OFFICE OF NAVAL RESEARCH

CONTRACT NO. N00014-75-C-0305

TECHNICAL REPORT NO. 39

Boranametallacarboranes. 1. Synthesis and Characterization
of (Borane)Cobalt(Carborane) Sandwich Complexes

Lester Borodinsky and Russell N. Grimes

Department of Chemistry

University of Virginia

Charlottesville, Va.   22901

Prepared for Publication in

Inorganic Chemistry

December 1981

Boranametallacarboranes. 1. Synthesis and

Characterization of (Borane)Cobalt(Carborane)

Sandwich Complexes[1]

Lester Borodinsky and Russell N. Grimes[*]

Abstract. The first known examples of borane-metal-carborane

sandwich complexes, in which a metal atom simultaneously

occupies vertices in a metallaborane and a metallacarborane

framework, have been obtained from reactions of $B_5H_8^-$ or $B_9H_{14}^-$

ions with $CoCl_2$ in THF, followed by addition of $R_2C_2B_4H_5^-$ ion

(R = $CH_3$ or $C_2H_5$).  With $B_5H_8^-$ and $(C_2H_5)_2C_2B_4H_5^-$, the

characterized products are $[2,3-(C_2H_5)_2C_2B_4H_4]-2-Co[B_5H_{10}]$

(I), $[2,3-(C_2H_5)_2C_2B_4H_4]-5-Co[B_9H_{12}-1-O(CH_2)_4]$ (II),

and $[2,3-(C_2H_5)_2C_2B_3H_5]-5-Co[B_9H_{12}-1-O(CH_2)_4]$ (III).

With $B_9H_{14}^-$ as the borane reagent, the products are

$[2,3-(C_2H_5)_2C_2B_3H_5]-6-Co[B_9H_{12}-2-O(CH_2)_4]$ (IV) and $[1,2-$

$(C_2H_5)_2C_2B_7H_7]-6-Co[B_9H_{12}-2-O(CH_2)_4]$ (V), as well as traces

of I, II, and III.  Except for I, an orange oil, all products

are crystalline solids.  Products I-V were characterized from

their FT NMR spectra obtained at 360 MHz for $^1H$ and 115.5 MHz

for $^{11}B$, their ir and mass spectra, and by X-ray diffraction

studies on II, III, and V which are reported in the accompanying

paper.  The syntheses of I-V are highly sensitive to reaction

conditions; simultaneous addition of the borane, carborane, and

metal reagents does not give boranametallacarboranes (as shown

in an earlier study by Hosmane and Grimes).  The yields of I-V

are maximized by short (~ 20 min.) reaction periods and low temperatures (~ -20°C) for the $CoCl_2$/borane interaction prior to addition of carborane.

| Accession For | |
|---|---|
| NTIS GRA&I | ☒ |
| DTIC TAB | ☐ |
| Unannounced | ☐ |
| Justification | |

| By | |
|---|---|
| Distribution/ | |

| Availability Codes | |
|---|---|
| Dist | Avail and/or Special |
| A | |

## Introduction

The insertion of metals into borane and carborane frameworks generates metallaboranes[2] and metallacarboranes,[3] respectively. These two compound classes encompass an enormous variety of species and constitute two large and quite distinct fields. While the metallaboranes and metallacarboranes have much in common structurally and obey the same electron-counting rules (which in fact extend to numerous non-boron clusters as well),[4] their synthetic origins are entirely different and their respective chemistries have developed along separate paths. As a general observation, interactions of metal reagents with carborane substrates are, to a degree, more predictable and stereospecific than are metal-borane reactions. Moreover, the cage carbon atoms in metallacarboranes provide loci for functional groups which permit the synthesis of specifically "tailored" derivatives; an elegant recent example is the preparation by Hawthorne and co-workers[5] of powerful metallacarborane catalysts for homogeneous hydrogenation. Rational development of metallaborane chemistry has proceeded more slowly, but this has been compensated by the discovery of a variety of novel structural features and unanticipated cage geometries which have aided the evolution of structural and bonding theory in clusters.

This paper is concerned with the interface between the metallaborane and metallacarborane fields, and describes the synthesis and characterization of the first borane-metal-carborane complexes, or "boranametallacarboranes," in which a metal atom

occupies vertices in metallaborane and metallacarborane frameworks simultaneously. Our interest in such species was stimulated by the possibility of effecting fusion of borane and carborane cages under mild conditions, in a manner similar to that previously demonstrated for bis(carborane) complexes of cobalt and iron.[2d,6] Although a previous study involving interactions of metal ions with the $2,3-(CH_3)_2C_2B_4H_5^-$ and $B_5H_8^-$ ions simultaneously[6c] did not lead to isolable borane-metal-carborane complexes, further investigation revealed that under proper conditions such mixed species can indeed be isolated. Here we report the synthesis and spectroscopic characterization of several boranametallacarboranes derived from $nido-R_2C_2B_4H_5^-$ ($R = CH_3$ or $C_2H_5$) and $B_5H_8^-$ or $B_9H_{14}^-$ ions. X-ray crystal structure determinations on three of these products are described in the following article.[7]

Results and Discussion
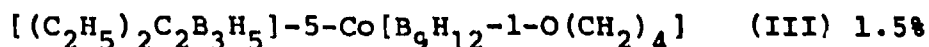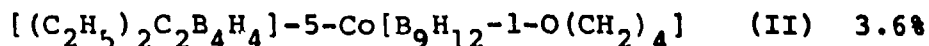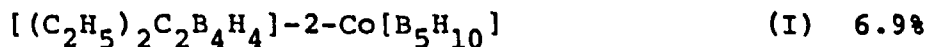
The choice of $nido-2,3-R_2C_2B_4H_5^-$ ions as the carborane substrates in this work was based on the facility with which these ions form $\eta^5$ - complexes with transition metal ions,[2d,2e,3b,6] their easy accessibility,[8] and the demonstrated propensity of $(R_2C_2B_4H_4)_2MH_x$ complexes ($R = CH_3$, $C_2H_5$, or $C_3H_7$; $M = Fe$, $x = 2$; $M = Co$, $x = 1$) to undergo fusion, forming $R_4C_4B_8H_8$ carboranes in high yield.[2d,6] As borane reagents, the $B_5H_8^-$ and $B_9H_{14}^-$ ions, both of which interact with transition metals to generate metallaboranes,[2] were utilized in separate experiments. In earlier published work from this laboratory,[6c] the simultaneous interaction of $CoCl_2$ with $B_5H_8^-$ and $(CH_3)_2C_2B_4H_5^-$ ions in

tetrahydrofuran (THF) solution at room temperature gave, as the sole isolated product (21% yield), the mixed-carborane complex $[2,3-(CH_3)_2C_2B_4H_4]CoH[2,3-(CH_3)_2C_2B_7H_7]$, a yellow, air-stable solid. In the present study, $B_5H_8^-$ ion and CoCl$_2$ were permitted to react first, with the carborane substrate added later; this procedure gave entirely different results and produced several borane-metal-carborane complexes (which, in fact, had been the original synthetic objective of the earlier investigation).

Reaction of $Na^+B_5H_8^-$ and CoCl$_2$ Followed by $Na^+R_2C_2B_4H_5^-$ $(R = CH_3, C_2H_5)$. As described elsewhere,[9] the formation of $B_5H_8^-$ on treatment of $B_5H_9$ with NaH in THF unavoidably generates some $B_9H_{14}^-$ as a byproduct; however, at low temperature ($<-30^oC$) and in the presence of at least a 2.5-fold excess of NaH over $B_5H_9$, this complication is minimized[10] and the borane ion formed is predominantly (> 90 mole %) $B_5H_8^-$.

Under these conditions the following sequence is observed:

$$B_5H_8^- + CoCl_2 \xrightarrow[\substack{20\ min \\ -23^oC}]{THF} \begin{bmatrix} dark\ green \\ solution \end{bmatrix} \xrightarrow[THF,\ 7\ hr^-]{Et_2C_2B_4H_5^-} \begin{bmatrix} dark\ brown \\ solution \end{bmatrix} \frac{H_2O}{O_2}$$

| | | |
|---|---|---|
| $[(C_2H_5)_2C_2B_4H_4]-2-Co[B_5H_{10}]$ | (I) | 6.9% |
| $[(C_2H_5)_2C_2B_4H_4]-5-Co[B_9H_{12}-1-O(CH_2)_4]$ | (II) | 3.6% |
| $[(C_2H_5)_2C_2B_3H_5]-5-Co[B_9H_{12}-1-O(CH_2)_4]$ | (III) | 1.5% |

The yields shown are calculated from carborane employed; the corresponding C,C'-dimethyl products are obtained from $(CH_3)_2C_2B_4H_5^-$ ion in essentially the same yields. The isolated products I, II, and III, all air-stable, were purified via thick-layer and preparative high-pressure column chromatography and characterized from their ^{11}B and ^{1}H FT NMR spectra obtained at 115.5 and 360 MHz,
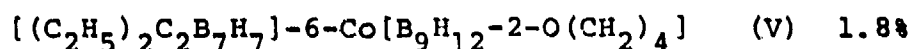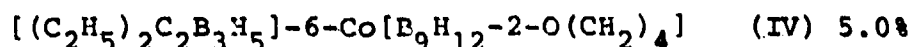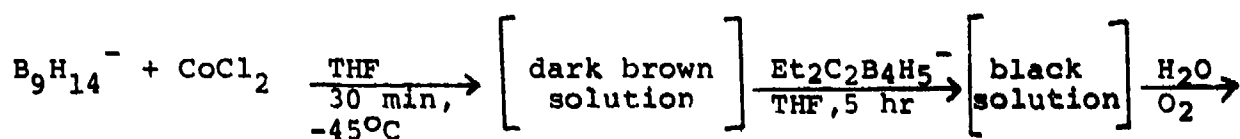
respectively, and from ir and mass spectra (Tables I-V),
as discussed below. In addition, X-ray crystal structure
determinations were conducted on II and III.[7] Figures 1-3 present
the assigned structures of all three species.

This reaction also generated a trace of $[2,3-(C_2H_5)_2C_2B_3H_5]$-
$CoH[2,3-(C_2H_5)_2C_2B_4H_4]$, analogous to the known complex
$[(CH_3)_2C_2B_3H_5]CoH[(CH_3)_2C_2B_4H_4]$[6b], which was isolated and
identified from its NMR spectra.

The yields of products I-III are sensitive to the length of
time elapsed between the initial reaction of $B_5H_8^-$ with $CoCl_2$
and the introduction of the carborane anion. When this period
is held to 20 min, the yields are as indicated above, but longer
intervals result in progressively lower yields for all three
species; thus, when the $B_5H_8^-/CoCl_2$ mixture is stirred at $-23^\circ C$
for 4 hr before addition of carborane, the quantities of I-III
are reduced by an order of magnitude or more. Temperature is
also a significant factor in this system. When the $B_5H_8^-/CoCl_2$
reaction mixture is maintained at $-78^\circ C$ for 20 min, the yields
of I, II, and III increase slightly to 7.3, 4.7, and 1.6 percent,
respectively.

