

Electrochemistry of Boron Compounds

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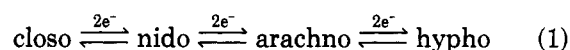
Contents

I. Introduction	51
II. Compounds Containing a Single Boron Atom	51
A. BX_3 and BR_3	51
B. BH_4^-	53
1. Industrial Applications of Tetrahydroborate Electrolysis	53
2. An Overview of the Aqueous Electrochemistry of Tetrahydroborate	53
3. Mechanistic Studies of the Electrochemical Oxidation of the Tetrahydroborate Ion	53
C. BH_3CN^-	57
D. BX_4^- and BR_4^-	58
E. Metalloxyano Complexes of BX_3	58
F. $L \cdot BH_3$ Complexes	58
III. Cyclic Boron Compounds	59
IV. Boranes, Borane Anions, and Metallaboranes	60
A. $B_3H_8^-$ and Its Derivatives	60
B. $B_9H_{14}^-$ and Its Derivatives	60
C. $B_{10}H_{14}$	61
D. $B_{10}H_{12}(NCCH_3)_2$	62
E. $B_nH_n^{2-}$ Anions and Their Substituted Derivatives	62
1. $B_9X_9^{2-}$	62
2. $B_{10}X_{10}^{2-}$	63
3. $B_{12}X_{12}^{2-}$	64
F. Metallaboranes	65
G. Heteroboranes and Their Metallaborane Derivatives	65
V. Carboranes and Their Derivatives	65
A. 1,2-, 1,7-, and 1,12- $B_{10}C_2H_{12}$ and Their Simple Derivatives	65
B. Monocarbon Carboranes and Derivatives	67
C. Heteroatom Carboranes	71
VI. Metallacarboranes	71
A. Mercury Derivatives of Carboranes	71
B. Transition-Metal Derivatives of Carboranes	72
VII. Metal Sandwich Complexes	73
VIII. References	74

I. Introduction

The application of electrochemical techniques to boron chemistry was covered briefly in previous review articles,¹⁻⁹ but the volume of published data now makes a comprehensive review necessary.

The scope of the work covers the formation of compounds at boron anodes, electrochemical behavior of simple boron compounds, anodic and cathodic processes on boranes and boron anions, and electrochemical properties of metallaboranes, carboranes, and metallacarboranes. It is important to survey the available electrochemical data in view of the formal structural relationship of borane clusters with the number of electron pairs available for bonding. The formal relationship suggests that oxidation-reduction processes should be able to induce structural change. The structural series that are formally related by such redox processes



are now well established in boron chemistry. Some of the earlier data dealt primarily with aqueous systems, but more recently, nonaqueous electrochemistry has become dominant. The review will not deal with the extensive literature involving the widely used tetrafluoroborate(-1) salts as supporting electrolytes, except where pertinent to other boron studies.

An attempt has been made to compile the basic electrochemical data of $E_{1/2}$, or other appropriate potential values, of compounds studied in the literature. Other information has been reported in the text. The nomenclature of the carboranes and their derivatives used in this review is that of the original authors.

II. Compounds Containing a Single Boron Atom

A. BX_3 and BR_3

The electrolysis of an ether solution of a Grignard reagent at a boron anode and an inert platinum or stainless steel cathode has been reported as a method of producing organoboranes of the general formula BR_3 .¹⁰ Thus triethylborane was prepared by electrolyzing a solution of $EtMgCl$ in Et_2O under nitrogen and distilling off the solvent after 8 h.



John Morris is a Senior Lecturer in Inorganic Chemistry at Strathclyde University, Glasgow, Scotland, where he joined the faculty in 1969. He was born and educated in Cardiff, Wales. He graduated with a B.Sc. in Chemistry from Nottingham University (1958) and gained a Ph.D. degree also from Nottingham (1961). After postdoctoral fellowships at Harvard University with F. G. A. Stone and University of Newcastle upon Tyne with N. N. Greenwood, he held faculty positions at Kingston-upon-Thames Polytechnic (formerly Kingston College of Technology). His major research interests are in chemical and electrochemical studies of boranes, metallaboranes, and boron heterocycles.



Henry Gysling was born in Philadelphia in 1941. He received his B.S. (1963) from St. Joseph's College (Philadelphia) and his Ph.D. (1967) from the University of Delaware for work with John Burmeister on linkage isomerism in inorganic complexes. After postdoctoral work with Minoru Tsutsui at New York University (organolanthanides, 1967–1968) and Norman Greenwood at the University of Newcastle upon Tyne (boron hydrides, 1968–1970), he joined the Kodak Research Laboratories, where he is currently a research associate in the Chemistry Division. His research interests include synthetic inorganic and organometallic chemistry (most recently coordination complexes with organotellurium ligands) and the applications of such materials in nonsilver imaging processes, electroless plating, and catalysis.

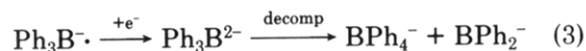
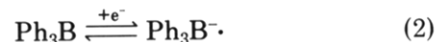
The electrochemical behavior of boron halides and tetrahaloborates in acetonitrile has been studied.¹¹ Table I gives half-wave potentials for oxidation and reduction at a dropping-mercury electrode (DME) with Et_4NClO_4 as supporting electrolyte and with reference to SCE. The oxidation of the halides was interpreted in terms of formation and subsequent oxidation of (solvent) BCl_3 , (solvent) $_2\text{BBr}_2^+$ and BBr_4^- , and (solvent) $_2\text{BI}_2^+$ and I^- . On reduction, 0.5 F per mole was consumed for either BCl_3 or BCl_4^- , and although the reduction product was not further characterized, it was inferred to be derived from 2 mol of each reagent.

Triarylboranes were reduced at a DME to arylborane



David Reed was born in England in 1954 and obtained his B.Sc. at Leeds University in 1975. He gained a Ph.D. at the same university in 1978, having worked with Professor N. N. Greenwood on boron hydride chemistry. He then took up a post as a Research Fellow with Dr. J. H. Morris, at Strathclyde University, working on the electrochemistry of boron hydrides. Since 1981 he has been associated with the national high-field NMR service centre at Edinburgh University.

anions.¹² Thus triphenylborane in THF with tetrabutylammonium perchlorate electrolyte gave a non-Nernstian, diffusion-controlled reduction wave at $E_{1/2} = -2.61$ V with respect to Ag/Ag^+ . A second wave at $E_{1/2} = -3.57$ V corresponded to the formation of Ph_3B^{2-} . Cyclic voltammetry indicated that the reduction to $\text{Ph}_3\text{B}^{\cdot-}$ was quasi-reversible, but that to Ph_3B^{2-} was nonreversible. The overall processes were represented by



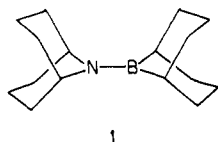
The oxidation of BR_3 derivatives at graphite anodes in CH_3OH with NaOMe and NaClO_4 gave the products ROME , R_2 , and cycloalkanes.^{13–17} When the solvent/electrolyte system was HOAc/NaOAc , the product was ROAc ($\text{R} = \text{pentyl, 2-methylbutyl, hexyl, octyl, phenethyl, cyclopentyl, cyclohexyl}$). A carbonium ion mechanism was proposed.

Electrolysis of trialkylboranes between two platinum electrodes in nitromethane solutions of tetraalkylammonium halide produced nitroalkanes RCH_2NO_2 in 76–150% yield.¹⁴ The nitroalkanes were formed by nucleophilic attack of O_2NCH_2^- , produced at the cathode, on the alkyl halides formed at the anode. Similarly, trialkylboranes were electrolyzed in MeCN solution to give corresponding aliphatic nitriles in good yield.¹⁵ In a similar undivided cell, electrolysis of trialkylboranes, BR_3 ($\text{R} = \text{Pr, Bu, pentyl, sec-Bu, cyclopentyl}$), in the presence of phenylacetylene in an electrolyte solution of Bu_4NI in THF gave $\text{PhC}\equiv\text{CR}$ in 70–94% yield,¹⁶ and this electrochemical reaction gave alkynes with retention of configuration with respect to the B–C bonds.¹⁶ Alkyne products were also obtained with 1-hexyne. When the trialkylborane was electrolyzed in acetonitrile solutions containing tetraalkylammonium halides and propenoic acid esters ($\text{CH}_2=\text{CHR}'\text{CO}_2\text{Et}$), carboxylic esters ($\text{RCH}_2\text{CHR}'\text{CO}_2\text{Et}$) were formed.¹⁸

TABLE I. Electrochemical Data for Boron Halides and Tetrahaloborates

compd	redn $E_{1/2}$, V	oxidn $E_{1/2}$, V
BCl_3	-1.08	+0.345
BBr_3	-0.547	+0.063; +0.471
BI_3	-0.666	-0.279; +0.196
BCl_4^-	-0.94	+0.40
BBr_4^-	-0.57	+0.066; +0.495
py· BCl_3	-1.23	not oxidized to +0.6
PhBCl_2	-1.116	+0.423
Ph_2BCl	-1.292	+0.444

The cyclic voltammograms of 9-(9-borabicyclo[3.3.1]nonyl)-9-azabicyclo[3.3.1]nonane, **1**, showed an irreversible oxidation, indicating that the radical cation derived from the compound was short-lived in solution.¹⁹



Electrolysis of organoboron compounds has also been used as a synthetic route to organometallic derivatives. A variety of anodes have been examined, including Pb, Hg, Bi, Mg, and Pt.²⁰⁻²⁴

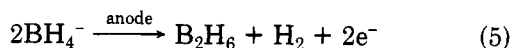
Inorganic applications include a study of the electrode processes of borate melts in which the electrochemical reduction of sodium tetraborate gave boron at nickel electrodes,²⁵ the electrochemical synthesis of boron carbide,²⁶ and electrochemical synthesis of zirconium diboride.²⁷

B. BH_4^-

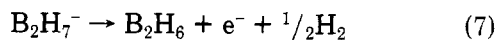
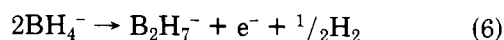
The tetrahydroborate anion has been the subject of a number of electrochemical studies in the aqueous phase and in the melt.²⁸⁻⁴³

1. Industrial Applications of Tetrahydroborate Electrolysis

The tetrahydroborate anion has been oxidized by electrolysis to diborane.³⁰



The reaction can be carried out in molten tetrahydroborate, because the mixed-alkali-metal tetrahydroborates have unusually low eutectic temperatures. The electrolysis of NaBH_4 in polyethylene glycol dimethyl ethers with a mercury cathode gave diborane in good yield. The formation of sodium heptahydrodiborate is indicated by a time lag in the release of diborane.³¹



Production of diborane by electrolysis of tetrahydroborate in DMF has also been patented,³² and such an electrolysis in dimethylamine produced dimethylamine-borane.³³ The latter process was carried out at an inert electrode such as platinum at the boiling point of the solvent (7 °C). Hydrogen was liberated at the anode, and the stable product was isolated by evaporation of the solvent, extraction with ether, and re-

crystallization. A similar reaction has been used to prepare ethylamine-borane.⁴³

2. An Overview of the Aqueous Electrochemistry of Tetrahydroborate

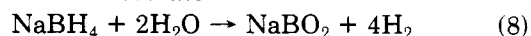
Several detailed studies of the electrolytic oxidation of NaBH_4 ³³⁻³⁹ and KBH_4 ^{36,40,41} in aqueous solution have been reported. These studies clearly demonstrate the need for extreme care in purifying materials used in detailed electrochemical studies and the need for equally extreme caution in interpreting electrochemical data.

This system is complicated by the presence of a competitive chemical reaction (hydrolysis) that gives products that are themselves oxidizable at somewhat more negative potentials than the parent ion. A further complication is introduced by the pH dependence of the rate of formation of these hydrolysis products (i.e., BH_3OH^- , $\text{BH}_2(\text{OH})_2^-$, $\text{BH}(\text{OH})_3^-$). As a final complication, the composition of the electrode surface, by virtue of its role as a heterogeneous catalyst for the hydrolysis reaction, also influences the overall composition of a tetrahydroborate analyte and thus its voltammetry.

In the discussion that follows, the studies of the tetrahydroborate system are presented chronologically to show the evolution of the understanding of the electrochemistry of this complex system. During this evolution, the application of ¹¹B NMR to establish the identity of the hydrolysis products was important in the elucidation of this system. The use of some independent spectroscopic technique to identify the various solution species is recommended, because the material in solution may not be the same chemically as that isolated in the solid state.

3. Mechanistic Studies of the Electrochemical Oxidation of the Tetrahydroborate Ion

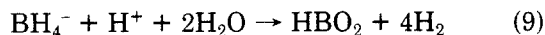
Marshall and Widing³⁴ reported two anodic polarographic waves for the oxidation of NaBH_4 in alkaline media. The wave at -0.15 V vs. the saturated calomel electrode (SCE) had 65 times the magnitude of the wave at -0.64 V vs. SCE. The authors found that the stability of the tetrahydroborate ion in aqueous alkaline solution at room temperature, its facile and complete decomposition in boiling or acid solution, and its favorable oxidation potential made it a useful substitute for the Jones reduction in the volumetric determination of uranium and in other analytical procedures involving the reduction of cations. The behavior of NaBH_4 at a DME was studied by adding the solid to various air-free buffered alkaline solutions in the cell. No wave was obtained by the electrolysis of "solutions" of NaBH_4 in acid or after alkaline solutions of NaBH_4 were acidified, and no cathodic wave was obtained from solutions of NaBH_4 after partial electrolytic oxidation at a large mercury electrode or from solutions of the hydrolysis product of NaBH_4 obtained by boiling a 0.5 M NaBH_4 solution until hydrogen evolution ceased. According to Hoekstra's equation³¹ for the hydrolysis of alkali metal tetrahydroborates, the hydrolysis solution would be 0.5 M sodium metaborate.



No cathodic wave, corresponding to the reduction of the oxidation products at the DME, has been obtained from electrolytically oxidized solutions of NaBH_4 . The absence of such a cathodic wave is a reliable criterion of thermodynamic irreversibility of the electrode reaction and agrees with the fact that the half-wave potential $E_{1/2}$ depends on the drop time of the DME and the concentration of sodium tetrahydroborate. The second anodic wave was assigned to an impurity in the NaBH_4 , a conclusion supported by a subsequent study.⁴⁰ The diffusion data of the first wave, calculated from the Ilkovic equation, were interpreted in terms of an electron-transfer number of 4.

The second smaller wave reported above was not obtained in later work by Pecsok,³⁵ who concluded that impurities were probably responsible for its presence, although the technical product used in his study was itself only 95% pure. He found that NaBH_4 in solutions buffered at pH 9 or greater gave a single highly irreversible anodic polarographic wave corresponding to the oxidation to a proton and a borate ion and involving eight electrons per mole, the half-wave potential following the relationship $E_{1/2} = +0.105 - 0.013\text{pH}$. At $\text{pH} < 9$ the solutions decompose so fast that polarograms are meaningless. The plot of $\log [(i_d - i)/i]$ vs. E_{DME} gave a straight line of slope 0.045 (for an eight-electron reaction the expected slope is 0.0075), indicating that the oxidation is highly irreversible, making it impossible to calculate thermodynamic properties from polarographic data alone. The limiting current was not strictly diffusion controlled. The ratio $i_d/h^{1/2}$ (i_d = diffusion current; h = height of mercury column), which is independent of h for a diffusion-controlled process, was 5.67 at 40 cm and 6.65 at 80 cm, indicating that the oxidation goes via several intermediate stages involving relatively slow reaction rates. The wave, which is well formed with a flat plateau, is proportional to the BH_4^- concentration over the wide concentration range in which BH_4^- is stable. Although the Ilkovic equation is applicable only to diffusion-controlled processes, the deviation is not sufficient here to invalidate its use to determine n . Assuming a value of $n = 8$, a diffusion coefficient, $D_{\text{BH}_4^-}$, of $3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ was calculated, a reasonable value compared with those of other ions. The value of $n = 4$, suggested by Marshall and Widing,³⁴ gives a diffusion coefficient of $10 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, a value larger than even that of the hydrogen ion ($D_{\text{H}^+} = 9.34 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$).

The hydrolysis reaction



was followed potentiostatically, the potential of the DME being kept at -0.05 V vs. SCE (well on the anodic plateau) and plots of i vs. t being recorded until the reaction was essentially over. For a series of experiments in the pH range 7.7–9.5 at 15, 25, and 35 °C, linear plots of t vs. $\log C$ were obtained, indicating that the hydrolysis is first order in BH_4^- , the slope being k' in the rate equation

$$\frac{-d[\text{BH}_4^-]}{dt} = k'[\text{BH}_4^-] \quad (10)$$

$$[k' = f(\text{pH})]$$

If the reaction is also first order in H^+ , k' should be

directly proportional to $[\text{H}^+]$, and, in fact, a linear plot of $\log k'$ vs. pH was observed at each temperature, the slope being k in the complete rate equation.

$$\frac{-d[\text{BH}_4^-]}{dt} = k[\text{BH}_4^-][\text{H}^+] \quad (11)$$

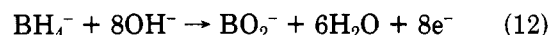
$$k = 8.7 \times 10^6 \text{ (15 °C)}$$

$$k = 1.5 \times 10^7 \text{ (25 °C)}$$

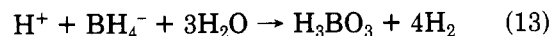
$$k = 2.4 \times 10^7 \text{ (35 °C)}$$

The hydrolysis, therefore, was postulated to involve a rate-controlling formation of a species of the formula $\text{HBH}_4 \cdot x\text{H}_2\text{O}$, which instantaneously lost hydrogen to give aquated borane radicals, which are known to hydrolyze rapidly.

Although the direct measurement of the standard EMF on the half-cell reaction (eq 12) was precluded by

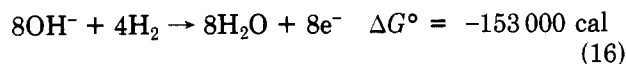
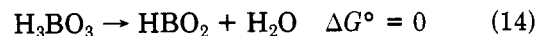


the highly irreversible nature of the electrode reaction, it was calculated from known thermodynamic parameters⁴⁴ (eq 13–16) to be 1.23 V vs. the standard hydrogen electrode. The entropies were known for all the species except BH_4^- , for which the BF_4^- value (40 eu) was used.

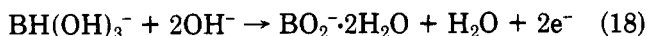
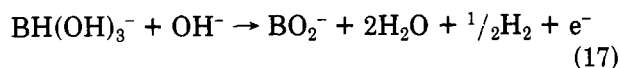


$$\Delta H_{\text{hyd}} = -63.9 \text{ kcal/mol}$$

$$\Delta G^*_{\text{hyd}} = -91\,700 \text{ cal}$$

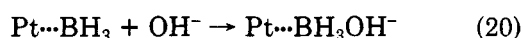
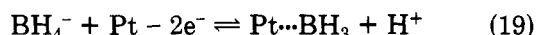


Mochalov and Gilmanshin²⁶ studied the polarographic behavior of NaBH_4 , KBH_4 , and LiBH_4 in aqueous NaOH solution (pH 9–11). The samples used in this study were purified and contained more than 98% tetrahydroborate. These workers examined the region $+0.2$ to -2.0 V (vs. SCE) and found that all three salts gave a single anodic wave with $E_{1/2} = -0.65 \text{ V}$ (vs. SCE). This wave decreased in height with time as the BH_4^- decomposed and finally completely disappeared. Technical-grade salts, containing chiefly the alcoholate as an impurity, gave identical polarograms. This anodic wave, which varied linearly with tetrahydroborate concentration (10^{-1} – 10^{-3} M) and was not completely diffusional, also had a strongly pH-dependent height. The height varied inversely with pH, and at $\text{pH} > 12.5$, where tetrahydroborates are quite stable, there was practically no wave. This behavior was interpreted to indicate that the observed wave was due not to BH_4^- but to some hydrolysis product of that ion. From a consideration of independent hydrolysis studies of BH_4^- and from the observation that $\text{NaBH}(\text{OCH}_3)_3$ gave an identical wave ($E_{1/2} = -0.65 \text{ V}$), the hydroborate species, $\text{BH}(\text{OH})_3^-$, was assigned to the observed wave, and the electrode reaction was formulated as eq 17 or 18.

