Volume 21
Number 7
July 1982

Inorganic Chemistry

© Copyright 1982 by the American Chemical Society

Contribution from the Department of Chemistry, University of Vermont, Burlington, Vermont 05405,
and Callery Chemical Company, Callery, Pennsylvania 16024

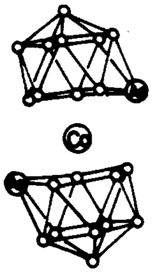
Electrochemical Study of High and Low Cobalt Oxidation States in Group-5-Substituted Borane Clusters

WILLIAM E. GEIGER,* DAVID E. BRENNAN, and JOHN L. LITTLE

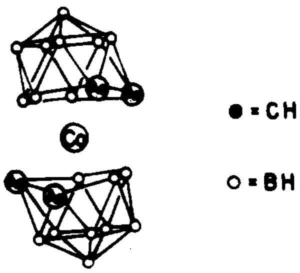
Received September 9, 1981

Electrochemical data are reported on nonaqueous solutions of a series of cobaltaboranes and cobaltacarboranes in which one or two of the borons has been replaced by a group 5 atom—either phosphorus or arsenic. One or more reversible electron-transfer reactions were found for each compound. 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. Direct-current polarography, cyclic voltammetry, and controlled-potential coulometry were the electrochemical techniques employed.

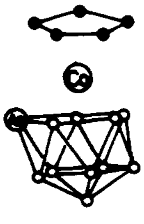
Although the oxidation and reduction properties of many metallacarboranes have been fruitfully studied,[1] little is known about how substitution of a group 5 heteroatom into the polyhedral cage will affect the stability of various metal oxidation states. The only published results in this area appear to be those contained in a paper by Little et al.,[2] which included $E°$ potentials of several iron and one cobalt phosphacarborane complexes. We report here the results of electrochemical measurements in nonaqueous solvents on a series of arsenic- and phosphorus-substituted metallaboranes (and one metallacarborane) in which substitution of a boron atom by arsenic or phosphorus allows formation of stable Co(IV), -(III), -(II), and -(I) complexes and even a short-lived Co(0) complex. The compounds studied[3] were the bis(arsaboranes) $(B_{10}H_{10}As)_2Co^{3-}$ (**1**) and $(B_9H_9As_2)_2Co^-$ (**2**), the "mixed sandwich" η^5-cyclopentadienyl (Cp) analogues $(B_{10}H_{10}As)CoCp^-$ (**3**) and $(B_9H_9As_2)CoCp$ (**4**), and the phosphaboranes $(B_{10}H_{10}P)CoCp^-$ (**5**) and $(1\text{-}CH_3\text{-}1,7\ PCHB_9H_9)_2Co$ (**6**). A



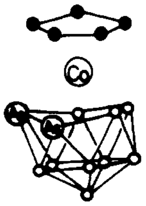
1



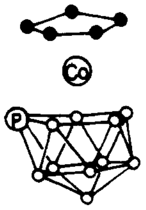
2



3



4



5

Table I. Redox Potentials[a,b] of Arsenic- and Phosphorus-Substituted Cobaltaboranes

compd	oxidn	redn	assignt
$(B_{10}H_{10}As)_2Co^{3-}$ (1)	+0.035		Co(IV)/Co(III)
	+0.67 (irrev)[c]		?/Co(IV)
$(B_9H_9As_2)_2Co^-$ (2)	+1.79 (irrev)		Co(IV)/Co(III)
		−1.00	Co(III)/Co(II)
		−1.82	Co(II)/Co(I)
		−2.58 (irrev)	Co(I)/Co(0)
$CpCo(B_{10}H_{10}As)^-$ (3)	+1.16[d]		Co(IV)/Co(III)
		−2.02	Co(III)/Co(II)
		−2.50 (irrev)	Co(II)/Co(I)
$CpCo(B_9H_9As_2)$ (4)		−0.99	Co(III)/Co(II)
		−1.80	Co(II)/Co(I)
$CpCo(B_{10}H_{10}P)^-$ (5)	+1.14	−2.00	Co(III)/Co(II)
		−2.50 (irrev)	Co(II)/Co(I)
$(1\text{-}CH_3\text{-}1,7\ PCB_9H_{10})_2Co$ (6)	+0.41		Co(III)/Co(II)
		−0.62[e]	Co(II)/Co(I)
		−1.93[e]	Co(I)/Co(0)