Reaction of $Na^+B_9H_{14}^-$ and $CoCl_2$ Followed by $Na^+R_2C_2B_4H_5^-$
$(R = CH_3, C_2H_5)$. Since the $B_9H_{14}^-$ ion is readily generated
from $B_5H_9$ and NaH at room temperature (with minimal amounts of
other borane species present),[9] a sequence analogous to that
described above was employed with $B_9H_{14}^-$. The major products,
IV and V, are species not obtained in the $B_5H_8^-$ reaction;
however, small quantities of I, II, and III are also obtained.

$$B_9H_{14}^- + CoCl_2 \xrightarrow[\substack{30 \text{ min,} \\ -45^\circ C}]{THF} \left[\begin{array}{c} \text{dark brown} \\ \text{solution} \end{array}\right] \xrightarrow[THF, 5 \text{ hr}]{Et_2C_2B_4H_5^-} \left[\begin{array}{c} \text{black} \\ \text{solution} \end{array}\right] \xrightarrow[O_2]{H_2O}$$

$[(C_2H_5)_2C_2B_3H_5]-6-Co[B_9H_{12}-2-O(CH_2)_4]$    (IV)   5.0%

$[(C_2H_5)_2C_2B_7H_7]-6-Co[B_9H_{12}-2-O(CH_2)_4]$    (V)   1.8%

+ traces of I, II, and III.

The spectroscopic and other characterization data for IV and V are given in Tables I-V, and a crystal structure analysis of V is reported in the following article.

Structural Characterization of Products. The proposed geometry of I (Figure 1), the major isolable product of the reaction of $B_5H_8^-$, $(C_2H_5)_2C_2B_4H_5^-$, and $CoCl_2$, is consistent with both the NMR data and the synthetic origin. The [11]B and ^{1}H spectra indicate local mirror symmetry in the $CoB_5$ (cobaltaborane) and $CoC_2B_4$ (cobaltacarborane) cage systems; as we have previously noted in other mixed-ligand sandwich complexes,[6c] the ligands do not perturb each other's chemical shifts to a detectable extent, and thus the relative orientation of the two ligands is not revealed by NMR evidence alone. However, the "twisted" arrangement in Fig. 1 is consistent with the crystallographically determined structures[7] of II, III, and V, all of which lack a molecular mirror plane.

Strong evidence for the proposed structure is given by the presence of ^{1}H NMR signals corresponding to two equivalent Co-H-B, two equivalent B-H-B, and a unique B-H-B bridge. Moreover, the nido-$CoB_5H_{10}$ grouping exhibits [11]B and ^{1}H spectra very similar

to those of the established compounds $2\text{-}(CO)_3FeB_5H_9$ [11],
$2\text{-}(\eta^5\text{-}C_5H_5)FeB_5H_{10}$ [12], and $2\text{-}(CO)_3MnB_5H_{10}$, [13] all of these species
being structural analogues of hexaborane(10), $B_6H_{10}$. After
assignment of the $^{11}B$ signals arising from the $B_5H_{10}^{-}$ ligand
(Table II), the remaining 1:1:2 pattern can be attributed to
the $(C_2H_5)_2C_2B_4H_4^{2-}$ group, whose spectrum resembles that of the
well-characterized $(\eta^5\text{-}C_5R_5)CoR'_2C_2B_4H_4$ species (R = H, $CH_3$;
R' = H, $CH_3$, $C_2H_5$). [14] The presence of only one set of $C_2H_5$
peaks in the $^1H$ spectrum indicates apparent equivalence of the
two C-ethyl units but, as noted above, does not imply overall
mirror symmetry in the molecule.

Compound I can be viewed as two polyhedra (closo 7-
vertex and nido 6-vertex) sharing a common vertex, or equivalently, as a
sandwich complex of $Co^{3+}$ with $[\eta^5\text{-}(C_2H_5)_2C_2B_4H_4]^{2-}$ and
$[\eta^3\text{-}B_5H_{10}]^{-}$ ligands. The proposed structure represents an
interesting illustration of Wade's electron-counting rules, [4]
in that it incorporates both (2n + 4)-electron (nido) and
(2n + 2)-electron (closo) frameworks. [15]

Compound II is formulated from its mass spectra and NMR
data as a THF-substituted derivative of a $[(C_2H_5)_2C_2B_4H_4]Co[B_9H_{13}]^{-}$
parent species; formal replacement of a terminal :$H^-$ by :$O(CH_2)_4$
generates II as a neutral derivative. The $^1H$ and $^{11}B$ patterns are
consistent with the presence of a closo $CoC_2B_4$ cage, as in I,
and the $^1H$ spectrum reveals three B-H-B and one Co-H-B signal
(identified from its high-field resonance), placing cobalt in the
5-position of a nido-$CoB_9$ cage. In order to establish the structure
and precisely locate the THF substituent group, an X-ray diffraction

study was undertaken[7] which disclosed the cage geometry shown in Figure 2. In this molecule, the 7-vertex $Co(C_2H_5)_2C_2B_4H_4$ unit is identical to that in I, while the $5\text{-}CoB_9H_{12}\text{-}O(CH_2)_4$ moiety is structurally analogous to $5\text{-}(\eta^5\text{-}C_5H_5)CoB_9H_{13}$, which was crystallographically characterized several years ago;[16a] both of these 10-vertex $CoB_9$ frameworks formally contain 24 (2n + 4) skeletal valence electrons and hence are nido cages, structurally similar to $B_{10}H_{14}$.

The molecule contains no overall symmetry plane, but as in I, the NMR spectra indicate local mirror symmetry in the carborane cage (particularly striking is the apparent equivalence of the two $C_2H_5$ groups). The $^{11}B$ NMR assignments in Table II are based, in part, on accumulated data from other $CoB_9$ and $Co_2B_8$ cage systems[16,10,17] and trends perceived in the earlier work; the $^{11}B$ spectrum of $B_{10}H_{14}$ itself[18] is also relevant. As expected,[19] substitution of a THF ligand for a terminal hydrogen produces a substantial shift of the corresponding $^{11}B$ resonance to lower field

Viewed as a sandwich complex of $Co^{3+}$, the ligands in II are $[\eta^5\text{-}(C_2H_5)_2C_2B_4H_4]^{2-}$ and $[\eta^4\text{-}B_9H_{12}\text{-}O(CH_2)_4]^-$. Further discussion of the structure of II appears in the accompanying article.[7]

The third product, III, is identifiable from its NMR and mass spectra as $[(C_2H_5)_2C_2B_3H_5]\text{-}5\text{-}Co[B_9H_{12}\text{-}O(CH_2)_4]$ (Figure 3), analogous to II with an $R_2C_2B_3H_5^{2-}$ ligand replacing $R_2C_2B_4H_4^{2-}$; thus the cobaltacarborane cage is a nido $CoC_2B_3$ (pentagonal pyramidal) unit. The borane ligand is again $[B_9H_{12}\text{-}1\text{-}O(CH_2)_4]^-$, identical to that in II. These deductions are based on the

close similarity in $^{11}$B and $^1$H NMR spectra of II and III, (Tables II and III), and on the fact that base-degradation of II produces III by removal of B(7')-H from the former (vide infra). Conclusive proof of this structure is given by an X-ray diffraction analysis whose details are reported in the following paper.[7]

The 360-MHz proton NMR spectrum of III clearly reveals the resonances of all six bridging protons, two of which [H(56)' and H(45)'] are equivalent owing to the local mirror plane in the $C_2B_3$ ring ligand and are assigned to the area-2 signal at $\delta$-4.00.

The $R_2C_2B_3H_5{}^{2-}$ ligand in III is isoelectronic with $C_5H_5{}^-$ and has previously been observed in the crystallographically characterized species $1-(CO)_3FeC_2B_3H_7{}^{20}$ and $[(CH_3)_2C_2B_4H_4]Co-[(CH_3)_2C_2B_3H_5]^-$.[21] As in the case of I and II, III can be described both in cluster terms (6- and 10- vertex nido cages linked at a common vertex) or as a sandwich of $Co^{3+}$ with $[\eta^5-(C_2H_5)_2C_2B_3H_5]^{2-}$ and $[\eta^4-B_9H_{12}-O(CH_2)_4]^-$ ligands.

Product IV, obtained from $B_9H_{14}{}^-$ ion as described above, is an isomer of III in which the cobalt atom occupies the 6-position in the $CoB_9$ cage (Figure 4). This produces local mirror symmetry in both the $CoB_9$ and $CoC_2B_3$ frameworks, and results in considerable simplification of the NMR spectra as compared to III. The location of cobalt in the cobaltaborane cage is established by the presence of two equivalent Co-H-B and two equivalent B-H-B bridges, as revealed by NMR. While the THF substituent could be attached to B(2), B(4), or B(9) and still preserve the local mirror symmetry, placement on B(2) is most consistent with the NMR data in comparison with the established structures II and III; moreover, attack of THF on

$MB_9$-type metallaborane cages invariably occurs at a boron adjacent to the metal[22]. The proton and boron NMR data on the $CoC_2B_3$ fragment correlate well with those of the corresponding portion of the established structure, III. Similarly, the signals arising from the $6-CoB_9$ cage closely resemble the spectra of known $6-(\eta^5-C_5R_5)CoB_9H_{13}$ species (R = H[23] and $CH_3$[10]).

Compound V, the other major product of the $B_9H_{14}^-$ reaction, is unique among the compounds obtained in this study, in that the carborane ligand is a $C_2B_7$ rather than a $C_2B_3$ or $C_2B_4$ system. The $^{11}B$ NMR spectrum exhibits 12 distinct resonances and is too complex for unambiguous interpretation. From the $^1H$ spectrum one can deduce the presence of two Co-H-B and two B-H-B bridges in equivalent pairs; assuming that the cobaltaborane cage is once again a $B_{10}H_{14}$- like $CoB_9$ system, this places the metal in the 6- position. However, definitive structural assignment of this molecule required an X-ray diffraction study[7] which established the geometry shown in Figure 5. As can be seen, the complex consists of closo 10-vertex $CoC_2B_7$ and nido 10-vertex $CoB_9$ cages sharing a common vertex at cobalt. The $CoC_2B_7$ unit, however, has an abnormally long C(2')- B(3') distance [2.192(9)Å] which suggests a weak bonding interaction; this may reflect electronic influence of the $B_9$ ligand, as discussed in the accompanying report.[7]

A variety of other closo $MC_2B_7$ metallacarborane systems has been reported,[3] but in none of these do the carbon atoms occupy the 1,2 vertices as in V. Curiously, even in the complex $[(CH_3)_2C_2B_4H_4]CoH[(CH_3)_2C_2B_7H_7]$, which was obtained in a closely related earlier study of the $CoCl_2/B_5H_8^-/(CH_3)_2C_2B_4H_5^-$

"simultaneous" reaction[6c] (see Introduction), the $CoC_2B_7$ cage
is different from that in V; although X-ray confirmation
of the earlier compound is not available, its $^{11}B$ NMR spectrum
lacks a low-field signal corresponding to that at $\delta$ 78.8 in
V. Furthermore, the $^1H$ NMR spectrum of the above-mentioned
bis⌒(carborane) complex shows that the C-R units in the
$CoC_2B_7$ cage are equivalent, in contrast to V.

