reaction is approximately 2 min at room temperature. The equilibrium is fully established in approximately 10 min. No formation of complex 1 has been detected. Computer simulation and addition of the standard solution of complex 1 to the above reaction mixture suggest that more than 3% conversion of complex 10 to complex 1 would be detectable.

Comparison of the Rate of Ethylene Oxidation in Mono- and Bimetallic Systems. A. Monometallic System. A Fisher-Porter tube was charged with complex 1 (89 mg, 0.33 mmol), evacuated, and pressurized (345 kPa) with ethylene. A degassed solution of *n*-undecane (4.53 mg, internal standard) in 1,2-dichloroethane (10 mL) was added with the aid of air-tight syringe. The reaction mixture was stirred at room temperature, the ethylene pressure was kept constant at 345 kPa, and samples were withdrawn at appropriate time intervals by using an air-tight syringe. The formation of acetaldehyde was monitored by GC using a 6 ft glass column packed with Poropack PS (Figure 1).

B. Bimetallic System. The procedure was analogous to that described above with the exception that the Fisher-Porter tube was charged with $(CH_3CN)_2PdCl_2$ (209 mg, 0.81 mmol) and py(TPP)CoNO₂ (248 mg,

0.31 mmol). The results are summarized in Figure 1.

Metal-Promoted Fusion and Linkage of $B_5H_8^-$, $1\text{-}XB_5H_7^-$ (X = D, CH₃), $B_{10}H_{13}^-$, and $(\eta^5\text{-}C_5H_5)CoB_4H_7^-$. Facile Routes to $B_{10}H_{14}$ and $(\eta^5\text{-}C_5H_5)_2Co_2B_8H_{10}$ Isomers[1]

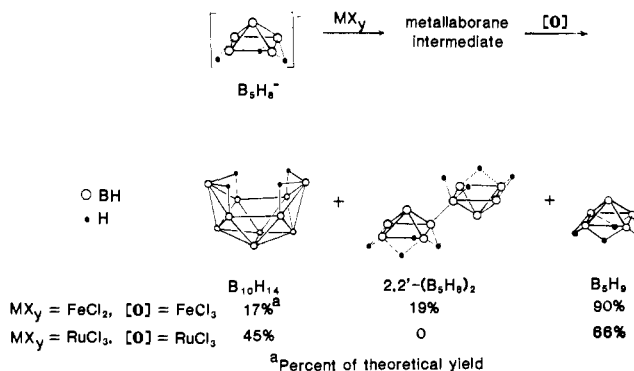**Cynthia T. Brewer and Russell N. Grimes***

Contribution from the Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901. Received December 5, 1984

Abstract: This study examined the conversions, via oxidative fusion or coupling, of $B_5H_8^-$ to $B_{10}H_{14}$ and 2,2'-$(B_5H_8)_2$ in the presence of $FeCl_2/FeCl_3$, of $B_5H_8^-$ to $B_{10}H_{14}$ alone in the presence of $RuCl_3$, and of $1\text{-}XB_5H_7^-$ (X = D and CH₃) to $2,4\text{-}B_{10}H_{12}D_2$ and $2,2\text{-}(1\text{-}CH_3B_5H_7)_2$ with $RuCl_3$ or $FeCl_2/FeCl_3$. The $B_{10}H_{13}^-$ ion was shown to form *n*- and *i*-$B_{18}H_{22}$ on treatment with $RuCl_3$ in THF and subsequent exposure to air. The $RuCl_3$-promoted fusions of the square-pyramidal cobaltaboranes 2-$(\eta^5\text{-}C_5H_5)CoB_4H_7^-$ and $1\text{-}(\eta^5\text{-}C_5H_5)CoB_4H_7^-$ (both analogues of $B_5H_8^-$) to give *nido*-$(\eta^5\text{-}C_5H_5)_2Co_2B_8H_{12}$ isomers were also studied. The 2-isomer yields primarily 5,8- 1,5-, and 1,7-$(\eta^5\text{-}C_5H_5)_2Co_2B_8H_{12}$, while the 1-isomer affords only 2,4-$(\eta^5\text{-}C_5H_5)_2Co_2B_8H_{12}$. All these observations support a fusion mechanism in which two square-pyramidal substrate molecules, facilitated by coordination to a common metal ion, are initially joined at their basal edges and then complete the fusion process to give a nido 10-vertex cage in which the original apex (1-vertex) atoms become the 2,4-vertexes in the product. The new compounds were characterized via infrared, ¹¹B and ¹H NMR, mass spectra, and in some cases by two-dimensional (2D) ¹¹B homonuclear NMR.

The application of transition metals as agents in synthesis, especially of organic compounds, has found wide acceptance and constitutes a tool of major importance in preparative chemistry.[2] A principal attribute of transition-metal ions is their ability, through coordination to substrates of interest, to facilitate processes that would otherwise be unfavorable. Moreover, metal-mediated reactions are often highly stereospecific, increasing still further their value in synthetic chemistry.

In the inorganic field, there are fewer examples of transition-metal ions as preparative agents per se; however, the boron hydride/carborane family, which like hydrocarbon chemistry features covalently bonded hydrogenated networks, seems particularly suited to such applications.[3] Our entry into this realm dates from the fortuitous discovery of the metal-induced fusion of $R_2C_2B_4H_4^{2-}$ carborane ligands (R = alkyl) to give $R_4C_4B_8H_8$ species.[4] In the

Scheme I

decade since our first report,[4a] we have observed similar fusion reactions with other carboranes and with metallacarboranes[5] and have elucidated some details of the conversion of $(R_2C_2B_4H_4)_2FeH_2$ to $R_4C_4B_8H_8$.[6] The likelihood that metal-

(1) Based in part on: Ph.D. Dissertation, Brewer, C. T. University of Virginia, 1984.

(2) Davies, S. G. "Organotransition Metal Chemistry: Applications to Organic Synthesis"; Pergamon Press: Oxford, 1982.

