

oven temperature, m/e value, relative abundance in parentheses, and probable assignment: $\text{Cp}_2\text{Mo}(\text{PhN}=\text{NPh})$ 130°, 408 (10) M^+ , 226 (40) Cp_2Mo , 184 (43) PhNHNHPh , 182 (14) $\text{PhN}=\text{NPh}$, 97 (42) $\text{C}_5\text{H}_5\text{N}_2\text{H}_4$, 93 (45) $\text{C}_5\text{H}_5\text{N}_2$, 92 (38) PhNH_2 , 77 (100) Ph , 71 (62) C_5H_{11} , 69 (61) C_5H_9 , 57 (90) C_4H_9 ; $\text{Cp}_2\text{Mo}[(\text{CO}_2\text{CH}_3)_2\text{NNCO}_2\text{C}_2\text{H}_5]$ 210°, 372 (30) M^+ , 328 (1) $\text{M}^+ - \text{CO}_2$, 268 (2) Cp_2MoNCO , 257 (2) $\text{Cp}_2\text{MoOCH}_3$, 240 (4) Cp_2MoN , 226 (100) Cp_2Mo , 116 (22) $\text{C}_3\text{H}_4\text{N}_2\text{O}_3$, 103 (51) $\text{CH}_3\text{NH}-\text{NCO}_2\text{CH}_3$, 102 (45) $\text{CH}_3\text{N}_2-\text{CO}_2\text{CH}_3$, 75 (50) $\text{NH}_2\text{CO}_2\text{CH}_3$, 65 (10) C_5H_5 , 59 (72) CO_2CH_3 ;

$\text{Cp}_2\text{Mo}[(\text{CO}_2\text{C}_2\text{H}_5)_2\text{NNCO}_2\text{C}_2\text{H}_5]$ 190°, 400 (23) M^+ , 356 (1) $\text{M}^+ - \text{CO}_2$, 328 (1) $\text{Cp}_2\text{Mo}(\text{CH}_3)(\text{CO}_2\text{CH}_3)$, 268–269 (1) $\text{Cp}_2\text{Mo}(\text{NCO}$ and $\text{NCOH})$, 256–257 (1) $\text{Cp}_2\text{MoOCH}_2$, 240 (3) Cp_2MoN or Cp_2MoCH_2 , 226 (65) Cp_2Mo , 104 (23) $\text{NH}_2\text{NHCO}_2\text{C}_2\text{H}_5$, 92 (68) C_7H_5 , 91 (100) C_7H_7 , 78 (68) C_6H_6 , 65 (15) C_5H_5 .

Acknowledgment. The authors are grateful for the experimental assistance of Messrs. H. Minamida, T. Koyama, and J. Izawa.

New 13-Atom Bimetallocarboranes Prepared by Polyhedral Subrogation

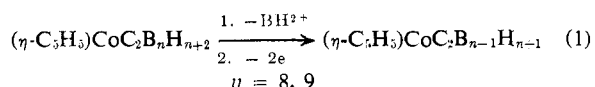
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Contribution No. 3252 from the Department of Chemistry, University of California, Los Angeles, California 90024. Received December 17, 1973

Abstract: The reaction of 13-vertex cobaltacarboranes, $(\eta\text{-C}_5\text{H}_5)\text{CoC}_2\text{B}_{10}\text{H}_{12}$, with ethanolic potassium hydroxide in the presence of cyclopentadiene and an appropriate metal salt produces new 13-vertex bimetallocarboranes. These bimetallic products, which may contain identical or dissimilar metals, have one less boron atom than does the original monometallic carborane. The preparation, characterization, and structures of these complexes are discussed.

We have recently reported^{1,2} an extension of the polyhedral contraction reaction^{3,4} in which $4\text{-}(\eta\text{-C}_5\text{H}_5)\text{-4-Co-1,8-C}_2\text{B}_{10}\text{H}_{12}$ ^{5,6} was degraded in the presence of ethanolic potassium hydroxide to form the $[3\text{-}(\eta\text{-C}_5\text{H}_5)\text{-3-Co-4-CB}_9\text{H}_9]^-$ anion.⁷ In an effort to learn more about the mechanism of this unusual reaction, we began a study of some of the side products that were isolated. Among these side products were metallocarboranes of unexpectedly high molecular weight suggesting that the metallocarborane frameworks contained more than one transition metal atom. It thus appeared that the polyhedral contraction reaction, or a modification thereof, might be useful in the preparation of polymetallocarboranes.

The polyhedral contraction process converts certain cobaltacarboranes to their next smaller homolog by the removal of a formal BH^{2+} unit from the polyhedral framework by base degradation followed by a two-electron oxidation (eq 1). If the degradation reaction



(1) D. F. Dustin and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 1329 (1972).

(2) D. F. Dustin and M. F. Hawthorne, *Inorg. Chem.*, **12**, 1380 (1973).

(3) C. J. Jones, J. N. Francis, and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 900 (1972).

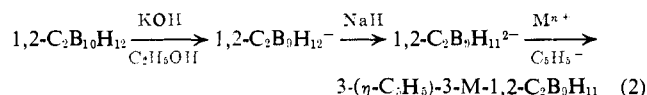
(4) C. J. Jones, J. N. Francis, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **94**, 8391 (1972).

(5) D. F. Dustin, W. J. Evans, C. J. Jones, R. J. Wiersema, H. Gong, S. Chan, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **96**, 3085 (1974).