The $^{11}B$ and $^1H$ NMR spectra of V are fully compatible with
the X-ray-determined structure; assignment of the individual
$^{11}B$ peaks is not obvious, other than for B(2)-THF (a singlet
resonance) and B(10')-H, which is a low-coordinate BH unit
adjacent to cobalt and probably generates the low-field
($\delta$ 78.8) signal.

Degradation of II to III. In light of the structures
established for products II and III, which differ only by the
presence of a "capping" BH group [i.e., B(7')] in II that
is replaced by two bridging hydrogen atoms in III, it appeared
likely that III is formed by removal of B(7')-H from II during
workup in aqueous media. Accordingly, treatment of II with
acidified aqueous THF was found to give III in 82% yield. Such
conversions of closo-$C_2B_4$ to nido-$C_2B_3$ ligands by base attack
at the apex boron have been noted elsewhere: $[(CH_3)_2C_2B_4H_4]_2CoH$
is similarly degraded to $[(CH_3)_2C_2B_4H_4]CoH[(CH_3)_2C_2B_3H_5]$,[6b]
and $(\eta^5-C_5H_5)CoR_2C_2B_4H_4$ species are readily converted to
$(\eta^5-C_5H_5)CoR_2C_2B_3H_5$ complexes.[24]

These observations raise the question of the origin of compound IV, which also contains an $R_2C_2B_3H_5^{2-}$ ligand. It can be assumed that this species forms similarly via degradation of the corresponding $R_2C_2B_4H_4^{2-}$ complex, i.e., $[(C_2H_5)_2C_2B_4H_4]$-6-$Co[B_9H_{12}$-2-$O(CH_2)_4]$; however, this latter species has not been observed. It seems a reasonable presumption that this compound is formed in the original reaction of $(C_2H_5)_2C_2B_4H_5^-$, $CoCl_2$, and $B_9H_{14}^-$ in THF, and during workup in aqueous THF undergoes complete conversion to product IV which is subsequently isolated.

Finally, we note that treatment of compounds I and V (both of which also incorporate an $R_2C_2B_nH_n^{2-}$ ligand) with aqueous THF does <u>not</u> lead to characterizable compounds, giving only intractable substances.

<u>Reaction of $B_3H_8^-$ with $CoCl_2$ and $R_2C_2B_4H_5^-$</u>. Investigation of the borane/$CoCl_2$/$R_2C_2B_4H_5^-$ reaction system (R = $CH_3$) with $B_3H_8^-$ as the borane substrate, following the sequence used in the $B_5H_8^-$ reaction, gave compounds II and III together with some $(R_2C_2B_4H_4)_2Co^-$, in very low yields; no I, IV, or V were observed. When $BH_4^-$ was employed as the borane reagent, the only isolable product was the known compound $(2,3$-$R_2C_2B_3H_5)CoH(2,3$-$R_2C_2B_4H_4)$. These results can be contrasted with earlier observations on the borane/$FeCl_2$/$(CH_3)_2C_2B_4H_5^-$ reactions in which the isolable products and yields were essentially independent of whether $B_5H_8^-$ or $B_3H_8^-$ was employed as the borane reagent.[6c]

<u>Reaction of $[2,3$-$(CH_3)_2C_2B_4H_4]_2CoH$ with $B_5H_8^-$</u>. As a control experiment, the carborane anion $(CH_3)_2C_2B_4H_5^-$ was permitted to react first with $CoCl_2$, generating the well-characterized red

complex[6b] $[(CH_3)_2C_2B_4H_4]_2CoH$, which was then stirred in THF

solution with $B_5H_8^-$ and the products worked up in aqueous THF

in air. No evidence of reaction was observed, other than

degradation to $[(CH_3)_2C_2B_4H_4]CoH[(CH_3)_2C_2B_3H_5]$ during workup.

## Conclusions

This work affords the first known examples of borane-metal-

carborane mixed-ligand complexes or boranametallacarboranes, and

in the process reveals some useful information which may guide

future efforts at synthesizing mixed-ligand species. It is

evident that $Co^{2+}$ interacts with $R_2C_2B_4H_5^-$ carborane anions

much more rapidly than with $B_5H_8^-$ (a similar conclusion was reached

earlier[6c] regarding $FeCl_2$ with the same substrates); hence, a

prerequisite for obtaining mixed-ligand products is that the

metal-borane reaction be conducted prior to introduction of the

carborane reagent. Simultaneous interaction of all three

reactants leads only to bis(carborane) metal complexes (though

the presence of the borane anion gives rise to larger carborane

ligands[6c] such as $R_2C_2B_5H_5^{2-}$ and $R_2C_2B_7H_7^{2-}$). The nature of the

metallaboranes generated initially in reactions of metal halides

with $B_5H_8^-$ in THF has not been established, although their extreme

reactivity and their activity as hydrogenation catalysts have been

reported.[25]

Since borane and carborane ligands in monometallaborane and

-metallacarborane complexes usually carry a formal -2 charge,

bis(ligand) complexes of cobalt (III) would normally be

monoanions. In both past and present work in this laboratory,

however, we have been fortunate to isolate neutral products

generated either by protonation to give such species as

$[R_2C_2B_4H_4]_2Co^{III}H$,[6b] or, as in the present study, by substitution of THF for a terminal hydrogen to give electrically neutral molecules which are soluble in organic media and can often be sublimed in vacuum.

The products obtained from $B_5H_8^-$ and from $B_9H_{14}^-$ in this work, viewed together with earlier investigations involving interactions of these ions with $CoCl_2$ and $C_5R_5^-$ (R = H,$CH_3$),[2d,10,16b] reveal a clear structural pattern which seems to have mechanistic implications. When the reagent is $B_5H_8^-$, a variety of cobaltaborane products are obtained, often including 10-vertex $CoB_9$ species; with $B_9H_{14}^-$, the products are invariably nido $CoB_9$ and/or $Co_2B_8$ cage systems. Thus far without exception, the $CoB_9$ products obtained from $B_5H_8^-$ have the metal in the 5-position, while in those generated from $B_9H_{14}^-$ the metal occupies the 6-position. Earlier studies by Gaines, et al.,[13,22] on manganaboranes are consistent with these trends. We think it likely, therefore, that the 6-substituted species, which include IV and V in this work and 6-$[\eta^5-C_5(CH_3)_5]CoB_9H_{13}$,[10] are formed by direct, stereospecific insertion of cobalt into the $B_9H_{14}^-$ ion; the 5-$CoB_9$ complexes, which include II and III in this study as well as 5-$(\eta^5-C_5H_5)CoB_9H_{13}$,[16b] evidently are generated by attack of $B_5H_8^-$ on a $CoB_4$ or $CoB_5$ species present in the reaction mixture. This suggestion is consistent with the fact that the principal species obtained from $B_5H_8^-$ in the present study is I, a $CoB_5$ complex.

Finally, compound I merits comment. That the major product of the $B_5H_8^-/CoCl_2/R_2C_2B_4H_5^-$ reaction is a mixed complex

incorporating $B_5H_{10}^-$ and $R_2C_2B_4H_4^{2-}$ ligands would perhaps be unremarkable, except for the fact that in no previous study of cobalt-$B_5H_8^-$ interactions[6c,10,16b] has a $CoB_5$ species been isolated [the vapor-phase reaction of $(C_5H_5)Co(CO)_2$ with $B_5H_9$ does, however, give 1-$(C_5H_5)CoB_5H_9$[26]]. In reactions of $B_5H_8^-$ with $CoCl_2$ and $C_5H_5^-$ or $C_5(CH_3)_5^-$, for example,[10,16b] the major products obtained are 2-$(C_5R_5)CoB_4H_8$ (R = H,$CH_3$), which are presumed to have formed from an unstable $(C_5R_5)CoB_5H_x$ precursor, but no such intermediate has been found. Thus, the isolation of I as a stable product suggests that the $R_2C_2B_4H_5^-$ carborane anion intercepts and stabilizes a $CoB_5$ intermediate species (perhaps dislodging one $B_5H_x$ ligand from a bis-ligand cobaltaborane formed in the $CoCl_2/B_5H_8^-$ reaction). Two inherent properties of $R_2C_2B_4H_5^-$ are of value here: the presence of an acidic bridging proton which is readily transferable to other ligands in a metal sandwich complex, and the capacity of the dinegative $R_2C_2B_4H_4^{2-}$ pyramidal ligand to bind strongly to metal ions via its $C_2B_3$ face. Both properties of the $R_2C_2B_4H_5^-$ anions are currently being exploited in our laboratory as a tool in the synthesis of new arene hydrocarbon ligands and metal-arene sandwich complexes.[27]

## Experimental Section

Materials. **2,3-dimethyl**-2,3-dicarbahexaborane(8) **2,3**-$(CH_3)_2C_2B_4H_6$, was prepared from $B_5H_9$, $(CH_3)_2C_2$ and $(CH_3CH_2)_3N$ as described elsewhere.[8] 2,3-diethyl-2,3-dicarbahexaborane(8), 2,3-$(C_2H_5)_2C_2B_4H_6$ was similarly prepared from $B_5H_9$, $(CH_3CH_2)_2C_2$ and $(CH_3CH_2)_3N$. Triethylamine was freed of primary and secondary amine impurities first by reflux and then by distillation from phthalic anhydride, and then dried by

distillation from BaO under a nitrogen atmosphere. 2-Butyne and 3-hexyne were purified by twice stirring over metallic sodium and distillation under nitrogen. Pentaborane(9), $B_5H_9$ (U.S. Government stockpile ), was utilized as received after assay by infrared spectroscopy. $(CH_3)_4NB_3H_8$ was prepared from $NaBH_4$ and $I_2$ as described elsewhere.[28] $CoCl_2$ was dried at high temperature in vacuo and tetrahydrofuran (THF) was rigorously dried over $LiAlH_4$ prior to use. NaH (Alfa, 50% in mineral oil) was washed twice with pentane prior to use. All other chemicals were reagent grade and were used as received. Column chromatography utilized silica gel 60 (Merck), and thin- and preparative-layer chromatography TLC and PLC respectively) were conducted on pre-coated plated of silica gel F-254 (Brinkman Instruments, Inc.).

