(31) F. E. Scarbrough and W. N. Lipscomb, *Inorg. Chem.*, **11**, 369 (1972), and references cited therein.
(32) L. J. Guggenberger, *Inorg. Chem.*, **9**, 367 (1970).
(33) T. A. Halgren, R. J. Anderson, D. S. Jones, and W. N. Lipscomb, *Chem. Phys. Lett.*, **8**, 547 (1971).
(34) S. J. Lippard and G. J. Palenik, *Inorg. Chem.*, **10**, 1322 (1971).
(35) A summary of the literature in this area and a more complete discussion of this phenomenon will be submitted shortly.
(36) C. P. Brock and J. A. Ibers, *Acta Crystallogr., Sect. B*, **29**, 2426 (1973).
(37) P. H. Davis, R. L. Belford, and I. C. Paul, *Inorg. Chem.*, **12**, 213 (1973).
(38) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 2970 (1968), and references cited therein.
(39) For a comparison of chloroform geometry see W. P. Schaeffer and R. E. Marsh, *Acta Crystallogr., Sect. B*, **25**, 1675 (1969).
(40) S. J. Lippard and D. Ucko, *Chem. Commun.*, 983 (1967).
(41) (a) The characterizations of several *nido*-metalloboranes are reviewed by E. L. Muetterties, *Pure Appl. Chem.*, **29**, 585 (1972), and by N. N. Greenwood and I. M. Ward, *Chem. Soc. Rev.*, **3**, 231 (1974). (b) *closo*-Metallocarboranes and -metalloboranes, which structurally parallel the bonding patterns of *nido*-metalloboranes noted in the text, are reviewed by M. F. Hawthorne, *Accounts Chem. Res.*, **1**, 281 (1968), and reported by (c) V. R. Miller and R. N. Grimes, *J. Amer. Chem. Soc.*, **95**, 5078 (1973), and references cited therein.
(42) D. R. Schultz and R. W. Parry, *J. Amer. Chem. Soc.*, **80**, 4 (1958).
(43) R. W. Parry and G. Kodama, Proceedings of the XVIth IUPAC Congress, Inorganic Section, Paris, 1957, p 483.
(44) W. N. Lipscomb, *J. Chem. Phys.*, **28**, 170 (1958).
(45) P. H. Wilks and J. C. Carter, *J. Amer. Chem. Soc.*, **88**, 3441 (1966).
(46) D. F. Gaines, *J. Amer. Chem. Soc.*, **91**, 6503 (1969).
(47) (a) T. J. Marks, W. J. Kennelly, J. R. Kolb, and L. A. Shimp, *Inorg. Chem.*, **11**, 2540 (1972); (b) L. Vaska, W. V. Miller, and B. R. Flynn, *Chem. Commun.*, 1615 (1971); (c) M. L. H. Green, H. Munakata, and T. Saito, *J. Chem. Soc. A*, 469 (1971); (d) K. M. Melmed, D. Coucouvanis, and S. J. Lippard, *Inorg. Chem.*, **12**, 232 (1973).
(48) (a) P. H. Bird and M. R. Churchill, *Chem. Commun.*, 403 (1967); (b) V. Plato and K. Hedberg, *Inorg. Chem.*, **10**, 590 (1971).
(49) E. R. Bernstein, W. C. Hamilton, T. A. Keiderling, W. J. Kennelly, S. J. La Placa, S. J. Lippard, T. J. Marks, and J. J. Mayerle, unpublished results.
(50) (a) E. R. Bernstein, T. A. Keiderling, S. J. Lippard, and J. J. Mayerle, *J. Amer. Chem. Soc.*, **94**, 2552 (1972); (b) E. R. Bernstein, W. C. Hamilton, T. A. Keiderling, S. J. LaPlaca, S. J. Lippard, and J. J. Mayerle, *Inorg. Chem.*, **11**, 3009 (1972).
(51) H. D. Kaesz, W. Fellmann, G. R. Wilkes, and L. F. Dahl, *J. Amer. Chem. Soc.*, **87**, 2753 (1965).
(52) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, p 65.
(53) D. F. Gaines and S. J. Hildebrandt, *J. Amer. Chem. Soc.*, **96**, 5574 (1974).
(54) I. Shapiro, R. E. Williams, and S. G. Gibbins, *J. Phys. Chem.*, **65**, 1061 (1961).
(55) J. P. Faust, *Advan. Chem. Ser.*, No. **32**, 69 (1961).
(56) E. L. Muetterties, "The Chemistry of Boron and Its Compounds," Wiley, New York, N.Y., 1967, pp 289–298.
(57) D. F. Gaines and T. V. Iorns, *J. Amer. Chem. Soc.*, **92**, 4571 (1970).
(58) (a) D. F. Lewis, S. J. Lippard, and P. S. Welcker, *J. Amer. Chem. Soc.*, **92**, 3805 (1970); (b) M. S. Weininger, I. F. Taylor, Jr., and E. L. Amma, *Inorg. Nucl. Chem. Lett.*, **9**, 737 (1973), and references cited therein.