[a] Volts vs. aqueous saturated calomel electrode. Solvent/electrolyte was $CH_3CN/0.1\ M\ Bu_4NPF_6$, unless otherwise noted. A platinum microelectrode was used for scans positive of +0.4 V, and a hanging mercury drop was used for all CV scans negative of that voltage. [b] Potentials without notation represent $E°$ values measured by dc polarography ($E_{1/2}$ potentials) or cyclic voltammetry (average of E_{pa} and E_{pc}) for reversible systems. Potentials given for irreversible (irrev) systems are CV peak potentials recorded at a scan rate of 0.2 V/s. [c] There is a third oxidation wave at $E° = +0.94$ V due to a product formed after the second, irreversible oxidation (see text). [d] At slow scan rates, this wave becomes irreversible and a product wave grows in at $E_p = +1.65$ V (irrev). [e] In dimethoxyethane/Bu_4NPF_6.

---

* To whom correspondence should be addressed at the University of Vermont.

(1) Geiger, W. E. In "Metal Interactions with Boron Clusters"; Grimes, R. N., Ed.; Plenum Press: New York, in press.

(2) Little, J. L.; Welcker, P. S.; Loy, N. J.; Todd, L. J. *Inorg. Chem.* **1970**, *9*, 63–69.

0020-1669/82/1321-2529$01.25/0 © 1982 American Chemical Society

summary of the electrochemical data is in Table I.

Oxidation of $(B_{10}H_{10}As)_2Co^{3-}$: A Stable Co(IV) Species. In virtually all previous studies of cobaltacarborane electrochemistry,[1] a reversible Co(III)/Co(II) couple has been reported. For five of the six compounds of the present study, this was also the case. However, **1**, $(B_{10}H_{10}As)_2Co^{3-}$, showed no reductions in the potential range investigated, which extended to −2.8 V (vs. SCE).[4] But this resistance to reduction was accompanied by a corresponding ease of oxidation. Direct-current polarography in CH_3CN/0.1 M Bu_4NPF_6 gave an $E_{1/2}$ potential for the oxidation of +0.035 V with a current-potential slope of 65 mV and a diffusion current constant of 2.98,[5] consistent with a reversible one-electron oxidation to the Co(IV) dianion. Cyclic voltammetry confirmed the reversibility ($E^\circ = +0.04$ V; $i_c/i_a = 1.0$ for scan rates, v, from 0.02 to 0.7 V/s), although the peak separation, ΔE_p, was somewhat larger (78 mV) than that expected (60 mV) for an electrochemically reversible process, at $v = 0.2$ V/s (Pt electrode). Controlled-potential coulometry at a Pt basket at +0.25 V gave an n value of 1.0 electrons as the solution went from yellow to green. Subsequent CV scans confirmed that the green solution contained only the Co(IV) species. Actual isolation of $(B_{10}H_{10}As)_2Co^{2-}$ was not attempted. There have been very few successful attempts at isolation of Co(IV) boranes or carboranes. Knoth reported a stable Co(IV) cluster, $(B_{10}H_{11}C)_2Co^{2-}$, which was generated from the corresponding Co(III) complex by oxidation with ceric ion.[6] Dustin and Hawthorne reported isolation of neutral, green $CpCo(B_7H_8C)$, which was stable if stored cold.[7]

There were further oxidations of the Co(IV) compound. Two waves of one-electron height at $E_{pa} = +0.67$ V and about +1 V ($v = 0.2$ V/s) were observed. The first wave was irreversible and considerably drawn out; the difference between the potential at the anodic peak, E_p, and that at half the current peak, $E_{p/2}$, was about 75 mV, larger than the 57 mV for a reversible wave.[8] The electrochemical transfer coefficient, α, calculated from this wave shape was 0.64.[9] The last oxidation wave was reversible, having an E° of 0.94 V. Bulk electrolysis at +0.80 V turned the solution a deeper green and confirmed that one more electron was involved ($n = 0.95$ e). The only wave remaining was the couple at +0.94 V. Further oxidation at +1.05 V released another 1.2 e and no voltammetric waves were present in the final solution.

This appears to be the first reported example of a cobaltaborane cluster which can be oxidized *beyond* the Co(IV) stage. This one-electron oxidation, which most likely involves a ligand-based orbital, gave rise to the final product with the reversible couple at +0.94 V.

