Arylborane Anions. An Electrochemical Study

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Abstract: The electrochemical reduction of triphenylborane, trimesitylborane, and tri-α-naphthylborane has been investigated in tetrahydrofuran (THF) and 1,2-dimethoxyethane solvents with tetrabutylammonium perchlorate (TBAP) and sodium perchlorate supporting electrolytes. The nature of the electrochemical reduction of the triarylborane varied with the aryl group and was found to be largely in accord with chemical reduction studies. In THF solutions with TBAP, triphenylborane, $(C_6H_5)_3B$ displayed a non-Nernstian, diffusion controlled, one-electron reduction wave ($E_{1/2} = -2.61$ V vs. Ag|Ag$^+$) at a dropping mercury electrode. A second polarographic wave corresponding to the dianionic species, $(C_6H_5)_3B^{2-}$, occurred at $E_{1/2} = -3.57$ V vs. Ag|Ag$^+$. Cyclic voltammograms indicated the $(C_6H_5)_3B\cdot^-$ radical to be quasi-reversible, whereas the dianion $(C_6H_5)_3B^{2-}$ was found to be chemically irreversible. The reduction of $(C_6H_5)_3B^{2-}$ was further complicated by the apparent adduct formation of $(C_6H_5)_3B\cdot^-$ with unreduced triphenylborane. Spectroscopic studies indicated tetraphenylborate and diphenylboronium ions to be primary degradation species following controlled-potential electrolysis, and that oxidation of tetraphenylborate led to the re-formation of triphenylborane. In most systems investigated, an equilibrium between free monoanion triarylborane radicals and diamagnetic ion pair aggregates was observed which was highly dependent on the boron substituent, the solvent, and the gegenion.

Several papers have appeared on the alkali metal reduction of triphenylborane, TPB. The first of these compounds to be reported was the yellow solid $NaBPh_3$, along with the disodium salt Na_2BPh_3.[1] Later, compounds were obtained with other alkali metals.[2] Mono- and disodium salts of triphenyl-,[1,3] tri-α-naphthyl-,[4-9] tri-β-naphthyl-,[10] and trimesitylborane[11-14] were investigated.

Although the BPh_3^- anion might be expected to be a free radical isoelectronic with the triphenylmethyl radical, several electron spin resonance and magnetic susceptibility studies indicated that the solid monosodium salt and its tetrahydrofuran solution were diamagnetic.[3,7] Molecular weight determinations and conductance measurements showed that the salt formed ion pairs leading to dimerization with spin pairing in solution. The extent of the association was found to depend both on solvent and the nature of the aryl group. In light of recent advances in the theories of the structure of ion pairs,[15] there are strong indications that the counteranion may also play a major role in the stabilization of these anion radicals, as the more bulky ions such as the tetraphenylstibonium cation tend to promote dissociation of ion pairs into free ions. However, the metathesis of tetraphenylstibonium triphenylborane from tetraphenylstibonium hydroxide and the sodium addition compound of triphenylborane unexpectedly led to the formation of a diamagnetic compound.[3]

Although previous work showed $BPh_3\cdot^-$ not to exist as a free radical in ether solvents, Leffler and coworkers recently reported[16] the electron spin resonance of BPh_3^- in 1,2-dimethoxyethane (glyme) with Na-K counteranions. They found the $BPh_3\cdot^-$ radical to be stable for weeks under air-free conditions. In addition an electron resonance study of tris(p-deuteriophenyl)-, tris(3,5-deuteriophenyl)-, tris(p-chlorophenyl)-, tris(p-dimethylaminophenyl)-, and tris(p-tolyl)borane was reported.

In order to further clarify the reduction mechanism of triphenylborane and to determine the exact nature of the solvent as well as the role of the gegenion in radical stabilization, an electrochemical investigation of triphenyl-, tri-α-napthyl-, and trimesitylborane is reported.

Experimental Section

All chemical and electrochemical procedures requiring rigorous exclusion of water and oxygen were performed using standard vacuum line and drybox techniques.[17] Working vacuums were maintained at 10^{-4} to 10^{-6} Torr. The helium-filled drybox was equipped with a recirculating system in which water and oxygen were removed, respectively, by molecular sieves and a copper catalyst in pellet form supplied by BASF Chemicals, Inc.

Instrumental. Electrochemical experiments were made using a Wenking Model 66TS10 potentiostat and a Chemtrix Type 800-A waveform generator in conjunction with a Plotamatic Model 715 x–y recorder or, for fast techniques, a Tektronix Type 564B storage oscilloscope. Some measurements were also performed on a Princeton Applied Research Corp. (PAR) electrochemical system, Model 170. A Varian Associates NMR spectrometer Model XL-100-15 was used for ^{11}B spectra. Proton NMR spectra were recorded on the same instrument or on a Varian A-60. EPR spectra were obtained using a Varian Associates Model V4500-10A spectrometer. Raman spectra were recorded on a Jarrell-Ash Model 25-500 lasar Raman, and ir spectra were recorded on a Perkin-Elmer Model 457 grating spectrophotometer. Uv-visible spectra were obtained on a Cary 17 spectrophotometer.

Electrochemical Measurements. The cell used for obtaining electrochemical measurements was of a three-electrode configuration and was vacuum tight allowing for rigorous exclusion of oxygen and water.[18] In addition to providing a system free of contamination, the cell is particularly well adapted to the use of solvents with low dielectric constant such as ethers. Polarograms were run using a 6–12-sec drop capillary while cyclic voltammograms utilized a platinum bead electrode. The design used in the construction of the dropping mercury, platinum bead electrode, and reference electrodes and the routine operation of the cell have been previously described.[18] Unless otherwise specified, E_p values for cyclic voltammograms of triarylboranes were performed at ambient temperature and are reported for sweep rates of 275 mV/sec. Assignments of E_p values for some anodic peaks may be approximate as their values varied upon concentration change. This is particularly true in cyclic voltammograms of triarylboranes in which sodium perchlorate was used as the supporting electrolyte as these solutions demonstrated very irreversible electron transfer characteristics. Controlled-potential coulometry was done at a mercury pool or platinum gauze electrode with a copper wire auxiliary electrode, sealed from the working solution by a glass sleeve with a glass frit. A platinum bead electrode was used to obtain cyclic voltammograms of electrolyzed solutions. The Ag wire|0.1 M Ag$^+$ tetrahydrofuran reference electrode was measured to be +0.49 V vs. SCE. All potentials recorded, however, were vs. the Ag|$AgClO_4$ electrode.