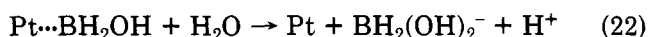


A subsequent study⁴⁰ showed that alkaline aqueous solutions of KBH_4 gave a reproducible static potential at platinum electrodes that was more positive than the theoretical value calculated for an eight-electron oxidation and did not correspond to the previously postulated equilibrium. The observed potential was independent of borate ion concentration, and it did not vary with tetrahydroborate and hydrogen ion concentrations in the way this equilibrium would predict. Also, on anodic polarization, although borate was an ultimate product of the oxidation, hydrogen gas was usually also evolved and the oxidation depended markedly on the nature of the anode material. Well-defined activation overpotentials were observed and studied over a wide current-density range. At electrodes that are inactive for the ionization of hydrogen, the tetrahydroborate ion was not readily oxidized until the potential approached that of oxygen evolution. Also, each gram ion of tetrahydroborate was oxidized by much less than 8 F. It was proposed, therefore, that BH_4^- reacts at certain surfaces only, such as platinum, setting up an equilibrium with an intermediate oxidation product, this equilibrium giving a characteristic static potential, and that further oxidation can occur on passage of current. From a general consideration of the overpotential and stoichiometric results, the following reaction scheme was proposed for the anodic behavior of the tetrahydroborate ion at a platinum surface.

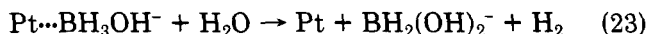
initial step



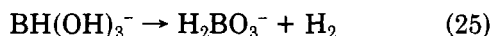
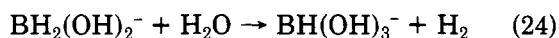
rate-determining step



slow hydrolysis



completion step



The competition between the slow electrochemical oxidation and the corresponding hydrolysis accounts for the different behavior at various electrode surfaces. For smooth platinum, platinized platinum, and gray platinum, reproducible static potentials of -0.827 , -0.828 , and -0.927 V, respectively (0.01 M KBH_4 , 0.1 M KOH), were measured, potentials substantially more negative than the reversible hydrogen potentials in the same solutions (e.g., -0.751 V in 0.1 M KOH). None of the

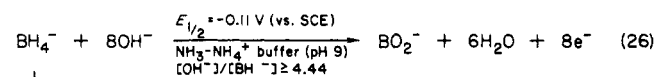
other electrodes studied (graphite, copper, amalgamated copper, palladium, and nickel) showed this behavior. With palladium, on immersion of the electrode in 0.1 M KBH_4 and 0.1 M KOH, the potential drifted towards the reversible hydrogen value but never actually attained it. At the other electrodes no steady potentials could be recorded, and the BH_4^- was not oxidized readily until the potential approached that of oxygen discharge (~ 0.8 V). Further support for the mechanism proposed (eq 19–25) was found in the similar polarization behavior of an aqueous solution of tetrahydroborate ion and aqueous diborane, both sources of borane radicals.

A study⁴¹ of the anodic oxidation of BH_4^- in alkaline solution ($[\text{BH}_4^-] \leq 10^{-2}$ M; pH 13) at a Pt electrode by a charging-curve oscillographic technique^{45,46} confirmed the conclusion of the above study that the sole electrochemical reaction in this system is the ionization of hydrogen from the parent ion and from the first hydrolysis product, BH_3OH^- , bound to the electrode surface. A similar mechanism, involving initial adsorption on a Pt electrode, followed by ionization of hydrogen from the adsorbate, has also been confirmed for the oxidation of methanol^{47,48} and hydrazine.⁴⁹ On the basis of these studies it has been suggested that any species taking part in such a low-potential oxidation must be able to release a proton.⁴⁸

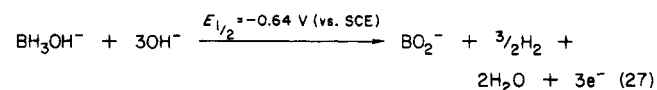
Analysis of the oscillographic traces indicated that a low-potential reaction occurs at Pt, the potential of which is independent of the quantity of current passed in each anodic pulse but is strongly dependent on current density (cd), the final decay potentials agreeing well with the static potential data.⁴⁰ This reaction has been assigned, by comparison with the well-established anodic charging curve for 0.1 M KOH,⁴⁶ to the irreversible ionization of hydrogen bound to the electrode surface by adsorption of BH_4^- and its first hydrolysis product BH_3OH^- . If the solution was not too dilute, this oxidation proceeded indefinitely at a potential below that of the formation of platinum oxide layers. However, on prolonged anodic polarization and/or a decrease in $[\text{BH}_4^-]$, oxide formation (platinum(II) oxide, platinum(IV) oxide, or both) became significant, inhibiting hydrogen ionization and gave rise to oxygen evolution, as was observed in the previous polarization study.⁴⁰ As expected for such a mechanism, introduction of an electrolytic poison, such as arsenious oxide or carbon disulfide (solutions 0.1 M in KOH and KBH_4 and 10^{-3} M in poison), inhibited hydrogen ionization.

Evidence was also presented for a similar mechanism at Pd and Ni electrodes.⁴¹

Gardiner, in a subsequent detailed study of the hydrolysis and electrolytic oxidation of the tetrahydroborate ion, has clarified this plethora of conflicting data.^{38,50} The anodic behavior of BH_4^- at a DME was explained by the following reaction scheme:



hydrolysis (see below)



A base-stabilized, partly hydrolyzed solution was prepared by dissolving NaBH_4 in an $\text{NH}_4^+ - \text{NH}_3$ buffer solution at pH 9.1 to give a 0.02–0.05 M ($\mu = 0.2$) solution, which was then allowed to hydrolyze for 5.5 min at 25 °C. The hydrolysis was then quenched by adjusting the pH to ≥ 12.5 with 20 M NaOH. The resulting solution contained $[\text{BH}_4^-]/[\text{BH}_3\text{OH}^-]$ in a ratio of ~ 25 , the half-life of BH_3OH^- in this medium being 3.7 h.

The n values of 8 and 3 for eq 26 and 27, respectively, were determined by constant-potential coulometry. This 8:3 ratio of n values was consistent with the ratio of diffusion-current constants for BH_4^- ($22.2 \mu\text{A mM}^{-1} \text{mg}^{-2/3} \text{s}^{1/2}$) and the hydrolysis intermediate BH_3OH^- ($9.35 \mu\text{A mM}^{-1} \text{mg}^{-2/3} \text{s}^{1/2}$)⁴¹ (i.e., $D_{\text{BH}_4^-}/D_{\text{BH}_3\text{OH}^-} = 2.37$). The identity of the hydrolysis intermediate as a BH_3 -containing species was independently established by ^{11}B NMR.⁵⁰ The 19.3-MHz ^{11}B NMR spectrum of a partly hydrolyzed BH_4^- solution consisted of a low-field borate singlet (final hydrolysis product), a high-field BH_4^- quintet ($J_{11\text{B}-1\text{H}} = 82 \text{ Hz}$), and an intermediate 1:3:3:1 quartet ($J_{11\text{B}-1\text{H}} = 82 \text{ Hz}$) 13.9 ppm upfield from the borate signal. The quartet was present only in the spectra of solutions having large limiting currents at -0.5 V , and the 1:3:3:1 intensity ratios indicate an interaction of three equivalent protons with a ^{11}B nucleus.

The anodic diffusion current for eq 26 was proportional to $[\text{BH}_4^-]$, but in unbuffered solutions it was strongly affected by the concentration of hydroxyl ion. When the ratio $[\text{OH}^-]/[\text{BH}_4^-]$ fell below 4.44, the slope of a current vs. $[\text{BH}_4^-]$ plot fell sharply. This decrease in the effective n value for eq 26 has been attributed to a local depletion of hydroxyl ions at the DME surface in such unbuffered solutions. Thus the stoichiometry of eq 26 could not be fulfilled, and a concurrent hydrolysis reaction becomes significant. Under such conditions, hydrogen also evolved.

The low n values and hydrogen evolution observed by Elder and Hickling⁴⁰ were attributed to the significant hydrolysis resulting from catalysis by the Pt electrode they used. The low value of n (i.e., 4) along with the considerable hydrogen evolution observed at a nickel electrode in a study of the use of NaBH_4 in concentrated aqueous NaOH as an anodic fuel³⁷ was similarly ascribed to electrode catalysis of the hydrolysis. The catalytic effect of Hg, however, must be negligible, since the kinetic data for the hydrolysis obtained chemically (iodate volumetric method) agree well with those obtained polarographically.

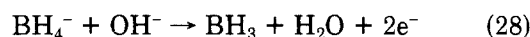
The failure of Mochalov and Gilmanshin³⁶ to observe the BH_4^- oxidation wave (-0.1 V) may have been due to their erroneous assignment of this wave to the anodic mercury wave. In the concentrated solutions they used (up to 0.08 M NaBH_4), the great height of the wave could easily have led them to assign it to the anodic dissolution of mercury. They did, however, correctly assign the wave at -0.65 V to the oxidation of a BH_4^- hydrolysis product, although a ^{11}B NMR study⁵⁰ has supported a BH_3OH^- formulation for this intermediate, rather than their postulated $\text{BH}(\text{OH})_3^-$ species.

Kinjo³⁹ has confirmed the conclusions of the study by Gardiner.^{38,50} He found that the tetrahydroborate ion underwent an overall eight-electron oxidation to produce hydrogen ion as a product, whereas its chief

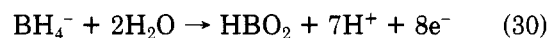
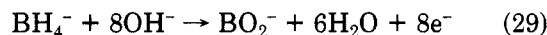
hydrolysis intermediate, trihydrohydroxyborate ion (BH_3OH^-), was oxidized to yield hydrogen gas by a three-electron process even at a potential where tetrahydroborate oxidation occurs.

Anodic oxidation of BH_4^- with an electrode made from Pd deposited on porous sintered Ni in 5 M NaOH solution gave three current peaks on the polarization curve at -0.07 , -0.30 , and 0.10 V with respect to Hg/HgO. Laser Raman spectroscopic investigation of the anodic solution at each peak potential showed only $\text{B}(\text{OH})_4^-$, and there was no detectable intermediate species $\text{BH}_x(\text{OH})_y^-$.⁵¹ Below -0.65 V the current efficiency increased with increasing duration of electrolysis.^{52,53}

An analysis of the single oxidation wave of BH_4^- in well-buffered alkaline media (pH 9–14) suggested that the rate-determining electron-transfer reaction involved two electrons and one hydroxide ion per mole of BH_4^- . The intermediate produced in this rate-determining step was postulated to be borane, BH_3 , instead of trihydrohydroxyborate ion, because the latter hydrolysis species produces hydrogen gas upon oxidation:

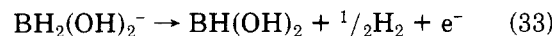
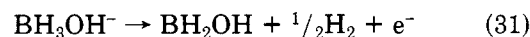


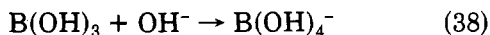
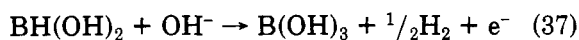
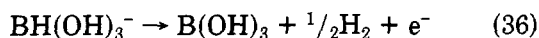
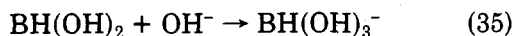
In an unbuffered alkaline medium (0.01 M NaOH, 0.49 M NaNO_3), BH_4^- oxidation occurred in two steps if the BH_4^- was in stoichiometric excess over hydroxide ion; the first step was the reaction with hydroxide ion ($E_{1/2} = -0.11 \text{ V}$ vs. SCE), and the second step was the reaction with water ($E_{1/2} = +0.47 \text{ V}$ vs. SCE):



In such a medium, however, considerable hydrolysis of BH_4^- also occurred at the electrode surface, owing to the decrease in pH as the electrode reaction proceeds and BH_3OH^- is produced. Since this hydrolysis species required no hydroxide ion for its oxidation, eq 29 for tetrahydroborate oxidation in an unbuffered medium proceeded beyond the extent predicted from the hydroxide ion concentration. As a result of this hydrolysis step, the total amount of tetrahydroborate ion oxidized at the electrode surface in eq 29 and 30 was less than that predicted from the bulk concentration.

The oxidation of BH_3OH^- was characterized by one, two, or three polarographic and chronopotentiometric waves, depending on factors such as solution pH and the presence or absence of maximum suppressors. The first polarographic wave was pH independent and appeared at -0.65 V vs. SCE; the other two were pH dependent and appeared at -0.44 and -0.31 V vs. SCE in 0.1 M KOH. On the basis of polarographic, chronopotentiometric, and controlled-potential coulometric methods, the oxidation of BH_3OH^- has been explained by the following series of electron-transfer steps and chemical reactions:



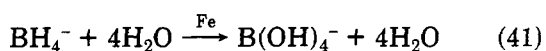
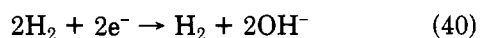
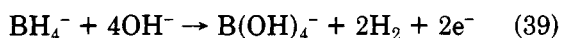


The pseudo-first-order rate constant for the first chemical step (eq 32) was determined by chronopotentiometry to be 27.5 s^{-1} in 0.1 M KOH.³⁹

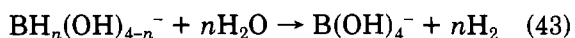
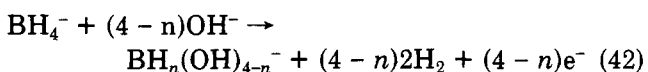
The other reports dealing with the electrochemistry of tetrahydroborates include the deposition of beryllium and beryllium boride by electrolysis of ethereal solutions of $\text{Be(BH}_4)_2$,^{54,55} the formation of $\text{Mg(BH}_4)_2(\text{NH}_3)_6$ by the electrolysis of a liquid-ammonia solution of NaBH_4 with a Mg anode and cathode,^{56,57} and the electrolysis of THF solutions of $\text{Ti(BH}_4)_3 \cdot \text{THF}$ to give cathodic titanium boride.⁵⁸

The electrolysis of NaBH_4 in liquid NH_3 at an Al anode and an Fe cathode separated by an anion exchange membrane gave $\text{Al(BH}_4)_3 \cdot 6\text{NH}_3$.⁵⁹

An electrochemical study of the catalytic decomposition of BH_4^- on the surface of iron-boron coatings has also been reported.⁶⁰ The Fe-B surface was deposited on a copper substrate at 40 °C from the following plating solution: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.036 M), sodium tartrate (0.35 M), NaBH_4 (0.26 M), NaOH (0.1 M). The rates of cathodic and anodic reactions of 0.15 M NaBH_4 in solutions of different alkalinity were determined potentiostatically at 20 and 50 °C with simultaneous measurement of the evolved H_2 . The rate of the catalytic decomposition of BH_4^- on the Fe-B surface decreased with increasing alkalinity. The data indicated that the decomposition of BH_4^- in 2–4 M NaOH solutions could be described as a catalytic process involving the following conjugated electrochemical reactions:



In 0.1–0.5 M NaOH solutions, however, a chemical mode of catalytic reaction prevailed. Based on the intermediates proposed in the earlier work of Elder and Hickling,⁴⁰ the BH_4^- oxidation was described in this pH region by consecutive electrochemical (~10%) and chemical (~90%) reactions.⁶⁰



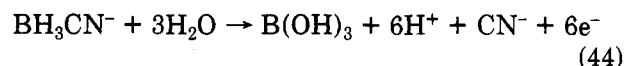
The potential of the Fe-B coating was more negative than that of the reversible hydrogen electrode in the same borohydride solution and was shifted in the negative direction with decreasing solution alkalinity. This latter effect, associated with the predominance of a chemical decomposition pathway at low alkalinity, has been attributed to the formation of surface iron hydride compounds.⁶⁰

The mechanism of the electrochemical reduction and oxidation of potassium borohydride has also been

studied at 20 and 80 °C at a nickel electrode [KBH_4 (0.001–0.04 M), ethylenediamine (1.0 M), NaOH (0.2–1.0 M)].⁶¹ With increasing concentration of KBH_4 (0.004–0.04 M) the steady-state potential of the Ni electrode is shifted sharply in the region of negative values at both 20 and 80 °C. The cathodic reduction of KBH_4 on the Ni electrode at different temperatures was controlled by both electrochemical (20 °C) and chemical (80 °C) reactions. The anodic process, independently of the electrolyte temperature, was controlled by electrochemical reactions.

C. BH_3CN^-

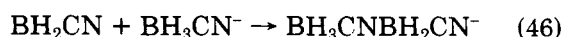
Cyclic voltammetry of 10^{-3} M aqueous solutions of the stable isomer KBH_3CN (0.1 M KCl supporting electrolyte, planar carbon paste working electrode, Pt foil auxiliary electrode, SCE as reference electrode) showed no evidence of oxidation or reduction in the range 1.6 to –1.6 V.^{62,63} However, BH_3CN^- was readily oxidized chemically by simple salts of Cu(II), Ag(I), and Hg(II).^{62,63} Addition of a neutral Ag(I) solution to a solution of BH_3CN^- produced a white precipitate, presumably AgNCBH_3 , which rapidly decomposed to metallic silver. However, ammoniacal solutions of Ag(I) were considerably more stable to BH_3CN^- ($t_{1/2} \approx 30$ min), suggesting that inner-sphere coordination of BH_3CN^- to the oxidant was necessary for a redox reaction. The oxidation half-reaction of BH_3CN^- does not require H^+ , so that the basicity of the solution itself cannot inhibit the reaction:



Aqueous Cu(II) was similarly reduced by BH_3CN^- ; the initially blue solution slowly became green, and CuCN precipitated in about 10 min. In the presence of excess BH_3CN^- , the white CuCN was reduced to Cu(0) in about 4 h. As observed for Ag(I), ammoniacal Cu(II) solutions were stable to BH_3CN^- for long times. Further evidence that BH_3CN^- was quite stable to oxidation in the absence of a reagent capable of inner-sphere reduction was its failure to react with the kinetically stable ($K_d = 10^{-31}$) Fe(CN)_6^{3-} , which is, however, a better oxidant than Cu(II).^{62,63}

The polarographic reduction of BH_3CN^- in 0.1 M KCl at a DME led to a reduction wave at $E_{1/2}$ of –0.35 V (SCE).⁶⁴ The cyanotrihydroborate anion is thus a good example of the importance of considering the redox mechanism rather than simply accepting a reduction potential, measured under specific experimental conditions, as an invariant and unequivocal parameter.

The cyclic voltammetry of BH_3CN^- in acetonitrile was examined as a function of electrode material.^{65–69} No obvious oxidation or reduction waves were observed at an "inert" working electrode (e.g., Pt), whereas several reactive electrodes (e.g., Fe, Cu, Co, Ni) led to the formation of metalocyanoborane derivatives. However, Mo or V electrodes resulted in oxidation of the BH_3CN^- at $E_p \sim +0.9$ V to give the ion $\text{BH}_3\text{CNBH}_2\text{CN}^-$ by the process





The chemical oxidation of BH_3CN^- in nonaqueous solution by Hg_2Cl_2 also led to the anion $\text{BH}_3\text{CNBH}_2\text{C}\cdot\text{N}^-$, whereas HgCl_2 yielded additionally the polymeric $[\text{BH}_2\text{CN}]_x$.⁶⁷

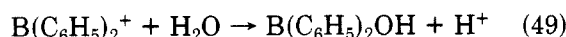
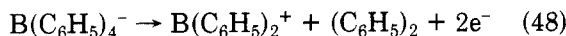
The anodic dissolution of iron in an acetonitrile solution of NaBH_3CN in the presence of $(\text{MeO})_3\text{P}$ or $(\text{EtO})_3\text{P}$ led to predominantly *cis*- $\text{Fe}[(\text{RO})_3\text{P}]_4(\text{NCBH}_3)_2$.⁶⁶ The *cis* and *trans* isomers showed similar electrochemical properties, and cyclic voltammetry gave irreversible behavior, with oxidation and reduction peaks at +1.0 and +0.46 V (Ag/AgNO₃), respectively.