(3) A recent example of metal-induced coupling of boranes is the conversion of B_5H_9 to 1,2'-$(B_5H_8)_2$ over PdBr₂: Corcoran, E. W. Jr.; Sneddon, L. G. *Inorg. Chem.* **1983**, *22*, 182.

(4) (a) Maxwell, W. M.; Miller, V. R.; Grimes, R. N. *J. Am. Chem. Soc.* **1974**, *96*, 7116. (b) *Inorg. Chem.* **1976**, *15*, 1343.

(5) For recent reviews, see: (a) Grimes, R. N. *Acc. Chem. Res.* **1983**, *16*, 22. (b) *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 55.

Metal-Promoted Fusion and Linkage of Boranes

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promoted fusion could be similarly applied to boranes appeared a logical next step for investigation and is the subject of this and the following paper.[7] A preliminary report on portions of this work has appeared.[8]
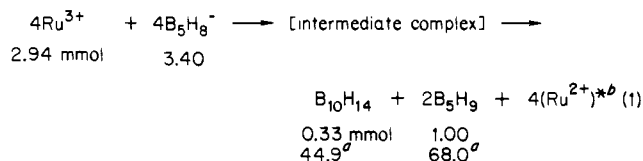
Results and Discussion

Fusion and Linkage of $B_5H_8^-$ Ions. As our initial subject for study, we chose the octahydropentaborate(1−) ion because of its ready availability via deprotonation of B_5H_9 with NaH, and of the possibility of producing $B_{10}H_{14}$ directly. This is an attractive synthetic goal since $B_{10}H_{14}$ is important as a precursor to *o*-carborane $(C_2B_{10}H_{12})$[9] and is currently prepared either via pyrolysis of B_2H_6[10a] or from B_5H_9 by improved multistep procedures[10b,c] involving a $B_9H_{14}^-$ or $B_{11}H_{14}^-$ intermediate. In our work, a THF (tetrahydrofuran) solution of $Na^+B_5H_8^-$ was treated with $FeCl_2$ to give a dark solution presumed to contain a ferraborane complex which was not isolable. The ^{11}B NMR spectrum of the solution exhibited only very broad signals centered at δ 89 and 211 relative to $BF_3 \cdot O(C_2H_5)_2$, indicating a paramagnetic species, possibly of the type $(B_5H_8)Fe^{III}(B_5H_7)$ or $[(B_5H_7)_2Fe^{III}]^-$.

Oxidation of the solution with $FeCl_3$ afforded $B_{10}H_{14}$ together with the linked-cage dimeric species[11] $2,2'$-$(B_5H_8)_2$ (Scheme I). The two metal reagents play separate roles in this sequence, the $FeCl_2$ serving to coordinate the B_5 anions and $FeCl_3$ functioning as an oxidant, inducing fusion. (Other oxidizers, including O_2 and I_2, can also be employed but are less efficient.) The reaction of $B_5H_8^-$ with $FeCl_2$ alone gave no isolable borane products; when only $FeCl_3$ was used, $2,2'$-$(B_5H_8)_2$ but no $B_{10}H_{14}$ was formed.

Under these conditions, it is clear that there are competing reactions involving cage fusion and cage linkage, respectively.[12] Since our primary interest centered on fusion, other metal reagents were investigated, and it was found that $RuCl_3$ effects fusion exclusively, giving $B_{10}H_{14}$ but no detectable $(B_5H_8)_2$ or other linked products. In this reaction system, it is evident that $RuCl_3$ functions both as a complexing agent and as an oxidant.

In both the $FeCl_2/FeCl_3$ and $RuCl_3$ reactions, little or no H_2 was formed but stoichiometrically significant quantities of B_5H_9 were generated. This suggests that the two hydrogen atoms which are necessarily lost in the course of $B_{10}H_{14}$ formation from $2B_5H_8^-$ are in fact taken up (as protons) by other $B_5H_8^-$ units to generate B_5H_9. The net process is then a four-electron oxidation, requiring 4 equiv each of Ru^{3+} and $B_5H_8^-$ per mole of $B_{10}H_{14}$ produced (eq 1). This idealized equation does not take into account the for-

$$4Ru^{3+} \ + \ 4B_5H_8^- \ \longrightarrow \ [\text{intermediate complex}] \ \longrightarrow$$
$$\begin{array}{cc} 2.94 \text{ mmol} & 3.40 \end{array}$$

$$B_{10}H_{14} \ + \ 2B_5H_9 \ + \ 4(Ru^{2+})^{*b} \ (1)$$
$$\begin{array}{cc} 0.33 \text{ mmol} & 1.00 \\ 44.9^a & 68.0^a \end{array}$$

^{a} Percent of theory based on $RuCl_3$. ^{b} Product not identified.

mation of unidentified nonvolatile borane products and is concerned only with the stoichiometric relation between the $B_5H_8^-$

(6) (a) Maynard, R. B.; Grimes, R. N. *J. Am. Chem. Soc.* **1982,** *104,* 5983. (b) Venable, T. L.; Maynard, R. B.; Grimes, R. N. *Ibid.* **1984,** *106,* 6187.

(7) Brewer, C. T.; Swisher, R. G.; Sinn, E.; Grimes, R. N. *J. Am. Chem. Soc.,* following paper in this issue.

(8) Brewer, C. T.; Grimes, R. N. *J. Am. Chem. Soc.* **1984,** *106,* 2722.

(9) (a) Heying, T. L.; Ager, J. W.; Clark, S. L.; Mangold, D. J.; Goldstein, H. L.; Hillman, M.; Polak, R. J.; Szymanski, J. W. *Inorg. Chem.* **1963,** *2,* 1089. (b) Hawthorne, M. F.; Andrews, T. D.; Garrett, P. M.; Olsen, F. P.; Reintjes, M.; Tebbe, F. N.; Warren, L. F.; Wegner, P. A.; Young, D. C. *Inorg. Synth.* **1967,** *10,* 91.