Electrochemical measurements on chemically reduced triarylboranes were obtained by syringing tetrahydrofuran solutions of the chemically reduced species into the electrochemical cell through an air-tight rubber septum cap. However, because of the extreme reactivity of chemically reduced triphenylborane solutions, it was necessary to make electrochemical measurements on samples of

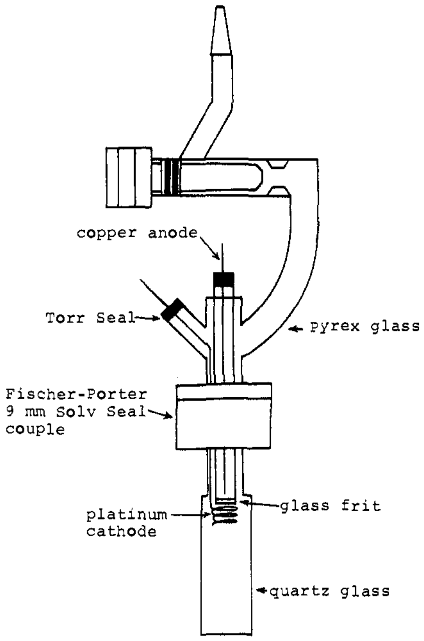


Figure 1. Uv-visible cell for electrochemical generation.

triphenylborane reduced directly in the electrochemical cell using sodium amalgam both as the reducing agent and as the auxiliary electrode.

Tetrahydrofuran, THF (Baker spectroscopic grade), and 1,2-dimethoxyethane, glyme (Matheson Coleman and Bell, reagent grade), were used in all chemical and electrochemical experiments. Water and oxygen were removed from the solvents by storage over Na-K alloy in a grease-free vessel similar to the one previously described.[18] The vessel could then be attached to the vacuum line, the solvent degassed and vapor transferred. To ensure removal of peroxides from the solvents, a number of experiments were performed with THF and glyme which was first distilled from $LiAlH_4$ and then stored over Na-K alloy. No presence of peroxides was noted. Complete removal of O_2 and H_2O from the solvent was determined by the formation of a persistent blue color indicating the presence of solvated electrons.

Tetrabutylammonium perchlorate and sodium perchlorate were used as supporting electrolytes in both solvents. The predried tetrabutylammonium perchlorate, TBAP (Southwestern Analytical Inc., Austin, Texas, polarographic grade), was further dried in vacuo in small quantities (~3 g) at 100° for 24 hr, and once dried was stored in the same vessel under vacuum. Sodium perchlorate was prepared from reagent grade NaOH and $HClO_4$ and recrystallized from water three times and was dried in the same manner as the TBAP. Supporting electrolyte solutions were prepared by vapor transferring an appropriate amount of solvent to the ampoule containing the supporting electrolyte to attain the desired concentration (0.2 *M*).

Uv-Visible and Ir Measurements. Uv-visible spectra of electrochemically generated reduction products and degradation species were obtained either by rapid transfer from the electrochemical cell to an air-tight quartz cell equipped with a high-vacuum Teflon stopcock for removal from the working cell or by direct electrochemical generation in a quartz cell. The latter method required the use of a specially designed two-electrode evacuable quartz cell (Figure 1). The cell consisted essentially of two parts separated by a Penton Coupling. The lower half of the cell was quartz, with the optical path portion constructed from 1-cm square quartz tubing. The upper portion was made entirely of Pyrex glass. It was fitted at the top with a standard joint for attachment to the vacuum line. Below the joint was a Teflon stopcock thus making the cell transferable. The anode (Cu wire) and the cathode (Pt wire) were inserted from the top of the cell and were sealed vacuum-tight by use of an epoxy resin, Torr Seal (Varian Associates). The anode was contained in a fritted-glass sleeve to prevent mixing of oxidized material with the reduced species. The design of the cell allowed for easy sample loading and freezing of the lower section to liquid nitrogen temperature for rapid vapor transfer. For a run, the cell was loaded in the drybox with an unmeasured amount of predried supporting electrolyte (~0.1 g) and substrate (~0.01 g). The cell was stoppered and transferred to the vacuum line and was evacuated to 10^{-5} Torr. Solvent was distilled from the Na-K solvent storage vessel into the cell. To minimize air leakage into the cell, the cell was warmed to room temperature and was brought to 1 atm by the addition of ultra-pure argon. Typical reductions were made by applying 15 V across the electrodes while maintaining a current of about 100 μA. In both uv-visible and ESR measurements of chemically reduced triarylboranes, freshly distilled sodium or sodium-potassium alloy was used as a reducing agent.

ESR Measurements. ESR measurements were also made by rapid transfer of reduced species from the electrochemical cell to an isolable attached ESR cell or by electrochemical generation in a specially designed two-electrode ESR cell. The cell design was basically that of West and Glass[19] with the added advantages that the cell was evacuable and could be sealed to ensure anaerobic conditions indefinitely. Also, the lower portion of the cell was made in such a manner that the metal-to-Pyrex glass seal could withstand liquid nitrogen temperature. This was achieved by using thin (0.005 mm) tungsten wire, treated with sodium nitrite, as a conductor to the larger gold or platinum wire (1 mm diameter) cathode. The ESR cells were 2 mm i.d. As with the two-electrode uv-visible cell, the ESR cell was loaded in the drybox, capped, and quickly transferred to the vacuum line. After solvent transfer, the cell was sealed at the glass constriction. During electrolysis the voltage across the copper-gold leads was held at about 50 V with a current reading of around 75 μA. These parameters, as well as those used in the two-electrode uv-visible cell, varied depending upon concentration of electroactive material and distance between electrodes. For calibration purposes, all ESR measurements were made with Fremy's salt as a reference.

Preparations. (**a**) **Triphenylborane,** $(C_6H_5)_3B$, was prepared by the method of Krause and Nitsche.[20] Bromobenzene 78 g (0.5 mol) was added dropwise to 12 g (0.5 mol) of magnesium turnings in 250 ml of dry diethyl ether. After completion of reaction (3 hr), 64 ml (0.5 mol) of BF_3-etherate was slowly added to the reaction mixture (~2 hr). The solution was then decanted and the solvent evaporated under N_2 atmosphere. The remaining solid was dried in vacuo at elevated temperature (~50°) and then distilled at 250–300°. The solid distillate was recrystallized from ether and stored in a drybox. The solid was identified by its melting point and NMR spectrum. However, in most chemical and electrochemical experiments, triphenylborane (mp 144–149°) obtained commercially from Alfa Products was used. Both unpurified TPB and samples crystallized from anhydrous ether produced identical electrochemical data.