The anodic dissolution of cobalt or nickel in acetonitrile solutions of NaBH_3CN led to the neutral complexes $[\text{Co}(\text{BH}_3\text{CN})_2(\text{CH}_3\text{CN})_4]$, $[\text{Co}(\text{BH}_3\text{CN})_2(\text{CH}_3\text{CN})_2]$, and $[\text{Ni}(\text{BH}_3\text{CN})_2(\text{CH}_3\text{CN})_4]$, or the anionic complexes $[\text{Co}(\text{BH}_3\text{CN})_4]^{2-}$, $[\text{Co}(\text{BH}_3\text{CN})_4(\text{CH}_3\text{CN})_2]^{2-}$, and $[\text{Ni}(\text{BH}_3\text{CN})_4(\text{CH}_3\text{CN})_2]^{2-}$, depending on the conditions.⁶⁸ In the presence of pyridine, the anodic dissolution gave the analogous neutral pyridine complexes.⁶⁹

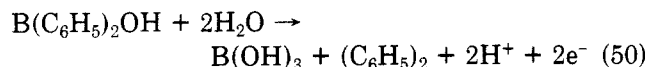
D. BX_4^- and BR_4^-

The electrochemistry of BX_4^- ions was discussed in section IIA.

The electrochemical oxidation of the BPh_4^- ion has been the subject of several investigations.⁷⁰⁻⁷³ It was earlier shown that biphenyl was a major product and that this arose by intramolecular dimerization during the oxidation of BPh_4^- . It was then shown that the oxidation at a stationary pyrolytic graphite electrode in aqueous solution gave two voltammetric waves. The first, which occurred at $E_{P/2} = 0.216$ V with respect to NaCl/calomel, involved two electrons and was pH independent. It was interpreted as



The second wave was less well defined, but involved the two-electron oxidation of $\text{B}(\text{C}_6\text{H}_5)_2\text{OH}$ and was linearly dependent on pH, such that $E_{P/2} = 0.92 - 0.057\text{pH}$. The slope of -0.057 indicated one H^+ per e^- liberated, and the reaction was interpreted as



The oxidation in nonaqueous solvents also involved two rather similar peaks, although the potentials were solvent dependent.

In contrast, the one-electron oxidation of BBu_4^- in CH_3CN at Pt, which occurs at a peak anodic potential, $E_p(a)$, of +0.35 V (these authors found for BPh_4^- , $E_p(a)$ +0.92 V referenced to standard aqueous calomel), resulted in the rapid decomposition to give butyl radicals, which could be identified in a spin trap by ESR.⁷³

The electrolysis of NaBEt_4 at a lead anode and a mercury cathode led to the formation of BEt_3 and PbEt_4 , which floated on the aqueous layer.⁷⁴ Similar electrolysis of alkali alkylalkoxyborates led to PbEt_4 .⁷⁵

The zwitterionic couples ferrocenyl(III) trisferrocenyl(II)borate, $\text{Fc}^+\text{BFc}_3^-$, showed four reversible oxidation potentials at -0.18, 0.09, 0.29, and 0.41 V (with respect to SCE). Controlled-current oxidation, in-

TABLE II. BX_3 Adducts of Metallocyano Complexes

compd	$E_{P/2}^a$
$\text{Fe}(\text{phen})_2(\text{CN})_2\text{BF}_3$	+0.8
$\text{Fe}(\text{phen})_2(\text{CNBF}_3)_2$	+1.12
$\text{Fe}(\text{phen})_2(\text{CNBH}_3)_2$	+1.18
$\text{Fe}(\text{phen})_2(\text{CNBBr}_3)_2$	+1.21

^a Half-peak potential vs. Ag/Bu₄NClO₄; CH₂Cl₂ solution.

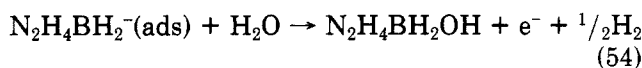
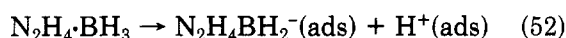
volving 1 F per mole, led to the cationic species, which in turn showed two negative oxidation potentials (-0.42 and -0.17 V) and two positive oxidation potentials (0.1 and 0.31 V). These data were consistent with one ferrocenyl(III) and three ferrocenyl(II) substituents in the zwitterion and two ferrocenyl(III) and two ferrocenyl(II) substituents in the cation.⁷⁶

E. Metallocyano Complexes of BX_3

A study⁷⁷ on a series of derivatives of the type $\text{Fe}(\text{phen})_2(\text{CNBX}_3)_2$ (Table II) showed that oxidation occurred reversibly (or nearly reversibly), and the oxidation potentials correlated with the charge-transfer electronic spectral shifts.

F. $\text{L}\cdot\text{BH}_3$ Complexes

The complexes of borane with neutral ligands often appear to be electrochemically inactive at Pt electrodes, and although few systematic studies have been reported, compounds of this type are often isolated as the products of electrochemical oxidation of other boranes in nonaqueous media. The oxidation of $\text{N}_2\text{H}_4\cdot\text{BH}_3$ has been studied in aqueous solution at a Pt electrode, and a rate equation has been proposed, consistent with the processes.⁷⁸



The potentiodynamic polarization curves were plotted to study the oxidation kinetics in acid and alkaline solutions.⁷⁹

In addition to the electrochemical properties of hydrazine-borane, the behavior of dimethylamine-borane has also been reported.⁸⁰ The use of dimethylamine-borane in electroless plating solutions (e.g., Cu,^{81,82} Ag,⁸² Au,⁸² Ni,⁸¹⁻⁸⁶ Co^{81,82,87}) has prompted a number of investigations into its electrochemical properties⁸⁸⁻⁹¹ including a potentiodynamic study on a platinum electrode, oxidation in an adsorbed layer, and the effect of adsorption potential, concentration, and temperature on its anodic behavior.

An electroless cobalt plating solution using diethylamine-borane has also been described,⁹² and methylamine-borane has been incorporated in an electroplating solution for an iron-boron alloy.⁹³

The cations derived from substituted dihydro(trimethylamine)(pyridine)boron(1+) salts underwent polarographic reduction in single one-electron waves which were diffusion controlled.⁹⁴ The shift of the polaro-

TABLE III. Polarographic Reduction Potentials at DME in Acetonitrile of Pyridine-Substituted (Trimethylamine)-*N*-pyridylboron(1+) Cations

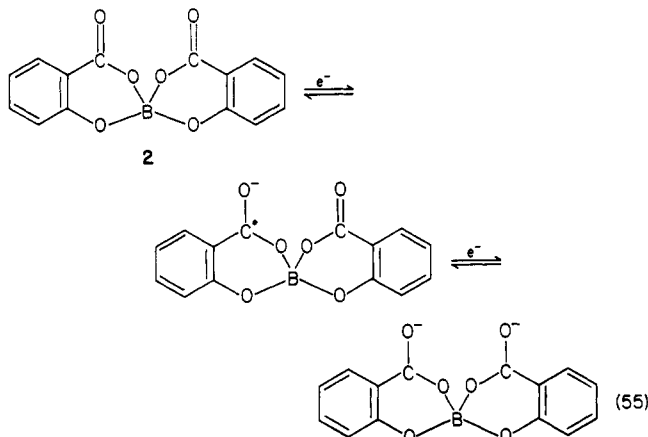
compd substituent	$-E_{1/2}, V^a$
2-F	1.33
2-Cl	1.215
3-Cl	1.198
3-Br	1.154
3-I	0.804
4-CN	0.77
4-Bz	1.53
4-COPh	0.766, 1.441
4-COMe	0.81, 1.527
4-Ph	1.28
2-OMe	1.89
3-OMe-4-CN	1.028
4-Me	1.602
2,3-CH=CH-CH=CH- ^b	1.05
3,4-Me ₂	1.66
2,4,6-Me ₃	1.583
H	1.473

^aSCE. ^bQuinoline.

graphic half-wave potentials of compounds with substituents on the pyridine ring vs. the unsubstituted (trimethylamine)-*N*-pyridylboron(1+) cation correlated with the sum of the Hammett substituent constants. The half-wave potential values are presented in Table III.

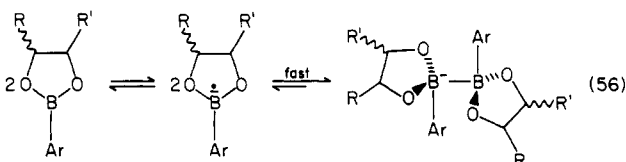
III. Cyclic Boron Compounds

A study of salicylic acid-borate complexes showed reversible reductive behavior in dimethylformamide.⁹⁵ The bis(chelate) complex (2) showed two one-electron reductions, localized on the carboxylate groups.



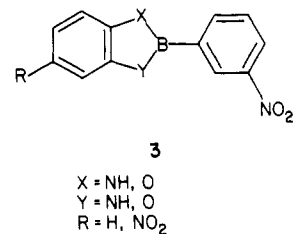
A number of boron acetylacetonate derivatives were investigated in the context of one-electron charge-transfer reactions,⁹⁶ since their electrochemical reduction behavior was previously shown to be highly irreversible.⁹⁷

The attempted preparative electrochemical reduction of a series of cyclic boronates derived from pinacols has been reported.⁹⁸ In most cases reduction was irreversible with $n \approx 1$, although aqueous workup resulted in substantial recovery of starting material, attributed to reoxidation of the dianion in the electrochemical scheme:

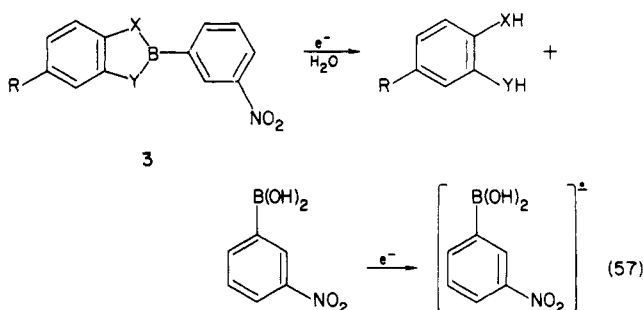


Pentaphenylborole gave a stable blue radical anion on reduction, although its electrochemical behavior was irreversible and gave complex cyclic voltammetric sweep data.⁹⁹

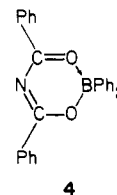
Several related boron chelates of type 3 reduced irreversibly and yielded substituted boronic acid derivatives.¹⁰⁰ The reduction occurred with two waves, and



exhaustive controlled-potential electrolysis at the plateaus of each wave showed two one-electron changes. The overall process was interpreted as in eq 57.



The chemical and electrochemical reduction of diphenylboron dibenzamide chelate, 4, led to a green



radical anion, which was significantly more stable than the ligand radical anion.¹⁰¹ The ESR spectrum of the chelate anion showed a highly resolved signal whose assigned hyperfine coupling constants indicated extensive delocalization of the unpaired spin over the ligand π system. The identity of (nitrophenyl)boronic acid was established by synthesis and polarographic reduction of the ortho, meta, and para derivatives to radical anions, which were examined by ESR.

Dc polarography of the chelate complexes Ni-(DMGBX₂)₂ (5) (X = F, Et) showed two reversible one-electron reduction waves, those of the BF₂ derivative occurring at more positive potentials than those of either the BEt₂ analogue or the parent Ni(DMGH)₂.¹⁰² These waves were interpreted as successive reductions to Ni(I) or Ni(0) complexes.

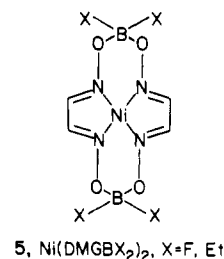
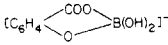
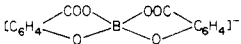
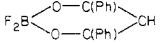
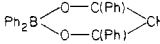
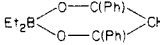
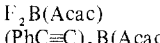
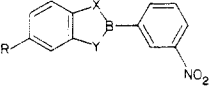


TABLE IV. Cyclic Boron Compounds and Derivatives

compd	$E_{1/2}$, V	comments	ref		
	-2.07 ^a	$n = 1$, reversible in DMF	95		
	-2.07, -2.35 ^a	both $n = 1$, reversible in DMF	95		
	-1.6, -2.66		97		
	-1.71, -2.74		97		
	-1.90		97		
	-2.80				
$F_2B(Acac)$	-2.08	highly irreversible, diffusion controlled	97		
$(PhC\equiv C)_2B(Acac)$	-2.16	highly irreversible, diffusion controlled	97		
$Ph_2B(Acac)$	-2.40	highly irreversible, diffusion controlled	97		
$Et_2B(Acac)$	-2.66	highly irreversible, diffusion controlled	97		
Ph_4C_4BPh	-2.8	$n = 2$, radical anion blue	99		
					
X	Y	R			
NH	NH	H	-1.75	cyclic voltammetry, irreversible	100
			-1.98 ^b	cyclic voltammetry, irreversible	
O	NH	H	-1.75	cyclic voltammetry, irreversible	100
			1.90 ^b	cyclic voltammetry, irreversible	
O	O	H	-1.50	cyclic voltammetry, irreversible	100
			-2.0 ^b	cyclic voltammetry, irreversible	
O	O	NO ₂	-1.75	cyclic voltammetry, irreversible	100
			-1.95 ^b	cyclic voltammetry, irreversible	100
$o\text{-NO}_2C_6H_4B(OH)_2$			-1.93 ^b	reversible	100
$m\text{-NO}_2C_6H_4B(OH)_2$			-1.55 ^b	reversible	100
$p\text{-NO}_2C_6H_4B(OH)_2$			-1.95 ^b	reversible	100
$Ph_3B_3N_3H_3$			-3.33 ^b	glyme (first wave only)	103
			-3.29 ^b	DMF	103
$Ph_2HB_3H_3N_3$			-3.37 ^b	glyme (first wave only)	103
			-3.32 ^b	DMF	103
$PhH_2B_3N_3H_3$			-3.40 ^b	glyme $n = 1$ (first wave only)	103
			-3.37 ^b	DMF	103
$H_3B_3N_3Ph_3$			$\geq -3.6^b$	glyme (no second wave)	103
			$\geq -3.45^b$	DMF	103
$Cl_3B_3N_3H_3$			-1.45 ^b		103
$Cl_3B_3N_3Ph_3$			-1.75 ^b		103

^a Hg pool reference. ^b Ag/Ag⁺ reference.

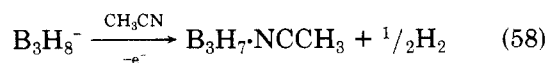
Polarographic studies on phenyl-substituted borazines indicated one-electron reduction on the first wave, and cyclic voltammetry of the boron-substituted derivatives indicated reversible charge transfer with rapid decomposition of the radical anion.¹⁰³ The radical anion from *N*-phenylborazine decomposed very quickly. A specific solvent effect was observed on the half-wave potentials.

Details of cyclic boron compounds are summarized in Table IV.

IV. Boranes, Borane Anions, and Metallaboranes

A. B₃H₈⁻ and Its Derivatives

The electrochemical properties of the octahydrotriborate ion have been the subject of several studies. In acetonitrile and DMF, B₃H₈⁻ underwent a one-electron oxidation at a platinum or gold anode to give B₃H₇N-CCH₃ and B₃H₇DMF,¹⁰⁴ respectively. The reaction, studied chronopotentiometrically and by exhaustive controlled-potential electrolysis and product identification, appeared to be



The chronopotentiometric oxidation wave occurred near +0.4 V (Ag/AgCl/LiCl; +0.19 V vs. SCE), and a diffusion coefficient of $(5.2 \pm 0.5) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at room temperature was calculated.¹⁰⁴

The cyclic voltammogram of B₃H₈⁻ in CH₃CN at a stationary Pt electrode was complex and highly irreversible, with oxidation waves near +0.4 and > +1.6 V (Ag/AgNO₃; +0.34 V vs. SCE)¹⁰⁵ although the potentials and appearance of the voltammograms were dependent on scan rate and the potential limits of the scans. Coulometry at the first oxidation wave showed a one-electron oxidation and isolation of B₃H₇N-CCH₃. At the higher potential, several electrons were involved in the oxidation process although the same product was isolated. Substitution of the B₃H₈⁻ ion by NCS⁻ or NCBH₃⁻ led to increased oxidative stability, with the first oxidation potential occurring near 1.32 V in B₃H₇NCS⁻ and 1.2 V in B₃H₇NCBH₃⁻. The first oxidation of B₃H₇NCS⁻ involved four electrons.

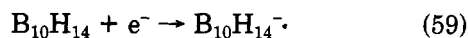
B. B₉H₁₄⁻ and Its Derivatives

Oxidation of CsB₉H₁₄ in acetonitrile (0.1 M LiBF₄) at a Pt electrode at low current density gave crystals that were identified by X-ray analysis as B₉H₁₃⁻NCCCH₃.¹⁰⁶

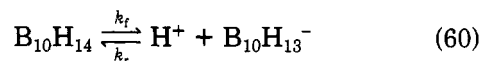
Cyclic voltammetry and ac voltammetry of $\text{Me}_4\text{NB}_9\text{H}_{14}$ in acetonitrile showed two irreversible oxidations at a Pt electrode. The peak potentials were 0.85 and 1.35 V (Ag/0.1 M AgNO_3 ; +0.34 V vs. SCE). Coulometry at the first oxidation potential confirmed a one-electron oxidation leading to isolation of $\text{B}_9\text{H}_{13}\text{NCCH}_3$.^{105a} The derivatives $\text{B}_9\text{H}_{13}\text{NCS}^-$ and $\text{B}_9\text{H}_{13}\text{SMe}_2$ both showed two-electron oxidations at 0.99 and 1.42 V, respectively (Ag/0.1 M AgNO_3 ; +0.34 V vs. SCE), although the products of oxidation were not characterized. B_9H_{12} in acetonitrile showed a one-electron oxidation at 1.03 V, although its only identifiable oxidation product was $\text{B}_9\text{H}_{13}\text{NCCH}_3$. In contrast, 0.5-electron oxidation in dichloromethane led to $\text{B}_{18}\text{H}_{21}^-$.^{105b}

C. $\text{B}_{10}\text{H}_{14}$

Decaborane itself has been studied most intensively with respect to electrochemical properties. The chemical reduction of $\text{B}_{10}\text{H}_{14}$ depended on both solvent and reaction time. With sodium in liquid ammonia, $\text{B}_{10}\text{H}_{14}^{2-}$ was the only product,¹⁰⁷ but in ether the reduction was accompanied by a transient red color, attributed to the radical anion $\text{B}_{10}\text{H}_{14}^{\cdot-}$, and the final product included $\text{NaB}_{10}\text{H}_{13}$ and $\text{Na}_2\text{B}_{10}\text{H}_{14}$. Reduction by sodium amalgam in ether¹⁰⁸ yielded $\text{Na}_2\text{B}_{10}\text{H}_{14}$ after 5 h; further reaction gave $\text{NaB}_{10}\text{H}_{13}$. Detailed electrochemical studies of the reaction in acetonitrile and glyme¹⁰⁹⁻¹²⁰ have shown that the apparently simple reduction of $\text{B}_{10}\text{H}_{14}$ is in fact mechanistically complex. Decaborane in glyme solution (0.1 M Bu_4NClO_4) gave two polarographic reduction waves at $E_{1/2} = -1.54$ and -2.75 V (Ag/AgNO₃ satd) and no oxidation waves.¹⁰⁹ Under the conditions studied, at the first wave, plots of instantaneous limiting current vs. (mercury column height)^{1/2} were linear with intercepts at or near the origin, indicating a diffusion-controlled process. A linear plot was also observed for $\log[(i_d - i)/i]$ vs. potential with a slope of 0.06 V. These data strongly suggested a primary reduction step involving a one-electron reduction of $\text{B}_{10}\text{H}_{14}$. The diffusion-controlled character of the lim-



iting-current first wave and total absence of kinetic character precluded the possibility of a chemical reaction preceding the charge-transfer step, such as



where the electroactive species is H^+ or $\text{B}_{10}\text{H}_{13}^-$. Figure 1 shows typical cyclic voltammograms for $\text{B}_{10}\text{H}_{14}$ in glyme after the application of several triangular wave cycles in a multicycle experiment in which the potential sweep did not encompass the second reduction wave.

