syntheses.[5] We have also found that congestion correlates well with observed stereospecificities in epoxidation and hydroboration of congested olefins[20] and expect that it will be applicable to other stereoselective reactions and perhaps to steric hindrance of ionization,[21] and structure–activity correlations.[22]

(20) W. T. Wipke, T. F. Brownscombe, and P. Gund, in preparation.
(21) H. C. Brown, ref 2, p 181.
(22) C. Hansch, *J. Med. Chem.*, **13**, 964 (1970).

W. Todd Wipke,* **Peter Gund**

Department of Chemistry, Princeton University
*Princeton, New Jersey 08540*

Synthesis of Bimetallocarboranes by Thermal Metal Transfer

Sir:

In the course of our investigation of the thermal rearrangements of metallocarboranes,[1,2] we have discovered a new preparative route to bimetallocarboranes of the formula $(C_5H_5)_2Co_2C_2B_8H_{10}$ based upon thermally induced intermolecular metal transfer (eq 1).

$$C_5H_5CoC_2B_8H_{10} \xrightarrow{\Delta} (C_5H_5)_2Co_2C_2B_8H_{10} \tag{1}$$

(six isomers)
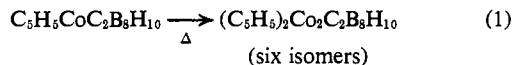
More surprisingly, similar products were obtained upon pyrolysis of the cobalticinium salt of the related commo metallocarborane, $[(C_5H_5)_2Co]^+[Co(C_2B_8H_{10})_2]^-$ (eq 2).

$$[(C_5H_5)_2Co]^+[Co(C_2B_8H_{10})_2]^- \xrightarrow{\Delta} (C_5H_5)_2Co_2C_2B_8H_{10} \tag{2}$$

(five isomers)
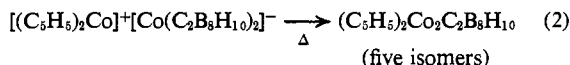
This discovery provides a new, experimentally convenient route to icosahedral bimetallocarboranes.

Rearrangement of $1-(\eta-C_5H_5)-1-Co-2,4-C_2B_8H_{10}$[3,4] to $1-(\eta-C_5H_5)-1-Co-2,3-C_2B_8H_{10}$[5] occurs at 350° under high vacuum in a hot tube[1] or at 145° in solution. Attempts to further rearrange $1-(\eta-C_5H_5)-1-Co-2,3-C_2-B_8H_{10}$ at 525° in a hot tube containing ceramic saddles resulted in an orange sublimate containing a mixture of products. Several species with mass spectral cutoffs at m/e 370 corresponding to the $^{11}B_8{}^{12}C_{12}{}^1H_{20}{}^{59}Co_2^+$ ion and isotopic distributions consistent with the formula $(C_5H_5)_2Co_2C_2B_8H_{10}$ were isolated. Increased yields resulted when the reaction was carried out in solution. After heating $1-(\eta-C_5H_5)-1-Co-2,3-C_2B_8H_{10}$ for 7 hr at 235° in hexadecane, five new red isomers and a green isomer of $(C_5H_5)_2Co_2C_2B_8H_{10}$ were produced in a total yield of 32% based on starting material consumed. Column and preparative thick-layer chromatography were used to purify the isomers which eluted in the order I–VI.[6] Three isomers were characterized by elemental analysis, while the formulas of the other

(1) M. K. Kaloustian, R. J. Wiersema, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **94**, 6679 (1972).
(2) D. F. Dustin, W. J. Evans, C. J. Jones, R. J. Wiersema, H. Gong, S. Chan, and M. F. Hawthorne, manuscript in preparation.
(3) C. J. Jones, J. N. Francis, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **94**, 8391 (1972).
(4) Formulas are numbered according to the guidelines outlined in R. M. Adams, *Pure Appl. Chem.*, **30**, 683 (1972).
(5) W. J. Evans, G. B. Dunks, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **95**, 4565 (1973).
(6) Melting points (deg): I, 132–135°; II, 225–227°; III, >310°; IV, 255–258°; V, 239–240°; VI (green), 275–277°.
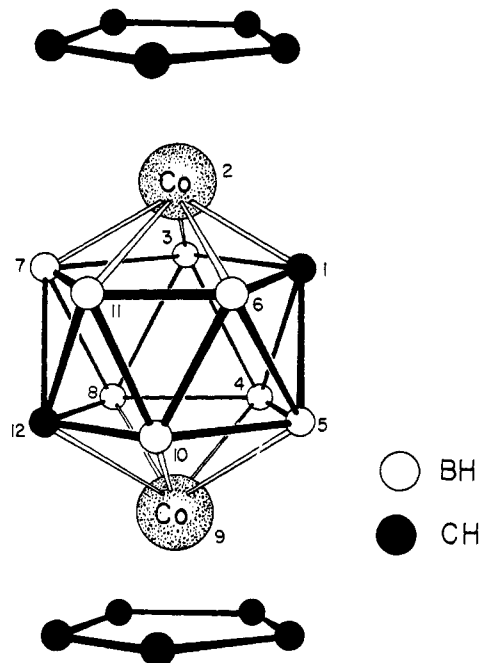
Figure 1. The structure of $2,9-(\eta-C_5H_5)_2-2,9-Co_2-1,12-C_2B_8H_{10}$.