(**b**) **Tri-α-naphthylborane, $(C_{10}H_7)_3B$.** The procedure for preparation of tri-α-naphthylborane was essentially that of Brown and Sujishi.[21] Aldrich Analyzed 1-bromonaphthalene was used to form the magnesium Grignard reagent. The tri-α-naphthylborane was recrystallized from warm benzene. The benzene of crystallization was removed by heating in vacuo at 140°. The remaining solid melted at 204–205° in an evacuated ampule.

(**c**) **Trimesitylborane, $(C_9H_{11})_3B$.** Trimesitylborane (mp 191–192°) obtained from Willow Brook Labs., Inc., required no further purification.

(**d**) **Tetraphenylboron Sodium, $(C_6H_5)_4BNa$.** Aldrich Analyzed tetraphenylboron sodium was used in electrochemical studies of the oxidation of authentic samples of the tetraphenylborate ion.

(**e**) **Diphenylboron Bromide, $(C_6H_5)_2BBr$,** was commercially obtained from Alfa Products and used without further purification.

Results

Triphenylborane, TPB. a. THF and Glyme Solvents with TBAP Supporting Electrolyte. Polarographic reduction with tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte in tetrahydrofuran (THF) solvent produced a diffusion-controlled, one-electron, non-Nernstian reduction wave ($E_{1/2} = -2.61$ V vs. Ag|Ag$^+$). A plot of $\log i/(i_d - i)$ vs. V yielded a slope of 120 mV. A second polarographic wave occurred at $E_{1/2} = -3.57$ V. Cyclic voltammetry at a platinum bead with TBAP supporting electrolyte showed similar electrochemical behavior in both THF and glyme solvents. During the cathode sweep the first wave occurred

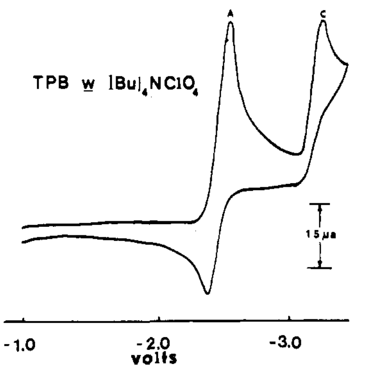


Figure 2. Cyclic voltammogram (275 mV/sec) of triphenylborane (2.1 $\times$ 10^{-3} *M*) in THF with TBAP supporting electrolyte.

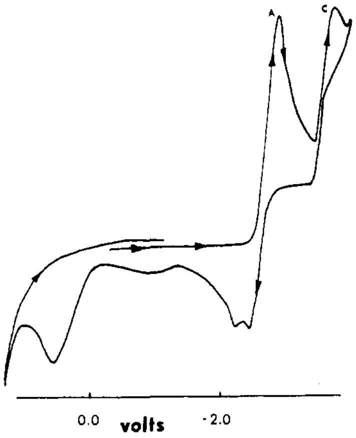


Figure 3. Cyclic voltammogram (275 mV/sec) of a glyme solution of triphenylborane in relatively high concentration (7.0 $\times$ 10^{-3} *M*) with TBAP supporting electrolyte.

at E_p = -2.7 V (A in Figures 2-5). This wave was chemically quasi-reversible as is indicated by the data in Table I which compares the cathodic and anodic peak heights vs. time. The first wave was followed by a transient wave occurring at -3.0 V (B in Figure 4). This wave was clearly evident only if a cyclic voltammogram was taken after partial coulometry (Figure 4). A third cathode wave which was totally irreversible appeared at -3.5 V (C in Figures 2-4). Coulometric determinations performed at -2.9 V yielded *n* values between 0.7 and 0.9. Because of the close proximity of the reduction wave at -3.5 V with the solvent cut-off potential, a quantitative relation between the peak heights of the reduction waves at -2.7 and -3.5 V could not be established although it appeared the peak height ratio (1:1) remained unchanged on varying the cathodic scan rates from 1 to 25 V/sec. Steady-state cyclic voltammograms (1-25 V/sec) resulted in a continued dramatic decrease in the peak height of the reduction of TPB (ca. one-fourth original height at 25 V/sec). Potential reversal following the cathodic sweep indicated four anodic waves at -2.5, -2.2, -0.7, and $+0.5$ V (Figure 3). The wave at -2.2 V was more prevalent at higher concentrations ($\sim 5 \times 10^{-3}$ *M*, Figure 3) or at lower temperatures (Figure 5). After exhaustive controlled-potential reduction of TPB in THF at -2.9 V, a cathodic scan revealed no reduced TPB remained in the electrochemical cell. The sequential anodic scan also indicated little of the species corresponding to wave C remaining, but again showed the presence of oxidation waves at -0.7 and $+0.5$ V. Repeated reduction scans demonstrated the re-formation of TPB after oxidation at $+0.5$ V. In situ electrogeneration of the TPB anion species in THF in the ESR cavity showed a 1:1:1:1 quartet (^{11}B, I = $^3\!/_2$) with a splitting of 9.8 G, containing some unresolved fine structure (Figure 6). The signal readily decayed after discontinuing electrogeneration. Similar ESR spectra were also obtained by controlled-potential coulometry in the electrochemical cell, followed by rapid transfer to an attached ESR cell. Such a procedure, however, was difficult and most often resulted in loss of the blue paramagnetic solution and replacement by a faint yellow-brown diamagnetic solution. If undisturbed, the light-blue (750 nm) solutions remained over at least a 24-hr period. Low temperatures (to $-50°$) had no effect on the splitting constant of the quartet.

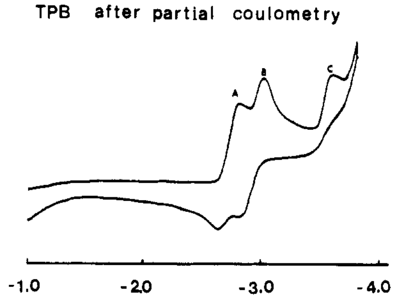


Figure 4. Cyclic voltammogram (275 mV/sec) of triphenylborane (2.1 $\times$ 10^{-3} *M*) in THF after partial coulometry at -2.9 V.

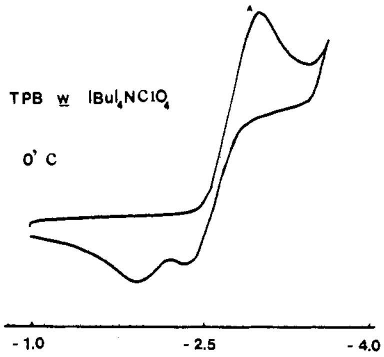


Figure 5. Cyclic voltammogram (275 mV/sec) at 0° of triphenylborane (2.1 $\times$ 10^{-3} *M*) in THF with TBAP supporting electrolyte.