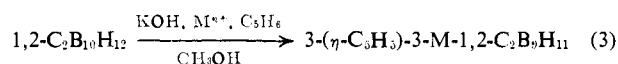
(6) Numbers accompanying formulas refer to the positions of the heteroatoms within the closo metallocarborane framework and to the positions of the exopolyhedral substituents, if any. Lowest numbers consistent with the molecular geometry are given to carbon in accordance with the inverse periodic order adhered to by the IUPAC Inorganic Nomenclature Committee; see R. M. Adams, *Pure Appl. Chem.*, **30**, 683 (1972). For example, in $4\text{-}(\eta\text{-C}_5\text{H}_5)\text{-4-Co-1,8-C}_2\text{B}_{10}\text{H}_{12}$, cobalt occupies position 4 while the carbon atoms are located at vertices 1 and 8. The cyclopentadienyl ring is π -bonded to the cobalt.

(7) K. P. Callahan, C. E. Strouse, A. L. Sims, and M. F. Hawthorne, *Inorg. Chem.*, in press.

takes place in the presence of excess metal ion, that metal ion may be inserted into the hole left by the departing boron atom in the polyhedral framework. We have termed this replacement of a boron atom by a metal atom the "polyhedral subrogation" reaction.⁸ The reaction itself is not a new one. In fact, the first metallocarboranes were prepared by the removal of a BH^{2+} unit from $1,2\text{-C}_2\text{B}_{10}\text{H}_{12}$ followed by the insertion of an appropriate metal atom.⁹ What was once a three-step procedure (eq 2) has recently¹⁰ been con-



densed into a one-step process (eq 3). A procedure



similar to that shown in eq 3 was used independently by two groups to prepare the icosahedral complex $3,6\text{-}(\eta\text{-C}_5\text{H}_5)_2\text{-3,6-CO}_2\text{-1,2-C}_2\text{B}_8\text{H}_{10}$ ^{10,11} and the heterobimetallocarborane $4,5\text{-}(\eta\text{-C}_5\text{H}_5)_2\text{-4-Co-5-Fe-1,8-C}_2\text{B}_9\text{H}_{11}$.¹² We now wish to report the syntheses of additional 13-vertex bimetallocarboranes and one trimetallic species each of which was prepared by the polyhedral subrogation reaction.

Results

The Preparation and Characterization of Homobimetallocarboranes Containing Cobalt. The polyhedral

(8) We have chosen the word "subrogation" rather than "substitution" so as not to confuse this reaction with those involving exopolyhedral substitution.

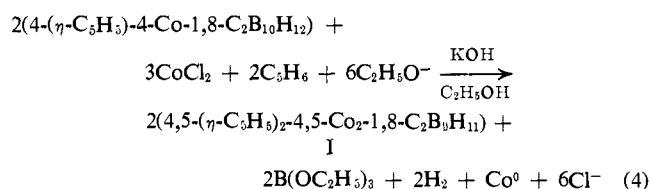
(9) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, and P. A. Wegner, *J. Amer. Chem. Soc.*, **90**, 879 (1968).

(10) J. Plešek, B. Štíbr, and S. Heřmánek, *Syn. Inorg. Metal-Organ. Chem.*, **3**, 291 (1973).

(11) C. J. Jones and M. F. Hawthorne, *Inorg. Chem.*, **12**, 608 (1973).

(12) D. F. Dustin, W. J. Evans, and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 805 (1973).

subrogation of 4-(η -C₅H₅)-4-Co-1,8-C₂B₁₀H₁₂ took place according to the following reaction scheme (eq 4).



Compound I, a dark green, diamagnetic complex, was isolated in 58% yield. The C,C'-dimethyl derivative of I, 4,5-(η -C₅H₅)₂-1,8-(CH₃)₂-4,5-Co₂-1,8-C₂B₉H₉, compound II, was prepared in an identical manner from 4-(η -C₅H₅)-1,8-(CH₃)₂-4-Co-1,8-C₂B₁₀H₁₀ in 43% yield.

The 60-MHz ¹H nmr spectrum of I (Table I) con-

Table I. 60-MHz ¹H Nmr Spectra

Compound	Resonance, τ^a (rel area)	Assignment
I ^b	4.67 (5)	Cyclopentadienyl protons
	4.89 (5)	Cyclopentadienyl protons
II ^b	4.67 (5)	Cyclopentadienyl protons
	4.91 (5)	Cyclopentadienyl protons
	7.53 (3)	Methyl protons
	7.92 (3)	Methyl protons
III ^b	4.88	Cyclopentadienyl protons
IV ^b	4.88 (10)	Cyclopentadienyl protons
	8.04 (3)	Methyl protons
	8.13 (3)	Methyl protons
V ^c	5.02 (10)	Cyclopentadienyl protons
VI ^{c,d}	6.90 (12)	Tetramethylammonium protons
	5.35 (5)	Cyclopentadienyl protons
VII ^{c,d}	5.99 (5)	Cyclopentadienyl protons
	5.33 (5)	Cyclopentadienyl protons
	6.01 (5)	Cyclopentadienyl protons
	7.79 (3)	Methyl protons
	8.32 (3)	Methyl protons

^a All resonances were singlets. Chemical shifts are relative to tetramethylsilane. ^b Determined in pyridine-*d*₅. ^c Determined in acetonitrile-*d*₃. ^d Reduced to an Fe(II) species.

sisted of two sharp singlets of equal area, and these were assigned to two nonequivalent cyclopentadienyl rings. Resonances of the carborane C-H units were not observed due to the limited solubility of the complex, but the ¹H nmr spectrum of II showed, in addition to two singlets of area 5, two singlets of area 3. These were attributed to the two nonequivalent carborane methyl groups. The 80.5-MHz ¹¹B nmr spectra of I and II are shown in Table II. The observation of five area 1 doublets, in addition to higher area signals due to coincidental overlap, establish the absence of molecular symmetry in these compounds. The elemental analyses (Table III) were consistent with the expected formulations of (C₅H₅)₂Co₂C₂B₉H₁₁ and (C₅H₅)₂Co₂C₂B₉H₉(CH₃)₂. The electronic and infrared spectra are given in Table IV and Table V, respectively.