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Electrolytic Reduction of *B*-Oxy Derivatives of 2,3-Dicarba-*closo*-undecaborane(11)

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Although the electrochemical reduction of 4,7-$(OH)_2$-2,3-$(CH_3)_2$-2,3-$C_2B_9H_7$ is a one-electron irreversible process, the reduction of the bis(oxy) derivatives 4,7-(ORO)-2,3-$(CH_3)_2$-2,3-$C_2B_9H_7$, R^1 = 1,2-ethanediyl, 1,2-phenyldiyl, or 1,3-dimethyl-1,3-propanediyl, consists of two one-electron wave reductions. The first electron reduction step is electrochemically reversible and produces a stable radical anion, which can be detected by electron spin resonance spectroscopy. Cyclic voltammetry and esr data indicate the addition of a second electron produces an unstable dianion species. A chemical reaction is associated with the addition of the second electron, which may involve an intramolecular rearrangement of the carborane dianion. The closo bis(oxy) derivatives, 4,7-(ORO)-2,3-$(CH_3)_2$-2,3-$C_2B_9H_7$, are regenerated by oxidation of the proposed dianion intermediates.

Introduction

The general reaction sequence involving the chemical reduction of a carborane followed by complexation with a transition metal to produce a monometallocarborane has led to the development of the polyhedral expansion reactions.[2a] The polyhedral expansion reaction has been extended to the metallocarboranes and is now an established procedure for producing bimetallocarboranes.[2b] The latter reaction is formally viewed as a M(III) → M(II) reduction followed by an additional two-electron reduction to form an anionic *nido*-metallocarborane species.[2b] The two-electron chemical reduction of the carboranes and the metallocarboranes has served as the basis for the polyhedral expansion reaction.

For the icosahedral carborane series, $B_{10}C_2H_{12}$, the reduction is accomplished by reaction with 2 equiv of an alkali metal[3–5] or by electrochemical methods.[6,7] The electrochemical reduction consists of a single two-electron irreversible process assuming the icosahedral carborane has no polarographically active substituents.[3] This reduction yields the dodecahydrodicarbadodecaborate(2−), $C_2B_{10}H_{12}^{2-}$, which then protonates to yield a stable tridecadicarba-*nido*-dodecaborate(1−), $C_2B_{10}H_{13}^-$, ion. Molecular orbital studies indicate retention of the cage structure for the dianion.[8] The structure of the *C,C*′-dimethyl-substituted *nido*-carborane anion has been published.[9] Prior publications on the electrochemical reductions of the carboranes have been concerned only with the icosahedral series.