Table I. 60-MHz ^1H and 80.5-MHz ^{11}B Nmr Spectra

Compound[a]	^1H C_5H_5, τ	^{11}B[b] chemical shift (rel intensity)
I	4.78, 4.96	−15.9 (2), −6.0 (1), −2.6 (1), +3.0 (1), +5.4 (1), +8.1 (1), +20.1 (1)
II	4.49, 4.92	−21.0 (2), −15.2 (1), −7.2 (1), −3.1 (2), +13.9 (2)
III	4.44	−1.4 (1), +6.4 (1)
IV	4.46, 4.98	−15.5 (1), −6.9 (1), +0.6 (1), +5.0 (1), +5.8 (1), +9.9 (1), +17.1 (1), +20.5 (1)
V	4.48, 4.71	−14.0 (1), −9.5 (1), −4.0 (1), −1.0 (1), +1.6 (1), +2.8 (1), +11.5 (1), +15.9 (1)
VI	4.08	−4.7 (1), +4.3 (2), +13.3 (1)

[a] In acetone-d_6. [b] Ppm *vs.* $BF_3 \cdot O(C_2H_5)_2$; all signals doublets with $J_{B-H} = 140 \pm 20$ Hz.

three were confirmed by exact mass measurement.[7] The ^{11}B nmr spectra and cyclopentadienyl proton resonances are listed in Table I.

The synthesis of I–V was also accomplished by heating $[(\eta-C_5H_5)_2Co]^+[1,1'-Co-(2,3-C_2B_8H_{10})_2]^-$[5] interspersed on ceramic saddles at 525° under high vacuum or by heating in hexadecane at 270°. Comparable yields were obtained from both neutral and ionic substrates. Higher molecular weight products including species believed to be alkylated bimetallics (based on mass spectral and electrochemical data) were also produced using the hexadecane method but not examined further.

Of the six isomers, the structure of III is specified uniquely by the nmr data as $2,9-(\eta-C_5H_5)_2-2,9-Co_2-1,12-C_2B_8H_{10}$ (Figure 1). This is the first example of an icosahedral metallocarborane containing metal atoms in the "para" positions.

Compound VI has been previously reported as a

(7) For example, Calcd for $(C_5H_5)_2Co_2C_2B_8H_{10}$: C, 39.10; H, 5.47; B, 23.46; Co, 31.97. Found: C, 39.40; H, 5.56; B, 22.42; Co, 31.54. Calcd m/e 370.0973. Found 370.0978 ± 0.0007.

product of the polyhedral expansion reaction,[5,8] and structurally characterized[9] as 2,3-(η-C$_5$H$_5$)$_2$-2,3-Co$_2$-1,7-C$_2$B$_8$H$_{10}$ by X-ray diffraction. The metal atoms occupy adjacent vertices in this isomer. While a large number of possible structures exist for I, II, IV, and V, we tentatively propose the following atomic arrangements based on a number of empirical observations of their spectral and physical properties; the carbon atoms are in 1,7 positions in all isomers, and cobalt positions are: I, 6,9; II, 3,9; IV, 2.5; and V, 3.6.[10]

Thermal polyhedral rearrangements of carboranes and metallocarboranes have been known for a number of years, but this is the first example of the preparation of an ($n + 1$)-vertex bimetallocarborane by pyrolysis of an n-vertex monometallocarborane. The synthesis of 12-vertex neutral species by pyrolysis of the cobalticinium salt of the commo-11-vertex complex is even more surprising.

Previous syntheses of (C$_5$H$_5$)$_2$Co$_2$C$_2$B$_8$H$_{10}$ isomers by polyhedral expansion[5,8] or contraction[12] produced at most two isomers. The thermal intermolecular metal transfer process described here occurs in an energetically rich environment and would be expected to afford a diversity of products. The predominant production of icosahedral bimetallocarboranes indicates the greater kinetic or thermodynamic stability of 12-vertex polyhedra and also expands the range of isomeric (C$_5$H$_5$)$_2$-Co$_2$C$_2$B$_8$H$_{10}$ species available for further investigation. Generalization of this method to other metallocarboranes is under investigation and may afford a new source of heretofore unknown polymetallocarboranes of diverse structures.