The structure proposed for compound I is shown in Figure 1. The gross geometry is identical with that established for a 13-vertex metallocarborane,¹³ and the structure differs from the starting material, 4-(η -C₅H₅)-4-Co-1,8-C₂B₁₀H₁₂, in that the high coordinate boron atom initially located at vertex 5 has been replaced by a cobalt atom.

Compound I has also been isolated as a side product

(13) M. R. Churchill and B. G. DeBoer, *J. Chem. Soc., Chem. Commun.*, 1326 (1972).

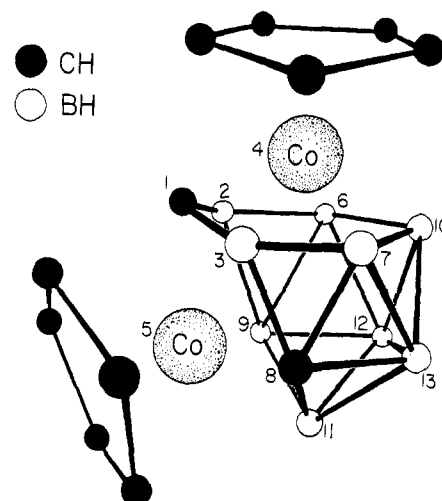


Figure 1. The proposed structure of I, 4,5-(η -C₅H₅)₂-4,5-Co₂-1,8-C₂B₉H₁₁.

Table II. 80.5-MHz ¹¹B Nmr Spectra

Compound	Relative intensities	Chemical shifts, δ^a (J_{B-H} in Hz)
I ^b	1:1:2:1:1:2:1	-17.2 (125), -17.0 (150), -13.1 (144), -7.4 (134), -2.6 (150), +1.6 (138), +9.2 (154)
II ^b	3:1:1:1:1:1:1	-15.0 (131), -12.7 (138), -11.5 (128), -7.2 (144), -5.8 (147), +0.2 (138), +5.3 (150)
III ^b	3:3:2:1	-9.7 (160), -6.4 (144), -2.3 (150), +6.3 (154)
IV ^b	3:5:1	-13.5 (154), -6.4 (134), +2.3 (158)
V ^c	4:4:1:1:2:1:2:1:1:1	-17.9 (134), -15.8 (141), -8.8 (134), -7.9 (153), -3.6 (140), -2.0 (144), +2.0 (153), +4.0 (150), +7.9 (150), +10.0 (144)
VI ^{c,d}	1:1:2:1:1:1:1:1	-11.8 (128), -6.7 (128), -3.5 (118), -2.5 (131), +4.5 (122), +4.8 (125), +11.3 (138), +14.2 (144)
VII ^{c,d}	2:1:3:1:2	-10.8 (134), -9.2 (138), -3.3 (132), -0.9 (140), +9.1 (128)

^a Relative to BF₃·O(C₂H₅)₂. ^b Determined in pyridine-*d*₅. ^c Determined in acetonitrile-*d*₃. ^d Reduced to an Fe(II) species.

Table III. Elemental Analyses

Compound		% C	% H	% B	% Co	% Fe	% N
I	Calcd	37.86	5.57	25.58	30.99		
	Found	37.99	5.78	25.63	30.83		
II	Calcd	41.14	6.17	23.83	28.86		
	Found	41.12	6.37	23.97	28.79		
III	Calcd	37.86	5.57	25.58	30.99		
	Found	38.06	5.84	25.34	30.37		
IV	Calcd	41.14	6.17	23.83	28.86		
	Found	41.05	6.45	22.99	28.45		
V	Calcd	33.45	6.87	30.13	27.38		2.17
	Found	33.03	6.82	29.54	26.82		2.31
VI	Calcd	38.17	5.61	25.79	15.62	14.80	
	Found	38.19	5.91	25.02	15.20	14.53	
VII	Calcd	41.45	6.22	24.01	14.54	13.78	
	Found	41.21	6.23	24.34	14.73	13.81	

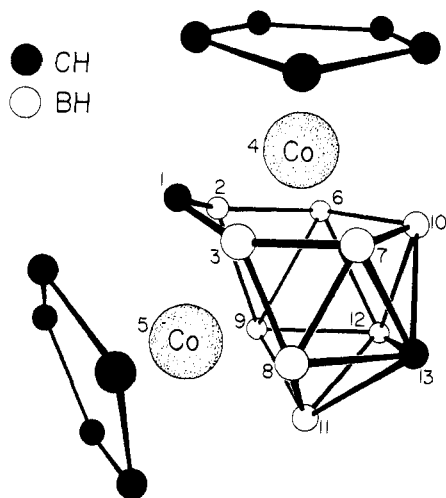


Figure 2. The proposed structure of III, 4,5-(η -C₅H₅)₂-4,5-Co₂-1,13-C₂B₉H₁₁.

Table IV. Melting Points, Mass Spectral Data, and Electronic Spectra

Compound	Mp, ^a °C	<i>m/e</i> cutoff	λ_{\max} , m μ (log ϵ) ^b
I	295–296	382	262 sh (3.9), 305 (3.9), 398 (3.4), 610 (2.7)
II	234–235	410	266 (3.9), 314 (3.9), 408 (3.3), 622 (2.7)
III	277–278	382	262 sh (3.8), 300 (3.9), 399 (3.4), 474 sh (2.9), 614 (2.8)
IV	270–272	410	252 sh (3.4), 324 (3.4), 390 (3.4), 478 sh (2.9), 617 (2.8)
V	>300		264 (4.2), 306 (4.2), 340 (4.1), 442 (3.8), 584 sh (3.3)
VI	>300	379	270 (3.9), 300 (3.9), 470 (3.2), 692 (2.7)
VII	>300	407	266 (3.9), 302 (3.9), 470 (3.2), 692 (2.8)

^a Sealed capillary. ^b In Spectroquality acetonitrile.