This paper presents both electrochemical and spectroscopic data on the nature of the oxidation–reduction reactions of the octadecahedral carborane 2,3-$(CH_3)_2$-2,3-$C_2B_9H_{11}$ and its *B*-oxy derivatives. The electrochemical behavior of the octadecahedral derivatives is distinctly different from that described for the icosahedral carboranes.[6,7]

Experimental Section

Physical Measurements. The polarograms were obtained with a Heathbuilt Model EUA-19 dropping-mercury electrode. The constant-potential electrolyses were performed using a Wenking Electronic potentiostat, Model 68 FR 0.5, and a cell similar to the design described by Headridge.[10] The cyclic voltammograms were obtained with an instrument designed and built by Professor R. Reed[11] and by use of a cell described in the literature.[12] Esr spectra were recorded on a Varian Associates Model E-12 spectrometer operating on the X-band. Assignment of the splitting factor values were based on simultaneous calibration using the nmr signal of water.

Reagents. Acetonitrile was Spectrograde and distilled from calcium hydride prior to use. Monoglyme and tetrahydrofuran were distilled from potassium–benzophenone prior to use. Tetrabutylammonium perchlorate and tetraethylammonium bromide were obtained from Eastman Kodak. The tetrabutylammonium perchlorate was dried at 60° for 24 hr and the tetraethylammonium bromide was recrystallized from ethanol and dried prior to use.

Table I. Reduction Behavior of Octadecahedral B-Substituted Carboranes

Carborane	$-E_{p/2}$, V, *vs.* sce	Total electrons transferred[a]
$2,3\text{-}(CH_3C)_2B_9H_9$ (I)	1.06	1.0
$4\text{-}OH\text{-}2,3\text{-}(CH_3C)_2B_9H_8$ (II)	1.08	0.87
$4,7\text{-}(OH)_2\text{-}2,3\text{-}(CH_3C)_2B_9H_7$ (III)	1.27	0.96
$4,7\text{-}(OCH_2CH_2O)\text{-}2,3\text{-}(CH_3C)_2B_9H_7$ (IV)	1.24 1.43	1.60
$4,7\text{-}(CH_3CH(O)CH_2CH(O)CH_3)\text{-}2,3\text{-}(CH_3C)_2B_9H_7$ (V)	1.25 1.64	2.02 2.02
$4,7\text{-}(OC_6H_4O)\text{-}2,3\text{-}(CH_3C)_2B_9H_7$ (VI)	1.03 1.39	1.95

[a] Reduction of approximately 0.05 mmol of material at −2.0 V *vs.* sce reference in acetonitrile solutions containing 0.1 *M* TBAP. Mercury pool cathode used in all cases. Integrated current in faradays per mole calculated by current integration using a strip-chart recorder and a standard resistor.

The carborane derivatives $2,3\text{-}(CH_3)_2\text{-}2,3\text{-}C_2B_9H_9$, I,[13] $4\text{-}OH\text{-}2,3\text{-}(CH_3)_2\text{-}2,3\text{-}C_2B_9H_8$, II,[14] $4,7\text{-}(OH)_2\text{-}2,3\text{-}(CH_3)_2\text{-}2,3\text{-}C_2B_9H_7$, III,[15] $4,7\text{-}(OC_2H_4O)\text{-}2,3\text{-}(CH_3)_2\text{-}2,3\text{-}C_2B_9H_7$, IV,[16] $4,7\text{-}(CH_3CH(O)CH_2CH(O)CH_3)\text{-}2,3\text{-}(CH_3)_2\text{-}2,3\text{-}C_2B_9H_7$, V,[17] and $4,7\text{-}(OC_6H_4O)\text{-}2,3\text{-}(CH_3)_2\text{-}2,3\text{-}C_2B_9H_7$, VI,[15] were all prepared according to literature methods.

The polarographic and cyclic voltammetric data were obtained at room temperature on solutions 10^{-3} *M* in electroactive species. The constant-potential electrolyses were also done at room temperature on approximately 0.05 mmol of electroactive species. The solution was subjected to exhaustive electrolysis at −2.00 V *vs.* sce.

