

Figure 1. Possible isomer structures of the  $(B_7C_2H_9)_2Co^-$  ion.

These nmr results prove that the  $B_7C_2H_9^{-2}$  ligand has very low symmetry with all carbon and boron atoms in unique environments.

A mixed complex (II) of formal cobalt(III) was prepared in 36% yield from the reaction of cobalt(II) chloride with the  $B_7C_2H_{11}^{-2}$  ion and a fivefold excess of the  $C_5H_5^-$  ion in diethyl ether. The red complex (II) was easily purified by sublimation or by recrystallization.

$C_5H_5^- + 1.5Co^{+2} + B_7C_2H_{11}^{-2} \longrightarrow$   
 $H_2 + 0.5Co^0 + (C_5H_5)Co(B_7C_2H_9)$

tion from hexane, mp 158–159°. *Anal.* Calcd for  $(B_7C_2H_9)Co(C_5H_5)$ : C, 36.12; H, 6.06; B, 32.80; Co, 25.31. Found: C, 36.10; H, 6.09; B, 32.90; Co, 25.07. High-resolution mass spectroscopy unequivocally verified the formulation  $CoB_7C_7H_{14}$ : calcd for  $^{59}Co^{11}B_7^{12}C_7^{1}H_{14}$ , 234.108; found, 234.109. The electronic spectrum was determined in acetonitrile [ $\lambda_{max}$  m $\mu$  ( $\epsilon$ ): 270 (15,400), 315 (4800), 365(sh) (1800), and 502 (345)].

The 60-Mc/sec  $^1H$  nmr spectrum of II contained a sharp cyclopentadienyl resonance at  $\tau$  3.9. The protons associated with the carbon atoms of the  $B_7C_2H_9^{-2}$  ligand were very broad and appeared at  $\tau$  2.31 and 6.23. The 32-Mc/sec  $^{11}B$  nmr spectrum resembled that obtained with the complex I and consisted of seven discrete doublets.

Since the nmr results, composition, and charge type of both I and II indicate that each carbon and boron atom carries one proton and that cobalt(III) couples two ligands (identical in the case of I), it is attractive to formulate the gross structures of I and II as species in which the metal ion completes a polyhedral surface containing one or two  $B_7C_2H_9^{-2}$  fragments. This being the case, one would expect the complex polyhedron to resemble the well-known  $B_{10}H_{10}^{-2}$ ,<sup>3</sup>  $B_9CH_{10}^-$ ,<sup>4</sup> and  $B_8C_2H_{10}^-$ <sup>5</sup> structures. Ruling out the possibility of carbon-atom nearest neighbors and giving cobalt a coordination number of 5, including two carbon atoms (one at an apex position since the  $^{11}B$  nmr spectrum indicated one apical boron atom at low field),<sup>6</sup> we were led to propose structures such as those shown in Figures 1 and 2. Preliminary X-ray diffraction results obtained by

(3) M. F. Hawthorne and A. R. Pitochelli, *J. Am. Chem. Soc.*, **81**, 5519 (1959).

(4) W. H. Knoth, *ibid.*, **89**, 1274 (1967).

(5) F. N. Tebbe, P. M. Garrett, D. C. Young, and M. F. Hawthorne, *ibid.*, **88**, 609 (1966).

(6) W. N. Lipscomb, A. R. Pitochelli, and M. F. Hawthorne, *ibid.*, **81**, 5833 (1959).

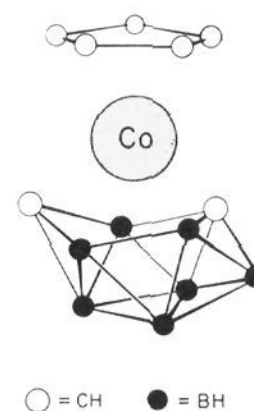


Figure 2. Proposed structure of  $(C_5H_5)Co(B_7C_2H_9)$ .

using tetraethylammonium(I) confirm<sup>7</sup> this gross structure of I and place the carbon-atom positions as shown in the antiisomer of Figure 1.

While only the complexes of formal cobalt(III) were presented here, further preliminary work suggests that many other polyhedral complexes may be prepared which incorporate the  $B_7C_2H_9^{-2}$  ligand. Further work is in progress.