(10) (a) Greenwood, N. N. "The Chemistry of Boron"; Pergamon Press: Oxford, 1973; pp 769–773 and references therein. (b) Toft, M. A.; Leach, J. B.; Himpsl, F. L.; Shore, S. G. *Inorg. Chem.* **1982,** *21,* 1952. (c) Dunks, G. B.; Barker, K.; Hedaya, E.; Hefner, C.; Palmer-Ordonez, K.; Remec, P. *Inorg.* **1981,** *20,* 1692.

(11) Rietz, R. R.; Schaeffer, R.; Sneddon, L. G. *Inorg. Chem.* **1972,** *11,* 1242.

(12) For purposes of this discussion, we define linkage as a coupling of two cages via a single atom on each unit, while fusion connotes a greater degree of connectivity (hence bonding interaction) between the cages.

Table I. ^{11}B FT NMR Data (115.8 MHz) (CH_2Cl_2 Solution)

compound	δ $(J, Hz)^a$	rel area
$5,8$-$(C_5H_5)_2Co_2B_8H_{12}$ (1)	33.2 (130), 26.1 (102), 11.0 (132), −11.3 (134)	2:2:2:2
$1,5$- or $1,7$-$(C_5H_5)_2Co_2B_8H_{12}$ (2)	36.1 (123), 32.3 (113), 16.7 (132), 12.0 (135)	1:1:1:1
	$6.3,^b$ $5.4,^b$ 1.1 (141), −14.4 (142)	1:1:1:1
$1,7$- or $1,5$-$(C_5H_5)_2Co_2B_8H_{12}$ (3)	41.1 (135), 27.5 (132), 18.5 (125), 9.2 (159)	1:1:1:1
	5.8 (∼130), 4.7 (∼130), −0.5 (135), −37.3 (145)	1:1:1:1
$2,4$-$(C_5H_5)_2Co_2B_8H_{12}$ (4)	21.5 (128), 12.3 (146), 3.5 (140)	2:2:4

$^a BF_3 \cdot O(C_2H_5)_2$ shift is 0; positive shifts are downfield. $^b J_{BH}$ coupling not measurable.

Table II. ^1H FT NMR Data (360 MHz)

compd	δ^a	rel area	assign
1 (C_6D_6)	4.56	10	C_5H_5
	−3.01	2	B-H-B
	−17.79	2	B-H-Co
2 ($CDCl_3$)	5.11	5	C_5H_5
	5.09	5	C_5H_5
	−2.91	1	B-H-B
	−3.98	1	B-H-B
	−4.62	1	B-H-B
	−20.1	1	B-H-Co
3 ($CDCl_3$)	5.17	5	C_5H_5
	5.09	5	C_5H_5
	−1.36	1	B-H-B
	−2.52	1	B-H-B
	−4.74	1	B-H-B
	−22.2	1	B-H-Co
4 ($CDCl_3$)	5.03	10	C_5H_5
	−4.30	4	B-H-B

^{a} Shifts in parts per million referenced to $(CH_3)_4Si = 0$.

ion and $B_{10}H_{14}$. Alternatively, since the B_5H_9 produced can be recycled, one can calculate the $B_{10}H_{14}$ yield on the basis of net consumption of B_5H_9; expressed in this manner, the yield of decaborane(14) is 27.5% theory.

A corresponding description of the $FeCl_2/FeCl_3$ reaction is given in the idealized balanced equation (2). Yields given in Scheme

$$6Fe^{3+} + 6B_5H_8^- \rightarrow B_{10}H_{14} + 2,2'\text{-}(B_5H_8)_2 + 2B_5H_9 + 6Fe^{2+} \tag{2}$$
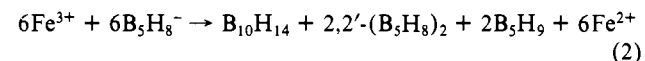
I are based on eq 2; on the basis of net B_5H_9 consumption, the yields of $B_{10}H_{14}$ and $B_{10}H_{16}$ are 24.8% and 27.4%, respectively. While no effort was undertaken to optimize conditions for $B_{10}H_{14}$ formation, metal-induced fusion of $B_5H_8^-$ under mild conditions appears to have promise as a simple, straightforward route to that hydride, particularly in view of the large stocks of B_5H_9 remaining in the U.S.

Fusion and Linkage of 1-$XB_5H_7^-$ Ions ($X = D$ and CH_3). In an attempt to cast some light on the fusion/linkage mechanisms of the $B_5H_8^-$–metal ion systems, the corresponding reactions of 1-deuterio- and 1-methylpentaborane derivatives (in which the substituent is on the apex boron) were examined. Treatment of $K^+(1$-$DB_5H_7)^-$ with $RuCl_3$ in THF solution gave a single product, $2,4$-dideuteriodecaborane(14), $2,4$-$D_2B_{10}H_{12}$, as determined from its ^{11}B NMR spectrum (Figure 1). The observation of this specific isomer, and no other, is significant and furnishes strong evidence that the B_5 units fuse in a highly stereospecific manner such that the apex boron atoms in the original species become the 2,4-borons in the decaborane product (Figure 2). While the possibility of deuterium migration exists in principle, this can be effectively discounted since only one isomer is seen; any significant scrambling of the D atoms in the course of the reaction would be immediately obvious in the proton-coupled ^{11}B spectrum of the product.

The reaction of 1-$CH_3B_5H_7^-$ ion with $FeCl_2/FeCl_3$ was examined and found to give only the linked-cage products $2,2'$-$(CH_3B_5H_7)_2$ and 2-$CH_3B_5H_8$; no $B_{10}H_{12}(CH_3)_2$ species was de-

Figure 1. Proton-coupled 115.8-MHz ^{11}B NMR spectra of (a) $B_{10}H_{14}$ and (b) 2,4-$D_2B_{10}H_{12}$ in C_6D_6.
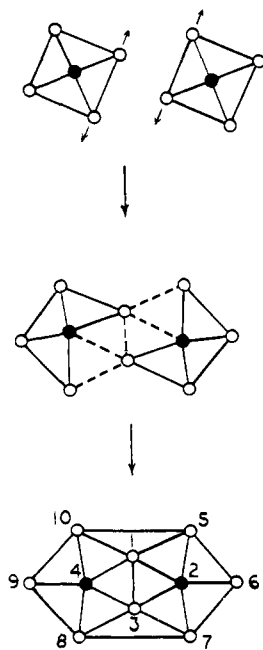

Figure 2. Proposed scheme for fusion of two square-pyramidal units (at top) to form a nido-10-vertex cage (bottom). Apical atoms of the original square pyramids are shown as solid circles. Hydrogen atoms are omitted.

tected, suggesting that the presence of the methyl substituents may inhibit the fusion process. The effect is evidently nonsteric, since the structurally analogous species 1-(η^5-C_5H_5)CoB$_4$H$_7^-$ does undergo fusion despite its bulky cyclopentadienyl ligand (vide infra).