The esr samples were degassed and sealed in esr tubes of design described in the literature.[18] The radical anions were generated by reaction of a solution of the carborane with a sodium mirror prior to transfer to the esr tubes. The concentration of carborane necessary and the reaction time for generating an adequate concentration of the radical anion are as follows: $2,3\text{-}(CH_3C)_2B_9H_9$, 0.1 *M*, 7 min; $4,7\text{-}(OC_6H_4O)\text{-}2,3\text{-}(CH_3C)_2B_9H_7$, 0.005 *M*, 1 min; $4,7\text{-}(CH_3CH(O)CH_2CH(O)CH_3)\text{-}2,3\text{-}(CH_3C)_2B_9H_7$, 0.05 *M*, 1 hr.

Results and Discussion

$2,3\text{-}(CH_3)_2\text{-}2,3\text{-}C_2B_9H_9$, I, and its B-substituted derivatives (see Table I) exhibit at least one polarographic reduction wave in solutions of 0.1 *M* TBAP in either acetonitrile or monoglyme. For the series of compounds shown in Table I the closo octadecahedral carborane I and the two *B*-hydroxy derivatives $4\text{-}(OH)\text{-}2,3\text{-}(CH_3)_2\text{-}2,3\text{-}C_2B_9H_8$, II, and $4,7\text{-}(OH)_2\text{-}2,3\text{-}(CH_3)_2\text{-}2,3\text{-}C_2B_9H_7$, III, exhibit a single one-electron, irreversible reduction, whereas the remaining *B*-oxy derivatives IV–VI each have two reduction waves separated by approximately 0.2–0.4 V. Compound I does exhibit a second reduction wave, but at a much more negative potential. Figure 1 indicates the structure and numbering scheme for the B-substituted derivatives. Half-wave potentials ($E_{p/2}$) of the first reduction wave vary from −1.06 V for $2,3\text{-}(CH_3)_2\text{-}2,3\text{-}C_2B_9H_9$ to −1.27 V for $4,7\text{-}(OH)_2\text{-}2,3\text{-}(CH_3)_2\text{-}2,3\text{-}C_2B_9H_7$ at 25° *vs.* sce. Although the shift of the half-peak potentials in the series I–VI is small, the trend indicates the *B*-oxy groups act as electron donors to the cage making the reduction of the *B*-oxy derivatives more difficult in comparison to the parent carborane, I. The wave height of the polarograms for I–VI increased linearly with an increase in concentration of the carborane sample. A plot of the limiting current *vs.* either the concentration or the square root of the height of the mercury column is linear with an intercept at the origin. These data indicate the reduction of this carborane series is a diffusion-controlled process and emphasize the lack of any kinetic character in the limiting current.[18] There are no noticeable prewaves or unusual drop oscillations at the foot of the waves indicating the absence of any adsorption effects for the mercury-dropping electrode. Serious adsorption effects occur with a platinum electrode indicating a lack of reversibility based on heterogeneous electron-transfer rates at the platinum electrode. However, the reversible behavior of IV–VI indicated by the cyclic voltammograms implies the reduced species are stable and have chemical reversibility.

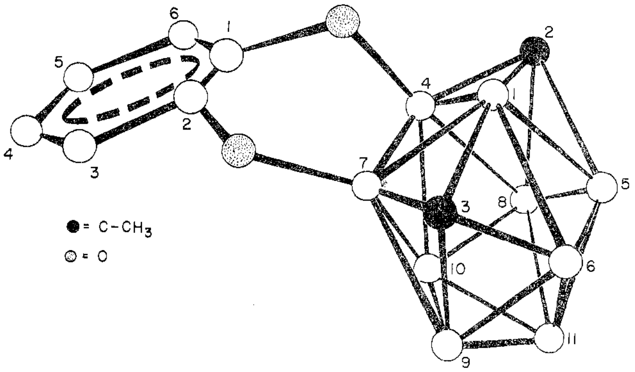

Figure 1. Structure and numbering system for 4,7-[1,2-phenyldiylbis(oxy)]-2,3-dimethyl-2,3-dicarba-*closo*-undecaborane(11), VI.