Wave B corresponded to the first reduction wave of $\text{B}_{10}\text{H}_{14}$, and waves A, C, and D did not appear unless wave B was included in the potential sweep, indicating that these waves are associated with the products of the first reduction step (wave B). The results suggested that the species producing wave C was not the product of the initial electron-transfer step [$\text{B}_{10}\text{H}_{14}^{\cdot-}$] but was due to some species that results from a unimolecular transformation of the primary electrolysis product. Unlike for wave C, the sweep-rate dependence of waves

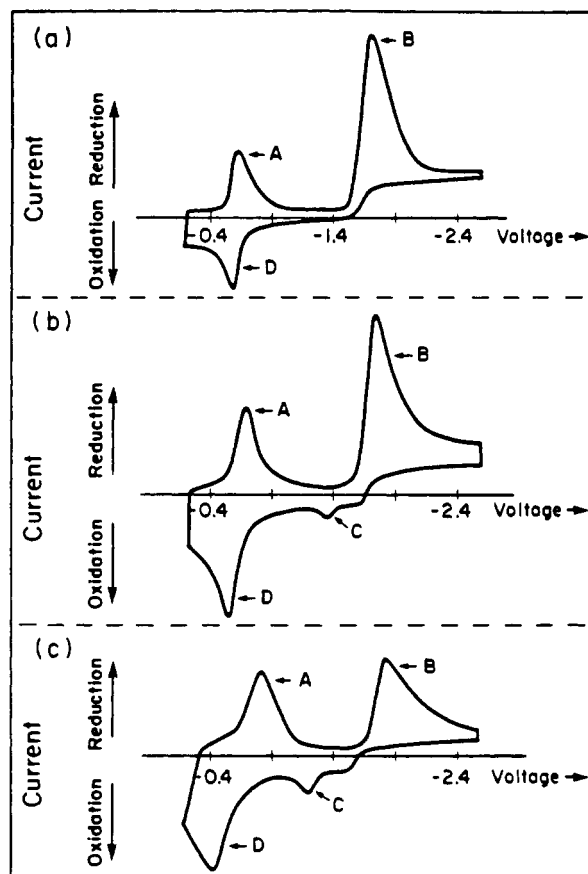
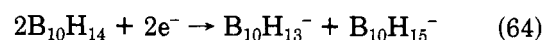
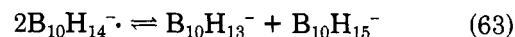
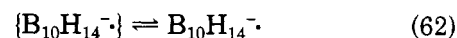
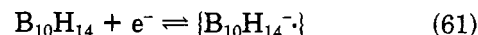


Figure 1. Cyclic voltammograms of $\text{B}_{10}\text{H}_{14}$ (0.49×10^{-3} M; 0.1 M Bu_4NClO_4 in 1,2-dimethoxyethane) with scan rates (a) 0.88, (b) 1.9, and (c) 5.5 V/s. These are scans after application of several triangular wave cycles (approximately steady state). Reproduced with permission from ref 109. Copyright 1967, American Chemical Society.

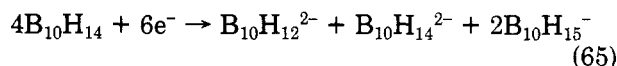
A and D suggested that they arose from a product of $\text{B}_{10}\text{H}_{14}$ reduction that was stable during the cyclic voltammetric experiment. These waves have been assigned to the redox processes of $\text{B}_{10}\text{H}_{13}^-$. The presence of $\text{B}_{10}\text{H}_{15}^-$ in the solution was deduced from the overall stoichiometry of the electrode reaction. Constant-potential electrolysis at the first reduction wave (B) gave a solution whose UV spectrum and polarogram supported the presence of equimolar amounts of $\text{B}_{10}\text{H}_{13}^-$ and $\text{B}_{10}\text{H}_{15}^-$. The overall mechanism proposed was¹⁰⁹



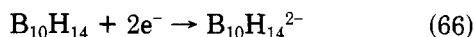
The oxidation wave due to the postulated $\{\text{B}_{10}\text{H}_{14}^{\cdot-}\}$ was not observed up to the limit of the instrumentation used, but polarographic data support such a unimolecular decomposition after the one-electron charge-transfer step. If the second-order decomposition (eq 64) were directly coupled to a reversible one-electron charge-transfer step (wave B), a linear $\log[(i_d - i)/i^{2/3}]$ vs. E plot with a slope of 0.06 V would have resulted. This was not the case.

The second reduction wave has also been studied in detail with glyme solutions.¹¹⁰ It was assigned to the

one-electron reduction of $B_{10}H_{13}^-$, with the resulting dianion, $B_{10}H_{13}^{2-}$, rapidly disproportionating to form $B_{10}H_{14}^{2-}$, which in turn reacted rapidly with bulk $B_{10}H_{14}$ to regenerate more electroactive $B_{10}H_{13}^-$. The overall reaction at the second reduction wave corresponded to

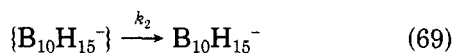
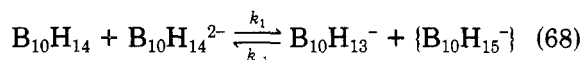
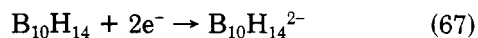


A reaction between $B_{10}H_{15}^-$ and $B_{10}H_{12}^{2-}$, generating $B_{10}H_{13}^-$, appeared to contribute to the electrode reaction over the longer times of constant-potential electrolysis experiments (1–2 h), so the net reaction under these conditions was



When $B_{10}H_{13}^-$ was reduced in the absence of bulk $B_{10}H_{14}$, the reaction stopped with the formation of $B_{10}H_{14}^{2-}$ and $B_{10}H_{12}^{2-}$.

The first reduction wave of $B_{10}H_{14}$ has also been studied in both acetonitrile and dichloromethane solutions.¹¹¹ Constant-potential coulometry at this wave gave an n value of about one electron per $B_{10}H_{14}$ molecule, and ¹¹B NMR showed that the electrolysis product was an equimolar mixture of $B_{10}H_{13}^-$ and $B_{10}H_{15}^-$. The reduction in these solvents, however, has been postulated as a two-electron irreversible step, on the basis of detailed analysis of the cyclic voltammograms, the formal reduction potential for the $B_{10}H_{14}/B_{10}H_{14}^{2-}$ couple in acetonitrile being -0.78 ± 0.02 V (vs. SCE).

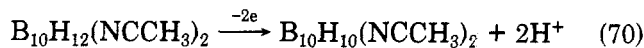


The kinetically important step after charge transfer both in the reduction of $B_{10}H_{14}$ and in the oxidation of $B_{10}H_{14}^{2-}$ was a proton transfer from $B_{10}H_{14}$ to $B_{10}H_{14}^{2-}$. The rate constant for this reaction in acetonitrile was $\sim 5 \times 10^4$ M⁻¹ s⁻¹ at 24 °C. Thus, on the short time scale of the polarographic experiment there is a considerable mechanistic difference in the redox characteristics of $B_{10}H_{14}$ in glyme¹⁰⁹ vs. acetonitrile¹¹¹ and dichloromethane.¹¹¹ The preferential solvation of the one-electron reduction species, $B_{10}H_{14}^-$, in glyme compared to acetonitrile may account for this difference. However, in both cases, on the time scale of a constant-potential electrolysis, the reaction products were the same.

D. $B_{10}H_{12}(NCCH_3)_2$

The cyclic voltammogram of $B_{10}H_{12}(NCCH_3)_2$ in CH_3CN at Pt gave two irreversible oxidation peaks at $E_p + 0.75$ and $+1.2$ V (Ag/AgNO₃) with no well-defined corresponding reduction waves.¹²¹ However, a broad reduction wave at $E_p - 0.8$ V, which appeared only after a scan to anodic potentials, is probably best interpreted as the reduction of H⁺. The appearance of the voltammogram was superficially similar to that of $B_{10}H_{10}^{2-}$. Exhaustive oxidation of $B_{10}H_{12}(NCCH_3)_2$ at $+0.9$ V showed that the first oxidation involves two electrons. Thin-layer chromatography showed about four prod-

ucts, of which the two minor components were identified as $B_9H_{13}(NCCH_3)$ and a species thought to be the nido derivative $B_{10}H_{10}(NCCH_3)_2$. The electrochemical oxidation was not simple, but at least part of the overall reaction may have proceeded as follows:



The cyclic voltammograms of $B_{10}H_{12}(SMe_2)_2$ and $B_{10}H_{12}[CH_3C(NEt_2)NH]_2$ were very similar to that of $B_{10}H_{12}(NCCH_3)_2$ and thus imply similar electrochemical behavior.

E. $B_nH_n^{2-}$ Anions and Their Substituted Derivatives

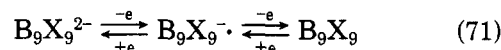
Muetterties et al. have reported polarographic data for several $B_nH_n^{2-}$ polyhedral anions^{112–115} and some halogenated derivatives of the B_{10} and B_{12} cages¹¹⁶ as a criterion of their comparative oxidative stabilities. The order of oxidative stability was $B_7 < B_8 < B_9 < B_8 < B_{11} < B_{10} < B_{12}$. The oxidation potentials and experimental conditions are listed in Table V. All of these studies were of anions in aqueous solution. The halogenation of the B_n cage increased the oxidative stability, although the nature of the various oxidation products was not studied in the original work.¹¹⁶ Substitution with OH⁻ decreased the oxidative stability of the anions.¹²²

1. $B_9X_9^{2-}$

More recently the electrochemical oxidations of $B_9X_9^{2-}$ ($X = Cl, Br, I$), $B_{10}Cl_{10}^{2-}$, and $B_{12}Cl_{12}^{2-}$ have been investigated in MeCN and CH_2Cl_2 ,¹¹⁷ and the products of one- and two-electron chemical reductions of $B_9X_9^{2-}$ ($X = Cl, Br, I$) have been isolated and characterized.¹¹⁸

The perhalogenated ions $B_9X_9^{2-}$ ($X = Cl, Br, I$) underwent two successive one-electron reversible oxidations in MeCN and CH_2Cl_2 (Table V). The initial oxidation was electrochemically reversible ($\Delta E_p \approx 60$ mV at sweep rates of 20–100 mV/s) and chemically reversible ($i_{pc}/i_{pa} = 1.0$). The second oxidation wave was chemically irreversible in MeCN but both chemically and electrochemically reversible in CH_2Cl_2 . These results, obtained by cyclic voltammetry (Table V), were also found by using differential and normal pulse voltammetry at a Pt wire electrode.

The redox behavior observed electrochemically¹¹⁷ is completely consistent with the previously reported¹¹⁸ chemical oxidation of $B_9X_9^{2-}$:



In the latter work¹¹⁸ the radical anions, $B_9X_9^-$ were isolated as air-stable highly colored $n\text{-Bu}_4N^+$ salts. Suitable chemical oxidants were $Tl(CF_3CO_2)_3$, N -chlorosuccinimide, and N -bromosuccinimide. Use of excess $Tl(CF_3CO_2)_3$ gave B_9X_9 ($X = Cl, Br$; a pure sample of B_9I_9 was not isolated by this reaction). Reduction back to the dianions is readily effected with stoichiometric amounts of ($n\text{-Bu}_4N$)I.

The enhanced chemical stability resulting from halogenation of the borane cage is especially marked in the $B_9X_9^{2-}$ system, $B_9H_9^{2-}$ exhibiting both air and hydrolytic instability, whereas the air-stable salt $Na_2B_9Cl_9$ is stable to both 12 N HCl and 6 N NaOH in aqueous solution.

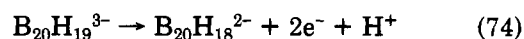
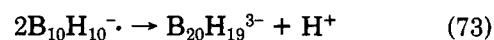
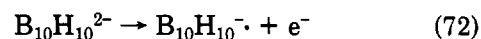
TABLE V. Boranes and Borane Anions

compd	$E_{1/2}$, V	comments	ref	compd	$E_{1/2}$, V	comments	ref
$B_3H_8^-$	+0.4	chronopotentiometric; vs. Ag/AgCl/LiCl-MeCN	104	$B_{10}Cl_9OH^{2-}$	+1.03	$E_{1/2}$; SCE, C paste, pH 4.5 (data also for pH 7 and 10)	122
		Pt-wire anode; MeCN/ Et_4NClO_4 ; irreversible		$B_{10}Cl_8(OH)_2^{2-}$	+0.74	$E_{1/2}$; SCE, C paste, pH 4.5 (data also for pH 7 and 10)	122
	>+1.6	CH_3CN ; Ag/AgNO ₃	105a	$B_{10}H_{14}$	-1.54	reduction in glyme; Ag/AgNO ₃	109, 110
$B_6H_6^{2-}$	-0.33	0.5 M aqueous K ₂ SO ₄ ; Pt; SCE	112		-2.75	reduction in CH ₃ CN; SCE	111
$B_7H_7^{2-}$		0.5 M aqueous K ₂ SO ₄ ; Pt; SCE	112	$B_{10}H_{12}(NCMe)_2$	+0.75	irreversible; CH ₃ CN; Pt; Ag/AgNO ₃	105
$B_8H_8^{2-}$	-0.04	0.5 M aqueous K ₂ SO ₄ ; Pt; SCE	112	$B_{11}H_{11}^{2-}$	+0.05	$E_{p/2}$ at stationary Pt; SCE; CH ₃ CN	125
$B_9H_9^{2-}$	-0.15	0.5 M aqueous K ₂ SO ₄ ; Pt; SCE	112	$B_{11}H_{14}^-$	+1.6	$E_{p/2}$ at stationary Pt; SCE; CH ₃ CN	125
$B_9Cl_9^{2-}$	+0.38	(<i>n</i> -Bu ₄)N ⁺ salt in MeCN/(<i>n</i> -Bu ₄)NClO ₄ ; cyclic voltammetry: 0.2 V/s; Pt-wire working electrode and AgCl-coated silver-wire reference	117	$B_{11}H_{13}^{2-}$	-0.45	$E_{p/2}$ at stationary Pt; SCE; CH ₃ CN	125
				$B_{12}H_{12}^{2-}$	+1.43	$E_{p/2}$; Pt, SCE	126, 127
$B_9Br_9^{2-}$	+0.64	(<i>n</i> -Br ₄)N ⁺ salt in MeCN/(<i>n</i> -Bu ₄)NClO ₄ ; cyclic voltammetry: 0.2 V/s; Pt-wire working electrode and AgCl-coated silver-wire reference	117		+1.50	RPE; CH ₃ CN; SCE	127
				$B_{12}H_{11}I^{2-}$	+1.88	$E_{p/2}$; Pt; SCE	127
				$B_{12}H_6Br_6^{2-}$	+2.00	$E_{p/2}$; Pt; SCE	127
				$B_{12}Br_{12}^{2-}$	>+2.2	$E_{p/2}$; Pt; SCE	127
				$B_{12}Cl_{10}H_2^{2-}$	>+2.2	$E_{p/2}$; Pt; SCE	127
				$B_{12}Cl_{12}^{2-}$	+2.34	Li ⁺ salt in MeCN/(Bu ₄ N)ClO ₄ ; differential pulse voltammetry at Pt-wire working electrode	117
$B_9I_9^{2-}$	+1.12	(<i>n</i> -Bu ₄)NClO ₄ ; cyclic voltammetry: 0.2 V/s; Pt-wire working electrode and AgCl-coated silver-wire reference	117	$B_{12}H_{12}^{2-}$	>+1.4	Li ⁺ salt in MeCN/(Bu ₄ N)ClO ₄ ; differential pulse voltammetry at Pt-wire working electrode	122
	+0.66			$B_{12}H_{11}OH^{2-}$	+0.98	Li ⁺ salt in MeCN/(Bu ₄ N)ClO ₄ ; differential pulse voltammetry at Pt-wire working electrode	122
				$B_{12}H_{10}(OH)_2^{2-}$	+0.76	Li ⁺ salt in MeCN/(Bu ₄ N)ClO ₄ ; differential pulse voltammetry at Pt-wire working electrode	122
$B_9H_{14}^-$			106				
$B_{10}H_{10}^{2-}$	+0.40	$E_{p/2}$; CH ₃ CN; Pt; SCE	119, 123	$B_{12}Br_{12}(OH)_2^{2-}$	+1.25	Li ⁺ salt in MeCN/(Bu ₄ N)ClO ₄ ; differential pulse voltammetry at Pt-wire working electrode	122
$2-B_{10}H_9I^{2-}$	+0.53	$E_{p/2}$; CH ₃ CN; Pt; SCE	123	$B_{20}H_{19}^{3-}$	+0.7	$E_{p/2}$ anodic; Pt; SCE	119
$1-B_{10}H_9I^{2-}$	+0.53	$E_{p/2}$; CH ₃ CN; Pt; SCE	123		-0.1	E_p cathodic; H ⁺ → ¹ / ₂ H ₂	
$2-B_{10}H_9NH_3^-$	+0.78	$E_{p/2}$; CH ₃ CN; Pt; SCE	123	$B_{20}H_{18}^{2-}$	-1.48	DME; SCE	119
$1-B_{10}H_9NH_3^-$	+0.75	$E_{p/2}$; CH ₃ CN; Pt; SCE	123	$B_{24}H_{23}^{3-}$	+1.74	Pt; CH ₃ CN; SCE	127
$2-B_{10}H_9NMe_3^-$	+0.90	$E_{p/2}$; CH ₃ CN; Pt; SCE	123	$B_{24}H_{21}I_3^{3-}$	+1.19		127
$1-B_{10}H_9NMe_3^-$	+0.88	$E_{p/2}$; CH ₃ CN; Pt; SCE	123	$B_{24}Br_7H_{16}^{3-}$	+0.78		127
$2-B_{10}H_9SMe_2^-$	+0.92	$E_{p/2}$; CH ₃ CN; Pt; SCE	123	$B_{24}Br_{10}H_{13}^{3-}$	+0.98		127
$1-B_{10}H_9SMe_2^-$	+0.92	$E_{p/2}$; CH ₃ CN; Pt; SCE	123	$B_{24}Br_{11}H_{12}^{3-}$	+1.14		127
$1-B_{10}H_9IC_6H_5^-$	-1.0	reduction at DME; SCE	124	$B_{24}Br_{14}H_8^{4-}$	+1.30		127
$B_{10}H_{10}^{2-}$	+0.85	$E_{p/2}$; SCE, C paste	122	$B_{24}Br_{16}H_4^{4-}$	+1.30		127
$B_{10}H_9OH^{2-}$	+0.60	pH 4.5 (data also for pH 7 and 10)	122	$B_{24}Cl_{18}H_4^{4-}$	+1.76		127
$B_{10}H_8(OH)_2^{2-}$	+0.47	$E_{p/2}$; SCE, C paste, pH 4.5 (data also for pH 7 and 10)	122				
$B_{10}Cl_{10}^{2-}$	>+1.1	$E_{p/2}$; SCE, C paste, pH 4.5 (data also for pH 7 and 10)	122				
	+1.43	Bu ₄ N ⁺ salt in MeCN/(Bu ₄ N)ClO ₄ ; cyclic voltammetry; 0.2 V/s; Pt-wire working electrode and AgCl-coated silver-wire reference	117				
	+2.16						

2. $B_{10}X_{10}^{2-}$

A variety of electrochemical techniques have been used to elucidate the mechanism and reaction products of the oxidation of $B_{10}H_{10}^{2-}$ at a platinum electrode in acetonitrile.¹¹⁹ This work represented the first application to boron hydride systems of nonaqueous polarography utilizing operational amplifier circuitry with a three-electrode system along with the methods of cyclic voltammetry and chronopotentiometry. The chemical oxidation of $B_{10}H_{10}^{2-}$ (by Fe³⁺ and Ce⁴⁺) gave $B_{20}H_{18}^{2-}$,¹²⁸⁻¹³² and under milder conditions the one-electron oxidation product, $B_{20}H_{19}^{3-}$, was isolated.¹³⁰⁻¹³² Voltammetry of $B_{10}H_{10}^{2-}$ at a rotating platinum electrode (RPE) produced two anodic waves. A variety of electrochemical techniques have been used to establish that the oxidation proceeded by an initial reversible one-electron transfer to form a free radical, which then

underwent a second-order chemical reaction to form $B_{20}H_{19}^{3-}$, which was further oxidized to $B_{20}H_{18}^{2-}$ at a slightly greater potential than $B_{10}H_{10}^{2-}$.¹¹⁹ The second-order rate constant for the chemical coupling reaction, as determined by chronopotentiometry with current reversal, was $k = 2.8 \times 10^3 \text{ mol}^{-1} \text{ s}^{-1}$. The overall reaction scheme was



The products of both eq 73 and 74 have been isolated by constant-potential electrolysis at a rotating platinum gauze electrode with 0.1 M LiClO₄ as the supporting electrolyte. The initial one-electron oxidation product was depleted too quickly by the bimolecular reaction

(eq 73) to be isolated, but fast-scan cyclic voltammetry has established the reversible nature of the oxidation. Cyclic voltammetry of a solution of $(\text{Me}_4\text{N})_3\text{B}_{20}\text{H}_{19} \cdot \frac{1}{2}\text{H}_2\text{O}$ showed an anodic peak at $\sim +0.7$ V and a cathodic peak at -0.1 V that increased on each cycle and was assumed to be due to the protons liberated by the oxidation of $\text{B}_{20}\text{H}_{19}^{3-}$ to $\text{B}_{20}\text{H}_{18}^{2-}$. The former wave corresponded to the second anodic wave of $\text{B}_{10}\text{H}_{10}^{2-}$. There was no evidence that the oxidation of $\text{B}_{20}\text{H}_{19}^{3-}$ was reversible within the scan rates and potential limits available. At a DME, a solution of $(\text{Me}_4\text{N})_2\text{B}_{20}\text{H}_{18}$ displayed a cathodic wave at 1.48 V (vs. SCE).