O BH   ●CH   •H
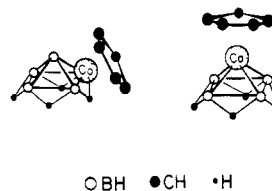
Figure 3. Established structures of 2-(η^5-C_5H_5)CoB$_4$H$_8$ (left) and 1-(η^5-C_5H_5)CoB$_4$H$_8$.

Table III. Infrared Absorptions (cm^{-1}, KBr Pellets)[a]

1	3100 (m), 2915 (s), 2850 (m), 2480 (s), 1720 (w, br), 1630 (w, br), 1450 (w), 1410 (m), 1030 (m), 970 (s), 825 (s), 780 (w), 750 (w), 700 (w), 670 (w), 470 (w), 410 (w)
2	3100 (m), 2920 (m), 2850 (m), 2490 (vs), 2450 (s), 1600 (w, br), 1520 (w, br), 1415 (m), 1350 (w, br), 1080 (w), 1050 (w), 1030 (w), 990 (m), 965 (w), 905 (m), 820 (s), 780 (m), 750 (w), 715 (w), 670 (w), 635 (w)
3	3100 (w), 2920 (s), 2850 (m), 2495 (s), 1850 (w, br), 1720 (w, br), 1630 (w, br), 1490 (w), 1460 (m), 1420 (m), 1195 (w), 1045 (w), 990 (s), 920 (w), 830 (s), 730 (w), 705 (w)
4	3100 (vw), 2920 (w), 2850 (w), 2500 (s), 2450 (m), 1870 (w, br), 1610 (w, br), 1420 (m), 1115 (w), 1090 (w), 1060 (w), 1010 (m), 980 (m), 946 (s), 910 (m), 850 (m), 820 (s), 770 (m), 730 (m), 705 (m), 660 (m), 620 (w), 570 (w)

[a] Key: s = strong, m = medium, w = weak, br = broad.

Fusion of *nido*-(η^5-C_5H_5)CoB$_4$H$_7^-$ Isomers. The cobaltaboranes 2-(η^5-C_5H_5)CoB$_4$H$_8$ and 1-(η^5-C_5H_5)CoB$_4$H$_8$ (Figure 3) are stable crystalline solids and have been fully characterized, including X-ray structure determinations.[13] These complexes are electronic and structural analogues of B_5H_9, consisting of square-pyramidal cage units in which a basal or apical BH unit in B_5H_9 has been replaced by Co(C_5H_5) (an electronic equivalent of BH[14]). Since both isomers can be deprotonated to give a (C_5H_5)CoB$_4$H$_7^-$ anion analogous to $B_5H_8^-$,[13,15] it was of interest to attempt the metal-promoted fusion of these ions in light of the $B_5H_8^-$/metal ion reactions described above.

The reaction of Na$^+$[2-(C_5H_5)CoB$_4$H$_7$]$^-$ with RuCl$_3$ in THF gave three main isolable products, characterized from NMR (Tables I and II), IR (Table III), and mass spectroscopy, as isomers of (η^5-C_5H_5)$_2$Co$_2$B$_8$H$_{12}$: brown **1**, amber **2**, and yellow-brown **3**. These compounds are isomeric (ignoring the C_5R_5 ligands) with the dicobaltaboranes 5,7- and 6,9-[η^5-C_5-(CH$_3$)$_5$]$_2$Co$_2$B$_8$H$_{12}$, reported earlier,[16] which were shown from NMR data[16] and X-ray diffraction studies[17] to be structural analogues of $B_{10}H_{14}$. Hence it is assumed that the new products **1–3** adopt similar *nido*-Co$_2$B$_8$ cage geometries. From the ^{11}B and ^{1}H NMR spectra of **1**, it is evident that the molecule has C_2 symmetry and that there are two B–H–B and two B–H–Co hydrogen bridges;[18] these requirements in a $B_{10}H_{14}$-type skeleton are met only by placing the Co(C_5H_5) units in the 5- and 8- (or equivalently the 7- and 10-) vertexes (Figure 4a). This conclusion is further supported by the two-dimensional (2D) ^{11}B NMR spectrum[19] of **1**, (Figure 5) whose pattern of cross peaks is entirely consistent with the proposed structure.[20]

The remaining isomers **2** and **3** cannot be unambiguously assigned from the available spectral information (sample size not

(13) Venable, T. L.; Sinn, E.; Grimes, R. N. *J. Chem. Soc., Dalton Trans* **1984**, 2275 and references therein.

(14) For discussions of the polyhedral skeletal electron-pair theory (PSEPT) rules governing contributions to framework bonding in clusters, see: (a) Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311. (b) O'Neill, M. E.; Wade, K. In "Metal Interactions with Boron Clusters"; Grimes, R. N., Ed.; Plenum Press: New York, 1983; Chapter 1 and references therein.

(15) Weiss, R.; Bowser, J. R.; Grimes, R. N. *Inorg. Chem.* **1978**, *17*, 1522.

(16) Venable, T. L.; Grimes, R. N. *Inorg. Chem.* **1982**, *21*, 887.

(17) Venable, T. L.; Sinn, E.; Grimes, R. N. *Inorg. Chem.* **1982**, *21*, 895.

