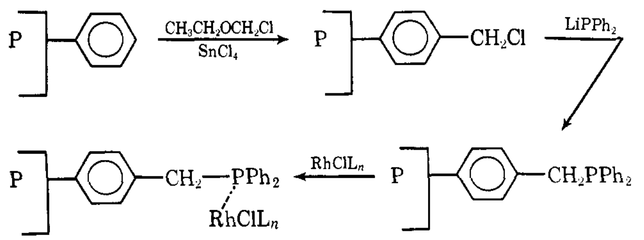
of tris(triphenylphosphine)chlororhodium(I)[5] for 2–4 weeks.



At the conclusion of the equilibration period the deep red beads were washed with deoxygenated benzene until the rinses were colorless for 3–5 successive cycles. Fresh oxygen-free benzene was then added and after equilibration of the catalyst under hydrogen at 1 atm for at least 1 hr, an olefin was added. A steady uptake of hydrogen then commenced and the reduced hydrocarbon could be observed by vpc analysis.

As can be seen from Table I, the rate of reduction depended on the molecular size of the olefin. Increasing the ring size of a cyclic olefin or going from an acyclic to a cyclic olefin decreased the rate of reduction. Large rigid olefins such as Δ^2-cholestene showed a dramatic decrease in reduction rate. We attribute this decrease in reduction rate to the restriction of the size of the solvent channels by the random cross-links in the polymer.[6] These observations also demonstrated that the major portion of the reductions was taking place inside of the polymer bead.[7] A surface reduction reaction would have shown a much lower specificity for the larger olefins (see Table I).

Table I

Olefin[a,d]	Beads rel rate[b]	$RhCl(Ph_3P)_3$ rel rate[b,c]
Cyclohexene	1	1.0
1-Hexene	2.55	1.4
Δ^2-Cholestene	1/32	1/1.4 (1/2.3)[e]
Octadecene (isom mix)	1/2.06	1/1.4
Cyclooctene	1/2.54	1.0
Cyclododecene (cis and trans)	1/4.45	1/1.5

[a] Measured by rate of hydrogen uptake at 1 atm. [b] 1 *M* olefin concentrations. [c] $(Ph_3P)_3RhCl$ 2.5 m*M*, in benzene at 25°. [d] The olefins were purified by distillation from sodium under nitrogen. [e] Ratio of H_2 uptake with 10% palladium on carbon.

The catalyst was easily recovered from the reagents by filtration and could be reused many times. The catalyst activity increased slowly to a maximum activity with use[8] and varied by ±5% over ten runs after the activity had maximized. The data given in Table I were obtained with one batch[9] of catalyst which reduced 1 *M* cyclohexene in benzene at a rate of 0.97 ml/min at 1 atm. The relative rates were determined by setting the rate of reduction of cyclohexene before and after the run on each olefin equal to 1.0. Different batches of the catalyst vary in activity.

Work is now in progress to further define the substrate specificity of these catalysts on the basis of substrate size, per cent of cross-linking in the polymer, and substrate polarity.

Acknowledgments. The authors wish to thank Mr. Terence K. Brunck for aid with the experimental work and The Dow Chemical Company, Midland, Mich., for a gift of the polymer beads used in this work.

Robert H. Grubbs,* LeRoy C. Kroll
Department of Chemistry, Michigan State University
East Lansing, Michigan 48823
Received March 9, 1971

---

(5) C. O'Conner and G. Wilkinson, *J. Chem. Soc. A*, 2665 (1968).

(6) A plot of average molecular size, as determined from molecular models, *vs.* corrected relative rates of reduction shows a reasonably linear relationship.

(7) R. B. Merrifield, *Science*, **150**, 178 (1965).

(8) R. L. Augustine and J. Van Pepper, *Chem. Commun.*, 571 (1970).