The evidence available strongly indicates the first reduction wave for I–VI involves a one-electron transfer to the carborane.

$$4,7\text{-}(ORO)\text{-}2,3\text{-}(CH_3C)_2B_9H_7 + e^- \rightarrow 4,7\text{-}(ORO)\text{-}2,3\text{-}(CH_3C)_2B_9H_7{}^{\cdot -} \qquad (1)$$

Since the limiting current contains no kinetic character under the experimental conditions cited, we preclude the possibility of any reaction or change in the carborane species prior to the charge-transfer step in eq 1. The initial product formed by electrolysis must then be a radical anion.

The cyclic voltammetry and esr data (*vide infra*) indicate the radical anions of the carboranes IV–VI are stable and have a prolonged lifetime. The *B*-hydroxy derivatives II and III are, however, extremely unstable and short-lived. The only identifiable product from the electrolysis of II and III is *arachno*-$1,3\text{-}(CH_3C)_2B_7H_{11}$, which indicates the B(OH) groups are easily extracted from the polyhedral surface. If the B(O) unit is protected by a terminal alkyl or aryl group, the radical anion produced is stable for a prolonged period of time.

For I and IV–VI the presence of the radical anion is confirmed by esr. Exposure of a solution of the carborane VI in tetrahydrofuran to a sodium mirror results in a bright yellow solution (see Experimental Section), which exhibits a strong esr signal. The intensity of the signal is directly related to the intensity of the color. The esr spectra of the carborane series I and IV–VI are all similar consisting of 10 broad lines (line width 25 g) of relative intensity 1:3:6:10:12:12:10:6:3:1 centered around the free electron splitting factor of $g = 2.00$. There is no discernible hyperfine structure as shown in Figure 2 for VI. The spectra were all recorded at room temperature in tetrahydrofuran and were not affected by changes in concentration and temperature (−60 → +25°).

If the highly colored solutions are exposed to an excess of the sodium mirror, the color fades, eventually becoming clear, with a corresponding loss of the esr signal. This indicates the second electron is added to the carborane unit and not to the organic substituent and forms the esr-inactive dianion $[4,7\text{-}(OC_6H_4O)\text{-}2,3\text{-}(CH_3C)_2B_9H_7]^{2-}$. Hydrolysis of the dianion intermediate has been shown previously to yield the *nido*-$7,9\text{-}(CH_3)_2\text{-}3,4\text{-}(OC_6H_4O)\text{-}7,9\text{-}C_2B_9H_8(1-)$.[14] The general polyhedral opening of the octadecahedron and its B-substituted derivatives has been discussed elsewhere.[14]

The esr data are consistent with a system in which three boron atoms are essentially equivalent. The splitting constants are unchanged and indicate the free electron is coupled to three boron atoms with $I = {}^3/_2$. The smaller coupling to the ^1H and ^{10}B isotope can be used, in part, to explain the broadness of

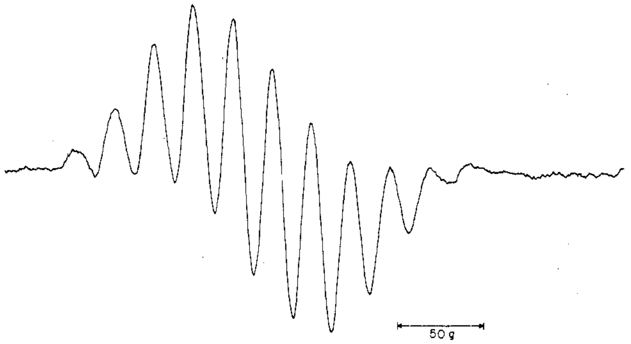

Figure 2. Derivative esr spectrum of the radical anion of 4,7-[1,2-phenyldiylbis(oxy)]-2,3-dimethyl-2,3-dicarba-*closo*-undecaborane-(11), VI, at room temperature in tetrahydrofuran.