(18) Protons bridging transition metals and boron are readily distinguishable by their large upfield shifts [usually $\delta < -10$ relative to BF$_3$·O(C$_2$H$_5$)$_2$]: see ref 16 and references therein.

(19) Venable, T. L.; Hutton, W. C.; Grimes, R. N. *J. Am. Chem. Soc.* **1984**, *106*, 29.

(20) Previous work[19] has shown that cross peaks between boron nuclei bridged by hydrogen [e.g., B(6)–B(7)] are normally absent; cross peaks between equivalent nuclei [e.g., B(1)–B(3)] cannot occur.

Metal-Promoted Fusion and Linkage of Boranes

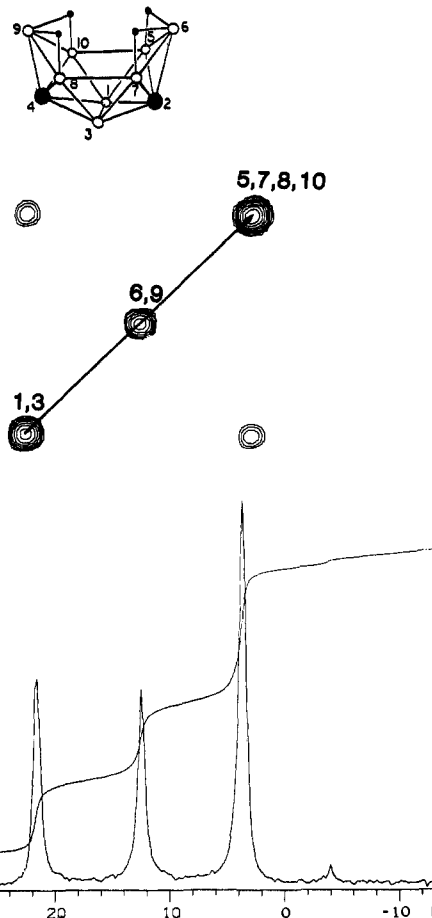*J. Am. Chem. Soc., Vol. 107, No. 12, 1985* 3555
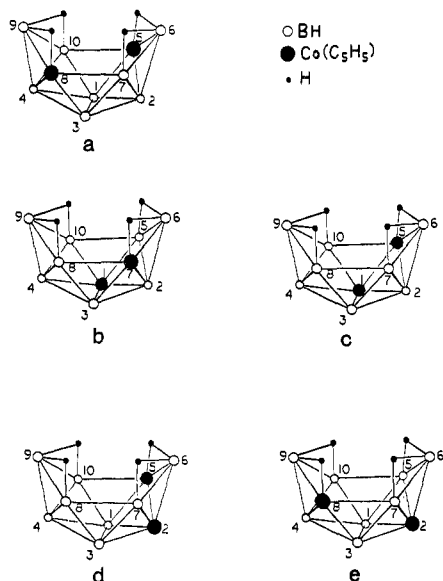
Figure 4. (a) Proposed structure of **1**. (b,c) Proposed structures of **2** and **3**. (d,e) Possible but less likely structures for **2** and **3** (see text). Equivalent and/or enantiomeric isomers, not shown, exist for each of the structures depicted.
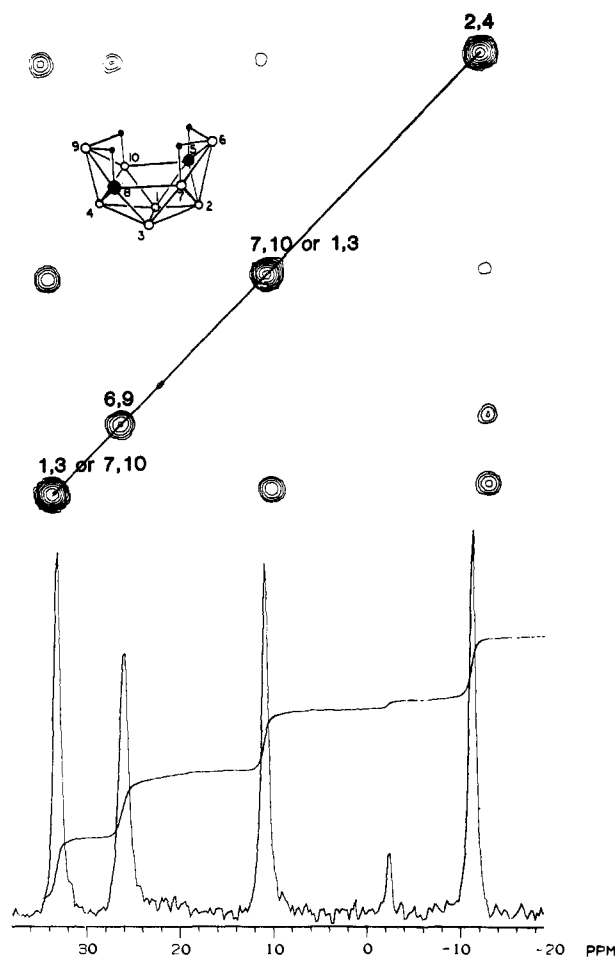
Figure 5. Two-dimensional (2D) proton-decoupled ^{11}B NMR spectrum of **1** at 115.8 MHz in CH_2Cl_2. Labeled peaks on diagonal correspond to the conventional 1D spectrum shown at bottom; off-diagonal (cross) peaks reveal scalar coupling between specific ^{11}B nuclei.[19]

Figure 6. Two-dimensional ^{11}B proton-decoupled NMR spectrum of **4** at 115.8 MHz in CH_2Cl_2, with 1D spectrum shown at bottom.

permitting 2D NMR analysis), but the possibilities are limited to four, as shown in Figure 4b–e. Each compound exhibits no cage symmetry (eight boron resonances) and has one Co–H–B and three B–H–B bridges; hence each has one cobalt in the 5- (or equivalent 7-, 8-, or 10-) vertex. The remaining cobalt must

then occupy vertex 1, 2, 3, or 4. Despite this ambiguity, we can present a mechanistic argument supporting the 1,7- and 1,5-structures (Figure 4b and c) for compounds **2** and **3**. If the scheme proposed for fusion of two B_5 units to generate a nido B_{10} cage (Figure 2) is assumed to hold for the $2(CoB_4) \rightarrow Co_2B_8$ conversion as well, then the apex boron atoms in the two CoB_4 moieties will constitute vertexes 2 and 4 in the Co_2B_8 product; hence these locations must be occupied by BH units in each isomer, ruling out structures such as the 2,5- and 2,8-species (Figure 4d and e). On this basis, **2** and **3** are assigned the 1,7- and 1,5-geometries (Figure 4b and c) with no prejudice as to which is which. Although the underlying mechanistic assumption has not been proved, it receives support from the fusion of $1\text{-}(C_5H_5)CoB_4H_7^-$ as follows.