Table V. Infrared Spectra

Compound	Frequency (cm ⁻¹ , Nujol mull)
I	3080 (m), 2495 (s), 1425 (m), 1420 (m), 1265 (w), 1195 (w), 1145 (w), 1115 (m), 1080 (m), 1060 (w), 1040 (w), 1015 (m), 1005 (m), 993 (m), 978 (m), 933 (w), 882 (w), 838 (s), 820 (s), 804 (w), 772 (w)
II	3070 (m), 2490 (s), 1410 (m), 1170 (w), 1120 (w), 1070 (w), 1020 (m), 987 (m), 942 (w), 890 (w), 873 (w), 841 (s), 824 (s), 797 (w), 769 (w)
III	3085 (m), 2485 (s), 1410 (m), 1185 (m), 1115 (m), 1060 (w), 1045 (m), 1030 (w), 1020 (m), 1010 (m), 970 (s), 942 (w), 900 (m), 843 (s), 816 (s), 792 (w), 775 (w), 749 (w)
IV	3090 (m), 2480 (s), 1410 (m), 1190 (w), 1115 (w), 1080 (w), 1020 (m), 986 (m), 958 (w), 929 (w), 904 (w), 889 (w), 862 (w), 841 (m), 818 (s), 788 (w)
V	3090 (m), 2490 (s), 1475 (s), 1405 (m), 1195 (w), 1150 (w), 1110 (w), 1080 (w), 1065 (w), 1020 (w), 1005 (m), 980 (m), 949 (m), 880 (w), 853 (w), 838 (m), 822 (s), 778 (w)
VI	3055 (m), 2495 (s), 1420 (m), 1160 (w), 1125 (w), 1095 (w), 1075 (w), 1065 (w), 1035 (w), 1030 (m), 993 (m), 972 (m), 933 (w), 879 (w), 835 (s), 826 (s), 802 (w), 742 (w)
VII	3085 (m), 2500 (s), 1405 (w), 1160 (w), 1120 (w), 1070 (w), 1025 (m), 1010 (m), 993 (w), 940 (w), 886 (w), 868 (w), 844 (m), 828 (s), 772 (w), 741 (w)

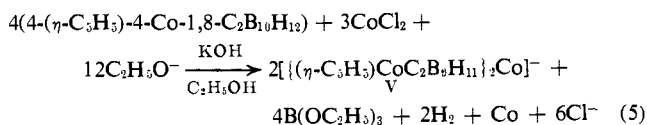
of the polyhedral expansion of 3-(η -C₅H₅)-3-Co-1,2-C₂B₉H₁₁.¹⁴ The principal product of this expansion was the isomeric complex, 4,5-(η -C₅H₅)₂-4,5-Co₂-1,3-C₂B₉H₁₁, and it has recently been shown¹⁵ that this isomer was converted to compound I *via* a thermal rearrangement.

Compounds I and II were also shown to undergo thermal rearrangements. At 150° in refluxing cyclooctane, I was converted to III in 80% yield in 15 hr, and, under identical conditions, II was converted to IV in 73% yield. The elemental analyses (Table III) and mass spectral cutoffs (Table IV) of III and IV indicated that they were indeed isomers of I and II, respectively. The ¹H nmr spectrum of III (Table I) consisted of only one sharp singlet and this was attributed to two equivalent cyclopentadienyl rings. The ¹H nmr spectrum of IV exhibited one sharp singlet of area 10 and two sharp singlets each of area 3. These resonances were assigned to two equivalent cyclopentadienyl rings and to two nonequivalent methyl groups. The ¹¹B nmr spectra (Table II) of III and IV were composed of overlapping doublets but indicated that both contained a plane of symmetry. The infrared spectra are presented in Table V.

The structure proposed for III is shown in Figure 2. The complex has the same geometry as compound I and is apparently formed by the migration of a carbon atom from vertex 8 to vertex 13. In light of our studies of thermal rearrangements of cobaltacarboranes,⁵ this was a predictable rearrangement since the carbon atom moved to a location that was further removed from both a cobalt atom and the other carbon atom. A kinetic study of this rearrangement was undertaken and the results appear in Table VI. Whereas the inclusion of a transition metal into a carborane substantially reduces the activation energy for rearrangement,⁵ the addition of a second metal atom to a metallocarborane seems to have a small and opposite effect.

The structure proposed for III is further confirmed by the fact that it was also prepared from 4-(η -C₅H₅)-4-Co-1,13-C₂B₁₀H₁₂ in exactly the same manner that I was prepared from 4-(η -C₅H₅)-4-Co-1,8-C₂B₁₀H₁₂. Once again, the boron atom initially located at vertex 5 was removed from the polyhedral environment and replaced by a cobalt atom.

One additional reaction was performed in an attempt to insert a second cobalt atom into a cobaltacarborane cage in place of a boron atom. An ethanol solution of 4-(η -C₅H₅)-4-Co-1,8-C₂B₁₀H₁₂ was treated with KOH and CoCl₂ but in the absence of cyclopentadiene. It was hoped that the reaction would produce a trimetallic species analogous to the [(η -C₅H₅)-CoC₂B₉H₁₁]₂Co]⁻ anion prepared in a similar manner from 3-(η -C₅H₅)-3-Co-1,2-C₂B₉H₁₁.¹¹ Compound V was prepared according to the following equation and isolated as the tetramethylammonium salt.