Schmitt¹²⁰ has given a more detailed discussion of the electrochemical oxidation of $\text{B}_{10}\text{H}_{10}^{2-}$ and some substituted derivatives of this anion [$(\text{B}_{10}\text{H}_9\text{L})^-$ (L = Me_2S , Me_3N , NH_3), 2- $\text{B}_{10}\text{H}_9\text{I}^{2-}$, 1- $\text{B}_{10}\text{H}_9\text{I}^{2-}$]. He found that the oxidation of the substituted analogues of $\text{B}_{10}\text{H}_{10}^{2-}$ paralleled the electrochemistry described above for the parent ion. A correlation was observed between the oxidation potentials and the inductive electron-withdrawing ability of the substituent. However, the position of isomeric substitution produced no detectable change in the potential. The rate of dimerization, however, in addition to exhibiting a substituent effect that correlated with the inductive electron-withdrawing ability of the substituents, also showed a dependence on the position of substitution, the 1-isomer showing an enhanced rate of chemical reaction.¹²³

The reduction of $\text{B}_{10}\text{H}_9\text{IC}_6\text{H}_5^-$ at a DME in acetonitrile occurred at about -1.0 V (SCE) but was not a reversible, diffusion-controlled process. Electrolysis at a mercury pool in CH_3CN at -1.2 V yielded $\text{B}_{10}\text{H}_9\text{I}^{2-}$ and benzene, with $n = 1.3$.¹²⁴

Two successive one-electron reversible oxidations of $\text{B}_{10}\text{Cl}_{10}^{2-}$ were observed in MeCN and CH_2Cl_2 ¹¹⁷ (Table V). Constant-potential electrolysis of $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ in MeCN at $+1.62$ V gave a purple solution (one-electron oxidation) characterized by visible absorption bands at 569 and 419 nm with poorly resolved more intense bands in the UV region. The purple solution was reasonably stable but the absorbance decreased by 10% over 1 h. A similar purple solution resulted from the chemical oxidation (e.g., Ce^{4+} or SOCl_2) of $\text{B}_{10}\text{Cl}_{10}^{2-}$ in MeCN (Li^+ salt) or CH_2Cl_2 ($n\text{-Pr}_4\text{N}^+$ salt).

The second oxidation of $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ was completely irreversible in MeCN by cyclic voltammetry (only the first oxidation could be observed in CH_2Cl_2 because of the anodic limit of this solvent). However, differential pulse voltammetry at a Pt electrode in MeCN/ $(n\text{-Bu})_4\text{NClO}_4$ showed two successive reversible one-electron oxidations with peak heights of 50 and 51 μA , respectively, and $E_{1/2}$ values consistent with the potentials observed by cyclic voltammetry (Table V).

These results were interpreted in terms of redox behavior analogous to that observed for the $\text{B}_2\text{X}_9^{2-}$ system (eq 71) rather than the oxidative boron polyhedron coupling observed for $\text{B}_{10}\text{H}_{10}^{2-}$ (eq 72–74).

3. $\text{B}_{12}\text{X}_{12}^{2-}$

The electrochemical oxidation of $\text{B}_{12}\text{H}_{12}^{2-}$ has been similarly studied. Voltammetry of $(\text{Et}_4\text{N})_2\text{B}_{12}\text{H}_{12}$ at an RPE in acetonitrile solution (0.1 M Et_4NClO_4) showed an anodic one-electron wave at $E_{1/2} = +1.5$ V (vs. SCE).^{126,127} Constant-potential electrolysis under nitrogen at $+1.45$ V with a graphite-cloth anode with no

TABLE VI. Metallaboranes and Anions

compd	$E_{1/2}$, V ^a		ref
	oxidn	redn	
2-CpCoB ₄ H ₄	+1.14 ^b	-1.40 ^c -2.52 ^b	141
[CpNiB ₁₁ H ₁₁] ⁻	+1.70 ^b	-1.50 ^c	139
CpNiB ₁₀ H ₁₃	+0.79 ^b		139
[CpNiB ₁₀ H ₁₂] ⁻	+0.61 ^d		139
[Cp ₂ CoNiB ₁₀ H ₁₀] ²⁻	+0.45 ^b +1.30 ^d	-1.55 ^d	139
(CpNi) ₂ B ₁₀ H ₁₀	+1.73 ^b	-0.27 ^c -1.35 ^c	139
[(2-CpNi)B ₉ H ₉] ⁻	+0.87 ^b	-1.42	139
[(1-CpNi)B ₉ H ₉] ⁻	+0.77 ^b	-1.52	139
[(2-CpNi)B ₉ Cl ₉] ⁻	-0.40 ^c		139
[(1-CpNi)B ₉ Cl ₉] ⁻	-0.35 ^c		139
[(B ₁₀ H ₁₂) ₂ Ni] ²⁻	+1.03 ^b		139

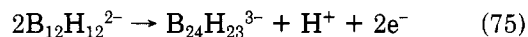
^a SCE, CH_3CN , Et_4NClO_4 , Pt. ^b Irreversible (E_p). ^c Reversible. ^d Quasireversible.

TABLE VII. Heteroboranes and Their Metalla Derivatives

compd	redox potentials, ^a V	ref
(B ₁₀ H ₁₀ S) ₂ Fe ²⁻	+0.21, reversible; RPE; CH_3CN ; SCE	132a
(B ₁₀ H ₁₀ S) ₂ Co ⁻	+1.35, +1.8 irreversible	132a
B ₉ H ₁₂ S ⁻	+0.90, Pt; CH_3CN ; SCE; irreversible	132a
B ₁₀ H ₁₁ S ⁻	+0.98	132a
(B ₁₀ H ₁₀ As) ₂ Co ³⁻	+0.035, +0.67 irreversible, +0.94 (product)	142
(B ₉ H ₉ As) ₂ Co ⁻	+1.79 irreversible	142
(B ₁₀ H ₁₀ As)CoCp ⁻	-1.00, -1.82, -2.58 irreversible	142
(B ₉ H ₉ As) ₂ CoCp	+1.16 irreversible at slow scans	142
(B ₁₀ H ₁₀ P)CoCp	-2.02, -2.50 reversible	142
(1-Me-1,7-PCHB ₉ H ₉) ₂ Co	-0.99, -1.80	142
(B ₁₀ H ₁₀ P)CoCp	+1.14, -2.00, -2.50 irreversible	142
(1-Me-1,7-PCHB ₉ H ₉) ₂ Co	+0.41, -0.62, ^b -1.93 ^b	142

^a $E_{1/2}$ for dc; E° for reversible CV; E_p for irreversible CV waves. ^b In dimethoxyethane/ Bu_4NPF_6 .

supporting electrolyte and precipitation of the oxidation product with CsF gave a product identified as $\text{Cs}_3\text{B}_{24}\text{H}_{23} \cdot 3\text{H}_2\text{O}$ on the basis of elemental analysis, a conductivity measurement, and ¹¹B NMR spectroscopy. A graphite anode was necessary because the oxidation produced severe filming on a platinum electrode. Because the product was ionic, the use of a supporting electrolyte with its accompanying separation problem was omitted, although the resulting diffusion loss decreased the typical yields to 80–85%. Another factor contributing to the less than quantitative yield was the acid-catalyzed reaction of $\text{B}_{12}\text{H}_{12}^{2-}$ with acetonitrile to give $\text{B}_{12}\text{H}_{11}\text{NCCH}_3^-$. The acid formed in the electrolysis reaction:



The structure of the dimeric oxidation product has been formulated as consisting of two B_{12} polyhedra joined by a bridge hydrogen, analogous to $\text{B}_{20}\text{H}_{19}^{3-}$.

Although $\text{B}_{24}\text{H}_{23}^{3-}$ is resistant to further oxidation without degradation, its partly halogenated derivative $[\text{B}_{24}\text{H}_{21}\text{I}_2]^{3-}$ (produced by the reaction of $\text{B}_{24}\text{H}_{23}^{3-}$ with iodine at room temperature in acetone-methanol)¹²⁷ underwent a two-electron oxidation in acetonitrile at $+1.3$ V (vs. SCE) to give $[\text{B}_{24}\text{H}_{20}\text{I}_2]^{2-}$,¹³³ a derivative of the hypothetical parent oxidation product $\text{B}_{24}\text{H}_{22}^{2-}$. Spectroscopic evidence¹³³ supported a structure for $\text{B}_{24}\text{H}_{20}\text{I}_2^{2-}$ analogous to that of the photoisomer of $\text{B}_{20}\text{H}_{18}^{2-}$.

TABLE VIII. Derivatives of *o*-Carborane

substituent	$E_{1/2}$, V vs. SCE	ref
unsubstituted compd	-2.51	143, 145-147
1-(<i>o</i> -C ₂ B ₁₀ H ₁₁)	-1.44	145
1-Me	-2.44	143, 145-147
1-Ph	-1.95	143, 145, 146
1-(<i>p</i> -MeC ₆ H ₄)	-2.12	145
1-(<i>p</i> -IC ₆ H ₄)	-1.60	147
	-2.00	
1-(CH ₂ =CH)	-1.89	145
1-(CH ₂ Cl)	-2.03	146
1-(CH ₂ Br)	-1.21	146, 149
1-Cl	-1.19	146
	-2.60	
1-Br	-0.56	146
	-2.53	
1-I	-0.12	147
	-0.39	
1,2-(Me) ₂	-2.35	145
1,2-(Ph) ₂	-1.14	145, 147
	-1.40	
1,2-(Cl) ₂	-1.36	149
1,2-(Br) ₂	-0.56	149
1,2-(I) ₂	-0.21	149
1-Me-2-Cl	-1.22	147
	-2.47	
1-Me-2-Br	-0.64, -0.42	146, 147
	-2.70, -2.45	
1-I-2-Me	-0.15	149
1-Ph-2-Br	-0.60	144, 147
	-2.30	
1-I-2-Ph	-0.2, -2.16	145, 149
1-Cl-2-(CH ₂ Cl)	-0.13	
	-1.28	149
	-1.90	
1-Br-2-(CH ₂ Cl)	-0.13	
	-1.27	149
	-1.82	
1-I-2(CH ₂ Cl)	-0.19	
	-1.28	149
	-2.00	
1-Me-2-(PhCH ₂)	-2.16	145
1-Ph-12-I	-1.51	145
1-Ph-12-Br	-1.63	144, 145
1-(CH ₂ =CH)-12-I	-1.52	144, 145
1-(CH ₂ =CH)-9-I	-1.52	144, 145
1,2-Me ₂ -3-(<i>m</i> -MeC ₆ H ₄)	-2.47	145
1,2-(Me) ₂ -9-I	-2.01	144, 145
1-(CH ₂ Cl)-10,12-(Cl) ₂	-1.68	149
1-(CH ₂ Cl)-9,10,11,12-(Cl) ₄	-1.60	149
3-Ph	-2.59	145
3-(<i>p</i> -MeC ₆ H ₄)	-2.67	145
3-(<i>m</i> -MeC ₆ H ₄)	-2.53	145
9-Cl	-2.34	143, 144, 147
9-Br	-2.21	143, 144, 147
9-I	-2.13	143, 144, 147
9,12-(Cl) ₂	-2.03	144
9,12-(Br) ₂	-1.90	144
9,12-(I) ₂	-1.81	144, 147
8,9,12-(Cl) ₃	-1.71	144
8,9,12-(Br) ₃	-1.66	144
8,9,12-(I) ₃	-1.41	144
10-Cl	-2.22	148
10-Br	-2.18	148
10-I	-2.15	148

As with the lower B_{*n*}X_{*n*}²⁻ species,¹¹⁷ halogenation of the B₁₂H₁₂²⁻ cage enhanced the oxidative stability. Although B₁₂Cl₁₂²⁻ gave no well-defined waves by cyclic voltammetry in MeCN, differential pulse voltammetry showed a wave at +2.34 V.¹¹⁷

The high thermal and redox stability of the salts Li₂B₁₀Cl₁₀ and Li₂B₁₂Cl₁₂ has led to their evaluation as nonaqueous electrolytes in solid-cathode lithium batteries.¹³⁴⁻¹³⁸

F. Metallaboranes

A series of *closo* metallaboranes were examined by cyclic voltammetry, and the qualitative features of the voltammograms were similar. The reduction waves were all one-electron reversible processes, and the oxidations were irreversible for the nickel compounds. By analogy with the Ni^{IV} carborane compounds (section VIB), the first reduction wave for the *closo*-nickelaboranes was assigned to the Ni^{IV}/Ni^{III} couple. Similarly, a quasi-reversible reduction wave in the Co-Ni bimetallic compound was assigned to the formal Co^{IV}/Co^{III} couple.¹³⁹ Details are presented in Table VI.

Electrolysis of B₃H₈⁻ at a variety of metal anodes led to anodic dissolution in a number of cases with the formation of metalloborane derivatives.^{65-69,105} The compounds (Ph₃P)₂CuB₃H₈ and (Ph₃P)₃AgB₃H₈ were prepared by using Cu or Ag anodes. At Zn or Cd anodes, electrolysis of Me₄NB₃H₈ led to metal dissolution, but only the cleavage products Ph₃PB₃H₇, Ph₃PBH₃, and (Ph₃P)₂B₂H₄ could be isolated.

The cyclic and ac voltammograms of (Ph₃P)₂CuB₃H₈ in CH₃CN at Pt also showed complex highly irreversible behavior. An oxidation wave near -0.6 V (Ag/AgNO₃), whose position and intensity depended on the electrochemical history of the sample, was probably oxidation of Cu⁰ to Cu^I; two other oxidation waves were observed, one broad and diffuse near +0.3 V and the other near +1.1 V, both of which were similar to those from the B₃H₈⁻ ion. Reduction waves were diffuse and difficult to identify.^{105a}

The cyclic voltammogram of [(B₁₀H₁₂)₂Ni]²⁻ in CH₃CN showed an irreversible oxidation at +1.03 V (SCE).^{139c}

Some of the data on metallaboranes have been reviewed recently.¹⁴⁰

G. Heteroboranes and Their Metalla Derivatives

Polarographic data have been obtained on salts of B₉H₁₂S⁻ and B₁₀H₁₁S⁻ and the iron and cobalt derivatives (B₁₀H₁₀S)₂Fe²⁻ and (B₁₀H₁₀S)₂Co⁻.^{139a} A series of phosphorus- or arsenic-substituted cobaltaboranes and carboranes was studied by dc polarography, cyclic voltammetry, and controlled-potential coulometry. Reversible processes involving Co(IV), Co(III), Co(II), Co(I), and Co(0) oxidation states were detected, with the favored oxidation state being determined largely by the formal charge on the borane ligand.^{140,142} Redox potentials are given in Table VII.

V. Carboranes and Their Derivatives

A. 1,2-, 1,7-, and 1,12-B₁₀C₂H₁₂ and Their Simple Derivatives

Electrochemical studies of carboranes themselves and their simple organo- and halo-substituted derivatives have been largely restricted to those compounds based on the 1,2-, 1,7-, and 1,12-dicarbododecahydro-*closo*-dodecaboranes *o*-, *m*-, and *p*-C₂B₁₀H₁₂, alternatively named *o*-, *m*-, and *p*-carborane, respectively.¹⁴³⁻¹⁴⁹ Tables VIII, IX, and X show electrochemical data obtained on derivatives of *o*-, *m*-, and *p*-carborane, respectively.

TABLE IX. Derivatives of *m*-Carborane

substituent	$E_{1/2}$, V vs. SCE	ref
unsubstituted compd	> -2.8	143, 145-147
1-(<i>m</i> -C ₂ B ₁₀ H ₁₁)	-2.62	145
1-Me	> -2.8	146
1-Ph	-2.45	143, 147
1-(<i>p</i> -IC ₆ H ₄)	-1.63	147
	-2.51	
1-Cl	-1.66	146
1-I	-0.35	149
1,7-(Ph) ₂	-2.35	145
1,7-(Cl) ₂	-1.30	149
1,7-(Br) ₂	-0.48	149
	-0.79	
1,7-(I) ₂	-0.25	149
	-0.39	
1-Cl-7-Me	-1.67	146
1-Br-7-Me	-0.66	146
1-I-7-Me	-0.36	149
1-I-7-Ph	-0.35	149
1-Ph-2-	-2.34	145
9-I	-2.71	145, 148
9,10-(Cl) ₂	-2.43	148
(I) ₃	-2.02	145
B-(Cl) ₄	-2.46	145
B-(Br) ₄	-2.23	145
B-oxy	-2.60	145

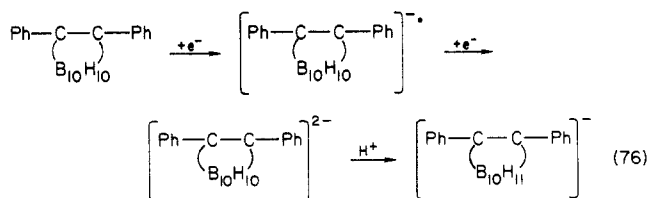
TABLE X. Derivative of *p*-Carborane

substituent	$E_{1/2}$, V vs. SCE	ref
unsubstituted compd	> -2.8	146, 148
1-Cl	-1.87	146, 148
1-Br	-0.78	146, 148
1-I	-0.53 ^a	148
1,12-(Cl) ₂	-1.84	146, 148
1,12-(Br) ₂	-0.75	146, 148
1,12-(I) ₂	-0.60 ^a	148
1-Cl-12-Me	-1.83	146, 148
1-Br-12-Me	-0.77	146, 148
1-I-12-Me	-0.50 ^a	148
2-I	-2.61	148

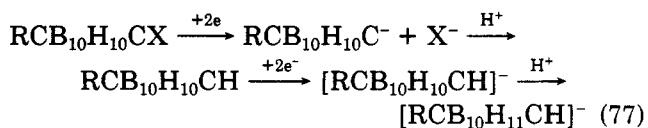
^a Supporting electrolyte was [N(C₁₀H₂₃)₄]⁺[ClO₄]⁻.

Under the conditions reported, *m*-carborane, its 1-methyl derivative, and *p*-carborane were not reduced polarographically down to -2.80 V, and in general *o*-carboranes were reduced more readily than *m*-carboranes, which in turn, reduced more readily than *p*-carboranes.

