nature of Krause's Adducts: The Structure of the 1:1 Adduct of Triphenylborane with Sodium Metal

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ABSTRACT

Triphenylborane (7) undergoes reductive dimerization with sodium metal in diethyl ether solution to form a yellow solid (3) having the empirical composition $Ph_3B \cdot Na \cdot (C_2H_5)_2O$. By ^1H NMR spectroscopy, 3 has now been shown to have the structure depicted. By the
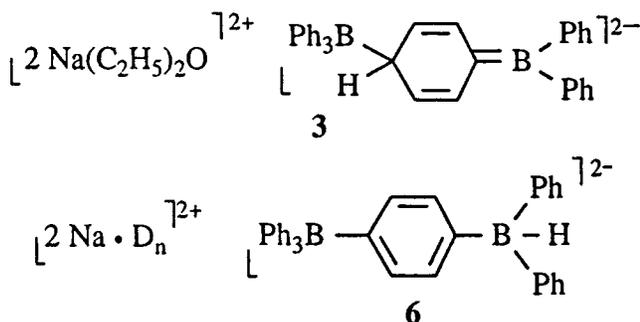
action of heat or strongly donor ethers, 3 rearranges into 6, whose structure was likewise determined by ^1H and ^{11}B NMR spectroscopy and by deuteriodeboronation with DOAc. Prolonged reaction of sodium metal with 7 or with diphenylboron chloride (8) in DME leads to biphenyl precursors, sodium tetraphenylborate (9), and sodium phenylborohydrides. All these results can be reconciled by the formation of the radical-anion 10 from 7 and its subsequent coupling or fragmentation. The coupling of 10 to form 3 and the rearrangement of 3 to yield 6 shows that there is a striking parallel in behavior between the isoelectronic $(Ph_3B \cdot)^-$ and the triphenylmethyl radical $(Ph_3C \cdot)$. In this light, the solution of the "hexa-

phenylethane riddle" is also applicable to the solution of the "hexaphenyldiborate dianion riddle," which was posed by the discovery of Krause's adduct over 68 years ago.

INTRODUCTION

Almost three-quarters of a century ago, the legendary Erich Krause and his students discovered that triarylboranes are capable of forming adducts with alkali metals in a 1:1 or a 1:2 ratio [1]. Such complexes formed solvates with ethers and, despite their salt-like composition, showed only weak electrical conductivity [2]. Cryoscopic molecular mass measurements have demonstrated that certain 1:1 adducts are monomeric [3], while others exist as monomers in equilibrium with oligomers [4]. Trimesitylborane, for example, forms a paramagnetic monomer in a benzene-tetrahydrofuran mixture but exists as a diamagnetic hexamer in benzene [3]. With the advent of ESR spectroscopy, the 1:1 paramagnetic adducts in strongly donor solvents, such as THF and DME, were shown to be radical anions having the unpaired electron spin delocalized over the tricoordinate boron and the ortho- and para-carbons of the aromatic ring [5]. The coupling constants in gauss (which are pro-

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portional to the electron spin densities) for the 1:1 sodium triphenylborane radical anion are shown in structure **1** and the possible spin delocalization suggested by structure **2**:

1
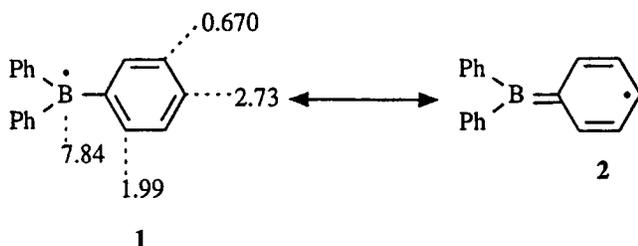
With this added information, it is evident that **1** deserves to be viewed as isoelectronic with Gomberg's triphenylmethyl free radical [6].

