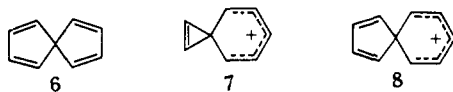


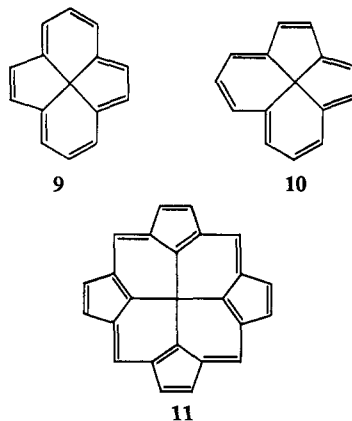
ceptor. The hypothetical molecule **5** combines these factors with destabilization of the tetrahedral form. Further favorable effects of an electronegativity differential are observed on Li substitution or replacement of C by N<sup>+</sup>.<sup>8</sup>

New types of stabilization in planar systems with tetracoordinate carbon may be probed with standard Hückel calculations. Thus the neutral spironon-tetraene **6** and the cations **7** and **8** in their planar geometries are stabilized 10-, 8-, and 10 $\pi$ -electron systems, respectively, superimposed on a positively charged  $\sigma$  core. Their highest occupied and lowest unoccupied



MO's are at +0.62 and -0.62 $\beta$  for **6**, +0.37 and -1.00 for **7**, +0.62 and -0.29 for **8**. In an extended Hückel calculation on **7** we find the tetrahedral form favored by only 1.1 eV. Chiral derivatives of **6** are known but do not racemize readily;<sup>9</sup> in these cases benzo fusion makes worse the steric problems apparent in a planar geometry of **6**.

Still more promising systems are created when a central carbon atom is fused to an annulene perimeter. For example, the chiral molecules **9** and **10**, highly



strained in their normal geometries, possess stable 16 $\pi$ -electron systems when planar. The porphyrin-like hydrocarbon **11** is also stabilized.<sup>10</sup>

(8) In any practical example a planar transition state for racemization must compete with pathways such as facilitated heterolytic or homolytic cleavage followed by recombination. The relative merits of the various mechanisms are, we feel, too delicate a question to evaluate given the available computational schemes. They must, of course, be considered in practice.

(9) Vespirenes: G. Haas and V. Prelog, *Helv. Chim. Acta*, **52**, 1202 (1969). The substituted achiral system **6** is also known: E. T. McBee, G. W. Calundann, and T. Hodgins, *J. Org. Chem.*, **31**, 4260 (1966).

(10) As a preliminary criterion for stability we take the absence of nonbonding molecular orbitals, the occupation of only bonding orbitals, and the presence of a sizable gap between highest filled and lowest unfilled molecular orbitals. Criteria for stabilization may be derived (C. F. Wilcox, to be published); it suffices to say at this time that most likely candidates fail these tests. If we denote these molecules by the rings involved (for example **6** would be [5,5], **7** = [3,6], **9** = [5,6,5,6], **10** = [5,5,6,6]) then other stabilized species we have found are [5,3,5], [5,7,5], [5,6,7], [3,5,5,5], [3,5,6,5], and [5,6,6,6].

For further prospects we turn to model transition metal complexes for the type **12**, e.g., M = Fe, X = CO.



The cyclopentadiene is acting as a four-electron ligand. If the group X is modified or removed, so that a six-electron donor is needed to satisfy the electronic demands of M, there could occur a rotation of the CY<sub>2</sub> group to fulfill this requirement.

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### Preparation and Crystallographic Characterization of the [B<sub>9</sub>C<sub>2</sub>H<sub>11</sub>·Co·B<sub>8</sub>C<sub>2</sub>H<sub>10</sub>·Co·B<sub>8</sub>C<sub>2</sub>H<sub>10</sub>·Co·B<sub>9</sub>C<sub>2</sub>H<sub>11</sub>]<sup>3-</sup> Anion. A System with Four Fused Icosahedra

Sir:

We wish to report the preparation and crystallographic characterization of a fused polyhedral system which contains three formal d<sup>6</sup> Co(III) ions sandwiched between two B<sub>8</sub>C<sub>2</sub>H<sub>10</sub><sup>4-</sup>  $\pi$ -bidentate ligands and two  $\pi$ -monodentate B<sub>9</sub>C<sub>2</sub>H<sub>11</sub><sup>2-</sup> ligands which serve as chain caps (Figure 1).