The corresponding treatment of the $1\text{-}(C_5H_5)CoB_4H_7^-$ ion with $RuCl_3$ yielded a single isolable product, **4**, easily identified from mass spectra as another $(C_5H_5)_2Co_2B_8H_{12}$ isomer. From the NMR data, it is evident that **4** has C_{2v} symmetry with no cobalt atoms adjacent to bridging hydrogens; hence the 1,3- and 2,4-isomers are the only possibilities. The 2D ^{11}B NMR spectrum of **4** (Figure 6) exhibits only one cross peak, a finding consistent with the 2,4- but not the 1,3-structure;[21] hence **4** is identified as $2,4\text{-}(\eta^5\text{-}C_5H_5)_2Co_2B_8H_{12}$. This conclusion is in line with the expectation noted above that fusion of square-pyramidal clusters to form nido-10-vertex cages places the apex units in the 2,4-positions in the product. The 2D spectrum of **4** also permits assignment of the peaks in the normal (1D) ^{11}B NMR spectrum, shown at the bottom. The cross peak between the resonances at δ 21.5 and 3.5 (the latter peak of area 4 arising from B(5,7,8,10)) identifies the former signal as due to B(1,3); hence the resonance at δ 12.3 is assigned to B(6,9).

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(21) In the 1,3-isomer, cross peaks are expected between B(2,4) and B-(5,7,8,10) and between B(2,4) and B(6,9); in the 2,4-isomer only the B-(1,3)–B(5,7,8,10) interaction is seen.

These observations support a geometric scheme for cage fusion of the 1- and 2-$(C_5H_5)CoB_4H_7^-$ ions that is similar to that proposed in Figure 2 for the $B_5H_8^-$ reaction. In each case, facilitated by complexation to a common metal ion, a basal atom (B or Co) from each square-pyramidal unit is inserted into the base of the other unit to form an open basket consisting of pentagonal-pyramidal moieties sharing an edge. The basal planes of these pyramids can then move closer together until bonds are formed between the 5–10- and 7–8-vertexes, producing a $B_{10}H_{14}$-like nido framework. This pathway causes the apex atoms of the original square-pyramidal units to occupy the 2- and 4-vertexes in the fused 10-atom cage, exactly as observed in each of the systems studied here. Thus, reactants labeled at the 1-position only, such as 1-$DB_5H_7^-$ and 1-$(C_5H_5)CoB_4H_7^-$, give rise to a single product; in contrast, species in which the basal atoms are not identical, like 2-$(C_5H_5)CoB_4H_7^-$, are expected to produce more than one fused product, as is also observed. In this latter case, the number of isomers actually isolated is likely to be influenced by steric constraints. Thus, if we assume that each Co_2B_8 product formed from merger of 2-CoB_4 units will have cobalts in vertexes other than 2 and 4 (these being reserved for the apex boron only, as noted above), then there are eight possible distinguishable isomers (ignoring enantiomers): (1,3), (1,5), (1,6), (1,7), (5,8), (5,9), (5,10), and (6,9). However, a further restriction can be imposed, based on earlier work which showed that when 2-$(C_5H_5)CoB_4H_8$ is deprotonated with NaH in THF, the proton is removed specifically from a Co–H–B rather than a B–H–B bridge.[15] Consequently, it is likely that the interaction of two 2-CoB_4 units occurs only at basal edges containing cobalt; this would exclude Co_2B_8 products having cobalt in the 6- or 9-vertex, reducing our list of possible isomers to just five. Of these, only the (1,5), (1,7), and (5,8) species have been isolated, as described above. What of the remaining two? It is probable that formation of the 1,3-complex is inhibited by crowding of the $Co(C_5H_5)$ units, and perhaps this is true of the 5,10-isomer as well; however, traces of these species may nevertheless form, as suggested by the observation of minor products which were not identified.

Conversion of $B_{10}H_{13}^-$ Ion to $B_{18}H_{22}$ in the Presence of $RuCl_3$. In order to examine the applicability of metal-induced fusion to larger borane substrates, a solution of $Na^+B_{10}H_{13}^-$ (derived from $B_{10}H_{14}$ and NaH) was treated with $RuCl_3$ in THF at low temperature. Formation of a dark-green solution indicated complexation of the borane by ruthenium. The complex could not be isolated, but its ^{11}B NMR spectrum was observed although the complexity of the spectrum (Experimental Section) precluded any structural interpretation. On removal of solvent and extraction with CH_2Cl_2 in air, two products identified as the known boranes n-$B_{18}H_{22}$[22] and i-$B_{18}H_{22}$[23] were isolated by plate chromatography.[24] Considerable $B_{10}H_{14}$ was also recovered from the reaction mixture.

This reaction is evidently more complex than those discussed above, involving net loss of boron from the original borane reagents. Nevertheless, the formation of the B_{18} products involves oxidation of one or more intermediate species which are presumed to be ruthenium–borane complexes. When workup of the green residue was conducted in an oxygen-free environment, no B_{18} hydride was obtained, demonstrating that the observed $B_{18}H_{22}$ products are formed only on oxidation of the metal complex(es) and not during the original reaction.