(8) W. J. Evans and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.,* 611 (1972).

(9) K. P. Callahan, C. E. Strouse, A. L. Sims, and M. F. Hawthorne, manuscript in preparation.

(10) Isomers II and V are also formed[2,11] by thermal rearrangement of 3,6-(π-C$_5$H$_5$)$_2$-3,6-Co$_2$-1,2-C$_2$B$_8$H$_{10}$[12] and similar rearrangements of the other isomers of (C$_5$H$_5$)$_2$Co$_2$C$_2$B$_8$H$_{10}$ are being examined to confirm the above assignments.

(11) B. Stibr, private communication.

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

William J. Evans, M. Frederick Hawthorne*

Contribution No. 3192
Department of Chemistry, University of California
Los Angeles, California 90024

Interconverting Cyclopropylcarbinyl Cations

Sir:

One of the longest sought after goals in mechanistic carbonium ion chemistry has been the nature of the intermediate involved in the rapid equilibration of cyclopropylcarbinyl, cyclobutyl, and homoallyl derivatives in protic solvents.[1] The suggestion, made more than a quarter of a century ago by Winstein and Adams,[2] that a cation might be involved has received

(1) For an excellent recent review see: K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe, III, in "Carbonium Ions," G. A. Olah and P. v. R. Schleyer, Ed., Vol. 3, Wiley, New York, N. Y., 1972, p 1295.

(2) S. Winstein and R. Adams, *J. Amer. Chem. Soc.,* **70,** 838 (1948).

overwhelming support and has led to two schools of thought. Reasoning primarily from product and rate data, the first preferred the existence of either one of the cyclopropylcarbinyl (I), cyclobutyl (II), or homoallyl cations *or* a rapid equilibration among two or more of them. More recently, however, Olah and his collaborators[3] have suggested the inadequacy of these "classical" representations.

While all indications point to classical structures for methyl and (geminally) dimethyl-substituted cyclopropylcarbinyl cations, with no sign of either degenerate rearrangement processes or equilibration with other forms taking place, the data seem not to be interpretable as such for the parent species. Rather, Olah best represents his (^{1}H and ^{13}C) nmr data in terms of a rapidly equilibrating set of σ delocalized structures.

It strikes these authors that Olah's strongest argument for such an assignment (or rather for deviation from a classical picture) rests not so much on direct structural evidence gathered for parent C$_4$H$_7^+$, but more on the observed lack of consistency between the nmr parameters for methyl-substituted ions and that for the parent itself.

In this communication we present evidence, resulting from theoretical *ab initio* molecular orbital calculations,[4] for a classical bisected cyclopropylcarbinyl type structure for all three ions. We suggest, moreover, that while parent C$_4$H$_7^+$ may readily undergo facile degenerate rearrangement interconverting the three equivalent cyclopropylcarbinyl valence tautomers, the introduction of either one or two (geminal) methyl substituents greatly enhances the stability of but one cyclopropylcarbinyl form effectively blocking the possibility of further rearrangement.

Recently we reported that all forms of the homoallyl cation collapsed without activation energy to bisected cyclopropylcarbinyl (I).[8] We have now resolved the structure of the puckered cyclobutyl cation (II) on this same potential surface. We find that like the homoallyl systems, the puckered cyclobutyl cation is unstable with respect to distortion in the direction of bisected cyclopropylcarbinyl, and hence may be thought of as one possible transition state to degenerate cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement. 4-31G level calculations indicate an activation of 9.4 kcal/mol (the difference in stabilities between groundstate cyclopropylcarbinyl and the puckered cyclobutyl

(3) G. A. Olah, C. L. Jeuell, D. P. Kelly, and R. D. Porter, *J. Amer. Chem. Soc.,* **94,** 146 (1972).

(4) The minimal STO-3G basis[5] has been used to calculate equilibrium and transition state geometries. Computations at interesting points on the resulting potential surface are then performed using the 4-31G extended basis set[6] in order to more accurately access relative molecular energetics. All calculations have been carried out using the GAUSSIAN 70 series of computer programs.[7]

(5) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.,* **51,** 2657 (1969).

(6) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.,* **54,** 724 (1971).

(7) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Ind., program no. 236.

(8) W. J. Hehre and P. C. Hiberty, *J. Amer. Chem. Soc.,* **94,** 5917 (1972).