Instrumentation. [11]B (115.5 MHz) and [1]H (360 MHz) pulse Fourier transform NMR spectra were recorded on a Nicolet NT-360 spectrometer equipped with a 1180E/293B data processor. Broad-band heteronuclear decoupling of ^{1}H was employed in recording the [11]B spectra, but the ^{1}H spectra were obtained without [11]B-decoupling. Unit resolution mass spectra (EI) were obtained on a Hitachi Perkin-Elmer RMU-6E mass spectrometer at 70eV. High resolution mass measurements[29] (EI) were conducted on a VG Micromass 70/70 HS mass spectrometer at 70eV, with a source temperature of 230° C. Peak matching versus perfluorokerosene as an internal reference was employed. Infrared spectra were recorded on a Beckman IR-8 instrument. Preparative-scale high pressure liquid chromatography (HPLC) was performed on a Prep-500 LC (Waters Associates), using a refractive index detector and a

PrePAK 500/silica gel cartridge. Melting ranges were determined on a Thomas-Hoover Unimelt capillary melting point apparatus (Thomas Co) or a Fisher-Johns melting point apparatus (Fisher Scientific Co).

Reaction of $B_5H_8^-$ and $CoCl_2$ Followed by $(C_2H_5)_2C_2B_4H_5^-$. Into storage tube B (Fig. 6) was placed 1.235g 2,3-$(CH_3CH_2)_2C_2B_4H_6$ (9.40 mmol), which was degassed and evacuated. The tip-in side-arm flasks were charged with 1.0222 g NaH (42.6 mmol) and 0.5736 g NaH (23.9 mmol) in flasks A and C respectively. A tip-in side-arm tube (E) was charged with 1.2238 g anhydrous $CoCl_2$ (9.43 mmol). The apparatus was assembled as in Figure 6 and evacuated. Flask A was cooled to $-196^O C$, and 1.187 g $B_5H_9$ (18.8 mmol) with about 35 ml dry THF were condensed in vacuo into it. The flask was warmed enough to liquefy the contents and was quickly immersed in a $-30^O C$ bath. Hydrogen gas was evolved over the course of 1.5 hr. The flask was cooled to $-196^O C$ and the $H_2$ pumped away, after which the contents of flask A were warmed to liquefaction and quickly filtered into flask D, kept at $-78^O C$. Stirring was begun at $-78^O C$ and the $CoCl_2$ in the tube E was tipped into flask D. The solution became blue immediately and after 2 min. became green-brown; essentially no gas was evolved. Flask D was cooled to and maintained at $-196^O C$. Flask C was then cooled to $-196^O C$, the contents of tube B tipped in, and about 35 ml dry THF was therein condensed in vacuo. The flask was warmed to room temperature and the contents evolved $H_2$ gas. When effervescence ceased (after 1 hr) the flask was cooled to $-196^O C$, the $H_2$ pumped away, and the flask re-warmed to liquefy its contents. The $(C_2H_5)_2C_2B_4H_5^-$ solution

FIGURE 6

was filtered in vacuo into flask D, which was then warmed to liquefaction. A -78°C bath was then placed around the reaction flask and the reaction resumed. The reaction mixture rapidly became black-brown and remained that color for the ensuing 7 hr. Partial solvent removal was begun in vacuo and after 1.5 hr a thick brown slurry remained in flask D. The reaction flask was filled with $N_2$ and removed from the rest of the apparatus. Its contents were exposed to the air, and to it was added 75 ml of a 2:1 mixture of $H_2O$ and THF; the mixture was stirred in the air for 30 min, which produced some effervescence and gave a dark brown suspension. This mixture was extracted with three 50 ml aliquots of a 1:1 $CH_2Cl_2$/hexane mixture to yield a brown organic phase and a dark pink aqueous phase. The solvent of the organic layer was removed on a rotary evaporator and the residue remaining was dissolved in a small amount of 10% $CH_2Cl_2$ in hexane. This solution was loaded onto a 4.5x14 cm silica gel column packed in hexane and was eluted with 100 ml portions of 0%, 10%, 25%, 50%, and 100% $CH_2Cl_2$ in hexane. A red-orange band was eluted in 10-50% $CH_2Cl_2$/hexane and further purified by PLC in 1:1 $CH_2Cl_2$/hexane giving primarily I (161.9 mg, 6.9% yield). A brown band was eluted in 50-100% $CH_2Cl_2$/hexane. This solution was rotary-evaporated to dryness and separated by PLC in 1:1 $CH_2Cl_2$/hexane. This gave primarily orange III (51.2 mg, 1.5% yield), and brown II (125.6 mg, 3.6%).

Reaction of $B_9H_{14}^-$ and $CoCl_2$ Followed by $(C_2H_5)_2C_2B_4H_5^-$. Storage tube B (Fig. 6) was charged with 1.111 g 2,3-$(CH_3CH_2)_2C_2B_4H_6$ (8.45 mmol), degassed, and evacuated. The tip-in side-arm

flasks A and C were charged with 0.2268 g NaH (9.45 mmol) and
0.4709 g NaH (19.6 mmol), respectively. Side-arm tube E
was charged with 1.1018 g anhydrous $CoCl_2$ (8.49 mmol). The
apparatus was assembled as in Figure 6 and evacuated. Flask
A was cooled to -196°C and 1.187 g $B_5H_9$ (18.8 mmol) and about
35 ml dry THF were condensed in vacuo into it. The flask was
warmed to ambient temperature and allowed to react for 12 hr,

during which $H_2$ was evolved and the solution became
yellow with an off-white flocculent material in suspension. The
flask was cooled to -196°C and the $H_2$ pumped away, after which
it was warmed to 24°C and the $B_9H_{14}^-$ solution filtered into flask
D, maintained at -78°C. An additional 15 ml dry THF was condensed
into flask A to rinse the insoluble material and this washing
was also filtered into flask D. Stirring was begun at -78°C
but much of the solid remained undissolved; consequently, the
temperature was raised to -45°C, which caused all of the solid
material to dissolve. The $CoCl_2$ was tipped in and a blue
solution immediately formed. The solution, which turned light
brown after five min, after thirty min was dark brown. The
reaction flask was cooled to -196°C and maintained at that
temperature. Flask C was then cooled to -196°C, the contents
of tube B tipped in, and into it about 35 ml dry THF was condensed
in vacuo. The flask was warmed to room temperature and the
contents evolved $H_2$. After about one hour, effervescence ceased
and the flask was cooled to -196°C. The $H_2$ was pumped off, the
flask re-warmed to liquefaction, and the 2,3-$(CH_3CH_2)_2C_2B_4H_5^-$
solution filtered into flask D. The reaction flask was warmed

to liquefaction and immersed in a $-45^{\circ}$C bath, resulting in a black-brown solution. Stirring was resumed and continued for five hr, at which point partial removal of the solvent was begun in vacuo. A thick brown slurry remained in the flask after 1.5 hr. The reaction system was filled with $N_2$, the reaction flask (D) was separated from the remainder of the apparatus, and its contents exposed to the air. Into it was placed 75 ml of a 2:1 mixture of $H_2O$ and THF, and the resulting mixture was stirred in air for 30 min with slight bubbling, producing a dark brown suspension. This mixture was extracted three times with 50 ml portions of a 1:1 $CH_2Cl_2$/hexane mixture to yield a brown organic phase and a dark pink aqueous phase. The organic phase was placed on a rotary evaporator and the solvent removed. The residues remaining were dissolved in a small amount of 10% $CH_2Cl_2$ in hexane. This solution was placed atop a 4.5x14 cm silica gel column packed in hexane and eluted with 250 ml hexane, 300 ml 10%, 300 ml 50% $CH_2Cl_2$ in hexane, and 200 ml $CH_2Cl_2$. An orange band was eluted in 10% $CH_2Cl_2$ in hexane and purified via TLC in 1:1 $CH_2Cl_2$/hexane, producing orange I (8 mg, 0.4% yield). A brown band was eluted in 50-100% $CH_2Cl_2$ in hexane, rotary-evaporated to dryness, and separated by PLC in 1:1 $CH_2Cl_2$/hexane, giving primarily orange III (4 mg, 0.1% yield), burgundy IV (153 mg, 5.0%), black-brown V (41 mg, 1.8%), and brown II (6 mg, 0.2%).

Reaction of $2,3-(CH_3)_2C_2B_4H_5^-$, $(CH_3)_4N^+B_3H_8^-$, and $CoCl_2$. A tipping storage tube was charged with 0.871 g $2,3-(CH_3)_2C_2B_4H_6$ (7.81 mmol) and degassed. A tip-in side-arm flask was charged

with 0.4641 g NaH (19.3 mmol), and another tip-in side-arm tube
was filled with 1.0143 g anhydrous $CoCl_2$ (7.81 mmol). The reaction
flask was charged with 2.686 g $(CH_3)_4N^+B_3H_8^-$ (23.4 mmol). The
apparatus was assembled and evacuated. About 40 ml dry THF was
condensed in vacuo into the reactor, warmed to liquefaction,
immersed in a $-23^{\circ}C$ bath, and stirring begun. The solid salt
would not completely dissolve and hence the temperature was raised
to $24^{\circ}C$, which effected solution. The $CoCl_2$ was tipped into the
reactor and the solution became blue immediately, but gradually
became green and evolved $H_2$ gas; after 45 min the solution had
become very dark green. The flask was then cooled to $-196^{\circ}C$
and kept at that temperature. The NaH and carborane were
combined at $-196^{\circ}C$ and 35 ml dry THF were condensed
in vacuo. The flask was warmed to room temperature and $H_2$
evolution ensued. When effervescence had ceased (after 1 hr),
the flask was cooled to $-196^{\circ}C$ and the $H_2$ removed. The flask
was warmed to liquefy the contents and the $(CH_3)_2C_2B_4H_5^-$ solution
was filtered into the reaction vessel. The reaction flask was
warmed to $-23^{\circ}C$, and stirring was resumed at that temperature
for three hours, at which point the solution was greenish-brown-black.
The solvent was partially removed in vacuo, a thick brown slurry
remaining after 1 hr. The flask was flooded with $N_2$ and its
contents exposed to the air; to the flask was added 25 ml of THF,
and then slowly and carefully 50 ml $H_2O$ was introduced. The
mixture exhibited much effervescence upon the initial additions
of $H_2O$, but gas evolution decreased after addition of the first
10 ml. Stirring this mixture for 20 min    in the air gave

a chocolate brown suspension which was extracted with two 50-ml aliquots of a 1:1 $CH_2Cl_2$/hexane mixture. The resulting brown organic phase was rotary-evaporated to dryness and the solids remaining dissolved in a small amount of 1:1 $CH_2Cl_2$/hexane. This solution was placed atop a 4.5x14 cm silica gel column packed in hexane. The column was eluted with 175 ml hexane, 175 ml 20%, 175 ml 60%, 200 ml 100% $CH_2Cl_2$ in hexane, and finally with 200 ml acetone. A yellow band was eluted in 20% $CH_2Cl_2$ in hexane and purified by TLC in 1:1 $CH_2Cl_2$/hexane to give yellow VI (12 mg).

A brown band was eluted in 60-100% $CH_2Cl_2$ in hexane and this solution was separated via TLC in 1:1 $CH_2Cl_2$/hexane, giving primarily orange III (2 mg) and brown II (4 mg). The acetone eluted an orange band which was rotary-evaporated to dryness. The resulting crystalline material was recrystallized by slow evaporation of 10% acetone in $CH_2Cl_2$ and was shown to be $(CH_3)_4N^+$ $(2,3-(CH_3)_2C_2B_4H_4)_2Co^-$ (32 mg).