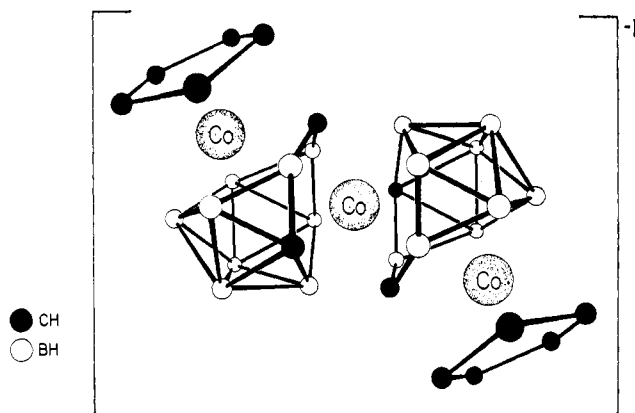


(14) W. J. Evans and M. F. Hawthorne, *J. Amer. Chem. Soc.*, submitted for publication.

(15) W. J. Evans, Ph.D. Dissertation, University of California, Los Angeles, Calif., 1973.

Table VI. Kinetic Data for the Rearrangements of 13-Vertex Mono- and Bimetallic Cobaltacarboranes

Reaction	Temp, °C	10^7k , sec ⁻¹	Activation parameters
4-(η -C ₅ H ₅)-4-Co-1,7-C ₂ B ₁₀ H ₁₂ \longrightarrow 4-(η -C ₅ H ₅)-4-Co-1,8-C ₂ B ₁₀ H ₁₂ ^a	35	2.30 \pm 0.07	$\Delta H^\ddagger = 30$ kcal/mol
	46	14.6 \pm 1	$\Delta S^\ddagger = 8$ eu
	58	73.0 \pm 5	
4-(η -C ₅ H ₅)-4-Co-1,8-C ₂ B ₁₀ H ₁₂ \longrightarrow 4-(η -C ₅ H ₅)-4-Co-1,13-C ₂ B ₁₀ H ₁₂ ^a	66	1.87 \pm 0.01	$\Delta H^\ddagger = 34$ kcal/mol
	81	16.0 \pm 0.05	$\Delta S^\ddagger = 14$ eu
	97	160 \pm 5	
	130	119 \pm 2	$\Delta H^\ddagger = 39$ kcal/mol
4,5-(η -C ₅ H ₅) ₂ -4,5-CO ₂ -1,8-C ₂ B ₉ H ₁₁ \longrightarrow 4,5-(η -C ₅ H ₅) ₂ -4,5-CO ₂ -1,13-C ₂ B ₉ H ₁₁	138	295 \pm 11	$\Delta S^\ddagger = 16$ eu
	149	1090 \pm 50	

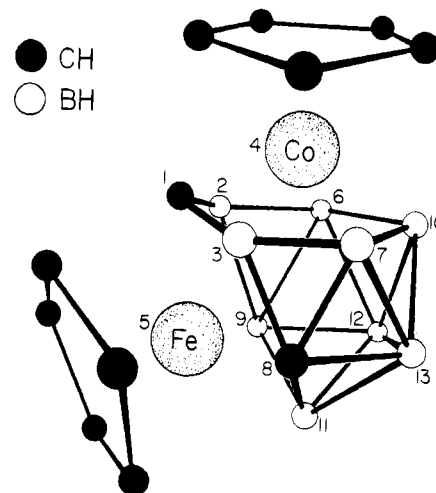
^a See ref 5.Figure 3. The proposed structure of the trans isomer of V, [(η -C₅H₅)CoC₂B₉H₁₁]₂Co⁻¹.

The 60-MHz ¹H nmr spectrum of V (Table I) exhibited two sharp singlets of area ratio 10:12. These were assigned to two equivalent cyclopentadienyl rings and to the tetramethylammonium ion protons, respectively. The electronic and infrared spectra are given in Tables IV and V.

The ¹¹B nmr spectrum of V (Table II) was qualitatively similar to the spectra of I and II but indicated 18 rather than 9 boron atoms. Repeated recrystallization of the product changed the relative size of the peak areas only slightly. The elemental analysis of V (Table III) has confirmed the formulation to be [(CH₃)₄N][(η -C₅H₅)CoC₂B₉H₁₁]₂Co, and the possibility of having a mixture of structural isomers was discounted since the reaction conditions were not severe enough to induce a thermal rearrangement. We have therefore ascribed this anomaly to the presence of a pair of diastereomers which would be expected to give similar but not identical ¹¹B nmr spectra.

The starting material in the reaction, 4-(η -C₅H₅)-4-Co-1,8-C₂B₁₀H₁₂, actually exists as a mixture of the 1,8 and 1,9 enantiomers. The removal of the boron atoms at vertex 5 from this mixture generated two enantiomeric [(η -C₅H₅)-CoC₂B₉H₁₁]₂⁻²⁻ species which apparently formed a bis complex with a central cobalt atom in either a cis or a trans fashion. The trans isomer is shown in Figure 3. The cis isomer is obtained by placing the high coordinate carbon atom in one of the carborane groups in an equivalent position on the opposite side of the open, six-membered ring adjacent to the central cobalt atom. Attempts to separate the two isomers have thus far been unsuccessful.