$(B_9H_9As_2)_2Co^-$ (2). The unusual susceptibility of **1** to oxidation undoubtedly is due at least in part to the high negative charge of the arsaborane ligand. The diarsaborane complex **2** carries two fewer negative charges than **1** and exhibits more ordinary redox behavior, displaying reversible one-electron reductions to Co(II) and Co(I) at −1.00 and −1.86 V, respectively (Figure 1). Bulk coulometry of the first reduction (E(applied) = −0.45 V) in THF/Bu_4NPF_6 (light yellow → pale green) gave an n value of 1.3 e.

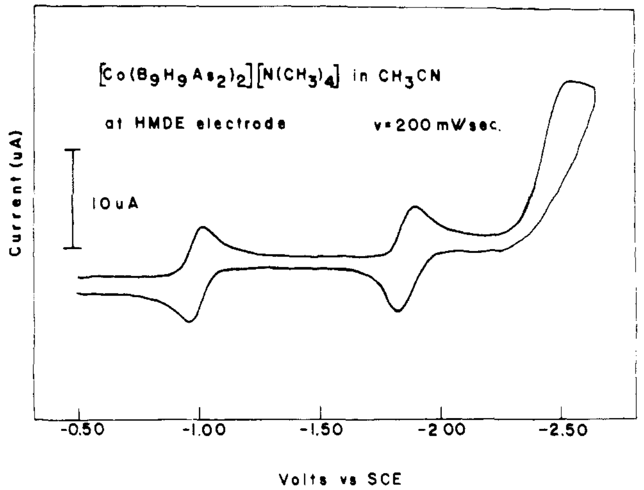


Figure 1. Cyclic voltammogram of $N(CH_3)_4[(B_9H_9As_2)_2Co]$ in CH_3CN/0.1 M Bu_4NPF_6: hanging-mercury-drop electrode, concentration = 3.0×10^{-4} M, $v = 0.20$ V/s.

Reduction of **2** beyond the Co(I) stage was evident from an irreversible wave just before electrolyte discharge, with $E_{pc} = -2.57$ V ($v = 0.2$ V/s). when background current was substracted, this cathodic wave was found to have a one-electron height. Thus, a formal Co(0) complex was formed, but it was highly unstable.

Attempted oxidation of **2** to a Co(IV) neutral compound gave a CV wave at $E_{pa} = +1.79$ V ($v = 0.2$ V/s), which was irreversible in either CH_3CN or CH_2Cl_2.

Half-Sandwich Compounds 3 and 4. Substitution of a cyclopentadienyl ring for a $(B_{10}H_{10}As)$ ligand resulted in a large (over 1 V) positive shift of the redox potentials of **3** compared to **1**. The Co(IV)/Co(III) oxidation at $E^\circ = +1.16$ V was not completely reversible, and CV scan rates in excess of 1 V/s were necessary to outrun the follow-up chemical reaction and obtain a value of unity for i_c/i_a. At slower scan rates an irreversible oxidation wave at +1.65 V (E_{pa}) grew in. That this wave was due to the decomposition reaction of neutral $CpCo(B_{10}H_{10}As)$ formed in the first oxidation was shown conclusively by bulk oxidation of the solution at +1.40 V, which resulted in release of one electron ($n = 1.1$ e, light yellow → mustard yellow) and the presence of only the wave at +1.65 V in subsequent CV scans.

Two one-electron reductions were noted for **3**. The second of these, the Co(II)/Co(I) couple, was irreversible. The half-sandwich version of the diarsaborane ligand, namely, $CpCo(B_9H_9As_2)$ (**4**), displayed reversible one-electron reductions at −0.99 and −1.80 V as the complex was sequentially reduced: Co(III)/Co(II)/Co(I). No oxidation waves were observed for this compound.

Phosphorus-Containing Cobalt Clusters: Formation of a Formal Co(0) Complex. The phosphaborane $CpCo(B_{10}H_{10}P)^-$ (**5**) had a redox behavior essentially the same as that of its arsenic analogue (**3**), with a Co(IV)/Co(III) oxidation which was reversible at high scan rates and a reversible Co(III)/Co(II) couple but an irreversible Co(II)/Co(I) process. The potentials of the corresponding waves were virtually identical. Thus, there was no indication of appreciable differences in the redox properties of analogous phospha- or arsametallaboranes.