Recently,<sup>1,2</sup> the complex ion [B<sub>9</sub>C<sub>2</sub>H<sub>11</sub>CoB<sub>8</sub>C<sub>2</sub>H<sub>10</sub>·CoB<sub>9</sub>C<sub>2</sub>H<sub>11</sub>]<sup>2-</sup> was reported to arise from the base degradation of the (B<sub>9</sub>C<sub>2</sub>H<sub>11</sub>)<sub>2</sub>Co<sup>-</sup> ion in aqueous media. The new tricobaltate complex reported here has been isolated from among the products of this reaction. Details of the preparation and unusual chemical properties of this new complex ion will be reported elsewhere.

The tetraethylammonium salt, [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N<sup>+</sup>]<sub>3</sub>[B<sub>9</sub>C<sub>2</sub>H<sub>11</sub>·Co·B<sub>8</sub>C<sub>2</sub>H<sub>10</sub>·Co·B<sub>8</sub>C<sub>2</sub>H<sub>10</sub>·Co·B<sub>9</sub>C<sub>2</sub>H<sub>11</sub>]<sup>3-</sup>, crystallizes from an acetone-water solution as deep red parallelepipeds belonging to the centrosymmetric triclinic space group *P* $\bar{1}$  (*C*<sub>1</sub><sup>1</sup>, no. 2) with unit cell parameters *a* = 12.248, *b* = 26.733, *c* = 20.428 Å,  $\alpha$  = 113.34,  $\beta$  =

(1) J. N. Francis and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **90**, 1663 (1968).

(2) D. St. Clair, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **8**, 2080 (1969).

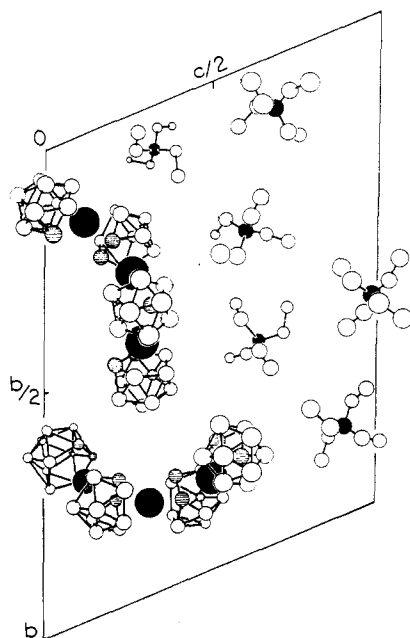


Figure 1. The asymmetric unit (two formula units of  $[(C_2H_5)_4N^+]_3 \cdot [B_9C_2H_{11} \cdot Co \cdot B_8C_2H_{10} \cdot Co \cdot B_8C_2H_{10} \cdot Co \cdot B_9C_2H_{11}]^{3-}$ ) projected on (100). Cobalt and nitrogen atoms are in black; carbon atoms of the carborane systems are shaded.

86.70,  $\gamma = 102.98^\circ$ .<sup>3</sup> The observed density,  $\rho_{\text{obsd}} = 1.19 \pm 0.01 \text{ g cm}^{-3}$  (by flotation in aqueous zinc iodide solution), is consistent with that calculated for  $M = 1073.72$  and  $Z = 4$  ( $\rho_{\text{calcd}} = 1.194 \text{ g cm}^{-3}$ ).

While good-sized crystals could easily be obtained, optical examination showed many to be hollow; all crystals examined gave unusually weak diffraction patterns. X-Ray data complete to  $\sin \theta = 0.63$  (Cu  $K\alpha$  radiation)<sup>4</sup> were collected with a 0.01 incrementing Supper-Pace Buerger Automated Diffractometer using a stationary-background,  $\omega$ -scan, stationary-background counting sequence. All data were corrected for absorption ( $\mu = 64.46 \text{ cm}^{-1}$ ) and the structure was solved, with considerable difficulty, by a combination of Patterson, Fourier, and least-squares refinement techniques. The asymmetric unit consists of two well-defined  $[B_9C_2H_{11} \cdot Co \cdot B_8C_2H_{10} \cdot Co \cdot B_8C_2H_{10} \cdot Co \cdot B_9C_2H_{11}]^{3-}$  anions and six poorly defined  $[(C_2H_5)_4N^+]$  cations. The present discrepancy index, after several cycles of positional and isotropic thermal parameter refinement for the 144 independent nonhydrogen atoms, is  $R_F = 14.1\%$  for 3994 independent nonzero reflections. Refinement is continuing. The crystallographic asymmetric unit is shown in Figure 1. (Carbon atoms of the icosahedral cages are identified by the following properties: (i) on electron density maps they appear as larger peaks than do the boron atoms; (ii) when all light atoms of the icosahedral cages are specified as boron atoms, refinement leads to negative isotropic thermal parameters for the carbon atoms; (iii) interatomic C-C and C-B distances are significantly shorter than B-B distances.)