Electrochemical measurements on recently prepared solutions of sodium-reduced TPB in THF solvent with TBAP supporting electrolyte initially exhibited two oxidation waves at -2.5 and -2.2 V. An anodic sweep following oxidation of the chemically reduced solution showed the re-formation of TPB, as evidenced by its initial reduction wave at -2.7 V.

b. THF Solvent with NaClO$_4$ Supporting Electrolyte. In THF solutions (Figure 7) with sodium perchlorate, TPB exhibited a chemically irreversible, one-electron reduction wave (-3.0 V) at a platinum bead electrode (275 mV/sec). No reduction wave corresponding to wave C in Figures 2-4 was evident due to the limited potential range of the sodium cation. A transient cathodic peak (-3.3 V), corresponding to wave B in Figure 4, however, was noted in cyclic voltammograms of solutions which had undergone partial coulometry. After current reversal following a slow cathodic scan (<1 V/sec), no anodic peak was evident corresponding to the reversible couple of wave A. An anodic wave due to oxidation of a secondary electrode product occurred at -1.9 V. At faster scan rates the decomposition of A could be partially preempted as was evidenced by the formation of a small anodic wave forming the oxidation portion of the oxidation-reduction couple.

Following exhaustive controlled-potential electrolysis the working cell solution was a bright yellow color. Repeated attempts to transfer this solution to attached uv-visible cells

Table I. Cyclic Voltammetric Data for the Reduction of Triphenylborane, TPB[a]

Sweep rate (mV/sec)	39	55	92	275	393	917	2750	3438	5500	13750
i_{pa}/i_{pc}	0.35	0.38	0.45	0.44	0.43	0.56	0.71	0.71	0.87	0.96

[a] The solution was $2.1 \times 10^{-3} M$ in TPB with TBAP supporting electrolyte in THF solvent. The data are for cyclic voltammograms of the wave with the cathodic couple at −2.7 V, wave A, Figure 2.

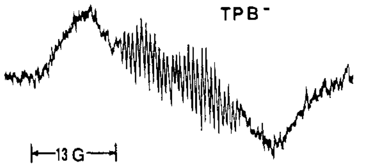


Figure 6. ESR spectrum of electrochemically generated triphenylborane anion radical in THF with TBAP supporting electrolyte. The radical was generated in situ in the spectrometer cavity at ambient temperature.

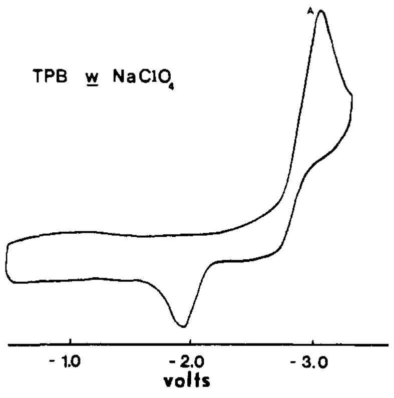


Figure 7. Cyclic voltammogram (275 mV/sec) of triphenylborane ($2.1 \times 10^{-3} M$) in THF with sodium perchlorate supporting electrolyte.

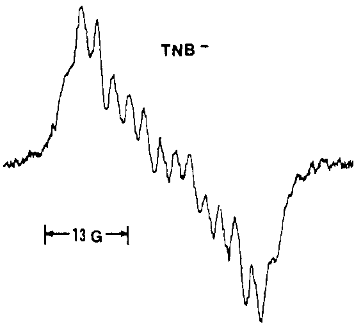


Figure 8. ESR spectrum of electrochemically generated tri-α-naphthylborane anion radical in THF with TBAP supporting electrolyte. The radical was generated at ambient temperature in situ.

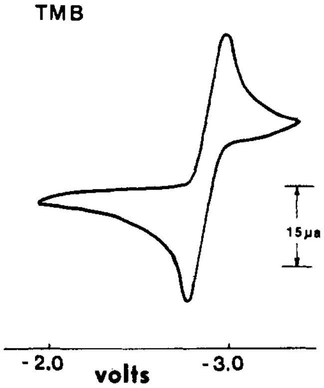


Figure 9. Steady-state cyclic voltammogram (275 mV/sec) of trimesitylborane ($1.5 \times 10^{-3} M$) in THF with TBAP supporting electrolyte.

resulted in loss of the bright yellow color and replacement with a much lighter yellow-brown diamagnetic solution. Uv-visible spectra of the latter solution showed peaks at 274, 276, and 333 nm. Electrolysis in a two-electrode uv-visible cell showed the former solution absorbed at 410 nm. Chemical reductions of triphenylborane in THF by sodium mirror, potassium-sodium amalgam as well as electrolysis in a two-electrode ESR cell with sodium perchlorate failed to give a detectable ESR signal attributable to a boron radical species; prolonged contact of TPB with chemical reductants produced biphenyl anion radicals.

c. Glyme Solvent with NaClO$_4$ Supporting Electrolyte. In glyme solutions with sodium perchlorate, cyclic voltammograms showed triphenylborane to reduce at $E_p = -2.9$ V. As in THF solutions with NaClO$_4$ supporting electrolyte, no second electron transfer was observed. Unlike THF solutions, however, an anodic scan at all scan rates showed two oxidation waves: one corresponding to the oxidation half of the reversible couple and the other at −2.1 V. Electroreductions in a two-electrode uv-visible cell produced species absorbing at ~410, ~700, and ~760 nm. Similar ESR studies identified a boron radical species with a splitting of ~10 G.

Tri-α-naphthylborane, TNB. In THF and glyme solvents with TBAP, the chemistry of tri-α-naphthylborane was similar to that of the reduction of triphenylborane. From cyclic voltammograms, TNB showed an initial one-electron, quasi-reversible electron transfer step at −2.7 V. The monoanion formed in this step was identified by ESR (Figure 8) and uv-visible spectra (445, 470, 635 nm) recorded on electrolyzed solutions. ESR spectra of the tri-α-naphthylborane anion were identical when sodium or tetrabutylammonium cations were present as counterions. A second chemically irreversible electron transfer step occurred at −3.5 V. Unlike TPB, TNB did not show a transient peak at (−3.0 V) after partial coulometry. In addition to the absence of a reduction wave at −3.0 V, the oxidation wave at ca. −2.2 V was also lacking.