However, the properties of the 1:1 adduct of triphenylborane with sodium, as formed in diethyl ether, are much at variance with this structure. As originally described by Krause [1] and reproduced by many others, such as Wittig et al. [7], Chu [8], and ourselves, this adduct (**3**) is bright yellow and definitely diamagnetic and, thus, yields a well-resolved ^{1}H NMR spectrum. It has long been concluded that this adduct must therefore be dimeric [8], but the suggested natures of such a dimer have strained structural credibility. One proposal has been that a boron–boron bond is formed (**4**), much like that originally suggested for the dimerization of the triphenylmethyl radical to hexaphenylethane [9].

$$\left[Ph_3B-BPh_3\right]^{2-} \qquad \left[\begin{array}{l} Ph_3B^- \ Na^+ \\ Na^+ \ ^-BPh_3 \end{array}\right]$$

4   **5**
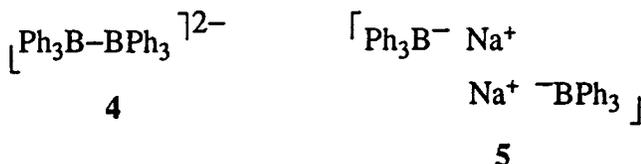
Another explanation proposed spin-pairing through ion-clustering (**5**) [3]. Since neither explanation seemed wholly convincing, we have undertaken a multinuclear NMR investigation of adduct **3**. From this, we find that the structural explanation for the properties of this 1:1 adduct is remarkably similar to the solution of the "hexaphenylethane riddle" [10].*

RESULTS

Structure of Adduct 3

Compound **3** was recrystallized from diethyl ether as yellow-orange needles of empirical composition

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*Note added in proof: Recently, Prof. Roland Köster of the Max-Planck-Institut für Kohlenforschung, Mülheim (Ruhr), Germany, informed us, in a private communication, that he suggested a coupling of the two Ph₃B-units via the boron center of one unit and the o or p-carbon of the second unit (*Houben-Weyl Methoden der Organischen Chemie*, Thieme Verlag, Stuttgart, Vol. XIII, *13b*, 1983, p. 811).

$(C_6H_5)_3B \cdot Na \cdot (C_aH_5)_2O$ that were only slightly soluble in diethyl ether-d_{10}. Such solutions were too dilute to give useful ^{11}B or ^{13}C NMR spectra in the FT-mode within a reasonable number of scans. Attempts to obtain more concentrated solutions by prolonged heating with ether in a sealed tube at 65°C caused **3** to isomerize into colorless **6**, whose ^{1}H and ^{11}B NMR spectra were most revealing (cf. infra).

The ^{1}H NMR spectrum of **3** could be obtained, however, and proved to be most informative. The spectrum can be uniquely interpreted in terms of the assignments

3
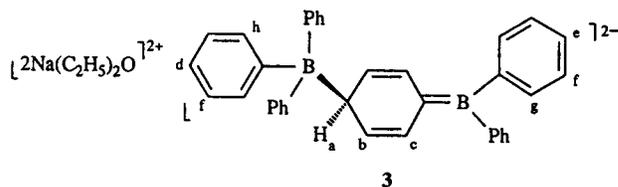
designated in **3**: H_a is the multiplet at 4.03, $2H_b$ is the doublet at 5.39, and $2H_c$ is the doublet of doublets at 6.58 ppm. The $3H_d$ triplet at 6.84 and the $2H_e$ triplet at 6.91 ppm are the *para*-phenyl protons of the three phenyl set to the left and the two phenyl set to the right in **3**. The $10H_f$ multiplet at 6.98 ppm represents the *meta*-phenyl protons, the $4H_g$ doublet of doublets at 7.08 the *ortho*-protons of the two identical phenyl groups, and the $6H_h$ multiplet at 7.41 ppm the *ortho*-protons of the three identical phenyl groups.