The polarographic reduction of *o*- and *m*-carboranes free of any polarographically active groups showed one two-electron wave. 1,2-Diphenyl-*o*-carborane, however, was reduced stepwise, with two one-electron waves, as shown.¹⁴³



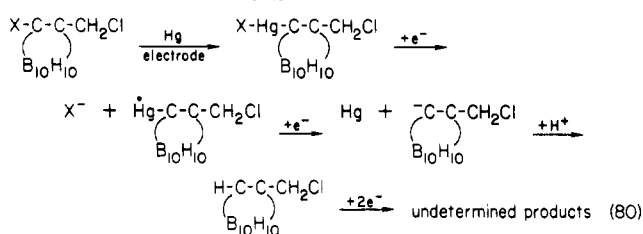
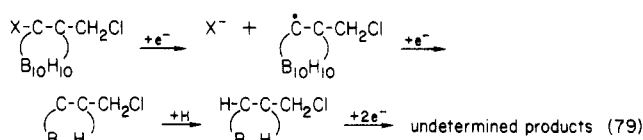
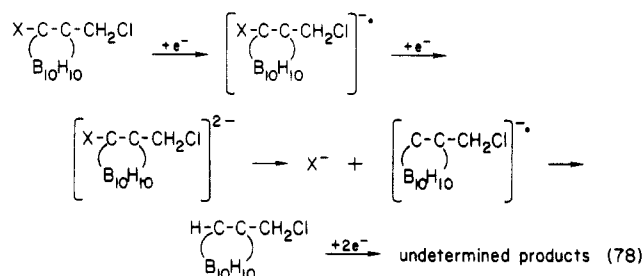
The polarographic reduction of C-substituted halogenocarboranes generally showed two equivalent two-electron waves, ascribed to (a) the reduction of the C-X bond and (b) the reduction of the carborane nucleus.¹⁴³



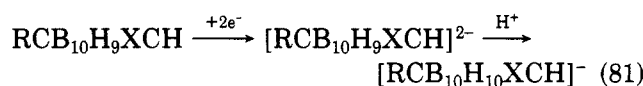
X = Cl, Br, or I

The ease of reduction of step a diminished in the order C-I > C-Br > C-Cl.

Where R = CH₂Cl, however, a slightly different behavior was observed.¹⁴⁸ Three reduction waves were found, and the potentials of these did not vary whether X was Cl, Br, or I. The first two waves were ascribed to two one-electron reductions, and the wave at the lowest potential was ascribed to a two-electron reduction. This latter reduction corresponded to that of 1-(CH₂Cl)-*o*-carborane. On assuming that the reduction of the C-X bond was affected by the presence of the CH₂Cl group, Stanko et al. proposed three alternative mechanisms (eq 78-80).¹⁴⁸



The reduction of the B-halo-substituted 9-halogenocarboranes showed just a single two-electron wave, as this reduction did not involve the B-X bond.^{143,144,147}



The reduction potentials of B-halo-substituted carboranes in general were independent of the nature of the halogen^{147,148} (e.g., 9-iodo-*o*-carborane showed a reduction potential of $E_{1/2} = -2.13$ V, the 9-Br derivative -2.21 V, and the 9-Cl derivative -2.34 V).

Carboranes other than *o*-, *m*-, and *p*-C₂B₁₀H₁₂ and their simple derivatives have been studied. The octadecahedral carborane 2,3-(Me)₂-2,3-C₂B₉H₉ and its B-oxy derivatives have been studied electrochemically by both polarography and cyclic voltammetry.¹⁵⁰ Table XI lists the polarographic data. Entries 1-3 gave single one-electron irreversible waves, whereas entries 4-6 each gave two reduction waves. The data suggested that the B-oxy derivatives were more difficult to reduce, implying that the B-oxy substituents acted as electron donors.

For entries 1-6, the first reduction wave was thought to involve a one-electron transfer to the carborane, with the formation of a radical anion

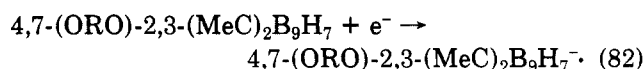


TABLE XI. Reduction Behavior of Octadecahedral B-Substituted Carboranes^a

compd	$E_{1/2}$, V vs. SCE	n^b
(1) 2,3-(MeC) ₂ B ₉ H ₉	-1.06	1.0
(2) 4-(OH)-2,3-(MeC) ₂ B ₉ H ₈	-1.08	0.87
(3) 4,7-(OH) ₂ -2,3-(MeC) ₂ B ₉ H ₇	-1.27	0.96
(4) 4,7-(OCH ₂ CH ₂ O)-2,3-(MeC) ₂ B ₉ H ₇	-1.43	
(5) 4,7-(OCH(Me)CH ₂ CH(Me)O)-2,3-(MeC) ₂ B ₉ H ₇	-1.25	2.02
	-1.64	
(6) 4,7-(OC ₆ H ₄ O)-2,3-(MeC) ₂ B ₉ H ₇	-1.03	1.95
	-1.39	

^a Reference 150. ^b Number of electrons transferred.

TABLE XII. Cyclic Voltammetry of Monocarbon Carboranes^a

compd	$E_{1/2}$, V vs. SCE	n^b
B ₁₁ CH ₁₂ ⁻	+2.4	
B ₁₀ CH ₁₃ ⁻	+1.65	2.0
B ₁₀ CH ₁₁ ⁻	+1.45	1.0
B ₉ CH ₁₀ ⁻	+1.85	1.0
B ₁₈ C ₂ H ₁₈ ²⁻	+2.35	

^a Reference 153. ^b Number of electrons transferred.

TABLE XIII. Polarographic Data on Carbaphospha- and Carbaarsaboranes^a

compd	$E_{1/2}$, V vs. SCE	compd	$E_{1/2}$, V vs. SCE
<i>o</i> -B ₁₀ H ₁₀ CHP	-2.30	<i>o</i> -B ₁₀ H ₁₀ CHAs	-2.60
<i>m</i> -B ₁₀ H ₁₀ CHP	-2.44	<i>m</i> -B ₁₀ H ₁₀ CHAs	-2.25
<i>p</i> -B ₁₀ H ₁₀ CHP	-2.51	<i>p</i> -B ₁₀ H ₁₀ CHAs	-2.43

^a Reference 154.

Entries 2 and 3 gave unstable radical anions, their ultimate electrolysis products being *arachno*-1,3-(MeC)₂B₇H₁₁, suggesting that the B(O) unit is protected by the presence of an organic group in entries 4–6. The formation of a radical anion was proven when the carboranes 1 and 4–6 were exposed to a sodium mirror, and ESR spectra were obtained.

The relative stabilities of the radical anions of entries 2 and 6 were illustrated by their cyclic voltammograms (Figure 2). An irreversible wave was found for entry 2, regardless of the scan rate, indicating the formation of an unstable radical anion. The voltammogram of entry 6, however, showed a reversible wave (at A and E), indicating the formation of a relatively stable radical anion.

The second reduction peak (at B) was assigned to the formation of the dianion *closo*-[4,7-(OC₆H₄O)-2,3-(MeC)₂B₉H₇]²⁻ and peak C to its subsequent oxidation back to the radical anion. The formation of a new peak D, at slower scan rates, was thought to be due to the oxidation of the product of the chemical transformation *closo*-[4,7-(OC₆H₄O)-2,3-(MeC)₂B₉H₇]²⁻ to *nido*-[3,4-(OC₆H₄O)-7,9-(MeC)₂B₉H₇]²⁻. The oxidation of this *nido* species again yielded the radical anion.

Electrolysis of an electrolyte containing nickel sulfamate, the C₂B₉H₁₂⁻ anion, NaCl, and H₃BO₃ at a current density of 1–8 A dm⁻² produced nickel–boron alloys.¹⁵¹ The B₉C₂H₁₁²⁻ anion has also been used in a silver–boron alloy electroplating solution.¹⁵²

B. Monocarbon Carboranes and Derivatives

The electrochemistry of the monocarbon carboranes B₁₁CH₁₂⁻, B₁₀CH₁₁⁻, B₁₀CH₁₃⁻, and B₉CH₁₀⁻ has been

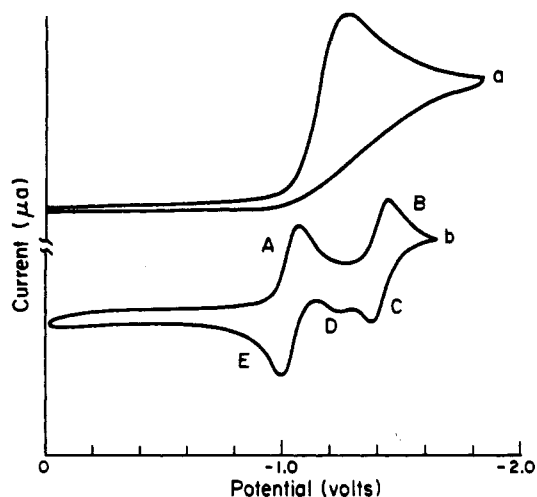


Figure 2. Cyclic voltammograms of 4-(OH)-2,3-(MeC)₂B₉H₈ (upper trace) and 4,7-(OC₆H₄O)-2,3-(MeC)₂B₉H₇ (lower trace). Reproduced with permission from ref 150. Copyright 1975, American Chemical Society.

TABLE XIV. Electrochemical Data of C-Mercurated Carboranes

R in R ₂ Hg	$E_{1/2}$, V vs. SCE	ref
<i>o</i> -HCB ₁₀ H ₁₀ C	-0.764	155, 157
<i>o</i> -1-MeCB ₁₀ H ₁₀ C	-0.822	155, 157
<i>o</i> -1-PhCB ₁₀ H ₁₀ C	-0.742	155, 157
<i>o</i> -10,12-HCB ₁₀ H ₈ Cl ₂ C	-0.857	157
<i>m</i> -HCB ₁₀ H ₁₀ C	-1.309	157
<i>m</i> -1-MeCB ₁₀ H ₁₀ C	-1.312	156, 157
<i>m</i> -1-PhCB ₁₀ H ₁₀ C	-1.197	157
<i>m</i> -9(10)-HCB ₁₀ H ₉ ClC	-0.990	157
<i>p</i> -HCB ₁₀ H ₁₀ C	-1.78	158
<i>o</i> -HCB ₁₀ H ₁₀ CCH ₂	-1.02	159

TABLE XV. Polarographic Characteristics of B-Mercurated Carboranes^a

compd	supporting electrolyte	$-E_{1/2}$, V		
		0.41	1.32	1.91
9(12)-ClHg- <i>o</i> -C(Ph)B ₁₀ H ₉ CH	TBAP	0.41	1.32	1.91
	TBAB	0.55	1.29	<i>b</i>
(9(12)- <i>o</i> -C(Ph)B ₁₀ H ₉ CH) ₂ Hg	TBAP			1.82
<i>o</i> -C(Ph)B ₁₀ H ₁₀ CH	TBAP			1.84
9-ClHg- <i>o</i> -CHB ₁₀ H ₉ CH	TBAB	0.66	1.42	<i>b</i>
	TBAP	0.48	1.53	<i>b</i>
9-BrHg- <i>o</i> -CHB ₁₀ H ₉ CH	TBAB	0.52	1.53	<i>b</i>
(9- <i>o</i> -CHB ₁₀ H ₉ CH) ₂ Hg	TBAP			2.58
<i>o</i> -CHB ₁₀ H ₁₀ CH	TBAB			2.55
9(12)-ClHg- <i>o</i> -CMeB ₁₀ H ₉ CH	TBAB	0.64	1.54	<i>b</i>
9-ClHg- <i>m</i> -CHB ₁₀ H ₉ CH	TBAB	0.63	0.49	
9-BrHg- <i>m</i> -CHB ₁₀ H ₉ CH	TBAB	0.69	1.81	
9-IHg- <i>m</i> -CHB ₁₀ H ₉ CH	TBAB	0.70	1.83	
2-ClHg- <i>p</i> -CHB ₁₀ H ₉ CH	TBAB	0.42	1.61	
(9- <i>m</i> -CHB ₁₀ H ₉ CH) ₂ Hg	TBAP			2.74
(2- <i>p</i> -CHB ₁₀ H ₉ CH) ₂ Hg	TBAP			2.55
<i>m</i> -CHB ₁₀ H ₁₀ CH	TBAB			2.8

^a Reference 160; DMF, 0.05 M Bu₄NBr or Bu₄NClO₄, 25 °C. ^b Ill-defined wave.

investigated,¹⁵³ and the results have been compared with those obtained for the electronically equivalent boranes, B₁₂H₁₂²⁻, B₁₁H₁₁²⁻, B₁₁H₁₃²⁻, and B₁₀H₁₀²⁻, respectively. Table XII shows the data obtained from cyclic voltammetry. The introduction of a carbon atom in place of a boron atom in going from boranes to monocarbon carboranes sharply increases the potentials required for oxidation. In other ways, however, they show similar behavior. For example, the controlled-potential electrolysis of Et₄NB₉CH₁₀ in acetonitrile at +1.95 V (vs. SCE) gave a one-electron oxidation to

TABLE XVI. Electrochemical Data of Transition-Metal/Carborane Complexes

compd ^a	$E_{1/2}$, V vs. SCE	oxidn/redn process	ref
Ti, Zr, Hf			
[4-(Cp)-4,1,6-Ti(C ₂ B ₁₀ H ₁₂) ⁻	+0.51	<i>b</i>	
	-1.78	Ti ^{III} + e ⁻ → Ti ^{II}	161
[3-(C ₈ H ₈)-3,1,2-Ti(C ₂ B ₉ H ₁₁) ⁻	-0.91	Ti ^{IV} - e ⁻ → Ti ^{IV}	161
3-(C ₈ H ₈)-3,1,2-Ti(C ₂ B ₉ H ₁₁)	-0.87	<i>b</i>	
	+1.70	Ti ^{IV} + e ⁻ → Ti ^{III}	161, 163
2-(C ₈ H ₈)-2,1,7-Ti(C ₂ B ₉ H ₁₁) ⁻	-0.87	Ti ^{IV} + e ⁻ → Ti ^{III}	163
4-(C ₈ H ₈)-4,1,6-Ti(C ₂ B ₁₀ H ₁₂)	-0.55	<i>b</i>	
	+1.77	Ti ^{IV} + e ⁻ → Ti ^{III}	161, 163
[4,4'-Ti(1,6-C ₂ B ₁₀ H ₁₂) ₂] ²⁻	-0.22	<i>b</i>	
	-2.03	Ti ^{II} - e ⁻ → Ti ^{III}	162, 163
[4,4'-Ti(1,6-(Me) ₂ -1,6-C ₂ B ₁₀ H ₁₂) ₂] ²⁻	-0.34	<i>b</i>	
	-2.10	Ti ^{II} → Ti ^I	162, 163
V, Nb, Ta			
[4,4'-V(1,6-C ₂ B ₁₀ H ₁₂) ₂] ²⁻	+0.4	V ^{II} - e ⁻ → V ^{III}	162, 163
	-1.79		
[4,4'-V(1,6-(Me) ₂ -1,6-C ₂ B ₁₀ H ₁₂) ₂] ²⁻	-0.12	V ^{II} - e ⁻ → V ^{III}	163
	-1.80		
Cr, Mo, W			
[4,4'-Cr(1,6-C ₂ B ₁₀ H ₁₂) ₂] ²⁻	-0.11		163
	-1.90		
[4,4'-Cr(1,6-C ₂ B ₁₀ H ₁₂) ₂] ⁻	-0.56	Cr ^{III} + e ⁻ → Cr ^{II}	163
	+1.41		
Mn, Tc, Re			
[4,4'-Mn(1,6-C ₂ B ₁₀ H ₁₂) ₂] ²⁻	-0.11		163
	-1.52		
Fe, Ru, Os			
[Fe(π-(3)-1,2-B ₉ C ₂ H ₁₁) ₂] ⁻	-0.424	Fe ^{III} + e ⁻ → Fe ^{II}	
[Fe(π-(3)1,2-C ₂ Me ₂ B ₉ H ₉) ₂] ⁻	-0.538	Fe ^{III} + e ⁻ → Fe ^{II}	164, 165
[Fe(π-(3)-1,2-C ₂ (Ph)B ₉ H ₁₀) ₂] ⁻	-0.464	Fe ^{III} + e ⁻ → Fe ^{II}	165
Fe(Cp)(π-(3)-1,2-C ₂ B ₉ H ₁₁)	-0.08	Fe ^{III} + e ⁻ → Fe ^{II}	165
[FeH(π-(3)-1,2-C ₂ B ₉ H ₁₁) ₂] ⁻	-0.44	Fe ^{II} - e ⁻ → Fe ^{III}	166
Fe(π-(3)-1,2-C ₂ B ₉ H ₁₀ SEt ₂) ₂	+0.48	Fe ^{II} - e ⁻ → Fe ^{III}	166
Fe(Cp)(C ₂ B ₁₀ H ₁₂)	+0.16		167
[Fe(C ₂ B ₁₀ H ₁₂) ₂] ²⁻	-0.02		167
4,5-(Cp)Fe ₂ -2,3-C ₂ B ₉ H ₁₁	-0.59		168
	+1.36		
[4-(Cp)-5-(η ⁵ -1,2-C ₂ B ₉ H ₁₁)-4,5-Fe ₂ -2,3-C ₂ B ₉ H ₁₁] ⁻	-0.70		168
	+1.07		
	+1.76		
(Cp) ₂ Fe ₂ C ₂ B ₆ H ₈	-0.80	oxidn	169
	-1.17	redn	
σ-2-Fe(CO) ₂ (Cp)-o-C ₂ (Me)B ₁₀ H ₁₀	-1.36		170
	-1.60		
σ-2-Fe(CO) ₂ (Cp)-o-C ₂ (Ph)B ₁₀ H ₁₀	-1.36		170
	-1.64		
	-2.10		
1-Fe(CO) ₂ (Cp)-m-C ₂ B ₁₀ H ₁₁	-1.59		170
	-2.34		
σ-2-CH ₂ Fe(CO) ₂ (Cp)-o-C ₂ (Me)B ₁₀ H ₁₀	-1.58		170
σ-B-Fe(CO) ₂ (Cp)-o-C ₂ B ₁₀ H ₁₁	-2.00		170
σ-B-Fe(CO) ₂ (Cp)-o-C ₂ (Me) ₂ B ₁₀ H ₉	-1.97		170
[(1,2-B ₉ H ₉ CHP) ₂ Fe] ²⁻	+0.08	Fe ^{III} → Fe ^{II}	171
[(1,7-B ₉ H ₉ CHP) ₂ Fe] ²⁻	+0.05	Fe ^{III} → Fe ^{II}	171
(1,2-B ₉ H ₉ CHPMe) ₂ Fe	+1.6	Fe ^{III} → Fe ^{II}	171
(1,7-B ₉ H ₉ CHPMe) ₂ Fe	+1.46	Fe ^{III} → Fe ^{II}	171
[(1,7-B ₉ H ₉ CHP)Fe(1,7-B ₉ H ₉ CHPMe)] ⁻	+0.74	Fe ^{III} → Fe ^{II}	171
1,2,3-CpFe(C ₂ B ₄ H ₆)	+1.20	Fe ^{IV} → Fe ^{III}	141
	-0.52	Fe ^{III} → Fe ^{II}	
(2,6-(CO) ₃ Fe(C ₂ B ₃ H ₆))	-1.25 (rev)		141
	-1.89 (irrev)		
Co, Rh, Ir			
4,5-(Cp) ₂ -4-Co-5-Fe-1,8-C ₂ B ₉ H ₁₁	+0.90	oxidn	172
	-0.42	redn	
1,2,3-CpCo(C ₂ B ₄ H ₆)	+1.52	Co ^{IV} → Co ^{III}	141
	-1.62	Co ^{III} → Co ^{II}	
	-2.50 (irrev)	Co ^{II} → Co ^I	
1,2,4-CpCo(C ₂ B ₄ H ₆)	+1.70	Co ^{IV} → Co ^{III}	141
	-1.43	Co ^{III} → Co ^{II}	
	<-2.75	Co ^{II} → Co ^I	
1,2,3-CpCo[(C ₂ B ₄ H ₄)(Me) ₂]	+1.43	Co ^{IV} → Co ^{III}	141
	-1.70	Co ^{III} → Co ^{II}	
	-2.70 (irrev)	Co ^{II} → Co ^I	
[(1,2-C ₂ B ₉ H ₁₁) ₂ Co] ⁻	+1.57	Co ^{IV} → Co ^{III}	165, 173, 175
	-1.36	Co ^{III} → Co ^{II}	
	-2.34	Co ^{II} → Co ^I	