<u>Reaction of I with THF/acidified ethyl acetate</u>. A 95.3 mg sample of I (0.378 mmol) was dissolved in 5 ml acidified ethyl acetate (prepared by shaking 25 ml ethyl acetate with 5 ml concentrated aqueous HCl and pipetting off the ethyl acetate layer), to give an orange solution. After about 15 minutes, no color change was observed. 5 ml THF was added to the solution. After another 10 minutes, the solvent was removed on a rotary evaporator, leaving a brown solid which was insoluble in hexane, $CH_2Cl_2$, and acetone and was not further investigated.

<u>Reaction of II with THF/acidified ethyl acetate</u>. 11.6 mg II (31.6 μmol) was dissolved in 5 ml of acidified ethyl acetate

(prepared as above), to give a brown solution. After stirring for 15 minutes in the air, no color change was observed. To this stirring solution was added 5 ml THF. After stirring for an additional 10 minutes, the solvent was removed on a rotary evaporator, and the brown residue was separated by TLC in 1:1 $CH_2Cl_2$/hexane to give orange III (3.1 mg, 82% yield based on starting material consumed) and unreacted II (7.7 mg).

Reaction of V with THF/acidified ethyl acetate. 25.2 mg V (62.2 μmol) was dissolved in 5 ml of acidified ethyl acetate (prepared as above), to give a brown solution. After stirring for 10 minutes, a black precipitate had formed. To this was added 5 ml THF, causing the formation of additional black precipitate. After an additional 10 minutes of reaction, the solvent was removed by rotary evaporation. The solid residue was not appreciably soluble in hexane, $CH_2Cl_2$, or acetone.

## References

(1) Taken in part from the Ph.D. dissertation of Lester Borodinsky, University of Virginia, 1982.

(2) Reviews: (a) Greenwood, N.N.; Ward, I.M. Chem. Soc. Rev. 1974, 3, 231; (b) Wegner, P.A. in "Boron Hydride Chemistry" (Muetterties, E.L., ed.); Academic Press: New York, 1975, Chapter 12; (c) Greenwood, N.N., Pure and Applied Chem. 1977, 49, 791; (d) Grimes, R.N., Acc. Chem. Res. 1978, 11, 420; (e) Grimes, R.N. Coord. Chem. Rev. 1979, 28, 47.

(3) Reviews: (a) Dunks, G.B.; Hawthorne, M.F., ref. 2b, Chapter 11; (b) Grimes, R.N., Organometal. React. Synth. 1977, 6, 63; also see refs. 2d and 2e.

(4) (a) Wade, K. Adv. Inorg. Chem. Radiochem. 1976, 18, 1; (b) Rudolph, R.W. Acc. Chem. Res. 1976, 9, 446; (c) Mingos, D.M.P. Nature (London) Phys. Sci. 1972, 236, 99.

(5) Delaney, M.S.; Knobler, C.B.; Hawthorne, M.F. Inorg. Chem. 1981, 20, 1341.

(6) (a) Maxwell, W.M.; Miller, V.R.; Grimes, R.N. Inorg. Chem. 1976, 15, 1343; (b) Maxwell, W.M.; Miller, V.R.; Grimes, R.N. J. Am. Chem. Soc. 1976, 98, 4818; (c) Hosmane, N.S.; Grimes, R.N. Inorg. Chem. 1980, 19, 3482.

(7) Borodinsky, L.; Sinn, E.; Grimes, R.N., following paper in this issue.

(8) Hosmane, N.S.; Grimes, R.N. Inorg. Chem. 1979, 18, 3294.

(9) (a) Savory, C.G.; Wallbridge, M.G.H. J. Chem. Soc., Dalton Trans. 1973, 179; (b) Leach, J.B.; Toft, M.A.; Himpsl, F.L., Shore, S.G. J. Am. Chem. Soc. 1981, 103, 988.

(10) Venable, T.L.; Grimes, R.N., Inorg. Chem., in press.

(11) Shore, S.G.; Ragaini, J.D.; Smith, R.L.; Cottrell, C.E.; Fehlner, T.P. Inorg. Chem. 1979, 18, 670.

(12) Weiss, R.; Grimes, R.N. Inorg. Chem. 1979, 18, 3291.

(13) Fischer, M.B.; Gaines, D.F. Inorg. Chem. 1979, 18, 3200.

(14) Grimes, R.N.; Beer, D.C.; Sneddon, L.G.; Miller, V.R.; Weiss, R. Inorg. Chem. 1974, 13, 1138.

(15) BH and CR units contribute 2 and 3 valence electrons respectively, to the framework, bridging hydrogen atoms contribute one electron, and cobalt contributes a total of three (of its total of nine valence electrons, six are assigned to "nonbonding" orbitals in the usual fashion;[4] the remaining three are available for skeletal bonding). Of the three Co skeletal electrons, assignment of 2 to the $CoC_2B_4$ cage and 1 to the $CoB_5$ framework produces electron counts of 16 (2n + 2) and 16 (2n + 4), respectively.

(16)(a) Pipal, J.R.; Grimes, R.N. Inorg. Chem. 1977, 16, 3251; (b) Miller, V. Weiss, R.; Grimes, R.N. J. Am. Chem. Soc. 1977, 99, 5646.

(17) Venable, T.L.; Sinn, E.; Grimes, R.N., Inorg. Chem., in press.

(18) Clouse, A.O.; Moody, D.C.; Roseberry, T.; Schaeffer, R. J. Am. Chem. Soc. 1973, 95, 2496.

(19) Eaton, G.R.; Lipscomb, W.N. "NMR Studies of Boron Hydrides and Related Compounds," Benjamin: New York, 1969.

(20) Brennan, J.P.; Grimes, R.N.; Schaeffer, R.; Sneddon, L.G. Inorg. Chem. 1973, 12, 2266.

(21) Pipal, J.R.; Maxwell, W.M.; Grimes, R.N. Inorg. Chem. 1978, 17, 1447.

(22) (a) Lott, J.W.; Gaines, D.F.; Shenhav, H.; Schaeffer, J. J. Am. Chem. Soc. 1973, 95, 3042; (b) Lott, J.W., Gaines, D.F. Inorg. Chem. 1974, 13, 2261.

(23) Zimmerman, G.J.; Hall, L.W.; Sneddon, L.G. Inorg. Chem. 1980, 19, 3642.

(24) Grimes, R.N.; Beer, D.C.; Sneddon, L.G.; Miller, V.R.; Weiss, R. Inorg. Chem. 1974, 13, 1138.

(25) (a) Bonny, A.; Beard, W.R.; Misener, C.M.; Kennedy, F.G.; Grimes, R.N., 180th National Meeting of the American Chemical Society, Las Vegas, Nevada, August 1980, Abstract I-252; (b) Grimes, R.N. Pure and Applied Chem., in press.

(26) Wilczynski, R.; Sneddon, L.G. Inorg. Chem. 1979, 18, 864.

(27) Maynard, R.B.; Grimes, R.N., 182nd National Meeting of the American Chemical Society, New York, New York, August 1981, Abstract I-11.

(28) Nainan, K.C.; Ryschkewitsch, G.E. Inorg. Nucl. Chem. Lett. 1970, 6, 765.

(29) Harvey Analytical Laboratories, Charlottesville, Virginia.

Table I. Boranacobaltacarborane Products

| Compound | Color | $R_f^a$ | m.p., °C |
|---|---|---|---|
| $[2,3-(C_2H_5)_2C_2B_4H_4]-2-Co[B_5H_{10}]$ (I) | orange | 0.78 | b |
| $[2,3-(C_2H_5)_2C_2B_4H_4]-5-Co[B_9H_{12}-1-O(CH_2)_4]$ (II) | brown | 0.45 | 89-91 |
| $[2,3-(C_2H_5)_2C_2B_3H_5]-5-Co[B_9H_{12}-1-O(CH_2)_3]$ (III) | orange | 0.60 | 141-143 |
| $[2,3-(C_2H_5)_2C_2B_3H_5]-6-Co[B_9H_{12}-2-O(CH_2)_4]$ (IV) | burgundy | 0.52 | 125-127 |
| $[1,2-(C_2H_5)_2C_2B_7H_7]-6-Co[B_9H_{12}-2-O(CH_2)_4]$ (V) | black-brown | 0.48 | 150(dec) |
| $[2,3-(C_2H_5)_2C_2B_3H_5]-CoH-[2',3'-(C_2H_5)_2C_2B_4H_4]^c$ (VI) | yellow | 0.82 | b |

a Chromatography on silica gel-60 TLC plates in 1:1 $CH_2Cl_2$/hexanes.    b Oil.    c The C-tetramethyl
analogue of this compound has been reported; see ref. 6b.

Table II. 115.5 MHz $^{11}$B FT NMR Data (CDCl$_3$ Solution)

| Compound | $\delta$, ppm $(J,Hz)$[a] | Rel Area |
|---|---|---|
| I | 34.1(112),[b] 13.1(151),[c] 5.5(139)[d], 2.2(161),[e] −47.7(148)[f] | 2,3,2,1,1 |
| II | 36.6,[g] 20.6(110), 142(128), 7.5(139), 5.3(133), −0.4(105), −3.5(151), −11.5(128), −27.1(139), −39.2(151) | 1,1,1,2,2, 2,1,1,1,1 |
| III | 36.7,[g] 19.2(110), 7.0(128), 3.2,[h] 1.4,[h] −0.7,[h] −2.2(116), −3.2,[h] −12.8(103), −26.4(116), −38.8(140) | 1,1,1,2,1 1,1,1,1,1,1 |
| IV | 10.7(124), 8.3(140), 4.4,[h] 1.7,[h] −3.1(130), −6.5(147), −38.4(154) | 2,2,3,1,2 1,1 |
| V | 78.8(165), 10.7(141), 8.5(126), 7.3,[h] 3.0,[g] −2.1(130), −3.9(124), −9.2(156) −18.8(137), −22.9(151), −24.8(140), −34.9(148) | 1,1,2,1,2 2,2,1,1,1 1,1 |

[a]$BF_3 \cdot O(C_2H_5)_2$ shift is 0; positive shifts downfield. [b]Assigned to B(3,6). [c]Assigned to B(4,5) and B(5') (superimposed). [d]Assigned to B(4',6'). [e]Assigned to B(7'). [f]Assigned to B(1). [g]Singlet in coupled spectrum; assigned to B−O(CH$_2$)$_4$. [h]$J_{BH}$ not measurable owing to peak overlap.