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### The $B_6C_2H_8^{-2}$ Ligand in a New Polyhedral Transition Metal Complex Containing Manganese

Sir:

The accompanying communication<sup>1</sup> describes the preparation of two polyhedral cobalt complexes which contain the  $B_7C_2H_9^{-2}$  ligand and in which the transition metal completes a bicapped Archimedean antiprism. We now wish to describe the preparation of what may prove to be a polyhedral complex which assumes a tricapped trigonal prism configuration with a  $B_6C_2H_8^{-2}$  ligand in conjunction with a transition metal.

The reaction of  $BrMn(CO)_5$ <sup>2</sup> with the  $B_7C_2H_{11}^{-2}$  ion<sup>1</sup> in tetrahydrofuran solution at the reflux temperature led to the formation of  $Mn_2(CO)_{10}$ , unidentified solids,  $H_2$ ,  $CO$ , and a 48% yield of a new anion (I). The  $Mn_2(CO)_{10}$  and sodium I were separated by using column chromatography on silica gel with hydrocarbon solvents. The tetramethylammonium or  $BH_2(py)_2^+$  salts of I were prepared by precipitation from water and recrystallized from organic solvents. Salts of I were stable indefinitely in the solid state in air but decomposed slowly in solution. The anion I was characterized as  $B_6C_2H_8Mn(CO)_3^-$ . *Anal.* Calcd for  $CsB_6C_2H_8Mn(CO)_3$ : B, 17.54; C, 16.27; H, 2.17; Cs, 36.03; Mn, 14.88. Found: B, 17.91; C, 16.22; H, 2.13; Cs, 34.85; Mn, 14.54. Calcd for  $(CH_3)_4NB_6C_2H_8Mn(CO)_3$ : equiv wt, 309.7. Found: equiv wt, 312. Calcd for  $(C_2H_5)_4NB_6C_2H_8Mn(CO)_3$ : formula wt, 366. Found: formula wt, 369, assuming 100% dissociation in acetone solution (osmometric). An infrared spectrum of the tetramethyl-

(1) M. F. Hawthorne and T. A. George, *J. Am. Chem. Soc.*, **89**, 7114 (1967).

(2) E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1501 (1959).

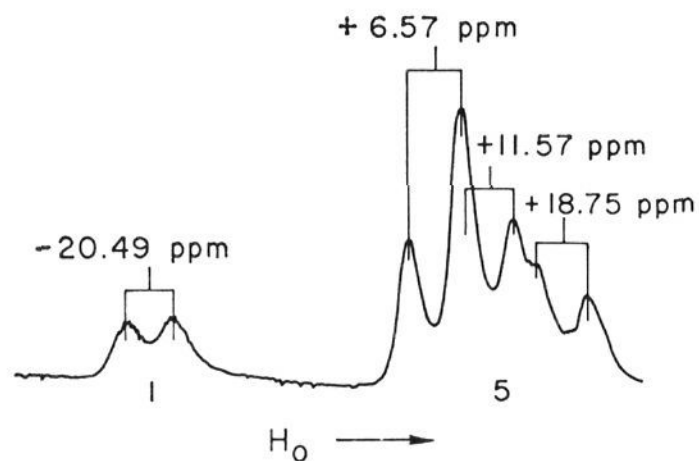


Figure 1. The  $^{11}\text{B}$  nmr spectrum of  $(\text{B}_6\text{C}_2\text{H}_8)\text{Mn}(\text{CO})_3^-$  in deuterioacetone at 32 Mc/sec. Chemical shifts measured relative to  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ .

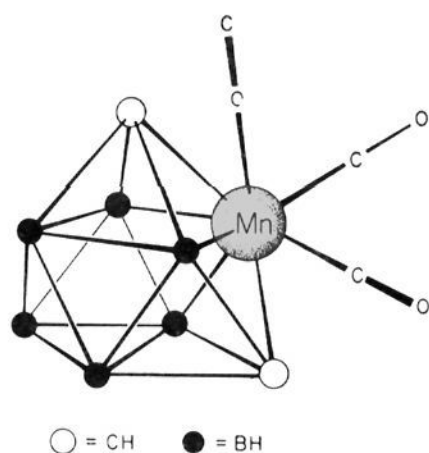


Figure 2. Proposed structure for  $(\text{B}_6\text{C}_2\text{H}_8)\text{Mn}(\text{CO})_3^-$ .

ammonium salt of I in tetrahydrofuran solution contained a band at  $2540\text{ cm}^{-1}$ , ascribed to B-H stretch, and carbonyl stretching bands at  $2000$  and  $1920\text{ cm}^{-1}$ . Electronic spectra were determined in acetonitrile solution [ $\lambda_{\text{max}}$   $m\mu$  ( $\epsilon$ ): 215 (sh) ( $\sim 36,000$ ), 287 (sh) (11,000), and 423 (4250)].