Cyclic voltammograms of tri-α-naphthylborane in THF with sodium perchlorate as a supporting electrolyte showed a reduction wave at −3.2 V. The reduction peak is only partially reversible due in part to the formation of a species oxidized at −1.9 V.

Trimesitylborane, TMB. As expected, we found that trimesitylborane in THF and glyme solvents with TBAP supporting electrolyte exhibited a reversible, one-electron reduction ($E_p = -3.0$ V) at a platinum electrode (Figure 9). ESR spectra of chemically and electrogenerated "free" radicals (Figure 10) confirmed earlier work. No other anodic or cathodic waves were present. Trimesitylborane in THF with NaClO$_4$ reduced at a platinum bead and displayed two anodic waves: one was the oxidation portion of the reduction-oxidation couple (−2.8 V), and another oxidation wave was at −1.8 V.

Discussion

Triphenylborane. The first anodic wave during the electroreduction of TPB at either a Pt bead or a dropping mercury electrode in glyme or THF solvent with TBAP or

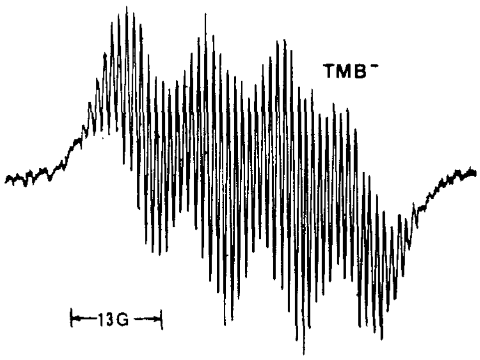


Figure 10. ESR spectrum of electrochemically generated trimesitylborane anion radical in THF with TBAP supporting electrolyte.

$NaClO_4$ supporting electrolyte corresponds to a one-electron transfer forming the $TPB\cdot^-$ anion radical.

$$TPB \xrightarrow{1e^-} TPB\cdot^-$$

This electron transfer step is assigned to wave A in Figures 2-5. Coulometric determinations yielded *n* values from 0.7 to 0.9, indicating reaction of some unreduced TPB with electrode products; however, the peak height of the first electron transfer to TPB is consistent with the peak height of the one-electron electroreduction of trimesitylborane, TMB (vide infra).

In THF or glyme solvent with TBAP supporting electrolyte the reduction to TPB is chemically quasi-reversible, as is indicated by the anodic wave at −2.5 V in Figures 2-4 and Table I. An ESR spectrum of the radical generated by controlled-potential electrolysis in the three-electrode electrochemical cell or in situ in the cavity of the spectrometer showed a 1:1:1:1 quartet with a coupling of 9.8 G arising from the ^{11}B nucleus (Figure 6). The extremely reactive blue radical exhibited a visible absorption band at 750 nm.

Although the electrochemical reduction of TPB with TBAP as a gegenion approximates the chemical reduction studies, perhaps the most compatible and illuminating electrochemical investigations involved the use of sodium as a counteranion. As in chemical reduction studies, such electrochemical examinations of the reduction of triarylboranes are complicated by the formation of ion pairs between the triarylborane anion and the sodium cation with the resultant association of these ion pairs into diamagnetic dimers or larger aggregates.

Thus in THF with $NaClO_4$ as the supporting electrolyte, the one-electron reduction of TPB to $TPB\cdot^-$ was totally irreversible at scan rates <1 V/sec. An oxidation wave, however, occurred at −1.9 V (Figure 7). This wave is assigned to the oxidation of a dimeric dianionic (or larger diamagnetic aggregate) ion pair. The assignment of this wave to a dimeric ion cluster of $TPB\cdot^-$ is made on the basis of the postulates of previous chemical reduction studies.[3,7] The size of the ion pair cluster, whether dimeric or larger, is unimportant to the argument, however. The chemical reduction of TPB in THF with Na has been reported to form $(Na^+TPB^-)_n$ ion pair clusters which exhibited an absorption at 410 nm. Consistent with the datum was an absorption at the same wavelength produced by electrolyzed solutions of TPB with $NaClO_4$ supporting electrolyte. Further confirming the absence of any paramagnetic "free" $TPB\cdot^-$ was the failure to find any ESR signal for THF solutions of reduced TPB where sodium (or potassium) was the counterion, whether chemically or electrochemically generated (see Experimental Section). Also supporting the assignment of these two oxidation waves to "free" and ion paired $TPB\cdot^-$ was the electrochemical behavior of a solution of sodium reduced TPB in THF with TBAP which exhibited the same two waves.

In glyme solutions with $NaClO_4$, cyclic voltammograms showed the reduction of TPB to be quasi-reversible, exhibiting two oxidation waves: one due to the oxidation of the monomeric anion radical and the other at −2.1 V corresponding to the oxidation of the ion pair species. The appearance of the monomeric triphenylborane anion species is apparently the result of the chelating ability of glyme[22] as compared to THF to more effectively solvate the sodium ion, thus preventing ion pair formation with triphenylborane anion radical and resultant dimerization through coulombic attraction of ion pairs. Electroreductions in a two-electrode uv-visible cell produced species absorbing at ~410 nm, compatible with an assignment to the aggregate species, and at 760 nm, compatible with an assignment to a monomeric anion radical. Similar ESR studies identified a boron radical species with a splitting of ~10 g. The appearance of the monomeric triphenylborane anion radical is in agreement with a previous chemical reduction investigation by Leffler et al.[16]

A wave corresponding to the oxidation of an ion pair cluster at −2.2 V was also observed in THF solvent with TBAP supporting electrolyte; the wave was relatively much smaller than when $NaClO_4$ was the supporting electrolyte, however. The wave was more prevalent when the concentration of TPB was high, $\sim 5 \times 10^{-3}$ *M* (Figure 3), or at lower temperatures (Figure 5). Although it was not possible to obtain a uv-visible spectrum of the ion pair aggregate formed by controlled-potential reduction at °0, a rust-red color eminated from around the platinum gauze electrode which turned blue as it dissipated into the bulk of the solution, thus indicating that fōrmation of the ion pair may only occur in regions of high $TPB\cdot^-$ concentration approximately in the vicinity of the electrode. A discussion of the forces involving the equilibrium between "free" $TPB\cdot^-$ anions and ion pair clusters will be made after the electroreduction of TMB and TNB has been described.