Table III.   360 MHz $^1$H FT NMR Data (CDCl$_3$ Solution) [a]

| Compound | $\delta$, ppm[b] | Rel Area | Assignment |
|----------|------------------|----------|------------|
| I | 2.17 quartet ($J_{H-H}$ = 8Hz) | 4 | CH$_2$ |
|   | 1.15 triplet ($J_{H-H}$ = 8Hz) | 6 | CH$_3$ |
|   | -1.12 broad | c | B-H-B |
|   | -5.19 broad singlet | 2 | B-H-B |
|   | -10.13 broad quartet ($J_{H_b-H_t}$ = 77 Hz) | 2 | Co-H-B |
| II | 4.51 multiplet | 4 | THF |
|    | 2.80 multiplet | 4 | THF |
|    | 2.19 multiplet | 4 | CH$_2$ |
|    | 1.35 triplet ($J_{H-H}$ = 8Hz) | 6 | CH$_3$ |
|    | -2.46 broad singlet | 1 | B-H-B |
|    | -3.99 broad singlet | 1 | B-H-B |
|    | -4.15 broad singlet | 1 | B-H-B |
|    | -15.33 broad singlet | 1 | Co-H-B |
| III | 4.40 multiplet | 4 | THF |
|     | 2.41 multiplet | 4 | THF |
|     | 2.09 unres. singlet | 4 | CH$_2$ |
|     | 1.26 unres. singlet | 6 | CH$_3$ |
|     | -2.29 broad singlet | 1 | B-H-B |
|     | -4.00 broad singlet | 2 | B-H-B |
|     | -4.87 broad singlet | 1 | B-H-B |
|     | -5.60 broad singlet | 1 | B-H-B |
|     | -14.57 broad singlet | 1 | Co-H-B |

| | | | |
|---|---|---|---|
| IV | 4.25 multiplet | 4 | THF |
| | 2.16 multiplet | 4 | THF |
| | 2.08 quartet $(J_{H-H} = 8HZ)$ | 4 | $CH_2$ |
| | 1.03 triplet $(J_{H-H} = 8Hz)$ | 6 | $CH_3$ |
| | -3.78 broad singlet | 2 | B-H-B |
| | -5.58 broad singlet | 2 | B-H-B |
| | -8.70 broad quartet $(J_{H_b-H_t} = 88Hz)$ | 2 | Co-H-B |
| V | 4.31 multiplet | 4 | THF |
| | 3.04 multiplet | 4 | THF |
| | 2.07 multiplet | 4 | $CH_2$ |
| | 1.61 triplet $(J_{H-H} = 8Hz)$ | 3 | $CH_3$ |
| | 0.41 triplet $(J_{H-H} = 8Hz)$ | 3 | $CH_3$ |
| | -5.53 broad singlet | 2 | B-H-B |
| | -12.99 broad singlet | 2 | Co-H-B |

[a] $^{11}B$-coupled.  [b] Shifts referenced to $(CH_3)_4Si$.  [c] Signal overlapped with several $H_t$ quartets.

Table IV.   Infrared Absorptions (cm$^{-1}$, KBr pellets)[a,b]

I   2980 s, 2940 s, 2880 m, 2860 s, 2580 s, 1880 w,
    1585 w, 1470 m, 1455 m, 1420 w, 1390 m, 1380 m,
    1070 sh, 1050 m, 1010 m, 930 m, 910 w, 875 m,
    710 m, 690 sh, 630 w

II   2976 s, 2940 s, 2880 m, 2560 s, 1880 w, 1530 sh,
     1450 s, 1380 m, 1360 m, 1340 sh, 1190 sh, 1150 w,
     1110 w, 1045 s, 1020 sh, 940 s, 915 s, 900 sh,
     875 m, 790 m, 670 m

III   2975 s, 2940 s, 2880 m, 2860 m, 2540 s, 1875 m,
      1560 sh, 1470 sh, 1460 m, 1450 m, 1380 w,
      1370 sh, 1355 w, 1115 sh, 1105 w, 1070 sh,
      1045 m, 930 s, 915 s, 890 w, 780 w, 670 w

IV   2980 s, 2940 s, 2935 s, 2880 m, 2870 m, 2570 s,
     1875 w, 1580 m, 1460 w, 1380 w, 1360 w, 1260 w,
     1050 m, 1015 sh, 1005 m, 960 m, 930 m, 915 m,
     825 w, 765 w, 725 m, 715 m, 690 w, 660 w, 625 w

V   2980 s, 2940 s, 2884 s, 2850 sh, 2570 s, 1880 m,
    1815 m, 1540 sh, 1455 s, 1430 sh, 1380 m, 1360 m,
    1190 sh, 1135 sh, 1115 w, 1065 m, 1050 m, 965 w,
    930 sh, 915 s, 875 m, 770 w, 690 w, 660 w

---

[a]$CCl_4$ solution vs $CCl_4$.

[b]Key:  s = strong, m = medium, w = weak, sh = shoulder

## Table V. High Resolution Mass Measurements

| Compound | Parent ion | Calculated Mass | Observed Mass |
|---|---|---|---|
| I | $^{59}Co^{12}C_6^{11}B_9^{1}H_{24}^{+}$ | 254.2047 | 254.2050 |
| II | $^{59}Co^{16}O^{12}C_{10}^{11}B_{13}^{1}H_{34}^{+}$ | 372.3151 | 372.3157 |
| III | $^{59}Co^{16}O^{12}C_{10}^{11}B_{12}^{1}H_{35}^{+}$ | 362.3136 | 362.3149 |
| IV | $^{59}Co^{16}O^{12}C_{10}^{11}B_{12}^{1}H_{35}^{+}$ | 362.3136 | 362.3149 |
| V | $^{59}Co^{16}O^{12}C_{10}^{11}B_{16}^{1}H_{37}^{+}$ | 408.3666 | 408.3698 |

## Figure Captions

Figure 1. Proposed structure of $[2,3\text{-}(C_2H_5)_2C_2B_4H_4]\text{-}2\text{-}Co[B_5H_{10}]$ (I)

Figure 2. Established structure[7] of $[2,3\text{-}(C_2H_5)_2C_2B_4H_4]\text{-}5\text{-}Co[B_9H_{12}\text{-}1\text{-}0(CH_2)_4]$ (II)

Figure 3. Established structure[7] of $[2,3\text{-}(C_2H_5)_2C_2B_3H_5]\text{-}5\text{-}Co[B_9H_{12}\text{-}1\text{-}0(CH_2)_4]$ (III)

Figure 4. Proposed structure of $[2,3\text{-}(C_2H_5)_2C_2B_3H_5]\text{-}6\text{-}Co[B_9H_{12}\text{-}2\text{-}0(CH_2)_4]$ (IV)

Figure 5. Established structure[7] of $[1,2\text{-}(C_2H_5)_2C_2B_7H_7]\text{-}6\text{-}Co[B_9H_{12}\text{-}2\text{-}0(CH_2)_4]$ (V)