TABLE XVI (Continued)

compd ^a	$E_{1/2}$, V vs. SCE	oxidn/redn process	ref		
[(1,7-C ₂ B ₉ H ₁₁) ₂ Co] ⁻	+1.68 (irrev)	Co ^{IV} → Co ^{III}	165, 173		
	-1.14	Co ^{III} → Co ^{II}			
	-2.54	Co ^{II} → Co ^I			
(Cp)Co(1,2-C ₂ B ₉ H ₁₁)	+2.07 (irrev)	as above	141, 165, 173		
	-1.21				
	-2.11				
[(1,2-C ₂ B ₉ H ₉ Br ₃) ₂ Co] ⁻	irrev	Co ^{IV} → Co ^{III}	165		
	-0.48	Co ^{III} → Co ^{II}			
	-1.58	Co ^{II} → Co ^I			
[(1,2-C ₂ B ₉ H ₉ (Me) ₂) ₂ Co] ⁻	irrev	Co ^{IV} → Co ^{III}	165		
	-1.13	Co ^{III} → Co ^{II}			
	-1.28	Co ^{III} → Co ^{II}			
[(1,2-C ₂ B ₉ H ₁₀ Ph) ₂ Co] ⁻	-1.28	Co ^{III} → Co ^{II}	165		
	[(C ₂ B ₉ H ₁₁)Co(C ₂ B ₉ H ₁₀)Co(C ₂ B ₉ H ₁₁)] ²⁻	+0.70		Co ^{IV} → Co ^{III}	173-175
		-1.48		Co ^{III} → Co ^{II}	
[(C ₂ B ₉ H ₁₁)Co(C ₂ B ₉ H ₁₀)Co(C ₂ B ₉ H ₁₀)Co(C ₂ B ₉ H ₁₁)] ³⁻	-2.36	Co ^{II} → Co ^I	175		
	+1.07				
	-1.36				
(Cp)Co(1,7-C ₂ B ₉ H ₁₁)	-1.03	Co ^{III} → Co ^{II}	176, 177		
(Cp)Co(1,11-C ₂ B ₉ H ₁₁)	-1.33	as above	176, 177		
(Cp)Co(1,6-C ₂ B ₉ H ₁₁)	-1.39	as above	176, 177		
(Cp)Co(5,11-C ₂ B ₉ H ₁₁)	-1.75	as above	176, 177		
(Cp)Co(1,12-C ₂ B ₉ H ₁₁)	-1.42	as above	176, 177		
(Cp)Co(1,10-C ₂ B ₉ H ₁₁)	-1.44	as above	176, 177		
(Cp)Co(1,2-C ₂ (Me) ₂ B ₉ H ₉)	-1.20	Co ^{II} → Co ^{II}	177		
(Cp)Co(1,7-C ₂ (Me) ₂ B ₉ H ₉)	-1.02	as above	177		
(Cp)Co(1,11-C ₂ (Me) ₂ B ₉ H ₉)	-1.38	as above	177		
(Cp)Co(1,6-C ₂ (Me) ₂ B ₉ H ₉)	-1.40	as above	177		
(Cp)Co(5,11-C ₂ (Me) ₂ B ₉ H ₉)	-1.75	as above	177		
(Cp)Co(1,12-C ₂ (Me) ₂ B ₉ H ₉)	-1.40	as above	177		
(Cp)Co(1,10-C ₂ (Me) ₂ B ₉ H ₉)	-1.45	as above	177		
(Cp)Co(1,2-C ₂ (-CH ₂) ₃ -B ₉ H ₉)	-1.14	as above	177		
(Cp)Co(1,6-C ₂ (-CH ₂) ₃ -B ₉ H ₉)	-1.43	as above	177		
(Cp)Co(5,6-C ₂ (-CH ₂) ₃ -B ₉ H ₉)	-1.70	as above	177		
(Cp)Co(5,10-C ₂ (-CH ₂) ₃ -B ₉ H ₉)	-1.80	as above	177		
4,5-(Cp) ₂ -4,5-Co ₂ -1,8-C ₂ B ₉ H ₁₁	+0.97	as above	172		
4,5-(Cp) ₂ -4,5-Co ₂ -1,8-C ₂ (Me) ₂ B ₉ H ₉	+0.92		172		
	-0.91				
4,5-(Cp) ₂ -4,5-Co ₂ -1,13-C ₂ B ₉ H ₁₁	+0.83		172		
	-1.25				
4,5-(Cp) ₂ -4,5-Co ₂ -1,13-C ₂ (Me) ₂ B ₉ H ₉	+0.87		172		
	-1.25				
{[CpCoC ₂ B ₉ H ₁₁] ₂ Co] ⁻	+0.56		172		
	-0.84				
4-Cp-4-Co-1,7-C ₂ B ₁₀ H ₁₂	-0.72		167, 178		
4-Cp-4-Co-1,8-C ₂ B ₁₀ H ₁₂	-1.15		167, 178		
4-Cp-4-Co-1,13-C ₂ B ₁₀ H ₁₂	-1.16		167, 178		
2,4-(Cp) ₂ -2,4-Co ₂ -1,7-C ₂ B ₈ H ₁₀	+1.41		179		
	-1.23				
4,10-(Cp) ₂ -4,10-Co ₂ -1,7-C ₂ B ₈ H ₁₀	+1.40		179		
	-1.65				
2,8-(Cp) ₂ -2,8-Co ₂ -1,12-C ₂ B ₈ H ₁₀	+1.45		179		
	-1.43				
4,12-(Cp) ₂ -4,12-Co ₂ -1,7-C ₂ B ₈ H ₁₀	+1.30		179		
	-1.50				
2,10-(Cp) ₂ -2,10-Co ₂ -1,7-C ₂ B ₈ H ₁₀	+1.37		179		
	-1.23				
2,9-(Cp) ₂ -2,9-Co ₂ -1,12-C ₂ B ₈ H ₁₀	+1.40		179		
	-1.35				
2,5-(Cp) ₂ -2,5-Co ₂ -1,7-C ₂ B ₈ H ₁₀	+1.40		179		
	-1.43				
1-Cp-1-Co-2,4-C ₂ (Me) ₂ B ₈ H ₈	-0.83		180		
	-1.64				
1-Cp-1-Co-2,3-C ₂ (Me) ₂ B ₈ H ₈	-1.23		180		
	-1.57				
10-Cp-10-Co-2,3-C ₂ (Me) ₂ B ₈ H ₈	-0.75		180		
	-1.66				
2-Cp-2-Co-1,6-C ₂ B ₇ H ₉	-1.03		178		
2-Cp-2-Co-1,7-C ₂ B ₇ H ₉	-1.33		178		
1,4-(Cp) ₂ -1,4-Co ₂ -2,3-C ₂ B ₇ H ₉	+0.87		28, 30		
	-0.87		179, 181		
1,10-(Cp) ₂ -1,10-Co ₂ -2,3-C ₂ B ₇ H ₉	+1.06		28, 30		
	-1.17		179, 181		
1,8-(Cp) ₂ -1,8-Co ₂ -2,3-C ₂ B ₇ H ₉	+0.75		181		
	-0.85				
8,9-(Cp) ₂ -8,9-Co ₂ -2,3-C ₂ B ₇ H ₉	+1.23		179		
	-1.41				

TABLE XVI (Continued)

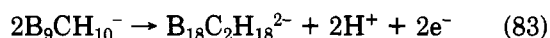
compd ^a	$E_{1/2}$, V vs. SCE	oxidn/redn process	ref
1,6-(Cp) ₂ -1,6-Co ₂ -2,4-C ₂ B ₇ H ₉	+0.80 -1.20		179
2,3,5-(Cp) ₃ -2,3,5-Co ₃ -1,7-C ₂ B ₇ H ₉	+0.65 -0.87		181
2-Cp-2-Co-4,5-C ₂ B ₆ H ₈	-0.84		178
2-Cp-2-Co-4,6-C ₂ B ₆ H ₈	-1.11		178
2,7-(Cp) ₂ -2,7-Co ₂ -1,10-C ₂ B ₈ H ₈	+1.37 -1.50		179
1,9-(Cp) ₂ -1,9-Co ₂ -4,5-C ₂ B ₅ H ₇	+0.82		181
1-Cp-1-Co-2,3-C ₂ B ₄ H ₆	+1.52 -1.62 -2.50	Co ^{IV} → Co ^{III} Co ^{III} → Co ^{II} Co ^{II} → Co ^I	182
1-Cp-1-Co-2,4-C ₂ B ₄ H ₆	+1.70 -1.43 <-2.75	Co ^{IV} → Co ^{III} Co ^{III} → Co ^{II} Co ^{II} → Co ^I	182
1,7-(Cp) ₂ -1,7-Co ₂ -2,3-C ₂ B ₃ H ₅	+1.72 +0.51 -1.44		182
1,7-(Cp) ₂ -1,7-Co ₂ -2,4-C ₂ B ₃ H ₅	-2.23 +0.89 -1.35 -2.30		182
[Co(<i>o</i> -C ₂ B ₁₀ H ₁₀) ₂] ²⁻	+0.62 -2.35	Co ^{II} → Co ^{II} Co ^{II} → Co ^I	183, 184
CpCoCB ₁₀ H ₁₁	+1.07	Co ^{III} → Co ^{IV}	185
2-(C ₁₀ H ₈)-2-Co-1-CB ₁₀ H ₁₁	-0.62 -1.31	Co ^{III} → Co ^{II} ligand redn	186
[2,11-(Cp) ₂ -2,11-Co ₂ -1-CB ₉ H ₁₀] ⁻	+0.20	Co ^{III} → Co ^{IV}	187
(1,2-B ₉ H ₉ CHPMe) ₂ Co	+0.43 -0.78	Co ^{III} → Co ^{II}	171
(1,7-B ₉ H ₉ CHPMe) ₂ Co	+0.41 -0.74	Co ^{III} → Co ^{II} Co ^{II} → Co ^I	171
2,10-(Cp) ₂ -2-Co-10-Ni-1-CB ₇ H ₈	-0.80	Co ^{II} /Ni ^{IV} → Co ^{III} /Ni ^{III}	186
6,8-(Cp) ₂ -6-Co-8-Ni-1-CB ₇ H ₈	-0.98	Co ^{II} /Ni ^{IV} → Co ^{III} /Ni ^{III}	186
6,10-(Cp) ₂ -6-Co-10-Ni-1-CB ₇ H ₈	-0.86	Co ^{II} /Ni ^{IV} → Co ^{III} /Ni ^{III}	186
6,9-(Cp) ₂ -6-Co-9-Ni-1-CB ₇ H ₈	-0.90	Co ^{II} /Ni ^{IV} → Co ^{III} /Ni ^{III}	186
2,3-Br ₂ -6,8-(Cp) ₂ -6-Co-9-Ni-1-CB ₇ H ₈	-0.73	Co ^{II} /Ni ^{IV} → Co ^{III} /Ni ^{III}	186
2-Br-3,10-(Cp) ₂ -3-Co-10-Ni-1-CB ₇ H ₇	-0.67	Co ^{II} /Ni ^{IV} → Co ^{III} /Ni ^{III}	186
Ni, Pd, Pt			
(π -(3)-1,2-C ₂ B ₉ H ₁₁) ₂ Ni	+0.25 -0.57 -2.10	Ni ^{IV} → Ni ^{III} Ni ^{III} → Ni ^{II} Ni ^{II} → Ni ^I	165, 173, 188
π -(3)-1,7-C ₂ B ₉ H ₁₁) ₂ Ni	+0.55 -0.91 -2.09	as above	165, 173, 188
(π -(4)-1,2-C ₂ B ₉ H ₁₁)(π -(3)-1,2-C ₂ B ₉ H ₁₁)Ni	0.00 -0.95	Ni ^{IV} → Ni ^{III} Ni ^{III} → Ni ^{II}	189
(π -(4)-1,2-C ₂ B ₉ H ₁₁) ₂ Ni	-0.19 -1.22	as above	189
(π -(3)-1,2-C ₂ B ₉ H ₁₁)(π -(3)-1,2-C ₂ (1-Me)B ₉ H ₁₀)Ni	+0.27 -0.64	as above	189
(π -(3)-1,2-C ₂ B ₉ H ₁₁)(π -(3)-1,2-C ₂ (1-Ph)B ₉ H ₁₀)Ni	+0.35 -0.52	as above	189
[(π -(3)-1,2-C ₂ (Me) ₂ B ₉ H ₉) ₂ Ni ^{III}] ⁻	+0.5 (irrev) -0.55	as above	189
(π -(3)-1,2-C ₂ (Me) ₂ B ₉ H ₉)(π -(4)-1,2-C ₂ (Me) ₂ B ₉ H ₉)Ni ^{IV}	+0.15 -1.02	as above	189
(π -(4)-1,2-C ₂ (Me) ₂ B ₉ H ₉) ₂ Ni ^{IV}	-0.10 -1.19	as above	189
[(π -(3)-1,2-C ₂ (CH ₂) ₃ -B ₉ H ₉) ₂ Ni ^{III}] ⁻	+0.60	as above	190
(π -(3)-1,2-C ₂ (CH ₂) ₃ -B ₉ H ₉) ₂ Ni ^{IV}	+0.30	as above	190
(π -(3)-1,6-C ₂ (CH ₂) ₃ -B ₉ H ₉)Ni ^{IV}	-0.80	as above	190
(π -(3)-1,6-C ₂ (CH ₂) ₃ -B ₉ H ₉) ₂ Ni ^{IV}	+0.02 -1.20	as above	190
3-CpNi-1,2-C ₂ B ₉ H ₁₁	+0.46 -0.52	as above	191
[π -C ₂ B ₁₀ H ₁₂) ₂ Ni] ²⁻	-0.03	Ni ^{II} → Ni ^{IV}	167
[Ni(<i>o</i> -C ₂ B ₁₀ H ₁₂) ₂] ²⁻	+0.86	Ni ^{III} → Ni ^{II}	184
12-CpNi-(η -7-CB ₁₀ H ₁₁)	-2.07 -0.27 -1.57 -2.43	Ni ^{II} → Ni ^I Ni ^{IV} → Ni ^{III} Ni ^{III} → Ni ^{II}	185
12-CpNi-(η -2-CB ₁₀ H ₁₁)	-1.52 -2.65	Ni ^{IV} → Ni ^{III} Ni ^{III} → Ni ^{II}	185
12-CpNi-(η -1-CB ₁₀ H ₁₁)	-0.92 -2.05	Ni ^{IV} → Ni ^{III} Ni ^{III} → Ni ^{II}	185
10-CpNi(η -1-CB ₈ H ₉)	-0.93	Ni ^{IV} → Ni ^{III}	192

TABLE XVI (Continued)

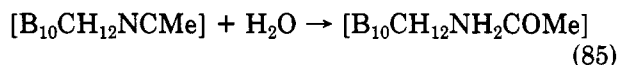
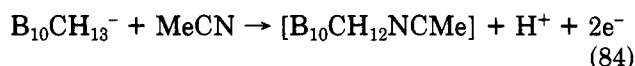
compd ^a	$E_{1/2}$, V vs. SCE	oxidn/redn process	ref
6,7,8-(CpNi) ₃ -2-Me-1-CB ₉ H ₅	+1.25 +0.95 +0.49		187
(π -(3)-1,2-C ₂ B ₉ H ₁₁) ₂ Pd	-0.95 -0.14	Ni ^{IV} → Ni ^{III} Pd ^{IV} → Pd ^{III}	193
[(π -(3)-1,2-C ₂ B ₉ H ₉ (Me) ₂) ₂ Pd ^{III}] ²⁻	-0.56 0.00	Pd ^{III} → Pd ^{II} Pd ^{IV} → Pd ^{III}	189
(π -(4)-1,2-C ₂ B ₉ H ₉ (Me) ₂) ₂ Pd ^{IV}	-0.44 -0.47 -0.71	Pd ^{III} → Pd ^{II} Pd ^{IV} → Pd ^{III} Pd ^{III} → Pd ^{II}	189
Cu, Ag, Au			
[(π -(3)-1,2-C ₂ B ₉ H ₁₁) ₂ Cu ^{II}] ²⁻	-0.35 -0.99	Cu ^{III} → Cu ^{II} Cu ^{II} → Cu ^I	194
[(π -(3)-1,2-C ₂ B ₉ H ₁₁) ₂ Cu ^{III}] ⁻	-0.35 -1.2	as above	193
[Cu(σ -C ₂ B ₁₀ H ₁₀) ₂] ²⁻	+0.15 -1.36	Cu ^{III} → Cu ^{II} ^a Cu ^{II} → Cu ^I	184
[(π -(3)-1,2-C ₂ B ₉ H ₁₁) ₂ Au ^{II}] ²⁻	-0.62 -0.92	Au ^{III} → Au ^{II} Au ^{II} → Au ^I ^b	193
[(π -(3)-1,2-C ₂ B ₉ H ₁₁) ₂ Au ^{III}] ⁻	-0.62 -0.84	as above ^c	193

^aThe numbering of all complexes is that cited in the original reference. ^bIrreversible wave. ^cQuasi-reversible wave.

(Et₄N)₂B₁₈C₂H₁₈. This is comparable to the formation of B₂₀H₁₈⁴⁻ from B₁₀H₁₀²⁻.^{119,123}



The controlled-potential electrolysis of 7-B₁₀CH₁₃⁻ at +1.80 V gave a two-electron oxidation to [B₁₀CH₁₂NHCOMe]⁻:



C. Heteroatom Carboranes

Heterocarboranes of the type B₁₀H₁₀MCH (M = P or As), which have icosahedral structures similar to those of the carboranes B₁₀C₂H₁₂, have been studied¹⁵⁴ (see Table XIII). The data show that carbaphosphaboranes and carbaarsaboranes have greater electron affinities than do their isostructural carboranes, but differences are found between the phospho and arsa compounds. In the phospho compounds, the electron affinities decreased in the order ortho > meta > para, whereas in the arsa compounds they decreased in the order meta > para > ortho.

VI. Metallocarboranes

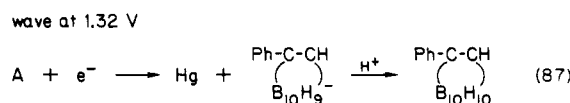
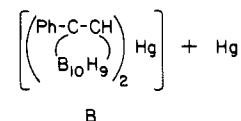
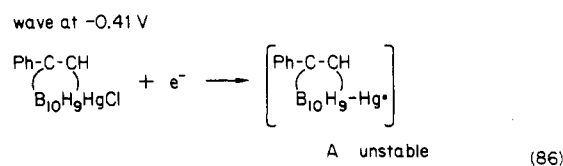
A. Mercury Derivatives of Carboranes

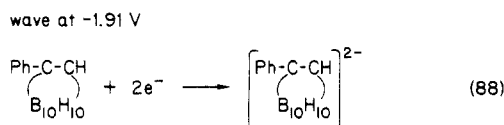
Much electrochemical work has been done on mercurated carboranes.¹⁵⁵⁻¹⁶⁰ These compounds can be effectively divided into two main types: C-mercurated carboranes and B-mercurated carboranes. Table XIV lists the C-mercurated derivatives, and Table XV lists the B-mercurated derivatives. The compound (9-*o*-C₂B₁₀H₁₁)₂Hg and the meta analogue each showed one polarographic reduction wave, the half-wave potentials of each being close to the values obtained for the respective unsubstituted carboranes. This suggests that the active center is the carborane cage rather than the

B-Hg bond. Comparison with their C-substituted analogues shows a reduction first in the C-Hg bond. Thus, for the *o*- and *m*-carboranes, the electrochemical activity falls off in the order C-Hg > carborane cage > B-Hg. That is, the electron-acceptor behavior of the carborane cage manifests itself at the substituent bound to a carbon atom but not at the substituent bound to a boron atom.