(9) Obtained by equilibrating 3.2 g of beads with 3.22 g of rhodium complex in 40 ml of benzene for 4 weeks under argon. Analysis showed 0.13 mmol of rhodium/g of beads.

An 11-Atom Polyhedral Metallocarborane Formed from 1,6-*closo*-$B_8C_2H_{10}$ by Polyhedral Expansion

Sir:

Recently the preparation of the $B_6C_2H_8^{2-}$,[1] $B_6C_2H_8^{4-}$,[2] and the $B_{10}C_2H_{12}^{2-}$ [3] ions by reduction of the corresponding *closo*-carboranes with sodium naphthalide and the reaction of these ions with transition metals have been reported. This method of creating polyhedral metallocarboranes may be called "polyhedral expansion" and may eventually prove to be a general reaction of *closo*-carboranes. We now wish to report the further extension of this synthetic method to form an 11-atom polyhedral complex containing formal Co(III) and the $B_8C_2H_{10}^{2-}$ ion, formed from 1,6-dicarba-*closo*-decaborane(10), 1,6-$B_8C_2H_{10}$.

Treatment of 1,6-$B_8C_2H_{10}$ in tetrahydrofuran (THF) at reflux with 2 equiv of sodium naphthalide, followed by addition of a fourfold excess of $Na^+C_5H_5^-$ and an excess of $CoCl_2$, yielded a mixture of products. A purple complex, formulated as $C_5H_5CoB_8C_2H_{10}$ (I), was isolated by column chromatography and recrystallized from hexane–dichloromethane in 38% yield, mp 297–300°. *Anal.* Calcd for $B_8C_2H_{10}CoC_5H_5$: B, 35.36; C, 34.37; H, 6.18; Co, 24.09. Found: B, 36.33; C, 34.03; H, 5.95; Co, 23.20. The mass spectrum exhibited a cutoff at *m/e* 246 corresponding to the $^{59}Co^{12}C_7{}^{11}B_8{}^1H_{15}{}^+$ ion. The electronic spectrum measured in acetonitrile was [λ_{max}, mμ (ϵ)] 230 (sh) (1100), 277 (3980), 352 (5820), 442 (382), 572 (455). The 32.1-MHz ^{11}B nmr spectrum in acetonitrile-d_3 contained doublets of relative area 1:2:1 at -8.5 (150), $+9.5$ (153), and $+21.7$ (139) [chemical shift, ppm, relative to $BF_3 \cdot O(C_2H_5)_2$ (coupling constant, Hz)]. The 60-MHz ^1H nmr spectrum consisted of a sharp singlet of area 5 at τ 4.32 and a broad singlet of area 1 at τ 3.28 which were assigned to the cyclopentadienyl and polyhedral C–H protons, respectively. A structure in which the cobalt completes an 11-member polyhedron with the carborane moiety is consistent with these data (Figure 1). This gross polyhedral geometry is seen in the $B_9C_2H_{11}$ carborane[4,5] and the isoelectronic $B_{11}H_{11}^{2-}$ ion.[6]

---

(1) G. B. Dunks, Ph.D. Dissertation, University of California, Riverside, Calif., 1970.

(2) G. B. Dunks and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **92**, 7213 (1970).

(3) G. B. Dunks and M. F. Hawthorne, *ibid.*, in press.

(4) T. E. Berry, F. N. Tebbe, and M. F. Hawthorne, *Tetrahedron Lett.*, **12**, 715 (1965).

(5) C. Tsai and W. E. Streib, *J. Amer. Chem. Soc.*, **88**, 4513 (1966).

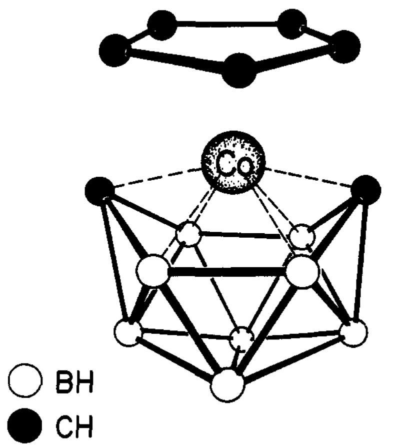


Figure 1. The proposed structure of $B_8C_2H_{10}CoC_5H_5$.