Figure 6. Apparatus for reaction of $Na^+ R_2C_2B_4H_5^-$ ($R = CH_3$ or $C_2H_5$), $Na^+ B_5H_8^-$, and $CoCl_2$. A, 100-ml round-bottom flask; B, 1 x 16.5-cm storage tube fitted with a Teflon stopcock; C, 100-ml round-bottom flask; D, 250-ml 2-neck round-bottom flask; E, 1.5 x 8 cm tube; F, coarse frit.
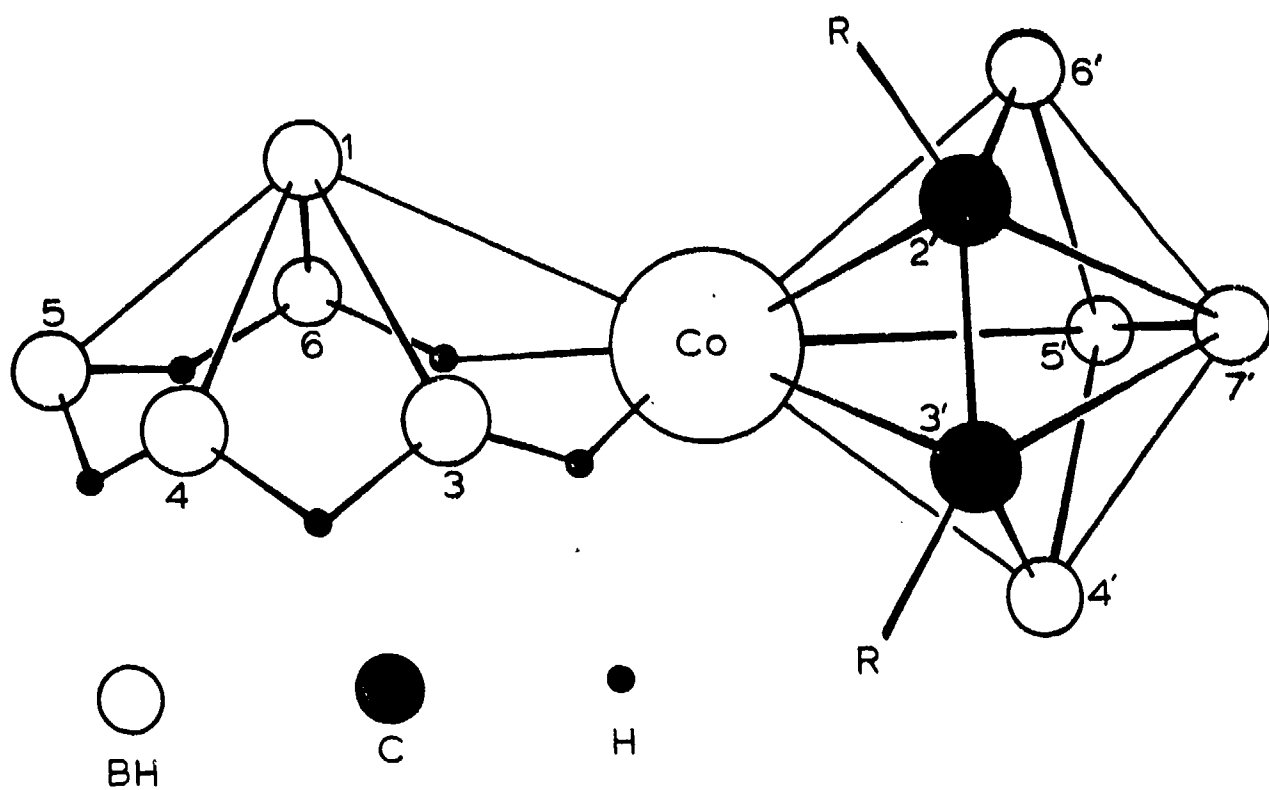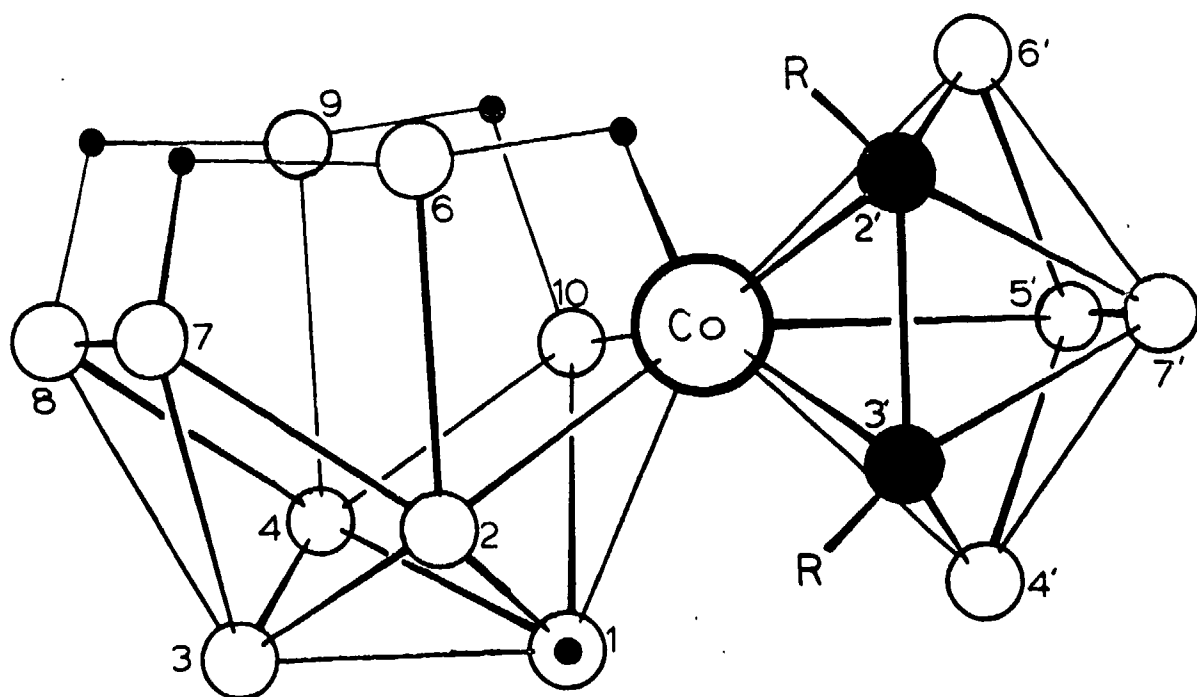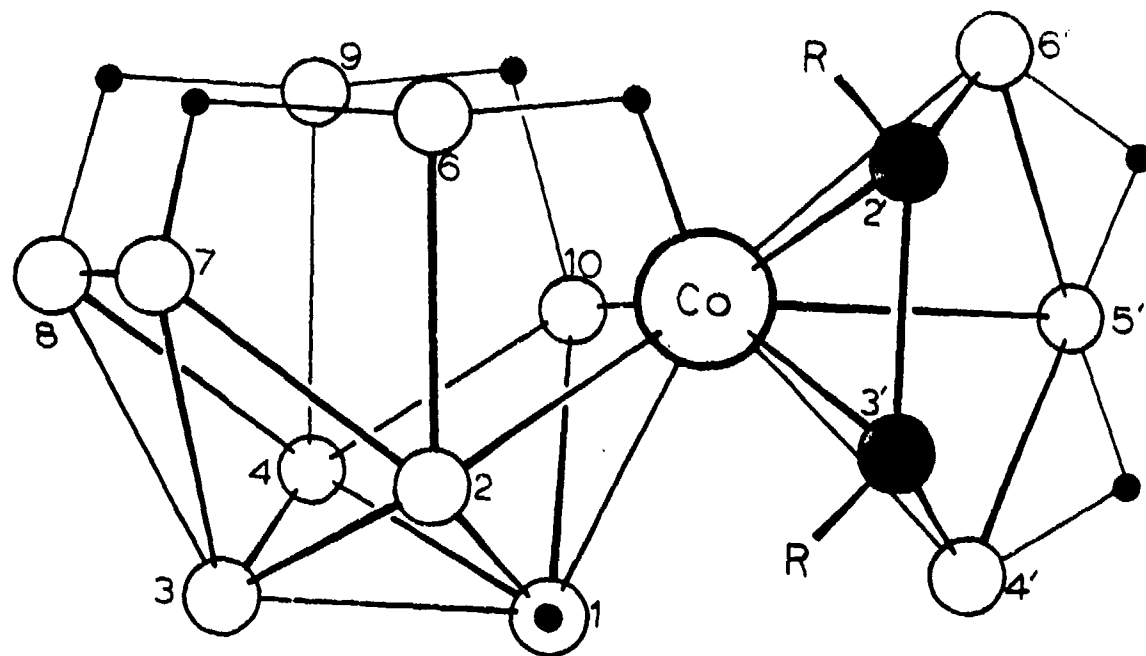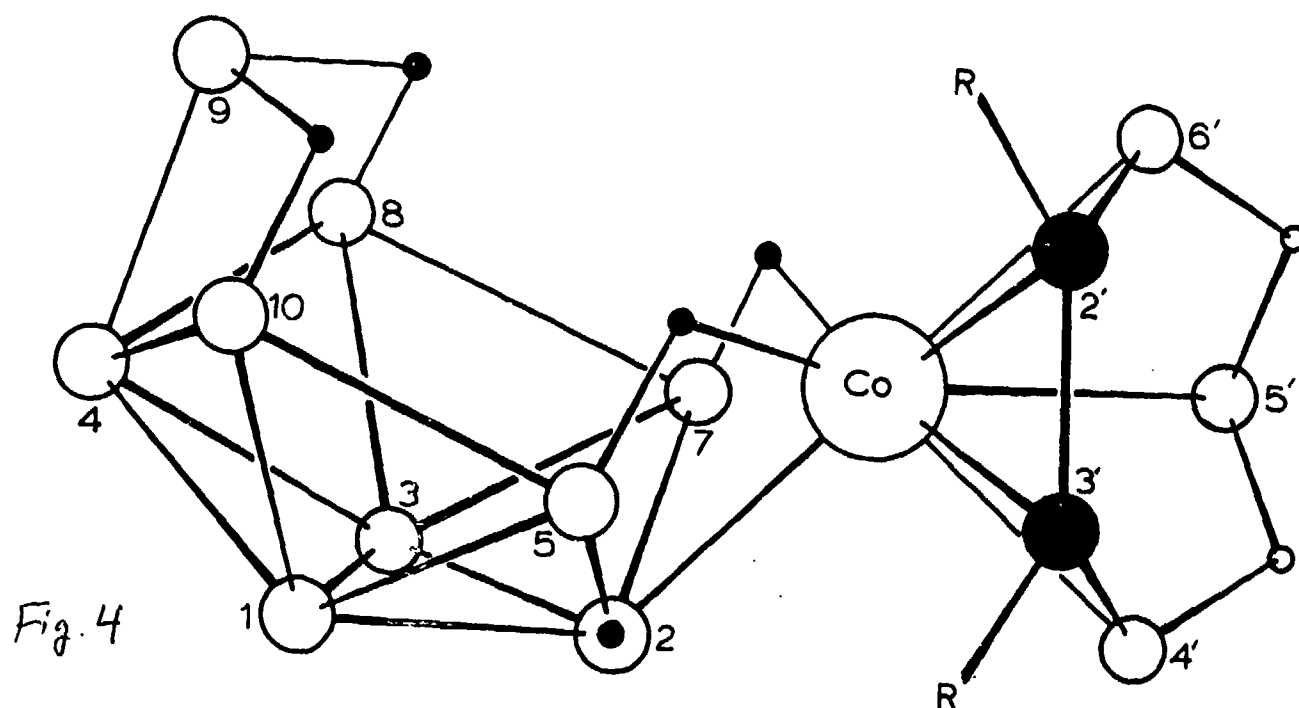
Fig. 1
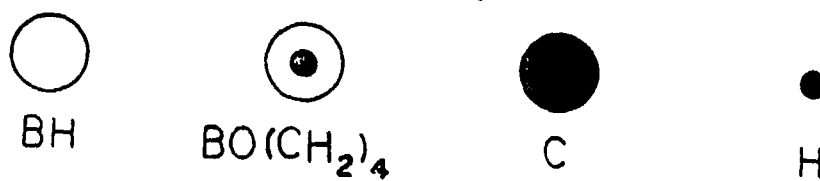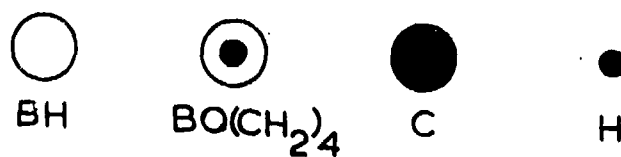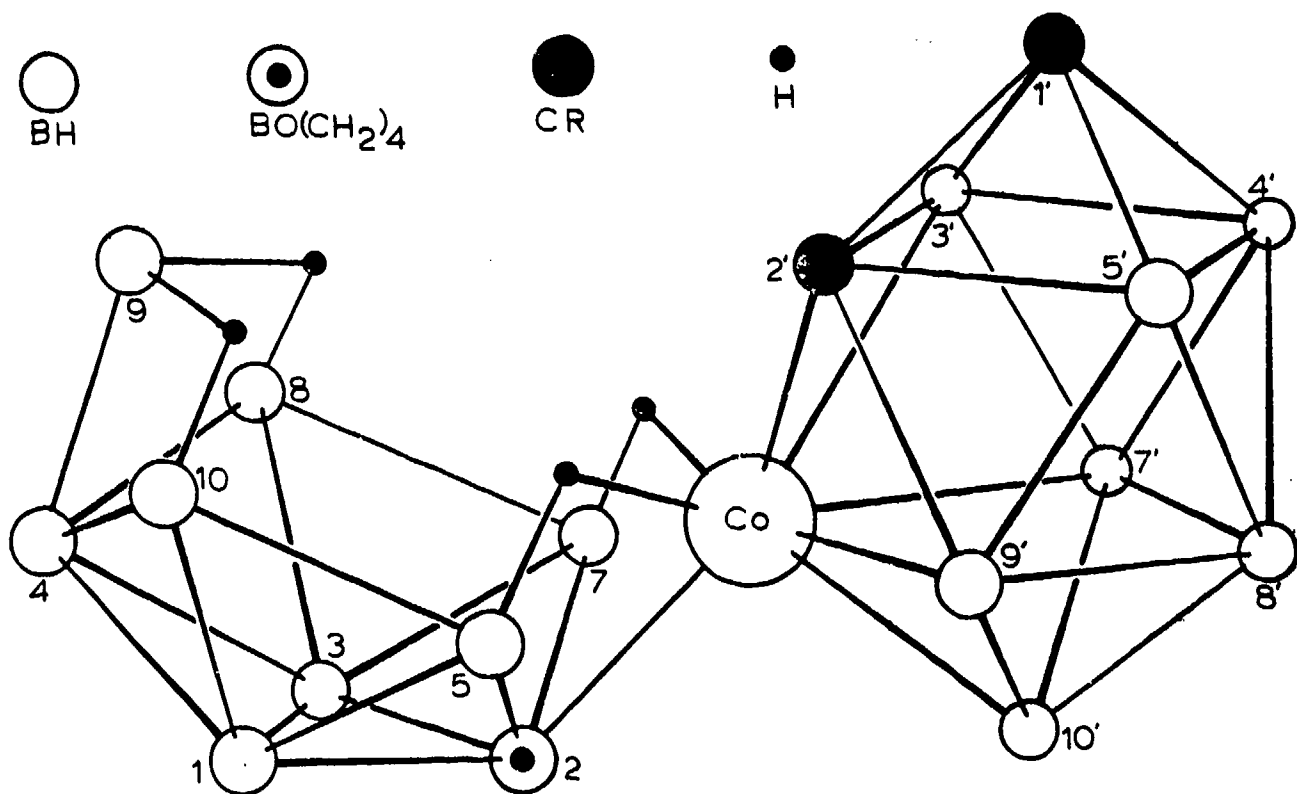
BH    C    H



Fig. 2.