A transient reversible wave (labeled B in Figure 4) appeared when a cyclic voltametric sweep was made after partial coulometry on THF solutions of TPB with TBAP supporting electrolyte. This wave is assigned to the reduction of an adduct formed

$$Ph_3B\cdot^- + Ph_3B \rightleftarrows Ph_3B\text{-}BPh_3\cdot^- \xrightarrow{+1e^-} Ph_3BBPh_3{}^{2-}$$

by the reaction of a TPB anion radical with unreduced triphenylborane, resulting in the formation of a boron-boron bond. Chemical reduction studies had led to postulations of such adduct formation as evidenced by disappearance of the anion solution color upon addition of unreduced TPB.[5] Additions of TPB to blue solutions of electrogenerated $TPB\cdot^-$ resulted in similar color discharge, but no significant effect could be ascertained by follow-up cyclic voltammograms. Adduct formation followed by decomposition is also consistent with the before-mentioned low coulometric values, as the concentration of triphenylborane would be effectively decreased. Although such adduct formation is not substantiated by ESR spectra of electrochemically generated TPB anion radicals,[3] Leffler et al.[16] found an intermittently occurring four-then-seven line ESR signal from the Na-K reduction of tris(*p*-dimethylaminophenyl)borane in glyme. A similar 1:2:3:4:3:2:1 ESR pattern was also observed following reductions of diphenylchloroborane by Na-K in glyme.[23] Such reductions of diarylchloroboranes are known to give radical signals due to the triarylborane anions[13] which could result in adduct formation with unreduced substrate. Leffler, however, assumed the seven line spectra to be caused by the reduction of in situ formed tetraaryldiborane(4). TPB in THF or glyme solvent with $NaClO_4$ also exhibited a reversible reduction wave after partial coulometry corresponding to the reduction of a $Ph_3B{-}BPh_3{\cdot}^-$ species.

A third cathodic wave (labeled C in Figures 2–4) appeared during the reduction of TPB in THF solvent with TBAP which was totally irreversible, and is consonant with the one-electron reduction of Ph_3B^-

$$Ph_3B{\cdot}^- \xrightarrow{1e^-} Ph_3B^{2-} \xrightarrow{\text{fast}} \text{(decomposition products)}$$

Formation of a disodium salt of triphenylborane from the sodium reduction of triphenylborane has been previously reported.[1,3] Steady-state cyclic voltammograms at varying scan rates showed that the lack of chemical reversibility of TPB^{2-} does not result from a simple electron transfer to unreduced TPB,

$$TPB^{2-} + TPB \not\rightleftharpoons 2TPB{\cdot}^-$$

The possibility that wave C could result from the reduction of a possible decomposition product of $TPB{\cdot}^-$, namely, tetraphenyldiborane(4), is unlikely in that at scan rates where the reduction of TPB is totally chemically reversible (1–25 V/sec), the formation of tetraphenyldiborane(4) should be insignificant and its reduction peak should not be observed. Although the isolation of tetraphenyldiborane(4) has not been reported, one would expect the boron atoms to be highly electron deficient and thus easily reducible. Biphenyl is also reduced at −3.5 V, but addition of biphenyl to solutions of TPB showed biphenyl to exhibit a reversible reduction wave at −3.5 V. Due to the limited potential range of the sodium cation, no reduction wave corresponding to the formation of TPB^{2-} was evident in either THF or glyme solvent with $NaClO_4$.

Potential reversal following a cathodic sweep of THF or glyme solutions of TPB with TBAP supporting electrolyte indicated four waves at −2.5, −2.2, −0.7, and +0.5 V (Figure 3). As discussed above, the wave at −2.2 V corresponds to the oxidation of the ion pair cluster of $TPB{\cdot}^-$. (The reduction–oxidation couple of the adduct $TPB{-}TPB{\cdot}^-$ was only observed after partial coulometry, vide supra). After controlled-potential coulometry of the solutions, only the oxidation waves at −0.7 and +0.5 V were present. Repeated reduction scans demonstrated the re-formation of TPB after oxidation at +0.5 V. The peak at +0.5 V is ascribed to the oxidation of tetraphenylborate in THF, as both reduced solutions of TPB and authentic Ph_4B^- solutions exhibited the same electrochemical behavior, namely, the occurrence of an oxidation wave at +0.5 V with the product of that oxidation being the re-formation of TPB. Further evidence for the existence of Ph_4B^- in electrolyzed solutions of TPB arose from uv-visible spectra of such solutions showing Ph_4B^- to be one of the primary absorbing species (274 and 276 nm), as well as the blue $TPB{\cdot}^-$ radical (750 nm) and a third species (absorbing at 333 nm). It is interesting to note that TPB is formed (at least indirectly) by the oxidation of BPh_4^- in an essentially water-free aprotic solvent, although it has been reported that TPB formation from the electrochemical oxidation of BPh_4^- resulted from the protonation of Ph_4B^-, with the proton source originating from the reaction of Ph_2B^+ (believed to be a primary oxidation product) with water.[24]

The anodic wave occurring at −0.7 V is tentatively assigned to a species similar to the diphenylboronium ion (Ph_2B^+) as described by Ramsey[25] and others.[26] There has been considerable controversy in the literature regarding the nature of the diphenylboronium ion.[25] Early investigators proposed a divalent cation Ph_2B^+, while later studies claimed the boron atom to be formally negative with the solvent molecules providing the extra electrons, i.e., $[Ph_2B^- (\text{solvent}^+)_2]^+$. However, regardless of the interpretation of the formal charge on the boron atom, all studies have assigned an absorption at ∼333 nm to the diphenylboronium ion. Certainly the origin of diphenylboronium anion is more easily understood in our system than would be a cation.

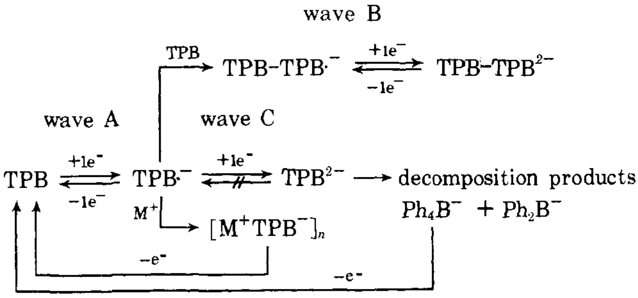
$$2Ph_3B^{2-} \rightarrow Ph_4B^- + Ph_2B^-$$

In this case, a boron anion is stabilized by two solvent-derived cations. Because of difficulties in synthesizing diphenylboronium perchlorate in THF (addition of $AgClO_4$ to Ph_2BBr resulted in the precipitation of AgBr and polymerization of the solvent), the electrochemistry of that species has not been definitive, but cursory experiments indicate a weak oxidation wave occurring at about −0.7 V. Uv-visible spectra of electrolyzed solutions of TPB confirmed the presence of the diphenylboronium ion (333 nm). Upon brief air exposure of the electrolyzed solutions, the spectra of phenylboric oxide was obtained, while the tetraphenylborate and diphenylboronium ion peaks disappeared. The fate of the tetraphenylborate and diphenylboronium ions is, as yet, undetermined; however, despite lack of Ph_3B formation from the metathesis of Ph_2BBr with $NaBPh_4$, there is some indication that as the electrolyzed solutions were exposed to air, BPh_3 was regenerated and then quickly oxidized to phenylboric oxide.