Finally, the reduction of the neutral Co(II) phosphacarborane (**6**) in dimethoxyethane was quite interesting. There was a highly reversible reduction at −0.62 V to the Co(I) complex and a further reduction at −1.93 V. The product of this second reduction was not completely stable ($i_a/i_c = 0.85$ at $v = 0.2$ V/s) but moderately rapid CV scans did outrun the rate of the chemical decomposition and simplify the process

---

(3) Little, J. L.; Pao, S. S. *Inorg. Chem.* **1978**, *17*, 584–587.

(4) Standard polarographic and cyclic voltammetric procedures were involved. For electrochemical procedures see: Bowden, W. L.; Holloway, J. D. L.; Geiger, W. E. *Inorg. Chem.* **1978**, *17*, 256–260. Each polarographic or cyclic voltammetric wave demonstrated diffusion-controlled mass transport, as shown by linear plots of dc plateau currents vs. square root of mercury column height (polarography) or cyclic voltammetric peak currents vs. square root of scan rate.

(5) Units of I are $\mu A\ mM^{-1}\ mg^{-2/3}\ s^{-1}$. The value for the one-electron reduction of the standard cobaltocenium ion was 3.6.

(6) Knoth, W. H. *Inorg. Chem.* **1971**, *10*, 598–605.

(7) Dustin, D. F.; Hawthorne, M. F. *Inorg. Chem.* **1973**, *12*, 1380.

(8) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706–723.

(9) From the relationship $E_p - E_{p/2} = 0.048\ V/\alpha n$.

Table II. Formal Charges of Group 5 Borane Ligands Employed in This Study

ligand	charge	ligand	charge
$B_{10}H_{10}As$	3−	$B_9H_9As_2$	2−
$B_{10}H_{10}P$	3−	$B_9H_{10}CP(CH_3)$	1−

to a reversible one-electron transfer. The dianion produced in this reduction appears to be the first evidence of a metallacarborane in a formal Co(0) oxidation state.

Conclusions. These results reveal that group-5-substituted cobaltaboranes are capable of extensive electron-transfer reactions. Accessibility of a particular cobalt oxidation state appears to depend largely on the formal ligand charge (Table II) which, of course, determines the overall charge of the complex in a particular metal oxidation state. In the complexes studied, the actual charge varies from 3− for **1** to 1+ for **6** in the formal Co(III) complexes. The electron-transfer reactions of these compounds involve a composite of five separate one-electron steps.

$$? \rightleftarrows Co(IV) \rightleftarrows Co(III) \rightleftarrows Co(II) \rightleftarrows Co(I) \rightleftarrows Co(0)$$

The number observed for any particular complex depends on its charge, which shifts the $E°$ potentials. A minimum of two waves (for trinegative **1**) and a maximum of four waves (for mononegative **2**) were found.

Acknowledgment. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation (Grant CHE80-04242). We thank Dr. L. J. Todd for providing a sample of **6**.

Registry No. **1**, 65036-28-4; **2**·$N(CH_3)_4$, 65036-33-1; **3**, 65015-72-7; **4**, 65036-34-2; **5**, 57091-19-7; **6**, 81245-18-3.

Contribution from the Department of Chemistry, Kent State University, Kent, Ohio 44242,
and the Ruhr-Universität Bochum, D4630 Bochum-Querenburg, Federal Republic of Germany

Electron Transfer. 54. Remote Attack in the Reductions of Carboxylato-Bridged Dicobalt(III) Complexes[1]

VANGALUR S. SRINIVASAN,[2a] A. N. SINGH,[2b] KARL WIEGHARDT,[2c] N. RAJASEKAR,[2b] and E. S. GOULD*[2b]