the individual lines. We suggest the odd electron is localized over the face defined by atoms B(1), B(5), B(6), C(2), and C(3). Simplified Hückel calculations, now in progress, support this assignment.[19] Hawthorne and Wiersema have also demonstrated that for paramagnetic metallocarboranes the planar C_2B_3 bonding face exhibits axial symmetry, in which the atoms are essentially equivalent.[20] Although the esr data suggest the odd electron is localized in the octadecahedron, the actual structure of the radical anion remains unassigned. Efforts to assign the structure are being made through a combination of Hückel-type calculations and spectroscopic data on the radical anion species.[19]

Figure 3 shows the cyclic voltammogram for II and VI. For II the reduction wave is clearly irreversible (Figure 3a) regardless of the scan rate employed indicating the radical anion formed undergoes a decomposition reaction. For VI the stability of the radical anion increases dramatically. In Figure 3b the cyclic voltammogram contains a wave at A and E corresponding to the reduction and oxidation peaks for the first wave. The separation of the half-peak potentials for A and E indicates the first wave is reversible. Controlled electrolysis at −1.2 V for a finite length of time followed by completion of the cyclic voltammogram shows no additional oxidation peaks or change in the peak shape of A and E indicating the radical anion is quite stable and that no chemical transformation is associated with the addition of the first electron.

The second reduction peak is indicated at point B. The separation of half-peak potentials for B and C is consistent with a reversible process, but the shape and peak height vary with the scan rate indicating the process is not truly reversible. Based on the esr data the second reduction process yields the dianion $[4,7\text{-}(OC_6H_4O)\text{-}2,3\text{-}(CH_3C)_2B_9H_7]^{2-}$, whose structure has not been identified. As the scan rate shows a new oxidation peak, D, appears, which is dependent on the existence of the dianion species. If the cyclic voltammogram is "clipped" at −1.50 V to exclude the production of B, the new peak at D disappears. The dependency of D on the scan rate indicates a chemical reaction is associated with the dianion species, B, which results in the appearance of two oxidation peaks at D and C. Regardless of the number of cycles completed the peak intensity for A and E remains constant. This lack of change in the entire voltammogram indicates the integrity of the octadecahedral carborane is maintained and that the chemical reaction at B does not involve degradation. Furthermore, the oxidation of either D or C results only in the regeneration of the closo octadecahedral carborane species. One explanation consistent with these data involves the chemical transformation of the *closo*-$[4,7\text{-}(OC_6H_4O)\text{-}2,3\text{-}(CH_3C)_2B_9H_7]^{2-}$ to a *nido*-$[3,4\text{-}(OC_6H_4O)\text{-}7,9\text{-}(CH_3C)_2B_9H_7]^{2-}$. Subsequent oxidation of either the closo or nido dianion to the radical anion produces the peaks at C and D, respectively. At sufficiently fast scan rates the fraction of the dianion at B undergoing the transformation to the nido dianion is very small and the peak at D virtually disappears. These data only suggest structural changes are involved in the generation of the dianion species. Confirmation of this process is being investigated through other spectroscopic methods.