The uv-visible spectrum of a solution of exhaustively reduced TPB in THF with $NaClO_4$ which had been transferred from the electrochemical cell also exhibited absorptions at 274 and 276 nm $(Ph_4B)^-$, and at 333 nm $(Ph_2B)^-$.

Bearing in mind the dependence of many of the equilibria on solvent and gegenion (supporting electrolyte), the TPB system can be diagrammatically summarized as shown in Scheme I.

Scheme I



Tri-α-naphthylborane, TNB. In THF and glyme solvents with TBAP the electrochemistry of tri-α-naphthylborane was similar to that of the reduction of triphenylborane. From cyclic voltammograms, TNB showed an initial one-electron, quasi-reversible electron transfer step at −2.7 V. The monoanion formed in this step has been identified by ESR[9] (Figure 8) and uv-visible spectra[7] (445, 470, 635 nm) recorded on electrolyzed solutions to be only that of the "free" radical $(\alpha\text{-}C_{10}H_7)_3B{\cdot}^-$, consistent with chemical reduction studies. ESR spectra of $TNB{\cdot}^-$ anion are identical when sodium or tetrabutylammonium cations are present indicating no splitting by the cation from formation of simple contact ion pairs. A second electron transfer step (−3.5 V) corresponds to the formation of the dianion followed by rapid decomposition. Unlike TPB, TNB did not show a transient peak at ca. −3.0 V after partial coulometry. Perhaps due to steric crowding of the naphthyl groups, adduct formation of the type $TNB{-}TNB{\cdot}^-$ was inhibited. In addition to the absence of a reduction peak at −3.0 V, the oxidation peak ascribed to the ion pair cluster (~2.2 V) was also lacking. Again this may be attributed in part to steric crowding by the larger napthyl groups as well as thermodynamic effects to be discussed. The sodium reduction studies in THF have shown TNB to form both mono- and disodium salts.[5,7] The monosodium salt is stable while the disodium salt (formed as a black precipitate) quickly decomposes to form naphthalene and dinaphthylborane anions.[9] Cyclic voltammograms of tri-α-naphthylborane in THF with sodium perchlorate as a supporting electrolyte showed a reduction wave at -3.2 V. (As noted in the Experimental Section, solutions with $NaClO_4$ often exhibited extreme irreversibility thus shifting cathodic waves to more negative potentials.) The reduction peak was only partially reversible due in part to the formation of another anodic species oxidized at -1.9 V. Although no exhaustive electrolysis studies were attempted, the peak is consonant with the formation of a dimeric, dianionic species and is in accord with sodium reduction studies of tri-α-naphthylborane in THF in which both a dimeric and monomeric species are known to be produced.[7]

Trimesitylborane, TMB, has shown to be an unusually stable borane due to steric hindrance around the boron atom.[11,12,27] It has also been shown to form blue paramagnetic solutions of the monosodium addition compound in THF which are stable for reasonable time periods. The disodium salt is not formed.[11] As expected, we found that TMB in THF and glyme with TBAP exhibited a reversible one-electron reduction at a Pt electrode. ESR spectra (Figure 10) of chemically and electrochemically generated free radicals confirmed earlier work.[13] No other cathodic or anodic waves were observed. However, when $NaClO_4$ was the supporting electrolyte, THF solutions of TMB showed two anodic waves, one corresponding to the oxidation of free $TMB\cdot^-$ and another more positive wave corresponding to the oxidation of an ion pair cluster. This is in accord with chemical reduction studies where the $TMB\cdot^-$ anion in ether has been shown upon standing to convert from a monomeric species to dimers and higher conglomerates such as tetramers, hexamers, etc., forming a red diamagnetic solution[11] (vide infra).

Ion Pairs. The occurrence of ion pairs and their subsequent formation to dimers and larger agglomerates through electrostatic attraction is widely known.[28] Because of the many investigations on the subject, an extensive discussion of the forces governing the phenomena of ion pair formation is not warranted here. However, a very limited and general discussion of the thermodynamic implications and ramifications of ion pairing as seen in the foregoing investigation can be pursued.

Previous reduction studies of the triarylboranes have employed the use of alkali metals as reducing agents. In general, these studies have shown the stability of the triarylborane anion radical to be dependent upon the nature of the solvent and the size of the triarylborane in question. In high dielectric, polar solvents the anion radical is stabilized while in solvents of low dielectric and low polarity the sodium addition products of the triarylboranes exist chiefly in the form of associated ion pairs. For example, the sodium reduction of trimesitylborane in THF forms a blue paramagnetic solution due to the stabilization of the anion radical $TMB\cdot^-$, but forms red diamagnetic ion clusters in benzene, the principal effects being the enhanced coulombic attraction of ion pairs and the decreased cation solvation in the low dielectric solvent.[11] The importance of anion size is most graphically illustrated in solutions of THF where sodium reductions of TMB form the anion radical $TMB\cdot^-$, while similar reductions of TPB form yellow diamagnetic solutions of ion clusters.[3,11]

In the electrochemical reductions of the triarylboranes, temperature, concentration, cation and anion, and solvent variations were noted to affect the stability of the anion radical.

In THF and glyme solutions with TBAP as the supporting electrolyte at 24°, the electrochemical reduction of triphenylborane indicates the primary reduction species to be the monomeric $TPB\cdot^-$ anion radical. At 0°, however, a substantial amount of diamagnetic dimer or higher aggregate was detected ($E_p = -2.1$ V), indicating the formation of ion pairs to be exothermic in this system.