Received November 10, 1981

Twelve carboxylato-bridged dicoalt(III) complexes of type I have been prepared and their reductions with the metal centers V^{2+}, Eu^{2+}, Cr^{2+}, $Ru(NH_3)_6^{2+}$, and U^{3+}, as well as with the radical (Rb·) and the dihydro derivative (RbH_2) of riboflavin, have been examined. In each of the dimeric oxidants, the carbonyl of the carboxyl group has been tied off by coordination, blocking off inner-sphere reduction of the type often encountered with monomeric carboxylato oxidants, but seven of the dimers feature a pendent carbonyl group in conjugation with the bridging carboxyl. Specific rates in each case appear to be determined by the reduction of the first of the two Co(III) centers. For those dimeric oxidants having no free carbonyl function, rate patterns for reactions with the five metal-center reductants correspond closely to those observed for other systems where only outer-sphere paths are possible. Incorporation of the conjugated carbonyl group enhances the rates of reduction with $Ru(NH_3)_6^{2+}$, Rb·, and RbH_2 (all outer-sphere reductants) only modestly (<10-fold) but accelerates reductions by Cr^{2+}, Eu^{2+}, and U^{3+} by 10^2–10^7, indicating strongly that a second (remote inner-sphere) path has come into play with these metal-center reductants. These experiments provide the first reported evidence for remote attack by U^{3+}. Reductions, using Eu^{2+}, of the carbonyl-substituted dimers yield considerably less than 1:1 Co^{2+}:Eu^{2+} even when the oxidant is taken in excess, indicating that reduction of the carbonyl group (and subsequent dimerization of the derived radical) competes with reduction of bound Co(III); this side reaction appears to occur both with the original dimer and with the monomeric Co(III) intermediate. In contrast, 1:1 stoichiometry is observed in reductions with $Ru(NH_3)_6^{2+}$ (which is too weak a reductant to reduce the carbonyl group) and with Cr^{2+} and U^{3+}, the oxidized forms of which (Cr^{III} and U^{IV}) presumably remain bound to the carbonyl function after the initial act of electron transfer. Rate comparisons between reductions of the dimers and carbonyl-substituted monomeric oxidants of the type $RCO_2Co(NH_3)_5^{2+}$ have been used to estimate the distribution between alternate reaction paths when carbonyl substitution in the monomers allows reduction, in part, by remote attack. It has thus been calculated that the remote path for Cr^{2+} reduction of the monomeric pyruvato complex comprises only 0.2% of the total reaction whereas that for the 2-formylbenzoato complex constitutes 15%.

Among the concepts contributing to the current picture of inner-sphere electron-transfer reactions, that of remote attack (the passage of an electron from one metal center to another through an extended portion of an organic molecule) has proved fascinating both to experimentalists and theoreticians but, at the same time, has suffered a rather checkered history. Early evidence in support of this concept[3] has been subjected to doubt[4] or to reinterpretation,[5] and the systems ultimately used to demonstrate this phenomenon[6] have, in some instances, been quite different from those to which it was originally meant to apply. An important difficulty was that much of the early work dealt with carboxylato derivatives of cobalt(III) having an unsaturated donor group (e.g., an aldehyde, ester, or pyridine function) lying in conjugation with $-COOCo^{III}$, which was presumed to offer a second (remote) path for electron transfer. It is now recognized, however, that such groups can greatly facilitate the more usual mode of transfer through the "adjacent" carboxyl,[4c,7] thus complicating the disentangling of the two competing inner-sphere contributions, unless, as in

---

(1) Sponsorship of this work by the National Science Foundation (Grant CHE 8022881) is gratefully acknowledged.

(2) (a) On leave from Vivekananda College, Mylapore, Madras, India. (b) Kent State University. (c) Ruhr-Universität Bochum.

(3) See, for example: (a) Fraser, R. T. M.; Taube, H. *J. Am. Chem. Soc.* **1961**, *83*, 2239. (b) Sebera, D. K.; Taube, H. *Ibid.* **1961**, *83*, 1785. (c) Gould, E. S.; Taube, H. *Ibid.* **1963**, *85*, 3706.

(4) See, for example: (a) Hurst, J. K.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1178. (b) Gould, E. S. *Ibid.* **1965**, *87*, 4730.

(5) Thamburaj, P. K.; Loar, M. K.; Gould, E. S. *Inorg. Chem.* **1977**, *16*, 1946.

(6) (a) Nordmeyer, F.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1162. (b) Gould, E. S.; Johnson, N. A.; Morland, R. B. *Inorg. Chem.* **1976**, *15*, 1929. (c) Balahura, R. J.; Purcell, W. L. *J. Am. Chem. Soc.* **1976**, *98*, 4457. (d) Hyde, M. R.; Wieghardt, K.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1976**, 690.

(7) See, for example: (a) Price, H. J.; Taube, H. *Inorg. Chem.* **1968**, *7*, 1. (b) Heh, J. C.-K.; Gould, E. S. *Ibid.* **1978**, *17*, 3138.

0020-1669/82/1321-2531$01.25/0