The ^{11}B NMR spectrum of the colorless isomer **6** formed by heating **3** displayed a singlet at −6.292 and a doublet at −7.568 ppm. The first signal is at a field very similar to the ^{11}B signal in NaBPh₄ (−6.3 ppm), and the ^{11}B doublet could be decoupled to a singlet from the proton it was bonded to, suggesting the presence of the grouping Ar_3BH^-. These data are consistent with the following isomeric structure for **6**:

6
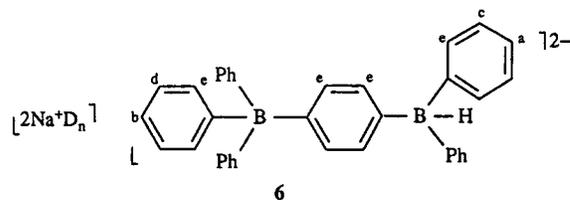
The ^{1}H NMR spectrum of **6** strongly supports this proposed structure: (1) the $2H_a$ triplet at 6.76 and the $3H_b$ triplet at 6.84 ppm stem from the *para*-phenyl protons; (2) the $4H_c$ triplet at 6.91 ppm represents one set of *meta*-phenyl protons and the $6H_d$ triplet at 6.99 ppm the other set of *meta*-phenyl protons; and (3) the $14H_e$ broad multiplet centered at 7.38 ppm arises from all the *ortho*-phenyl protons.

Deuteriodeboronation of **6** with O-deuterioacetic acid would be expected to yield HD (which

it did) and a 5:1 ratio of benzene-d_1 and benzene-d_2. Because the acetic acid used was only 98% isotopically pure and because of a significant kinetic isotope effect, the benzene obtained consisted of 12.9% of benzene-d_0, 74.3% of benzene-d_1, and 12.8% of benzene-d_2. The ratio of benzene-d_1 to benzene-d_2 actually obtained was 5.8:1.0.

Isomeric salt **6**, when produced and studied in diethyl ether, was solvated with one ether per sodium ion (**6**: D_n = $(C_2H_5)_2O$). If, however, it was prepared in ether, the ether was pumped off and then DME was added and any excess DME removed, the resulting salt **6** found to be complexed with two moles of DME per sodium.

Reactions of Triphenylborane with Sodium Metal

The reactions of sodium with either triphenylborane (**7**) directly or with triphenylborane generated from diphenylboron chloride (**8**) proved capable of pursuing a variety of courses. First, the formation of sodium tetraphenylborate (**9**) from **7** suggests that either the radical-anion **10** undergoes cleavage, as depicted in equation 1,

(1)

or that **6** is cleaved by sodium at the phenylene-$BHPh_2$ bond.

Second, the formation of biphenyl among the hydrolysis products from **7** and sodium metal indicates that radical anion **10** can also couple through both para-positions (equation 2) [12]. As with **3** rearranging to **6**, **12** should likewise rearrange to **13**. Intermediate **12**, like **3**, would also be expected to be yellow, and, indeed, we observed in this work that yellow precipitates from 1:1 interactions of **7** and Na in DME did yield biphenyl upon hydrolysis.

(2)

Dimeric anion **13** itself might then add 2 moles of sodium with the formation of a disodium biphenyl derivative; most biphenyl adducts are dark green in color [11]. Such a course of reaction may explain the observation by Chu that triphenylborane forms a dark green 1:2 sodium salt when exposed to sodium amalgam for a prolonged period in THF [8].

Third, the formation of phenylborohydrides from **7** or **8** and sodium metal is consistent with the transitory formation of boron radicals (such as **11** in equation 1), which abstract hydrogen atoms from the ether solvent (S–H, equations 3 and 4).

DISCUSSION

Solution of the Hexaphenyldiborate Dianion Riddle

From the work of Leffler et al. [5], the formation of radical-anion **10** is the first step of the reaction of triphenylborane (**7**) with sodium. Such radical-anions then couple to form diamagnetic dimers. If **10** couples to form a B–B bond (**4**), steric factors should cause **4** to redissociate, just as such factors are presumed to cause any transitory hexaphenylethane to redissociate into triphenylmethyl radicals [6]. The covalent radii of boron (0.80 Å) and sp^3-hybridized carbon (0.77 Å) should make the instability of the E–E bond quite comparable. A sterically more acceptable coupling would be the union of the boron center of **10** with the para-carbon of a second unit of **10**, both centers of which have relatively high electron spin densities. This would nicely explain the formation of **3**. However, the formation of biphenyl as a hydrolysis product from the prolonged action of sodium on triphenylborane strongly indicates that **3** can also redissociate into radical anions **10**, which can couple through two para-carbons (**12** equation 2) and that **12** would be expected to rearrange into **13** by hydride shifts, quite analogous to the isomerization of **3** into **6**. At the present time, it is not known whether such hydride shifts occur intraionically, by a thermally allowed 1,5-suprafacial sigmatropic rearrangement, or whether they take place interionically by an elimination and readdition of sodium hydride to the tricoordinate boron center. There are observations that suggest that this isomerization is not only promoted by heat but also by more strongly donor solvents, such as DME or THF.