Electroreduction of TPB in THF with sodium perchlorate supporting electrolyte showed the formation of diamagnetic clusters (dimers) of ion pairs to be favored. The preference of ion pair formation when sodium is used as a counteranion again stems from the culmination of complicated enthalpy and entropy factors. Because of the high charge density of the sodium cation as compared to the more diffuse tetrabutylammonium cation, the enhanced coulombic attraction of ion pairs should result in favored formation of an aggregate of the type shown below:

$$\begin{bmatrix} Na^+\,TPB^- \\ TPB^-\,Na^+ \end{bmatrix}$$

Entropy effects in the formation of simple ion pairs would also seem to be substantial. The small charge density of the sodium cation causes a tight, well-structured solvent shell (four THF molecules) to form around it. In forming an ion pair, this structure is replaced by one less rigorous, resulting in a gain in entropy and thus favoring ion pair formation. Such entropy effects become more insignificant in formation of higher aggregates. The entropy effects involving formation of ion pairs with tetrabutylammonium cations would also be less significant in leading to ion pair formation.

The electroreduction of TMB and TNB in THF with sodium perchlorate supporting electrolyte results in the formation of both ion pairs and separated ions at the surface of the electrode. The formation of the separated anion radical species, in contrast to the similar TPB reduction, apparently is due to the larger, more diffuse nature of $TNB\cdot^-$ and $TMB\cdot^-$.

The electroreduction of TPB with sodium perchlorate in glyme, in distinction to the results obtained in THF, shows the presence of both separated ions and ion pairs. The presence of separated ions is probably a result of a combination of higher heat of solvation of the sodium cation in glyme over THF and a lower entropy increase in the formation of an ion pair, assuming only two solvent molecules are used (bidentate nature of glyme) in contrast to four THF molecules in forming a solvent cage around the free cation.

With respect to the preceding discussion, the electrogenerated triarylborane anions investigated in this study were shown to form an equilibrium mixture of "free" ions and ion clusters in solution which, due to favorable thermodynamic factors, can be shifted to either extreme. Because of the complexity of the variables (solvent, anion and cation, concentration, and temperature), prediction of such factors cannot be determined without a thorough systematic study of the effect of each variable. However, in general, bulky cations (tetrabutylammonium vs. sodium) and chelating solvents (glyme vs. THF) favor the "free" ions, while the reverse situation favors ion pair aggregates.

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Chemistry of Monocarbon Metallocarboranes Including Polyhedral Rearrangements in Mixed-Metal Bimetallocarboranes

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Abstract: The synthesis and characterization of four isomers of the mixed-metal bimetallocarborane $(C_5H_5)_2CoNiCB_7H_8$ are reported. These species have been found to undergo novel thermal polyhedral rearrangements wherein metal atoms migrate to adjacent polyhedral vertices and remain there, constituting the first example of a thermally stable metal-metal interaction in a metallocarborane. Also described are some brominated derivatives and their thermal rearrangements. A general rearrangement scheme for ten-vertex polyhedra is developed and used in the analysis of polyhedral rearrangements and assignment of structures. In an attempt to synthesize a larger homologue of this mixed-metal species, we have iolated $(\eta\text{-}C_{10}H_8)Co^{III}CB_{10}H_{11}$, the first metallocarborane containing a neutral arene ligand bound to the metal.

The scope of metallocarborane chemistry was recently expanded when we reported[1] the synthesis of the first mixed-metal bimetallocarborane, a monocarbon species containing formal Co(III) and Ni(IV) in the polyhedral framework, $(C_5H_5)_2CoNiCB_7H_8$. Shortly thereafter[2,3] we reported mixed-metal species containing iron and cobalt, $(C_5H_5)_2CoFeC_2B_nH_{n+2}$ ($n = 7, 9$). To date, these are the only known mixed-metal metallocarboranes. As with the mixed-valence metallocenes,[4] their electrical and magnetic properties are of interest, particularly the aspect of metal-metal interactions within the polyhedron.

Because of the electron-deficient nature of the neutral Co(III)-Fe(III) species above, they are not expected to undergo polyhedral rearrangements.[5] Thus, an attempt to effect a polyhedral rearrangement in $4,5\text{-}(\eta^5\text{-}C_5H_5)_2\text{-}4\text{-}Co\text{-}5\text{-}Fe\text{-}1,8\text{-}C_2B_9H_{11}$ resulted in complete decomposition[3] under the same conditions that $4,5\text{-}(\eta^5\text{-}C_5H_5)_2\text{-}4,5\text{-}Co_2\text{-}1,8\text{-}C_2B_9H_{11}$ did rearrange.[3] It has been previously stated[6] that $\{C_5H_5Ni\}$ is formally isoelectronic with $\{CH\}$ with regard to the number of electrons donated to polyhedral bonding, just as $\{C_5H_5Co\}$ is similar to $\{BH\}$. Therefore, the monocarbon Co-Ni mixed-metal species is similar to a two-carbon carborane, $C_2B_nH_{n+2}$, or a two-carbon cobaltacarborane, $(C_5H_5Co)_xC_2B_nH_{n+2}$, and thus may undergo polyhedral rearrangement. We report here the preparation and novel polyhedral rearrangement of the heterobimetallocarborane $(C_5H_5)_2CoNiCB_7H_8$, along with the first report on the derivative chemistry of a bimetallocarborane including the physical properties of mono- and dibromo-substituted derivatives. We also report that an attempt to synthesize a larger homologue of this bimetallocarborane yielded instead the neutral complex $(\eta\text{-naphthalene})Co^{III}CB_{10}H_{11}$, the first metallocarborane containing a neutral arene ligand bound to the metal.

Results and Discussion

Synthesis and Characterization of the $(C_5H_5)_2CoNiCB_7H_8$ Isomers. The anionic metallocarborane[7] $[3\text{-}(\eta^5\text{-}C_5H_5)\text{-}3\text{-}Co\text{-}4\text{-}CB_7H_8]^-$ consumed 3 equiv of sodium naphthalide over a period of several days and was then treated with NaC_5H_5 and Ni(II) in tetrahydrofuran (THF). Whether the reduction/reaction temperature was −78°, 0°, 25°, or reflux, three isomers of $(C_5H_5)_2CoNiCB_7H_8$ were invariably isolated and separated by column and preparative thick-layer chromatography. A fourth isomer appeared consistently when the reaction was performed at −78°, and capriciously when done at 0°. Relative yields of isomers varied with temperature and can be found in the Experimental Section. While I, II, and IV were always observed, III was sometimes not formed in appreciable yield

$$[(CH_3)_4N][(C_5H_5)CoCB_7H_8] \xrightarrow[\text{THF}]{3Na^+C_{10}H_8^-} \xrightarrow[\text{NiBr}_2]{C_5H_5^-} \underset{\textbf{I-IV}}{(C_5H_5)_2CoNiCB_7H_8}$$