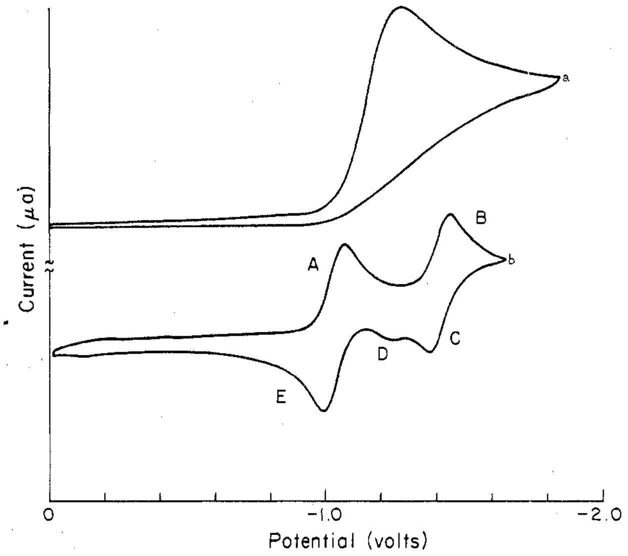

Figure 3. (a) The cyclic voltammogram of 4-hydroxy-2,3-dimethyl-2,3-dicarba-*closo*-undecaborane(11), II, in acetonitrile (0.1 *M* TEAB), scan rate 2 V/sec. (b) The cyclic voltammogram of 4,7-[1,2-phenyldiylbis(oxy)]-2,3-dimethyl-2,3-dicarba-*closo*-undecaborane(11), VI, in acetonitrile (0.1 *M* TEAB), scan rate 2 V/sec.

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Registry No. I, 17764-85-1; II, 51716-75-7; III, 40618-03-9; IV, 54062-07-6; V, 54062-08-7; VI, 40736-40-1; VI radical anion, 54062-09-8.

References and Notes

(1) The numbers accompanying formulas refer to the positions of the atoms in the closo octadecahedron and to the locants on the divalent radical exopolyhedral substituents. The divalent radicals bonded to the carborane, *i.e.*, $-OCH_2CH_2O-$, are indicated by the suffix diylbis(oxy) with locants for the radical position numbered as low as possible. Previous publications[14,15] have used the alternate numbering scheme for the octadecahedron, which has not been approved by IUPAC Inorganic Nomenclature Committee; see R. M. Adams, *Pure Appl. Chem.*, **30**, 683 (1972).
(2) (a) W. J. Evans, G. B. Dunks, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **95**, 4565 (1973); (b) W. J. Evans and M. F. Hawthorne, *Inorg. Chem.*, **13**, 869 (1974).
(3) L. I. Zakharkin, V. N. Kalinin, and A. P. Snyakin, *Dokl. Akad. Nauk SSSR*, **195**, 1357 (1970).
(4) D. G. Grafstein and J. Dvorak, *Inorg. Chem.*, **2**, 1128 (1963).
(5) M. Fein, J. Bobinski, N. Mayes, N. Schwartz, and M. S. Cohen, *Inorg. Chem.*, **2**, 1111 (1963).
(6) L. I. Zakharkin, V. N. Kalinin, and L. S. Podvisotskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2310 (1967).
(7) L. I. Zakharkin, *Pure Appl. Chem.*, **29**, 513 (1972).
(8) R. Hoffmann and W. N. Lipscomb, *Inorg. Chem.*, **2**, 231 (1963).
(9) M. R. Churchill and B. G. De Boer, *Inorg. Chem.*, **12**, 2674 (1973).
(10) J. B. Headridge, "Electrochemical Techniques for Inorganic Chemists," Academic Press, New York, N.Y., 1970, p 58.
(11) R. C. Reed, *Diss. Abstr. Int. B*, **32**, 2570 (1971).
(12) See ref 7, p 16.
(13) M. F. Hawthorne, T. D. Andrews, P. M. Garrett, F. D. Olsen, M. Reintjes, F. N. Tebbe, L. F. Warren, P. A. Wegner, and D. C. Young, *Inorg. Syn.*, **10**, 100 (1967); F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **90**, 869 (1968).
(14) G. D. Mercer and F. R. Scholer, *Inorg. Chem.*, in press.
(15) G. D. Mercer and F. R. Scholer, *Inorg. Chem.*, **12**, 2102 (1973).
(16) G. D. Mercer, Ph.D. Thesis, Cornell University, Ithaca, N.Y., 1974.
(17) D. Gladkowski and F. R. Scholer submitted for publication in *J. Organometal. Chem.*
(18) A. J. Fry, "Synthetic Organic Electrochemistry," Harper and Row, New York, N.Y., 1972.
(19) E. A. McNeil and F. R. Scholer, unpublished data.
(20) R. J. Wiersema and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **96**, 761 (1974).