It is noteworthy that the behavior of the tri-

phenylborane radical-anions (10) observed here, namely, their coupling to form 3 and the subsequent rearrangement of 3 into 4, exactly parallels the behavior of triphenylmethyl free radicals (14) [10]. Instead of coupling to form hexaphenylethane, as was assumed for almost 70 years, 14 radicals actually couple to form quinoid 15, as was first demonstrated by Lankamp et al. in 1968 [13]. Likewise, 15 undergoes an acid-catalyzed rearrangement to 16, the so-called Ullmann-Borsum hydrocarbon (equation 5).

$$ \tag{5} $$

This striking parallel in the behavior of these isoelectronic radicals 10 and 14 again illustrates how electronically similar tricoordinate boron and trivalent carbon centers are.

A further demonstration that dimer 3 is in equilibrium with radical-anion 10 is the report by Krause that his yellow adduct 3 reacts quantitatively with iodine or with mercury metal with the reformation of triphenylborane (7, eq. 6):

$$ \tag{6} $$

Further Pieces of the Puzzle

The existence of this equilibrium, especially in strongly donor ethers where 3 is more soluble, seems responsible for the complex reactions that can occur between triphenylborane 7 and an excess of sodium metal, such as the alternative coupling of radical-anion 10 leading to biphenyl derivatives (equation 2) and the generation of sodium tetraphenylborate (equation 1) and sodium phenylborohydrides (equations 3 and 4).

Although solutions of radical-anion 10 in DME were found by Leffler and coworkers to be stable for weeks, prolonged contact with Na-K alloy led to decomposition to biphenyl and a minor amount of benzene [5]. The benzene could have arisen from the phenyl anion generated in equation 1, but the biphenyl produced under these conditions could not have stemmed from the coupling depicted in equation 2. Leffler and coworkers showed that both phenyl groups of the biphenyl originated from the same Ph_3B unit. Accordingly, an alternative, acceptable explanation may involve a SET-mechanism with dianion 3 (Scheme 1):

This scheme would bear some resemblance to the cerium ion oxidation of sodium tetraphenylborate to biphenyl; here also, both phenyl groups stem from the same BPh_4 unit [14].

The formation of sodium tetraphenylborate (9) sodium triphenylborohydride (17), and sodium diphenylborohydride (18) from Ph_3B (7) or Ph_2BCl (8) and excess sodium metal could be initiated by fragmentation of the radical-anion (17) (equation 7), in which the more electronegative group departs as the anion:

Alternatively, 17 could form dianion 18, which would cleave into two anions (equation 8). In either event, boryl radical 11 should readily abstract hydrogen atoms from the ether solvent, or diphenylborate(II) anion 19 could abstract protons from ethers by virtue of either its high basicity [15] or its carbene character [16]. The phenylboron hydrides could then be readily converted into borate anions (equations 3 and 4). The precise determination of the mechanistic roles of such postulated boryl radicals, anions, and carbene analogs in organoborane chemistry stands as a formidable puzzle yet to be solved.

EXPERIMENTAL

General Procedures and Starting Materials

All solvent purification and all procedures or reactions involving organoboron compounds were carried out under an atmosphere of anhydrous, oxygen-free nitrogen or argon in accordance with established procedures [17].