Conclusions

This work establishes that the concept of transition-metal-promoted ligand fusion is applicable as a synthetic tool to boron hydrides and to metallaboranes as well as carboranes. Within these categories, it remains to be seen what kinds of species, in
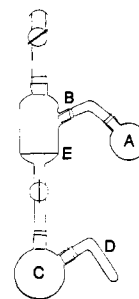

Figure 7. Pyrex apparatus employed in fusion reactions.

terms of structure and composition, are most amenable to fusion and also what metal ions and reaction conditions are most favorable. Some information on these questions is available from earlier work on carborane and metallacarborane fusion, and additional insight is given by the accompanying report[7] on the synthesis of $B_{12}H_{16}$ from $B_6H_9^-$. Metal-promoted synthesis is potentially a method of major importance for boron chemistry since it allows, in principle, stereochemical control over the construction of skeletal frameworks of specific desired geometry. Thus, the same advantages, mentioned in the introduction, that metal reagents bring to organic chemistry are applicable to boranes as well. Our investigations in this area are continuing.

Experimental Section

Materials. Pentaborane(9) was obtained from U.S. Government stockpiles. 1-DB_5H_8 was prepared from B_5H_9 and C_6D_6 by the method of Heppert and Gaines,[25] and 1-$CH_3B_5H_8$ was obtained by the method of Ryschkewitsch et al.[26] $nido$-2-$(C_5H_5)CoB_4H_8$ was prepared via the reaction of $B_5H_8^-$ with $CoCl_2$ and $C_5H_5^-$,[27] and its 1-isomer was prepared by thermolysis of 2-$(C_5H_5)CoB_4H_8$ as described elsewhere.[13,27] Other reagents were obtained commercially. Potassium and sodium hydrides were obtained as dispersions in mineral oil and were washed with hexane prior to use. Tetrahydrofuran (THF) was dried over lithium aluminum hydride and distilled under vacuum. Thin-layer chromatography was carried out on precoated 0.25-mm silica gel (F-254) plates.

Instrumentation. ^{11}B and ^1H NMR spectra were recorded on a Nicolet Magnetics Corp. NT-360/Oxford spectrometer, and data manipulation utilized standard Nicolet software with a 1280/293B data system. Infrared spectra were obtained with a Perkin-Elmer 1430 infrared spectrophotometer. Mass spectra were recorded on a Finnigan MAT 4600 GCMS spectrometer employing an Incos Data System.

Reaction of $Na^+B_5H_8^-$ with $FeCl_2$ and $FeCl_3$. The apparatus employed is illustrated in Figure 7. A 10.0 mmol sample of B_5H_9 was condensed in vacuo onto 0.67 g of NaH (28 mmol) at -196 °C in flask A followed by 50 mL of THF, and the mixture was warmed to -78 °C to allow deprotonation of the pentaborane. The flask was tipped up by rotation on the greased joint B, and the solution of $Na^+B_5H_8^-$ in the THF was filtered quickly in vacuo through the coarse frit E onto 0.76 g of $FeCl_2$ (6 mmol) in flask C, which had been cooled to -196 °C. Flask C was warmed to -78 °C, and the reaction mixture was stirred 1–2 h. A 1.72-g sample of $FeCl_3$ (10 mmol) was added via tip-in tube D attached to flask C, and the mixture was stirred for 4 h, after which the solvent was removed under vacuum while the reaction mixture was allowed to warm to room temperature. The residue was extracted with hexane in a drybox under N_2, and the solvent was removed from the extract by evaporation under vacuum. The flask containing the residue was evacuated at -78 °C, and $B_{10}H_{14}$ (35 mg) and 2,2'-$(B_5H_8)_2$[11] (40 mg) were obtained by vacuum sublimation/distillation and identified from their mass and ^{11}B NMR[11] spectra. B_5H_9 was observed in the recovered THF solvent and measured as 3.0 mmol by ^{11}B NMR analysis.

Reaction of $Na^+B_5H_8^-$ with $RuCl_3$. This procedure was conducted in an apparatus similar to that of the $FeCl_2/FeCl_3$ reaction (Figure 7), except that flask C contained no attached tube (D). Pentaborane(9) (3.4 mmol) was condensed onto 0.36 g of NaH (15 mmol) in flask A at -196 °C followed by THF. The flask was warmed to -78 °C. After all the pentaborane was deprotonated (evolution of H_2 had ceased), the THF solution of $Na^+B_5H_8^-$ was quickly filtered onto 0.61 g and $RuCl_3$ (2.94

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mmol) in flask C at −78 °C. The mixture was stirred at this temperature for 3 h and then was warmed to room temperature and stirred for an additional 30 min after which the solvent was removed under vacuum. The dark-green residue was extracted with hexane in air to give a yellow solution which was evaporated. The oily residue was placed on the vacuum line, and 40 mg (0.33 mmol) of $B_{10}H_{14}$ was obtained by sublimation. B_5H_9 recovered in the THF solvent was measured by ^{11}B NMR as 1.0 mmol.

Reaction of Na⁺(1-DB₅H₇)⁻ with RuCl₃. In a procedure identical with that described for the preceding reaction, a THF solution of Na⁺ (1-D-B_5H_7)⁻, prepared as described elsewhere,[25] was treated with RuCl₃. The fused decaborane product was identified as $2,4-B_{10}H_{12}D_2$ from its mass spectrum and ^{11}B NMR spectrum (vide supra).