The Preparation and Characterization of Heterobimetalliccarboranes Containing Iron and Cobalt. The

Figure 4. The proposed structure of VI, 4,5-(η -C₅H₅)₂-4-Co-5-Fe-1,8-C₂B₉H₁₁.

substitution of ferrous chloride for cobaltous chloride in eq 4 resulted in the formation of VI, a brownish purple compound formulated as 4,5-(η -C₅H₅)₂-4-Co-5-Fe-1,8-C₂B₉H₁₁.¹² Compound VII, the C,C'-dimethyl derivative, was prepared in a similar manner from 4-(η -C₅H₅)-1,8-(CH₃)₂-4-Co-1,8-C₂B₁₀H₁₀. Both VI and VII were paramagnetic having effective magnetic moments of 1.88 and 1.87 BM, respectively. Each was reduced to a green diamagnetic, monoanionic species, presumably containing a formal iron(II).

The ¹H nmr spectra (Table I) of the reduced complexes each exhibited two sharp singlets of area 5 attributed to nonequivalent cyclopentadienyl rings. In addition, the spectrum of VII showed two resonances, each of area 3, assigned to two nonequivalent methyl groups. Each 80.5-MHz ¹¹B nmr spectrum (Table II) was complicated by overlapping signals, but which indicated all boron atoms were unique. The elemental analyses (Table III) and mass spectral cutoffs (Table IV) were consistent with the formulations of (C₅H₅)₂CoFeC₂B₉H₁₁ and (C₅H₅)₂CoFeC₂B₉H₉(CH₃)₂ for VI and VII, respectively. The electronic and infrared spectra are given in Tables IV and V.

The structure proposed for VI is shown in Figure 4 and is similar to that proposed for I. It is consistent with the nmr data in that the molecule is totally asymmetric. An attempt was made to thermally rearrange VI to the corresponding 1,13 isomer. Heating VI to 150° for 15 hr in cyclooctane resulted in complete decomposition, and no rearranged product was detected. The inability of VI to undergo a thermal re-

arrangement gives further credence to the earlier proposition¹⁶ that the most stable closo bimetallo-carboranes are those having $2n + 26$ electrons (n = number of polyhedral vertices) participating in cage bonding. VI, having only 51 or $2n + 25$ electrons, would therefore probably not be expected to undergo the usual reactions of closo metallocarboranes such as rearrangement, expansion, or contraction.

Electrochemical Studies of Bimetallocarboranes. The potentials for oxidation and reduction for the known 13-vertex bimetallocarboranes are listed in Table VII.

Table VII. Electrochemical Data

Compound	$E_{p/2}$ (V) vs. sce ^a	
	Oxidation wave	Reduction wave
4,5-(η -C ₅ H ₅) ₂ -4,5-Co ₂ -1,3-C ₂ B ₉ H ₁₁ ^b	+0.77	-0.85
I	+0.97	-0.92
II	+0.92	-0.91
III	+0.83	-1.25
IV	+0.87	-1.25
V	+0.56	-0.84
VI	+0.90	-0.42
VII	+0.92	-0.47

^a Cyclic voltammetry in acetonitrile, with 0.1 *F* tetraethylammonium perchlorate as supporting electrolyte using a platinum button electrode, indicated one-electron redox processes. ^b See ref 14 and 15.

Although each complex consists of a metallocarborane cage having two transition metal atoms, only a single one-electron oxidation and a single one-electron reduction were observed. Even the trimetallic complex, V, exhibited the same behavior. The fact that each metal atom did not undergo an autonomous oxidation and reduction suggests that neither behaves as an independent entity and that the redox properties of one metal are strongly influenced by the presence of the other. An alternative view of this phenomenon is that the bimetallocarboranes, rather than behaving as two metal atoms bridged by a carborane ligand, must actually be considered as heteroboranes. The extensive electron delocalization throughout the entire cage causes the complex to function as a single entity much in the same way that certain transition metal cluster compounds act as single metal centers.

In the past, considerable use has been made of the correlations between the structures of monometallocarboranes and the values of their corresponding potentials for reduction.^{5,17} In complexes for which more than one isomer is known, knowledge of the reduction potential is helpful in assigning the locations of the carbon atoms since the proximity of the carbon atoms to the metal appears to have a direct bearing on the ease with which the metal is reduced. The three isomers of (η -C₅H₅)₂Co₂C₂B₉H₁₁ indicated that there is some correlation between structures and redox potentials of bimetallocarboranes—at least those with 13 vertices. As the rearrangements progress from the 1,3 to 1,8 to the 1,13 isomer, the high coordinate carbon, initially at vertex 3, increases its separation from both cobalt atoms. At the same time the reduction

potentials were observed to decrease indicating that the complex became more difficult to reduce. Of course, this is only one example and the full extent of the correlations, if any, of reduction potentials with structures of bimetallocarboranes is one of the topics under investigation in his laboratory.

Conclusion

The development of the polyhedral subrogation reaction represents an important advance in the synthesis of bimetallocarboranes. Previously, bimetallic species were prepared predominantly by the polyhedral expansion of monometallocarboranes.¹⁴ We now have an alternate method by which we can synthesize bimetallocarboranes, some of which are inaccessible by the polyhedral expansion reaction. Currently under investigation is the possibility that bimetallocarboranes may also undergo this reaction to produce polymetallic species.

Furthermore, we are now in a position to suggest a possible mechanism by which 4-(η -C₅H₅)-4-Co-1,8-C₂B₁₀H₁₂ is degraded to [3-(η -C₅H₅)-3-Co-4-CB₇H₈]⁻, at least in terms of which atoms are removed from the starting material. On the basis of this work, we can confidently say that one step in the mechanism is the removal of the boron atom initially at vertex 5, B(5). Since the carbon atom in the degraded product is located in a position nonadjacent to the cobalt atom,⁷ it is likely that C(1) was also removed from the 13-vertex polyhedron. It was observed in the polyhedral contraction reaction^{3,4} that a boron atom adjacent to carbon, but nonadjacent to cobalt, was always removed. There are only two such boron atoms left that satisfy these requirements: B(11) and B(13). These are the two remaining boron atoms that would be expected to be removed from the polyhedron by an attack of the nucleophilic ethoxide ion.