(3) We have recently discovered a monoclinic modification, space group  $P2_1/c$ , with  $a = 19.998$ ,  $b = 14.110$ ,  $c = 21.369 \text{ \AA}$ ,  $\beta = 101.52^\circ$ ,  $Z = 4$ . Crystallographic studies on this polymorph are presently in progress.

(4) The use of copper radiation was necessary in order to resolve adjacent reflections and to obtain diffraction data of reasonable intensity.

The two crystallographically independent  $[B_9C_2H_{11} \cdot Co \cdot B_8C_2H_{10} \cdot Co \cdot B_8C_2H_{10} \cdot Co \cdot B_9C_2H_{11}]^{3-}$  ions show essentially identical features. The terminal formal cobalt(III) ions are each linked to a  $C_2B_3$  face of a  $B_9C_2H_{11}^{2-}$  ligand and to a  $C_2B_3$  face of a  $B_8C_2H_{10}^{4-}$  ligand; the central cobalt(III) ion is bonded to  $C_2B_3$  faces of two  $B_8C_2H_{10}^{4-}$  ligands. Average dimensions within the anions are (in  $\text{\AA}$ ):  $Co \cdots Co = 3.80$ ,  $Co-C = 2.05$ ,  $Co-B = 2.14$ ,  $C-C = 1.60$ ,  $C-B = 1.75$ , and  $B-B = 1.83$ .

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### Vapor Phase Fluorination with Xenon Difluoride. Facile Substitution of Fluorine into Aromatic Compounds<sup>1</sup>

Sir:

We wish to report that  $XeF_2$  is an efficient and well-behaved fluorinating agent for aromatic compounds in the vapor phase. In particular we have shown that it causes facile substitution of fluorine into such molecules as benzene, nitrobenzene, and substituted fluorobenzenes.

Specific instances of fluorination by  $XeF_2$  have already been reported from this and other laboratories.<sup>2,3</sup> Shieh, Yang, and Chernick<sup>2a</sup> studied the addition reactions of xenon fluorides with several olefins, e.g.,  $XeF_4$  with perfluoropropylene and  $XeF_2$  and  $XeF_4$  with ethylene and propylene. Recently Hyman, *et al.*, used  $XeF_2$  to carry out substitution of benzene neat and in  $CCl_4$  solution,<sup>2b</sup> and toluene, fluorobenzene, and benzotrifluoride in  $CCl_4$  solution.<sup>2c</sup>

Our previous work<sup>3</sup> showed that a very smooth and efficient addition of two fluorine atoms occurred when  $XeF_2$  vapor was heated at 100-200° with octafluoronaphthalene or hexafluorobenzene vapor. Similar results were subsequently obtained with decafluorobiphenyl, so this vapor phase addition reaction is presumably general for perfluoroaromatics. We have since addressed ourselves to the possibility, suggested by the work of Hyman, *et al.*,<sup>2b,c</sup> that fluorine substitution of aromatic hydrocarbons might be general with the use of  $XeF_2$  under appropriate conditions, such as vapor phase and moderate temperature. The compounds we have used are benzene, nitrobenzene, *o*-

(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

(2) (a) T. Shieh, N. C. Yang, and C. L. Chernick, *J. Amer. Chem. Soc.*, **86**, 5021 (1964); (b) M. J. Shaw, H. H. Hyman, and R. Filler, *ibid.*, **91**, 1563 (1969); (c) M. J. Shaw, J. A. Weil, and H. H. Hyman, Paper FLUO-2, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969.

(3) Annual Report, Nuclear Engineering Department, Brookhaven National Laboratory, BNL 50082 (S-70), Dec 31, 1967, p 33.