In contrast, (2-*p*-C₂B₁₀H₁₁)₂Hg reduced at a half-wave potential of -2.55 V, whereas *p*-carborane itself did not reduce within the limits of the supporting electrolyte. Therefore, in this case the electrochemical activity falls off in the order C-Hg > B-Hg > carborane cage. This behavior was ascribed to the fact that there is an electron-deficient carbon atom adjacent to the B-Hg bond in this compound, whereas in the *o*- and *m*-carborane compounds the carbon atoms are farther from the B-Hg bonds.

Table XV shows that unsymmetrical B-mercurated carboranes show much more complicated polarographic behavior than the symmetrical compounds. For example, three reduction waves were observed for 9(12)-ClHg-*o*-1-Ph-C₂B₁₀H₁₀ in dimethylformamide (DMF) with Bu₄NClO₄ as supporting electrolyte. The waves at -0.41 and -1.32 V were one-electron reductions, and the wave at -1.91 V was a two-electron reduction, as shown by comparison with the height of the two-electron reduction wave of *o*-1-phenylcarborane. The mechanism proposed for these reductions is as follows:





The wave at -1.91 V was ascribed to the reduction of *o*-1-phenylcarborane on the basis of the similarity between the polarographic reduction wave obtained and that found for the carborane itself.

B. Transition-Metal Derivatives of Carboranes

Electrochemical data have been obtained on many transition-metal carborane complexes, particularly complexes of Fe, Co, and Ni. Table XVI lists the electrochemical properties of transition-metal carboranes and, where possible, assignments have been indicated. These assignments usually take the form of an $M^{n+}/M^{(n-1)+}$ redox couple; however, these complexes are delocalized systems, and these are *formal* metal oxidations/reductions and are not meant as an absolute guide to the processes occurring. This point is particularly relevant in a consideration of carborane derivatives containing more than one metal atom. Much of this work was done by Hawthorne and co-workers^{195,196} over several years, and during this time cyclic voltammetry and polarography gave much useful information on the structures of these complexes. Some of this work concerning complexes of Co has been discussed in recent reviews.^{140,197} A number of general points relating to structural features have emerged from the data in Table XVI:

(1) As carbon atoms move out of the ring adjacent to the transition-metal atom, the potential for reduction is lowered (i.e., the system is more difficult to reduce). This property has proven particularly useful in aiding structure determination of the many isomers obtained by thermal rearrangement reactions in the $\text{CpCoC}_2\text{B}_9\text{H}_{11}$ system¹⁷⁵ and the $\text{Ni}(\text{C}_2\text{B}_9\text{H}_{11})_2$ system^{178,189} (see later) ($\text{C}_2\text{B}_9\text{H}_{11}^{2-}$ = dicarbollide).

(2) $\text{C}_2\text{B}_{10}\text{H}_{12}$ complexes show lower reduction potentials than the analogous dicarbollide complexes.¹⁶¹⁻¹⁶³ This suggests that the C_2B_{10} system donates fewer electrons to the metal.¹⁶³ This has been ascribed to the more diffuse electronic environment of the C_2B_{10} system, which has six electrons in the open face among six sp_3 orbitals. This compares with six electrons among five sp^3 orbitals in the dicarbollide system.

(3) In complexes containing more than one metal, the metals do not appear to behave independently of one another, even where different metals are present.¹⁷¹ This suggests that either the metals have a strong influence over one another or the compounds must be considered as heteroboranes.

The nickel dicarbollide systems mentioned above are particularly interesting and illustrate point 1. The reaction sequence and electrochemistry of the bis(π -1,2-(μ -trimethylene)-1,2-dicarbollyl)nickel system are shown in Scheme I.

The notation used in eq 89-91 means that $\text{TM}_2\text{Ni-A}$ isomers are $(\pi\text{-}(3)\text{-}1,2\text{-C}_2(\text{TM})\text{B}_9\text{H}_9)_2\text{Ni}$, $\text{TM}_2\text{Ni-B}$ isomers are $(\pi\text{-}(3)\text{-}1,2\text{-C}_2(\text{TM})\text{B}_9\text{H}_9)(\pi\text{-}(3)\text{-}1,6\text{-C}_2(\text{TM})\text{B}_9\text{H}_9)\text{Ni}$, and $\text{TM}_2\text{Ni-C}$ isomers are $(\pi(3)\text{-}1,6\text{-C}_2(\text{TM})\text{B}_9\text{H}_9)_2\text{Ni}$.

The lowering of the $\text{Ni}^{\text{III}}/\text{Ni}^{\text{IV}}$ and $\text{Ni}^{\text{III}}/\text{Ni}^{\text{II}}$ redox

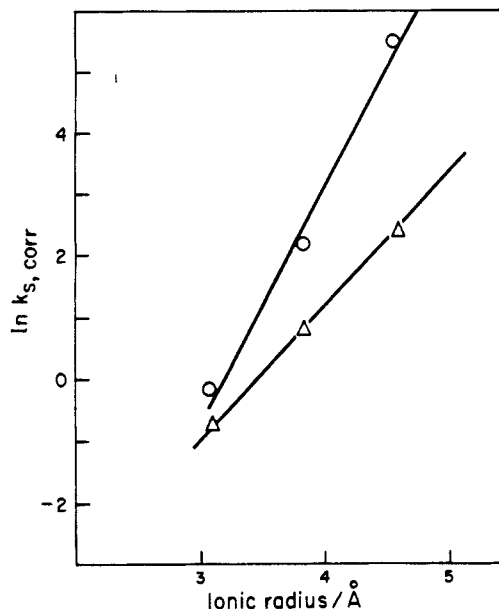


Figure 3. Plot of the logarithm of the rate constant corrected for double-layer charge vs. ionic radius (O = entries 2, 4, and 6; X = entries 1, 3, and 5, Table XVII). Reproduced with permission from ref 194. Copyright 1974, Elsevier Sequoia.

couple potentials on going from a B_3C_2 face adjacent to the metal atom to a B_4C face suggests that the B_4C face donates more electron density to the metal atom, thus stabilizing the higher (4+) oxidation state. It similarly destabilizes the lower (2+) oxidation state.¹⁸⁹

Few of the systems described above have been studied kinetically. However, heterogeneous electron-transfer kinetic parameters have been obtained for a series of electrode reactions at a mercury/acetonitrile interface involving cobalt and nickel π complexes composed of cyclopentadienide and dicarbollide ligands.¹⁹⁴ Table XVII lists the compounds studied and the data obtained.

Two general observations were made from the data:

(1) α values (with one unexplained exception) were close to 0.5, regardless of all other factors.

(2) Despite variations among compounds, k_s values were consistently large, the smallest value listed ($0.14 \text{ cm}^2/\text{s}$) being considered indicative of a moderately rapid electrode process.

These observations indicated that the electrode processes involved low activation-energy barriers that would be determined by transformations such as solvent reorganization or minor molecular conformational changes, as opposed to more apparent changes in molecular bonding.

As stated previously, significant differences in k_s, corr values are observed, and from Table XVII three main trends become apparent:

(1) As the cyclopentadienide ligand was replaced by dicarbollide, the value of k_s, corr increased, even in redox couples of the same ionic charge (e.g., entries 2 and 3, or 4 and 5 from Table XVII).

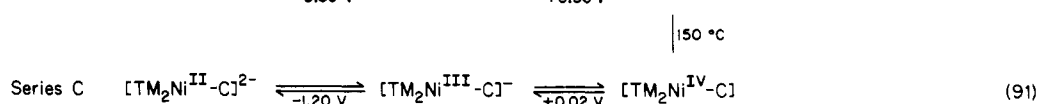
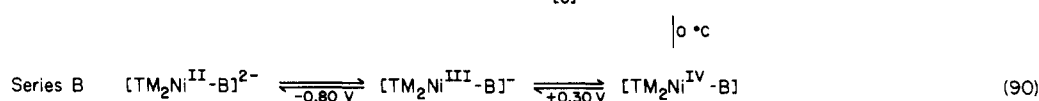
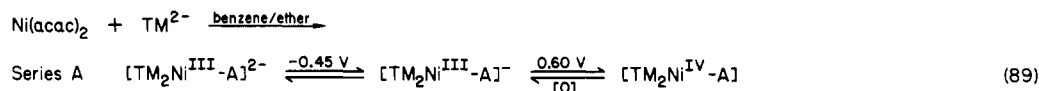
(2) As the ionic charge was increased by successive reductions (e.g., entries 3 and 4, 5 and 6, or 7 and 8), the value of k_s, corr increased. This can be compared with entries 1 and 2, where reduction did not lead to an increase in absolute ion charge, and the change in k_s, corr values was correspondingly small.

(3) The $(\pi\text{-}(3)\text{-}1,2\text{-dicarbollyl})\text{nickel}$ complex gave

TABLE XVII. Heterogeneous Charge-Transfer Rate Parameters for Some Metal "Sandwich Compounds" in Acetonitrile Containing 0.3 M Tetrabutylammonium Hexafluorophosphate at 25 °C^a

redox couple ^b	$E_{1/2}$, V vs. SCE ^c	D , ^d cm ² s ⁻¹	$k_{s,app}$, ^e cm s ⁻¹	q , ^f μC cm ⁻²	ϕ , ^g V	$k_{s,corr}$, ^h cm s ⁻¹	α ⁱ
(1) Cp ₂ Co ⁺ /Cp ₂ Co	-0.94	3.6×10^{-5}	0.86	-3.21	-0.034	0.46	0.52
(2) Cp ₂ Co/Cp ₂ Co ⁻	-1.88	3.6×10^{-5}	0.27	-6.50	-0.060	0.86	0.50
(3) Cp(<i>o</i> -B ₉)Co/Cp(<i>o</i> -B ₉)Co ⁻	-1.21	5.3×10^{-5}	1.00	-4.20	-0.043	2.3	0.50
(4) Cp(<i>o</i> -B ₉)Co ⁻ /Cp(<i>o</i> -B ₉)Co ²⁻	-2.11	5.3×10^{-5}	0.26	-7.30	-0.065	8.9	0.40
(5) (<i>o</i> -B ₉) ₂ Co ⁻ / <i>o</i> -B ₉) ₂ Co ²⁻	-1.36	3.2×10^{-5}	0.82	-4.70	-0.047	12	0.48
(6) (<i>o</i> -B ₉) ₂ Co ²⁻ / <i>o</i> -B ₉) ₂ Co ³⁻	-2.24	3.2×10^{-5}	0.37	-7.75	-0.067	2.5×10^2	0.48
(7) (<i>o</i> -B ₉) ₂ Ni/ <i>o</i> -B ₉) ₂ Ni ⁻	+0.25	3.4×10^{-5}	0.43	+6.35	+0.059	0.14	0.50
(8) (<i>o</i> -B ₉) ₂ Ni ⁻ / <i>o</i> -B ₉) ₂ Ni ²⁻	-0.57	3.4×10^{-5}	0.66	-1.60	-0.018	1.9	0.50
(9) (<i>m</i> -B ₉) ₂ Ni ⁻ / <i>m</i> -B ₉) ₂ Ni ²⁻	-0.92	3.0×10^{-5}	1.60	-3.15	-0.034	11	0.47

^a Reference 194. ^b Cp = C₅H₅⁻ (cyclopentadienide ion); *o*-B₉ = π-(3)-1,2-B₉C₂H₁₁²⁻ (*o*-dicarbollide ion); *m*-B₉ = π-(3)-1,7-B₉C₂H₁₁²⁻ (*m*-dicarbollide ion). ^c dc polarographic half-wave potentials (reversible); approximately equal to ac polarographic peak potentials in all cases. ^d Diffusion coefficients calculated from dc polarographic limiting currents using Ilkovič equation. ^e Apparent standard heterogeneous charge-transfer rate constant. ^f Diffuse double-layer charge calculated by integrating differential capacity curve. ^g Outer Helmholtz plane potential calculated assuming absence of specific adsorption. ^h Standard heterogeneous charge-transfer rate constants after invoking Frumkin correction assuming outer Helmholtz plane corresponds to plane of closest approach. ⁱ Charge-transfer coefficient.

SCHEME I

lower $k_{s,corr}$ values than the corresponding 1,7 complex or the cobalt analogues.

For a closer look at the processes influencing the electron-transfer rates, plots of $\ln k_{s,corr}$ vs. ionic radius (of each complex) were obtained (see Figure 3). These showed that the three Co^{III}/Co^{II} reductions fall on one line and the three Co^{II}/Co^I reductions on another straight line. This was taken as evidence to confirm that the cobalt reductions were solvent-reorganization controlled and also that the metal oxidation state might have an effect on the required changes in solvent dielectric.

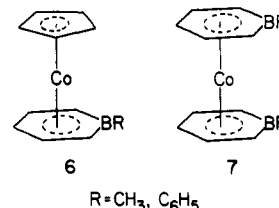
The low rate constants obtained for the Ni^{IV}/Ni^{III} and Ni^{III}/Ni^{II} reductions involving the 1,2-dicarbollide ligand and were thought to be due to the finite contribution of inner-sphere reorganizations. This view is supported by crystal structure determinations,^{189,193,198} which show that the 1,2-isomer goes from a symmetrical π complex in the Ni^{IV} state to a "slipped sandwich" structure in the Ni^{III} state.

Electrochemical studies on a series of small iron or cobalt metallocarborene clusters containing five to seven vertices indicated that, in contrast to their larger dicarbollide analogues, the small clusters stabilized high metal oxidation states and destabilized low oxidation states. Thus, cobalt compounds of the type CpCo-(C₂B₄H₆) underwent one oxidation and two reductions, all involving one electron. 1,2,3-CpFe(C₂B₄H₆) was reversibly reduced to formal Fe(II) at about 0.8 V negative of Cp₂Fe⁺ and also underwent an irreversible oxidation.¹⁴¹

VII. Metal Sandwich Complexes

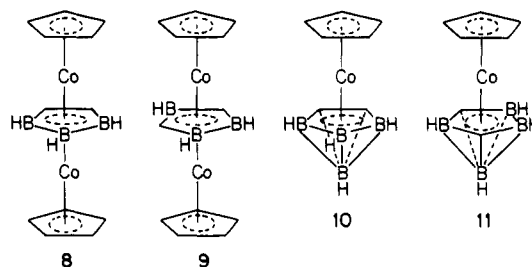
Cyclic voltammetry of borabenzene-cobalt complexes of the type 6 and 7 in acetonitrile showed reversible

one-electron oxidations at platinum to the respective



cations and reversible one-electron reduction to the anions.¹⁹⁹ The potentials are given in Table XVIII. Cyclic voltammetry of analogous iron, chromium, and vanadium complexes has also been studied,²⁰⁰ irreversibility was noted with some of the complexes, and the details are presented in Table XIX.

The electrochemical behavior of the triple-decker and sandwich compounds of the types 8–11 was studied.²⁰¹



The compounds showed a series of reversible one-electron oxidations and reductions in which the redox processes are diffusion controlled. The potentials are given in Table XX. The electrochemical results strongly favor delocalized electronic structures.

Other triple-decker complexes studied include bis(cyclopentadienylmetal)-μ-1,3-diborolenyl complexes with 29–34 valence electrons and, in particular, complexes 12–15.²⁰²

TABLE XVIII. Voltammetric Redox Potentials of Cobalt Metal Sandwich Complexes

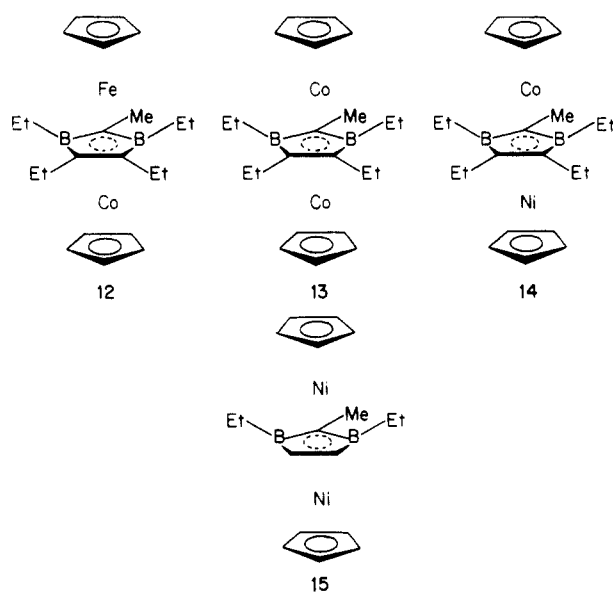
	\bar{E} , V ^a	neutral complex		neutral complex		
		$E^a - E_p^c$, mV	i^a/i^c	\bar{E} , V	$E_p^a - E_p^c$	i^a/i^c
[Co(Cp)(C ₅ H ₅ BPh)] ⁺	-0.435	70	1.0	-1.460	90	1.2
Co(CpBPh) ₂	+0.045	85	1.0	-1.105	70	1.04
CoCp(CpBMe)	-0.460	60	0.93	-1.570	80	0.62
Co(CpBMe) ₂	-0.018	65	0.96	-1.245	70	1.0

^a SCE.TABLE XIX. Voltammetric Parameters of Fe, Cr, and V Metal Sandwich Complexes^a

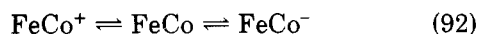
	E_p^a , V ^b	E_p^c , V	\bar{E} , V	i_p^a/i_p
FeCp(C ₅ H ₅ BMe)	0.89	0.79	0.84	0.8
FeCp(C ₅ H ₅ BPh)	0.92	0.84	0.88	0.9
Fe(C ₅ H ₅ BMe) ₂	1.22	0.98	1.10	
Fe(C ₅ H ₅ BPh) ₂	1.20	1.07	1.13	
Cr(C ₅ H ₅ BMe) ₂	0.54	0.36	0.45	1.0
Cr(C ₅ H ₅ BPh) ₂	0.58	0.49	0.53	0.97
	-0.96	-1.06	-1.01	1.05
V(C ₅ H ₅ BMe) ₂	+0.76			irrev
	-1.28	-1.41	-1.34	1.02

^a Reference 200. ^b SCE.TABLE XX. Reduction and Oxidation Potentials^a of Cobalt Triple-Decker and Sandwich Compounds 8-15

compd	red ₁	red ₂	ox ₁	ox ₂	ref
1,7,2,3-Cp ₂ Co ₂ C ₂ B ₃ H ₅ (8)	-1.44	-2.23	+0.51	+1.72	201
1,7,2,4-Cp ₂ Co ₂ C ₂ B ₃ H ₅ (9)	-1.35	-2.30	+0.89		201
1,2,3-CpCoC ₂ B ₄ H ₆ (10)	-1.62	-2.50	+1.52		201
1,2,4-CpCoC ₂ B ₄ H ₆ (11)	-1.43		+1.70		201
(CpFe)(CpCo)- (C ₃ B ₂ Et ₄ Me) (12)	-1.76		-0.06		202
(CpCo) ₂ (C ₃ B ₂ Et ₄ Me) (13)	-1.53	+2.56	-0.57	+1.74	202
(CpCo)(CpNi)- (C ₃ B ₂ Et ₄ Me) (14)	-1.63		+0.06	+1.00	202
	(-1.58) ^b			(+1.08) ^c	
(CpNi) ₂ (C ₃ B ₂ Et ₄ Me) (15)	-1.30		-0.13	+1.26	202

^a Volts vs. SCE. ^b THF. ^c CH₂Cl₂.

Compound 12 was reversibly oxidized and reduced to a monocation and a monoanion, respectively, and this may be represented by



Compound 13 (CoCo) underwent four one-electron redox processes, two oxidations and two reductions,

whereas 14 and 15 (CoNi and NiNi) underwent one reduction and two oxidations each. Details are given in Table XX.

Abbreviations Used throughout This Review

Ac	acetyl
Acac	acetylacetonate
Bu	butyl
Bz	benzyl
Cp	η^5 -cyclopentadienide
DME	dropping mercury electrode
DMF	dimethylformamide
EMF	electromotive force
ESR	electron spin resonance
Et	ethyl
Fc	ferrocenyl
glyme	1,2-dimethoxyethane
<i>m</i>	meta
Me	methyl
NMR	nuclear magnetic resonance
<i>o</i>	ortho
<i>p</i>	para
Ph	phenyl
phen	1,10-phenanthroline
py	pyridine
RPE	rotating platinum electrode
SCE	standard (saturated) calomel electrode
THF	tetrahydrofuran

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