With the removal of the four contiguous polyhedral vertices, C(1), B(5), B(11), and B(13), one can visualize the collapse of the remaining nine vertices to form a tricapped trigonal prism. The vertices of the trigonal prism would be the cobalt atom, B(3), B(7), B(6), B(9), and B(12) and the atoms constituting the three low coordinate caps would be B(2), B(10), and C(8).

Experimental Section

Physical Measurements. Ultraviolet-visible spectra were measured with a Beckman DB spectrophotometer. Infrared spectra were determined using a Perkin-Elmer Model 137 sodium chloride spectrophotometer. Proton nmr spectra were obtained by means of a Varian A-60D and the 80.5-MHz ¹³B nmr spectra with an instrument designed and constructed by Professor F. A. L. Anet of this department. Electrochemical data were obtained from an instrument which has been previously described.¹⁸ Mass spectra were obtained using an Associated Electrical Industries MS-9 spectrometer and magnetic susceptibilities measured utilizing a Cahn Model RG electrobalance. Kinetic data were measured by a previously described procedure.⁵

Elemental analyses were performed by Schwarzkopf Micro-analytical Laboratories, Woodside, N. Y.

Materials. 4-(η -C₅H₅)-4-Co-1,7-C₂B₁₀H₁₂, 4-(η -C₅H₅)-4-Co-1,8-C₂B₁₀H₁₂, and 4-(η -C₅H₅)-4-Co-1,13-C₂B₁₀H₁₂ and their C,C'-dimethyl derivatives were prepared according to literature methods.⁵ With the exception of the Spectroquality acetonitrile used in determining the electronic spectra, all solvents were reagent grade and were used without further purification. Sodium borohydride was purchased from Ventron. FeCl₂·4H₂O and CoCl₂·6H₂O were

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obtained from Mallinckrodt. Anhydrous CoCl_2 was prepared from the hydrate by heating under vacuum. Tetramethylammonium chloride was purchased from Matheson Coleman and Bell. Dicyclopentadiene was obtained from Aldrich Chemical Co. and was converted to cyclopentadiene immediately prior to use. Merck "Silica Gel 60," 70–230 mesh, was employed for column chromatography.

4,5-(η - C_5H_5)₂-4,5- Co_2 -1,8- $\text{C}_2\text{B}_9\text{H}_{11}$ (I). To a 250-ml, three-necked, round-bottom flask fitted with a mechanical stirrer and a reflux condenser topped with a nitrogen inlet, were added 0.268 g (1 mmol) of 4-(η - C_5H_5)-4- Co -1,8- $\text{C}_2\text{B}_{10}\text{H}_{12}$ and 125 ml of absolute ethanol. KOH (5 g, 85% pellets) was added directly as a solid followed by 2.6 g (20 mmol) of anhydrous CoCl_2 as a slurry in 25 ml of ethanol. Freshly distilled C_5H_6 (5 g, 75 mmol) was then added and the reaction mixture was stirred at the reflux temperature for 40 hr. The dark green solution was filtered through Celite and the solvent was removed from the filtrate by rotary evaporation. The dark brown-green oil was dissolved in 250 ml of water and the aqueous solution was extracted with five 125-ml portions of dichloromethane. The CH_2Cl_2 solution was dried with MgSO_4 and then stripped onto 30 g of silica gel. The solid was placed atop a silica gel chromatography column which was prepared with hexane. The column was eluted with hexane gradually enriched with dichloromethane. The first major band to be eluted was dark green and afforded 0.220 g (0.58 mmol, 58%) of black crystals of I.

4,5-(η - C_5H_5)₂-1,8-(CH_3)₂-4,5- Co_2 -1,8- $\text{C}_2\text{B}_9\text{H}_9$ (II). II was prepared in nearly the same manner as described for I, above. 4-(η - C_5H_5)-1,8-(CH_3)₂-4- Co -1,8- $\text{C}_2\text{B}_{10}\text{H}_{10}$ (0.60 g, 2 mmol), 150 ml of ethanol, 10 g KOH, 2.6 g CoCl_2 , and 5 g of C_5H_6 were combined in the flask and heated to the reflux temperature for 48 hr. The reaction mixture was filtered through Celite and the filtrate stripped to an oil. The oil was redissolved in water which was then extracted with five 125-ml portions of CH_2Cl_2 . The nonaqueous phase was stripped onto silica gel which was then chromatographed. Three weak bands, in order, green, yellow, and purple, were first to be eluted and were not characterized. An intense brown-green band was next to be eluted and from this band was isolated 0.35 g (0.86 mmol, 43%) of black crystals of II.

4,5-(η - C_5H_5)₂-4,5- Co_2 -1,13- $\text{C}_2\text{B}_9\text{H}_{11}$ (III). (a) **From 4-(η - C_5H_5)-4- Co -1,13- $\text{C}_2\text{B}_{10}\text{H}_{12}$.** 4-(η - C_5H_5)-4- Co -1,13- $\text{C}_2\text{B}_{10}\text{H}_{12}$ (0.54 g, 2 mmol) was dissolved in 150 ml of absolute ethanol with 10 g of KOH, 2.6 g CoCl_2 , and 5 g of C_5H_6 and the mixture stirred at reflux for 72 hr. The reaction mixture was worked up as described above for both I and II and then chromatographed. The first band to be eluted was very pale yellow and was discarded. The second was a bright green band which yielded 0.030 g (0.08 mmol, 4%) of green crystals of III.