Reaction of Na⁺(1-CH₃B₅H₇)⁻ with FeCl₂/FeCl₃. A sample of 1-$CH_3B_5H_8$ (0.70 g, 9.0 mmol) in THF solution was combined with NaH (1.52 g, 63 mmol) at −78 °C and warmed to −34 °C, at which temperature H_2 was rapidly evolved. When the technique and apparatus described above were used, the filtered THF solution of Na⁺(1-CH₃B₅H₇)⁻ was added to FeCl₂ (0.66 g, 5.2 mmol) at −78 °C and stirred for ~1 h. A 1.63-g (10 mmol) sample of FeCl₃ was added to the reaction mixture, and the mixture was stirred at −78 °C for 1.5 h. The THF solvent was removed in vacuo and saved, and the residue was removed under N_2 and extracted with *n*-hexane, and the solvent was stripped off to give a yellow oil, from which the volatiles were distilled through a −78 °C trap on the vacuum line. The residue was extracted with hexane, and the ^{11}B NMR spectrum was that of a complex mixture, with many poorly resolved resonances which were not interpretable. The −78 °C condensate and the THF solution from the reaction exhibited essentially identical ^{11}B NMR spectra, which indicated a mixture of $2,2'-(1-CH_3B_5H_7)_2$ and $2-CH_3B_5H_8$, identified from data previously reported.[28,29]

Reaction of Na⁺B₁₀H₁₃⁻ with RuCl₃. In a reactor identical with that employed in the previous reaction, THF was condensed onto 0.20 g (1.64 mmol) of $B_{10}H_{14}$ and 0.13 g (5 mmol) of NaH in flask A at −196 °C, after which the flask was warmed to room temperature. After deprotonation of $B_{10}H_{14}$ had ceased, the solution of $Na^+B_{10}H_{13}^-$ in THF was filtered onto 0.43 g of RuCl₃ (2 mmol) in flask C, which had been cooled to −35 °C. The reaction mixture was stirred at this temperature for 1.5 h, after which the solvent was distilled under vacuum while the mixture was allowed to warm to room temperature. The residue was extracted with dichloromethane and the extract filtered to give a dark green–brown solution whose proton-decoupled ^{11}B NMR spectrum at 115.8 MHz exhibited a complex pattern containing over 20 signals between δ 20 and −45 relative to $BF_3 \cdot O(C_2H_5)_2$ (THF solution).

The solution was chromatorgraphed on silica gel plates in 9:1 dichloromethane/hexane. A broad colorless band at the solvent front was identified as decaborane(14) (0.10 g). Two smaller green bands which were barely resolved from the origin were scraped off and washed with dichloromethane to give $n-B_{18}H_{22}$ (14 mg) for the first band and $i-B_{18}H_{22}$ (2 mg) for the second, the overall yield corresponding to 0.073 mmol, 17.8% of theory assuming a 4:1 ratio of starting borane to fused product

as in the $B_5H_8^-$ reactions described above. Alternatively, the $B_{18}H_{22}$ yield calculated on the basis of net $B_{10}H_{14}$ conversion (with a 2:1 $B_{10}H_{13}^-$/$B_{18}H_{22}$ ratio assumed) is again 17.8%.

Reaction of K⁺2-(C₅H₅)CoB₄H₇⁻ with RuCl₃. In a procedure corresponding to that employed for the $B_5H_8^-$ reaction, 20 mL of THF was condensed onto 0.080 g (2.0 mmol) of KH and 0.081 g (0.47 mmol) of $2-(C_5H_5)CoB_4H_8$ in flask A (Figure 7) at −196 °C. The flask was warmed to room temperature and allowed to stand 2–3 h during which period the solution changed from orange–red to purple–red. The contents of flask A were filtered onto 0.12 g of RuCl₃ (0.60 mmol) in flask C and stirred at room temperature for ~10 h. Solvent was removed under vacuum, and the residue was extracted with 1:1 benzene/hexane. The extract was filtered, reduced in volume, and chromatographed on silica gel plates in 1:1 benzene–hexane. Four major bands were observed: a red–orange band, $R_f = 0.66$, identified as $2-(C_5H_5)CoB_4H_8$ (53 mg, 0.30 mmol); yellow–brown 3 (2.3 mg), $R_f = 0.45$; amber 2, $R_f = 0.28$ (1.5 mg); and brown 1, $R_f = 0.14$ (3 mg). The electron-impact (EI) mass spectra of products 1–3 are very similar, exhibiting high mass cutoffs at m/e 347 corresponding to the $^{13}C^{12}C_9^{59}Co_2^{11}B_8^{1}H_{20}^+$ ion (parent-2) with some contribution from $^{12}C_{10}^{59}Co_2^{10}B^{11}B_7^{1}H_{21}^+$ and are consistent with the intensity pattern calculated for a $Co_2B_8C_{10}$ species from natural isotope abundances. Extensive hydrogen loss is evident (base peak at m/e 341), as are envelopes corresponding to loss, of 1, 2, and 3 BH units from the parent species. The spectra resemble those of crystallographically characterized $nido-(C_5R_5)_2Co_2B_8H_{12}$ species.[16,17] The total yield of 1, 2, and 3 based on a 4:1 ratio of $2-(C_5H_5)CoB_4H_7^-$ to $(C_5H_5)_2Co_2B_8H_{12}$ product (vide supra) is 16.6% theory; based on net consumption of $2-(C_5H_5)CoB_4H_8$ starting material (2:1 ratio), the total yield is 23%.

Reaction of K⁺1-(C₅H₅)CoB₄H₇⁻ with RuCl₃. The above procedure was followed with use of $1-(C_5H_5)CoB_4H_8$ (0.16 mmol) and 0.50 mmol of KH. Deprotonation of the cobaltaborane required 15–30 min at room temperature (monitored by evolution of H_2). The solution of K⁺1-(C₅H₅)CoB₄H₇⁻ was filtered onto 0.07 g (0.34 mmol) RuCl₃ and stirred at room temperature for 1 day. Solvent was removed under vacuum, and the residue was extracted with 1:1 benzene/hexane. The extract was filtered, reduced in volume, and chromatographed on silica gel plates in 1:1 benzene/hexane. One major, bright yellow band at $R_f = 0.73$ was isolated and identified as $2,4-(CpCo)_2B_8H_{12}$ (8 mg, 0.023 mmol), corresponding to 57% of theory assuming a 4:1 reactant/product ratio as discussed above. The EI mass spectrum of 4 is similar to those of 1–3 (vide supra) except that the high mass cutoff is at m/e 348 corresponding to the $^{13}C^{12}C_9^{59}Co_2^{11}B_8^{1}H_{21}^+$ (P − 1) ion. Again, loss of hydrogen and 1–3 BH units is evident in the spectrum.

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