Commercially available triphenylborane was recrystallized from anhydrous diethyl ether to yield colorless crystals, mp 147–148°C. Sodium sand was prepared from carefully cleaned pieces of sodium by refluxing them in toluene; the toluene was removed from the cooled suspension and the sodium sand dried in vacuo. The commercial O-deuterioacetic acid employed was of 98% deuterium content.

The GC analyses were performed on a Hewlett-Packard instrument, model 5880A; GC-MS measurements were made with a Hewlett-Packard apparatus, model 5992B; and multinuclear NMR data were collected with a Bruker spectrometer, at 360 MHz.

Reaction of Triphenylborane with Sodium

Although this reaction has been described by various authors after Krause's original detailed report

SCHEME 1

[7,8], we give our own observations with some completeness, because the reaction can take different courses, depending on the solvent, the amount of sodium, the temperature, and the duration of the interaction.

The reaction was conducted in a glass two-chamber apparatus, which was constructed by fusing two 50 mL, pear-shaped flasks to the two arms of a Y-shaped glass tubing and fusing a ground-glass neck bearing a three-way stop to the third aperture of the tubing. The apparatus was first thoroughly purged of air and moisture by alternately evacuating and refilling with argon thrice. Then, in a dry box, one chamber of the apparatus was charged with 290 mg (12.6 mmol) of sodium sand and a glass-sealed stirring bar and the other chamber with 220 g (0.91 mmol) of pure triphenylborane in 20 mL of pure diethyl ether. At room temperature, the apparatus was now tilted to allow the solution of the triphenylborane to flow onto the sodium in the other chamber. Upon magnetic stirring, a bright yellow precipitate formed. After 1 hour, the yellow suspension was carefully decanted from the sodium and poured back into the other chamber. After this yellow solid had settled out, the colorless supernatant layer was decanted off and poured back into the chamber containing the sodium. Restirring again for 1 hour led to the formation of more yellow solid. The processing of transferring the yellow solid to the other chamber and pouring the supernatant layer back onto the sodium was repeated until no more yellow precip-

itate formed. This signals the complete consumption of the triphenylborane. As already reported by Krause [1] and reproduced by others [7,8], this yellow solid is a 1:1 adduct of the composition $(C_6H_5)_3B \cdot Na \cdot (C_2H_5)_2O$.

This product can be recrystallized from ether by sealing the adduct and diethyl ether in a glass ampule (*Caution*: use a glass shield face protection and leather gauntlets in manipulating sealed tubes) and placing it in a water bath at 60°C. The resulting solution is slowly cooled in a Dewar flask containing water at 20°C. On one occasion, yellow octahedral crystals were formed; on other occasions, yellow-orange needles resulted.

These orange needles were only slightly soluble in ether at 25°C, but a solution in diethyl ether-d_{10} did yield a most informative ^{1}H NMR spectrum (no useful ^{13}C or ^{11}B NMR spectra could be obtained): 1.08, q, 12H (J = 7 Hz); 3.33, t, 8H (J = 7 Hz); 4.03, m, 1H; 5.39, br d, 2H (J = 8.6 Hz); 6.58, d of d, 2H (J_1 = 2.0 Hz, J_2 = 10.6 Hz); 6.84, t, 3H (7.0 Hz); 6.91, t, 2H (J = 4.8 Hz); 6.98, m, 10H; 7.08, d of d, 4H (J_1 = 1.5 Hz, J_2 = 8Hz); 7.41, m, 6H.

In attempting to form a more concentrated solution of the orange needles for measuring the ^{13}C and ^{11}B NMR spectra, the compound was heated in a sealed glass ampule at 65°C with pure diethyl ether-d_{10} (cf. supra for Caution). After 2 days at 65°C, the solution had changed in color from orange to yellow and the ^{1}H NMR spectrum began to exhibit new signals and show diminution in the previous

signals. After 4 days at 65°C, a colorless solution resulted, whose ^1H NMR spectrum was very different from that of the orange needles. Clearly, a thermal reaction had taken place and the colorless solid formed was much more soluble in ether: ^1H NMR (diethyl ether-d_{10}): 6.76, disordered t, 2H (J = 7 Hz); 6.84, disordered t, 3H (J = 7 Hz), 6.91, disordered t, 4H (J = 7.1 Hz); 6.99, disordered t, 6H (J = 7 Hz); 7.3–7.45, m, 14H. ^{11}B NMR: −6.292 ppm (upfield from $BF_3 \cdot OEt_2$), s, 1B; −7.568, d, 1B, J_{B-H} = 71 Hz; the latter could be decoupled from the proton to provide a boron singlet.