BH    BO(CH₂)₄    C    H

Fig. 3

BH  BO(CH₂)₄  C  H

Fig. 4

BH  BO(CH₂)₄  C  H

Fig. 5

A

B

C

D

E

F
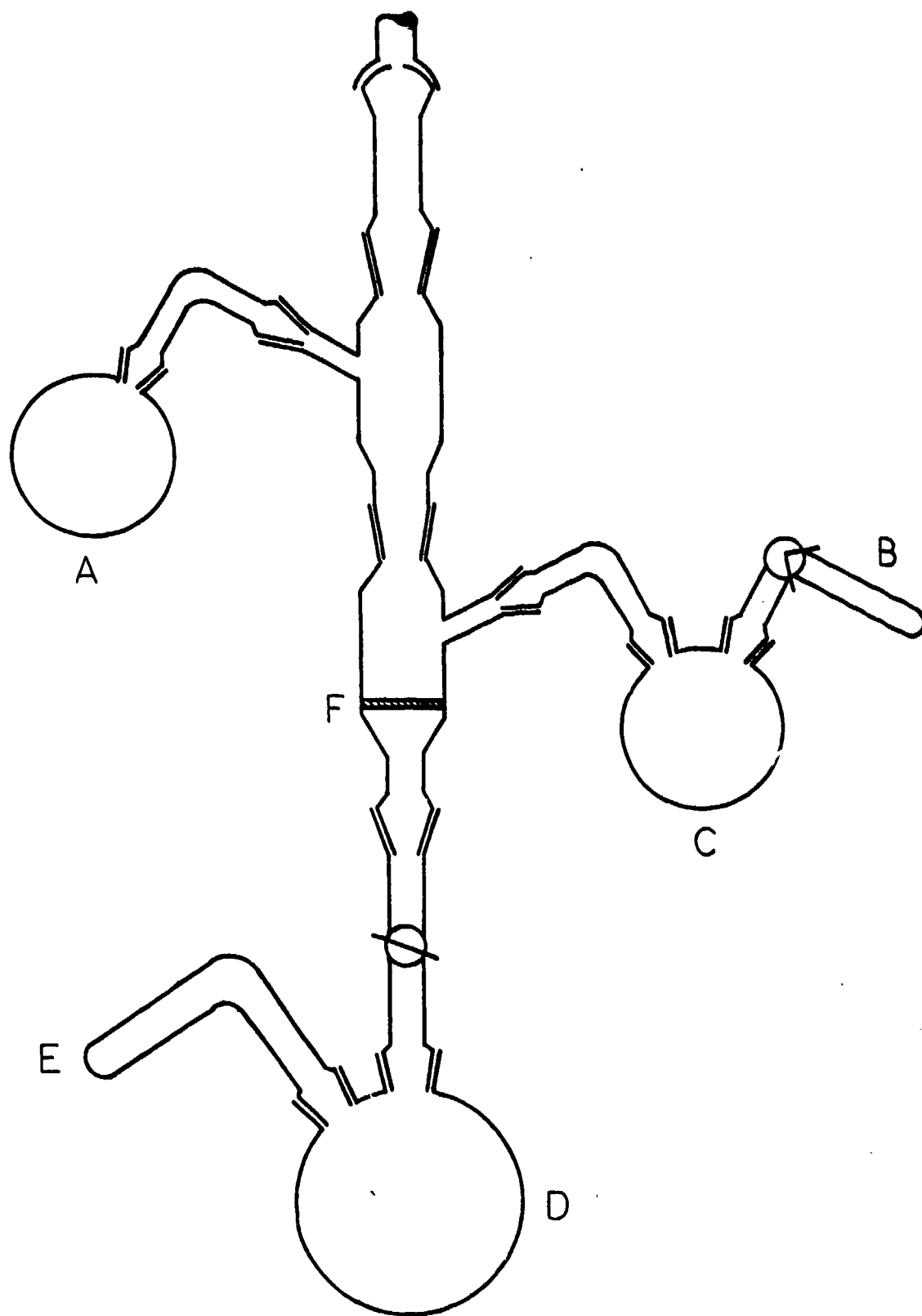
| REPORT DOCUMENTATION PAGE | READ INSTRUCTIONS BEFORE COMPLETING FORM |
|---|---|

| 1. REPORT NUMBER | 2. GOVT ACCESSION NO. | 3. RECIPIENT'S CATALOG NUMBER |
|---|---|---|
| Technical Report No. 39 | AD-A109 384 | |

| 4. TITLE (and Subtitle) | 5. TYPE OF REPORT & PERIOD COVERED |
|---|---|
| Boranametallacarboranes. 1. Synthesis and Characterization of (Borane)Cobalt(Carborane) Sandwich Complexes | Interim |
| | 6. PERFORMING ORG. REPORT NUMBER |

| 7. AUTHOR(s) | 8. CONTRACT OR GRANT NUMBER(s) |
|---|---|
| Lester Borodinsky and Russell N. Grimes | N00014-75-C-0305 |

| 9. PERFORMING ORGANIZATION NAME AND ADDRESS | 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS |
|---|---|
| University of Virginia Department of Chemistry Charlottesville, VA 22901 | NR-053-569 |

| 11. CONTROLLING OFFICE NAME AND ADDRESS | 12. REPORT DATE |
|---|---|
| Chemistry Branch Office of Naval Research Arlington VA 22217 | December 1981 |
| | 13. NUMBER OF PAGES |
| | 37 |

| 14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) | 15. SECURITY CLASS. (of this report) |
|---|---|
| | Unclassified |
| | 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE |

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Boranametallacarborane      Cobaltaborane
Metallaborane      Cobaltacarborane
Metallacarborane      Borane-Metal Complex

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

See pages 1 and 2

TECHNICAL REPORT DISTRIBUTION LIST, 053

No.
Copies

No.
Copies

Dr. B. Foxman
Department of Chemistry
Brandeis University
Waltham, Massachusetts   02154                1

Dr. M. F. Hawthorne
Department of Chemistry
University of California
Los Angeles, California   90024          1

Dr. T. Marks
Department of Chemistry
Northwestern University
Evanston, Illinois   60201                    1

Dr. D. B. Brown
Department of Chemistry
University of Vermont
Burlington, Vermont   05401              1

Dr. J. Zuckerman
Department of Chemistry
University of Oklahoma
Norman, Oklahoma   73019                      1

Dr. D. Venezky
Chemistry Division
Naval Research Laboratory
Code 6130
Washington, D.C.   20375                 1

Professor O. T. Beachley
Department of Chemistry
State University of New York
Buffalo, New York   14214                     1

Dr. J. Adcock
Department of Chemistry
University of Tennessee
Knoxville, Tennessee   37916             1

Professor K. M. Nicholas
Department of Chemistry
Boston College
Chestnut Hill, Massachusetts   02167          1

Dr. A. Cowley
Department of Chemistry
University of Texas
Austin, Texas   78712                    1

Professor R. Neilson
Department of Chemistry
Texas Christian University
Fort Worth, Texas   76129                     1

Dr. W. Hatfield
Department of Chemistry
University of North Carolina
Chapel Hill, North Carolina   27514      1

Professor M. Newcomb
Texas A&M University
Department of Chemistry
College Station, Texas   77843                1

Dr. D. Seyferth
Department of Chemistry
Massachusetts Institute of
  Technology
Cambridge, Massachusetts   02139         1

Professor Richard Eisenberg
Department of Chemistry
University of Rochester
Rochester, New York   14627                   1

Dr. M. H. Chisholm
Department of Chemistry
Indiana University
Bloomington, Indiana   47401             1

## TECHNICAL REPORT DISTRIBUTION LIST, GEN

| | No. Copies | | No. Copies |
|---|---|---|---|
| Office of Naval Research<br>Attn: Code 472<br>800 North Quincy Street<br>Arlington, Virginia 22217 | 2 | U.S. Army Research Office<br>Attn: CRD-AA-IP<br>P.O. Box 1211<br>Research Triangle Park, N.C. 27709 | 1 |
| ONR Western Regional Office<br>Attn: Dr. R. J. Marcus<br>1030 East Green Street<br>Pasadena, California 91106 | 1 | Naval Ocean Systems Center<br>Attn: Mr. Joe McCartney<br>San Diego, California 92152 | 1 |
| ONR Eastern Regional Office<br>Attn: Dr. L. H. Peebles<br>Building 114, Section D<br>666 Summer Street<br>Boston, Massachusetts 02210 | 1 | Naval Weapons Center<br>Attn: Dr. A. B. Amster,<br>Chemistry Division<br>China Lake, California 93555 | 1 |
| Director, Naval Research Laboratory<br>Attn: Code 6100<br>Washington, D.C. 20390 | 1 | Naval Civil Engineering Laboratory<br>Attn: Dr. R. W. Drisko<br>Port Hueneme, California 93401 | 1 |
| The Assistant Secretary<br>of the Navy (RE&S)<br>Department of the Navy<br>Room 4E736, Pentagon<br>Washington, D.C. 20350 | 1 | Department of Physics & Chemistry<br>Naval Postgraduate School<br>Monterey, California 93940 | 1 |
| Commander, Naval Air Systems Command<br>Attn: Code 310C (H. Rosenwasser)<br>Department of the Navy<br>Washington, D.C. 20360 | 1 | Scientific Advisor<br>Commandant of the Marine Corps<br>(Code RD-1)<br>Washington, D.C. 20380 | 1 |
| Defense Technical Information Center<br>Building 5, Cameron Station<br>Alexandria, Virginia 22314 | 12 | Naval Ship Research and Development<br>Center<br>Attn: Dr. G. Bosmajian, Applied<br>Chemistry Division<br>Annapolis, Maryland 21401 | 1 |
| Dr. Fred Saalfeld<br>Chemistry Division, Code 6100<br>Naval Research Laboratory<br>Washington, D.C. 20375 | 1 | Naval Ocean Systems Center<br>Attn: Dr. S. Yamamoto, Marine<br>Sciences Division<br>San Diego, California 91232 | 1 |
| | | Mr. John Boyle<br>Materials Branch<br>Naval Ship Engineering Center<br>Philadelphia, Pennsylvania 19112 | 1 |

Mr. A. M. Anzalone
Administrative Librarian
PLASTEC/ARRADCOM
Bldg 3401
Dover, N.J. 07801