(b) **From 4,5-(η - C_5H_5)₂-4,5- Co_2 -1,8- $\text{C}_2\text{B}_9\text{H}_{11}$.** A 0.206-g sample of 4,5-(η - C_5H_5)₂-4,5- Co_2 -1,8- $\text{C}_2\text{B}_9\text{H}_{11}$ was added to 50 ml of cyclooctane and the solution was heated at 150° for 15 hr. The solvent was removed using a mechanical vacuum pump and the solid was redissolved in 20 ml of dichloromethane. The solution was stripped onto silica gel and the solid was mounted upon a silica gel chromatography column which was eluted with hexane gradually enriched with dichloromethane. The first band was bright green and contained 0.165 g (80% conversion) of 4,5-(η - C_5H_5)₂-4,5- Co_2 -1,13- $\text{C}_2\text{B}_9\text{H}_{11}$ (III). A trace amount of compound I was next to be eluted.

4,5-(η - C_5H_5)₂-1,13-(CH_3)₂-4,5- Co_2 -1,13- $\text{C}_2\text{B}_9\text{H}_9$ (IV). The reaction of 4-(η - C_5H_5)-1,13-(CH_3)₂-4- Co -1,13- $\text{C}_2\text{B}_{10}\text{H}_{10}$ with ethanolic potassium hydroxide produced no compound IV; thus it was prepared solely *via* the thermal rearrangement of 4,5-(η - C_5H_5)₂-1,8-(CH_3)₂-4,5- Co_2 -1,8- $\text{C}_2\text{B}_9\text{H}_9$, compound II. A 0.103-g sample of compound II was dissolved in 25 ml of cyclooctane and stirred at

159° for 15 hr. Column chromatography of the reaction mixture produced a pale orange band which was discarded followed by a green band which yielded 0.075 g (73%) of green crystals of II.

[(CH_3)₄ N^+][(η - C_5H_5)₂ $\text{CoC}_2\text{B}_9\text{H}_{11}$]₂ Co (V). To 150 ml of ethanol were added 0.270 g (1 mmol) of 4-(η - C_5H_5)-4- Co -1,8- $\text{C}_2\text{B}_{10}\text{H}_{12}$ and 10 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. KOH (5.0 g) was added and the mixture was heated at reflux for 20 hr. The solvent was removed by rotary evaporation and the brown solid was redissolved in 150 ml of 50% acetone–water. The resulting slurry was filtered through Celite and the filtrate was added to 100 ml of a tetraethylammonium chloride solution in water. The acetone was removed by rotary evaporation and the dark suspension was filtered through Celite. The pale yellow filtrate was discarded. The filter cake was washed first with water and then with ethanol. When the ethanol washings became colorless, the Celite was extracted with five 100-ml portions of dichloromethane. The addition of hexane followed by the slow evaporation of the dichloromethane produced 0.055 g (0.085 mmol, 17%) of black crystals of V.

4,5-(η - C_5H_5)₂-4- Co -5- Fe -1,8- $\text{C}_2\text{B}_9\text{H}_{11}$ (VI). A 0.540-g (2 mmol) sample of 4-(η - C_5H_5)-4- Co -1,8- $\text{C}_2\text{B}_{10}\text{H}_{12}$ was dissolved in 150 ml of ethanol. KOH (10 g) and 4.0 g (20 mmol) of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were added directly as a solid and dissolved. Freshly distilled C_5H_6 (5.0 g, 75 mmol) was added and the mixture was heated to the reflux temperature and stirred for 20 hr. After the reaction mixture had cooled to room temperature, oxygen was bubbled through for 1 hr with occasional stirring. The dark brown liquid was then filtered through Celite, and the solvent was removed from the filtrate by rotary evaporation. The dark yellow-brown oil was redissolved in 300 ml of water and was then extracted with four 200-ml portions of dichloromethane. The CH_2Cl_2 phase was dried with MgSO_4 and then stripped onto silica gel. The resulting solid was chromatographed with hexane. The first band to be eluted consisted of ferrocene. The second band was a brownish purple color and produced 0.140 g (0.38 mmol, 19%) of black crystals of VI.

4,5-(η - C_5H_5)₂-1,8-(CH_3)₂-4- Co -5- Fe -1,8- $\text{C}_2\text{B}_9\text{H}_9$ (VII). VII was prepared in exactly the same manner described for VI immediately above. 4-(η - C_5H_5)-1,8-(CH_3)₂-4- Co -1,8- $\text{C}_2\text{B}_{10}\text{H}_{10}$ (0.60 g, 2 mmol) was used. Column chromatography of the CH_2Cl_2 phase produced three bands. The first was yellow and contained ferrocene. The second was a pale yellow-green band which was discarded. A brownish purple band was next to be eluted, and removal of the solvent from this band gave 0.230 g (0.56 mmol, 28%) of 4,5-(η - C_5H_5)₂-1,8-(CH_3)₂-4- Co -5- Fe -1,8- $\text{C}_2\text{B}_9\text{H}_9$.

Reduction of Cobaltferracarboranes. Both iron–cobalt complexes were reduced in the same manner in order to obtain nmr spectra. A 50-mg sample of either VI or VII was dissolved in 20 ml of acetonitrile in a 100-ml round-bottom flask to which 150 mg of NaBH_4 was added followed by 20 ml of water. The resulting mixture was heated on a steam bath for 30 min causing the color to change from brownish purple to green. The flask was transferred to a vacuum line where all of the solvent was removed. The flask was removed to a nitrogen-filled drybox, and the solid residue was scraped from the inside of the flask and placed in a small filter. This residue was washed with 2 ml of CD_3CN and the filtrate transferred to an nmr tube.

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