The major product resulting from treatment of 1,6-$B_8C_2H_{10}$ in THF at −78° with 2 equiv of sodium in the presence of a catalytic amount of naphthalene, followed by the addition of excess $CoCl_2$, was a green complex formulated as $Co(B_8C_2H_{10})_2^-$ (II). Complex *II* was isolated by column chromatography and recrystallized from acetone–water as its Cs^+ salt in 48% yield, mp 324° dec. *Anal.* Calcd for $[(B_8C_2H_{10})_2Co]^-Cs^+$: B, 39.96; C, 11.10; H, 4.62; Co, 13.61; Cs, 30.70; equiv wt, 433. Found: B, 40.07; C, 11.19; H, 5.00; Co, 13.14; Cs, 29.71; equiv wt, 457. The electronic spectrum determined in acetonitrile was [λ_{max}, mμ (ϵ)] 236 (28,000), 320 (16,100), 637[7] (155). The 32.1-MHz ^{11}B nmr spectrum of *II* was similar to that of I, having doublets of area ratio 1:2:1 at −8.9 (151), +7.5 (153), and +24.6 (136). The 60-MHz ^1H nmr spectrum contained a broad resonance at τ 4.57. These results suggest that the structure of the $B_8C_2H_{10}^{2-}$ ion in II is identical with that in I.

An X-ray diffraction study is planned to determine precisely the nature of the $B_8C_2H_{10}^{2-}$ ion. A number of additional products from these reactions are currently being investigated.

Acknowledgment. The authors wish to thank Dr. G. B. Dunks for helpful discussion. This research was supported in part by the Office of Naval Research and the Army Research Office (Durham).

---

[6] F. Klanberg and E. L. Muetterties, *Inorg. Chem.*, **5**, 1955 (1966).

[7] Broad, two overlapping unsymmetrical peaks.

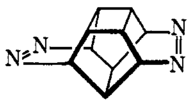
William J. Evans, M. Frederick Hawthorne*
Contribution No. 2795, Department of Chemistry
University of California, Los Angeles, California 90024

Received March 19, 1971

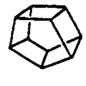
Synthesis and Reactions of 2,3,7,8-Tetraazahexacyclo-[7.4.1.$0^{4,12}$.$0^{5,14}$.$0^{6,11}$.$0^{10,13}$]tetradeca-2,7-diene[1]

Sir:

The thermal and photoinduced decomposition of alkyl cyclic azo compounds has been a subject of considerable interest.[2] We wish to report the synthesis and reactions of a cyclic bisazo compound, 2,3,7,8-tetraazahexacyclo[7.4.1.$0^{4,12}$.$0^{5,14}$.$0^{6,11}$.$0^{10,13}$]tetradeca-2,7-diene (**1**), an attractive and potential precursor of the hitherto unknown pentaprismane[3] **2**.