Deuteriolysis of the 1:1-Adduct of Triphenylborane with Sodium Metal

In accordance with the method described previously, 800 mg of triphenylborane was transformed into its yellow adduct with sodium metal and the adduct was recrystallized from ether. ^1H and ^{11}B NMR spectra showed that the pale yellow solid had been transformed largely into the foregoing colorless isomer.

An ethereal solution of this isomer was heated under argon with 5 mL of CH_3CO_2D (98% isotopically pure), so as to distill off the ether and let the compound be heated in refluxing acetic acid for 2 hours. The volatiles were then distilled, and all such volatiles were collected. The resulting mixture of ether, benzene, and acetic acid was then extracted with aqueous NaOH and dried over $MgSO_4$. The organic layer was carefully concentrated, and the residual ether-benzene layer was analyzed by GC-MS. The benzene was found to consist of 12.9% of benzene-d_0, 74.3% of benzene-d_1, and 12.8% of benzene-d_2. From the amount of benzene-d_0 (12.9%) and the adjusted amount of benzene-d_1 resulting from Ph–B bonds (72.6%), the k_H/k_D ratio for cleaving the Ph–B bonds is calculated at 7.2 (12.9/72.6 · 98/2 = k_H/k_D). From the estimated amount of benzene-d_1 resulting from diborylbenzene units (1.7%) and the amount of benzene-d_2, the k_H/k_D ratio for cleaving the second C–B bond in B–C_6H_4–B units is 6.5 (1.7/12.8 · 98/2 = k_H/k_D).

Related Reactions of Phenylboranes with Sodium Metal. Triphenylborane in (7) Ethers

When triphenylborane was allowed to stir with an excess of sodium sand for 24–36 hours in diethyl ether, the initially formed yellow suspension turned a yellow-green. When 1,2-dimethoxymethane was employed as solvent, a dark green color formed after 24 hours. In both cases, hydrolysis of the reaction mixture after appearance of the green color yielded biphenyl.

Diphenylboron Chloride (8)

The reaction of 15 mmol of pure Ph_2BCl with 30 mmol of sodium sand in 20 mL of 1,2-dimethox-

yethane yielded a golden-colored solution and a quantitative precipitation of NaCl. The separated, clear golden solution evolved dihydrogen gas upon treatment with glacial acetic acid, and benzene could be detected. When the golden solution was allowed to stand under argon, a pale yellow precipitate formed. This precipitate, which did not contain any NaCl, was treated with glacial acetic acid, and the resulting organic products were then washed with aqueous NaOH. Both benzene and biphenyl were identified as hydrolysis products.

A sample of the golden solution, after separation from the yellow precipitate, was reexposed to sodium sand. The solution eventually turned a deep greenish-blue.

The preceding reaction was also monitored by ^{11}B NMR spectroscopy. The appearance of singlet signals at +68.0 and −6.3 ppm verified the formation of triphenylborane and sodium tetraphenylborate, respectively. Peaks at +45, −6.0, and −15.2 ppm could not be assigned.

Finally, the reaction was carried out with an excess of sodium sand in DME with one equivalent of 15-crown-5-ether. After 9 hours of stirring, the supernatant deep blue solution was examined by ^{11}B NMR spectroscopy. The absence of a peak at +68 showed that the triphenylborane had been completely consumed. Prominent peaks were observed at −6.3 ($NaBPh_4$), −7.8, doublet (J = 80Hz, $NaBPh_3H$) and −14.6 ppm, triplet (J = 77 Hz, $NaBPh_2H_2$). Peaks at +5.8 and +2.8 ppm could not be assigned.

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