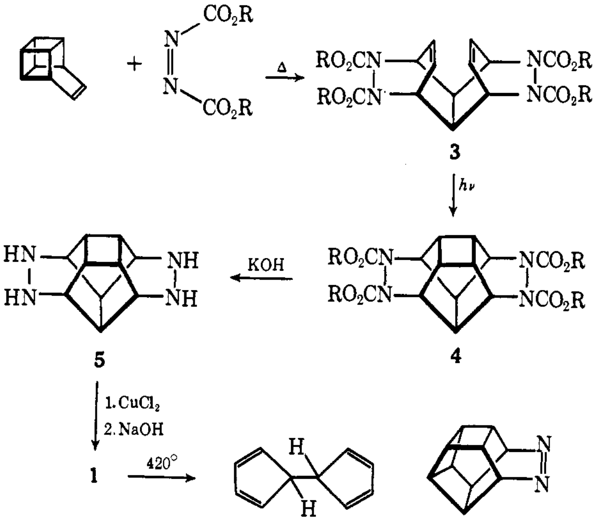
1



2

Reaction of pentacyclo[4.4.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]dec-9-ene[4] with diethyl azodicarboxylate (*cf.* Scheme I) (2.5:1 mole ratio) at 76° yielded the 2:1 adduct **3** in 85% yield: mp 190–191°; τ ($CDCl_3$) 3.5–6.2 (m, 4 H), 4.9–5.5 (m, 4 H), 5.77 (q, 8 H), 7.07 (broad S, 2 H), 8.75 (t,12 H).[5] When **3** was photolyzed in dry acetone (Vycor filter) for 5 hr, **4** was obtained in 90% yield: mp 155–156°; τ ($CDCl_3$) 5.72 (q, 8 H), 5.69 (under 5.7 quartet, 4 H), 7.00 (m, 6 H), 8.68 (t,12 H). Hydrolysis–decarboxylation of **4** with hot potassium hydroxide in methanol gave hydrazine **5**. Treatment of **5** with cupric chloride in water gave a dark brick red cuprous chloride complex of **1**. Bisazo compound **1** was generated by dissolving the cuprous complex in alkaline aqueous solution and extracting with chloroform (60% yield; mp 320° (sealed tube); τ ($CDCl_3$) 4.32 (m, 4 H), 7.52 (m, 4 H), 8.24 (m, 2 H); ν_{max}^{KBr} 1518 cm^{-1} (-N=N-); $\lambda_{max}^{CH_3CN}$ 360 mμ (ϵ ~540)).

Scheme I



Compound **1** was thermally stable ($t_{1/2}$ = 0.53 hr at 250°). Flash vacuum pyrolysis (FVP) of **1** at 420° gave 9,10-dihydrofulvalene[6] as the only identifiable

---

[1] K. W. Shen and L. J. Winters, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971, Abstract ORGN 57.

[2] (a) P. D. Bartlett and N. A. Porter, *J. Amer. Chem. Soc.*, **90**, 5317 (1968); (b) E. L. Allred and R. L. Smith, *ibid.*, **89**, 7311 (1967); (c) *ibid.*, **91**, 6766 (1969); (d) W. R. Roth and M. Martin, *Tetrahedron Lett.*, **39**, 3865 (1967); (e) J. A. Berson and S. S. Olin, *J. Amer. Chem. Soc.*, **91**, 777 (1969); (f) C. G. Overberger and J. W. Stoddard, *ibid.*, **92**, 4922 (1970); (g) P. D. Condit and R. G. Bergman, *Chem. Commun.*, 4 (1971); (h) R. J. Crawford, *Can. J. Chem.*, **48**, 628 (1970); (i) P. S. Engel and P. D. Bartlett, *J. Amer. Chem. Soc.*, **92**, 5883 (1970), and references cited in these papers.

[3] H. P. Schultz, *J. Org. Chem.*, **30**, 1361 (1965).

[4] (a) S. Masamune, H. Cuts, and M. G. Hogben, *Tetrahedron Lett.*, 1017 (1966); W. G. Dauben and D. L. Whalen, *ibid.*, 3743 (1966); (b) E. LeGoff and S. Oka, *J. Amer. Chem. Soc.*, **91**, 5665 (1969); H. H. Westberg, E. N. Cain, and S. Masamune, *ibid.*, **91**, 7512 (1969).

[5] After hydrolysis–decarboxylation of **3**, followed by oxidation with mercuric oxide, *cis*-9,10-dihydronaphthalene was obtained. This further confirms the structure of **3** as shown: K. W. Shen, *Chem. Commun.*, 391 (1971).