Figure 1 presents the 32-Mc/sec  $^{11}\text{B}$  nmr spectrum of tetramethylammonium I in deuterioacetone solution. Taking the low-field doublet of relative intensity 1, a 1:2:2:1 pattern of doublets is easily discerned. Similar  $^{11}\text{B}$  nmr spectra of the  $\text{BH}_2(\text{py})_2^+$  salt of I gave essentially the same result except for the fact that the high-field array integrated with a relative intensity of 6 due to the broad  $^{11}\text{B}$  resonance of the cation.<sup>3</sup> The  $^1\text{H}$  nmr spectrum of tetramethylammonium I contained a sharp singlet at  $\tau$  6.27 of relative intensity 12 which was assigned to the cation and a single resonance of relative intensity 2 at  $\tau$  4.3. The latter resonance was assigned to two equivalent protons attached to the carbon atoms of the  $\text{B}_6\text{C}_2\text{H}_8^{-2}$  ligand.

The equivalence of the two carbon atoms and the 1:2:2:1  $^{11}\text{B}$  nmr population coupled with the other characterization data suggests that the structure presented in Figure 2 approximates the structure of I. In this structure the  $\text{Mn}(\text{CO})_3$  moiety occupies a position between two equivalent apical carbon atoms. The third apical position must then be occupied by a boron atom, and this atom appears to reside at low field in the  $^{11}\text{B}$  nmr spectrum.<sup>4</sup>

The appearance of  $\text{Mn}_2(\text{CO})_{10}$  in the reaction products suggests that  $\text{BrMn}(\text{CO})_5$  functions as an oxidizing agent

(3) G. E. Ryschkewitsch, *J. Am. Chem. Soc.*, **89**, 3145 (1967).

(4) W. N. Lipscomb, A. R. Pitochelli, and M. F. Hawthorne, *ibid.*, **81**, 5833 (1959).

which degrades either the  $\text{B}_7\text{C}_2\text{H}_{11}^{-2}$  ion or an intermediate which contains seven boron atoms to produce the observed  $\text{B}_6$  ligand.

Further work is in progress with this and similar systems which will be reported elsewhere.

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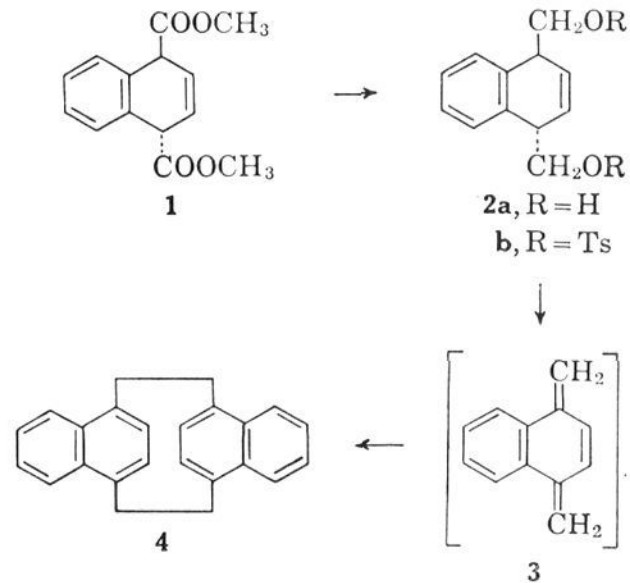
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## A Novel Synthesis of [2.2]Paracyclophanes

Sir:

[2.2]Paracyclophanes (e.g., **4**, **8**) are an interesting group of substances since they exhibit unusual transannular effects.<sup>1</sup> Unfortunately, all the methods known for the synthesis of simple members<sup>2-6</sup> involve a cyclization step which proceeds in rather unsatisfactory yield (not above 25%).<sup>7</sup> We now describe a new synthesis of this class of compound using a cyclization step which proceeds in considerably higher yield than those obtained previously.

Methyl *trans*-1,4-dihydronaphthalene-1,4-dicarboxylate (**1**)<sup>8</sup> was reduced with lithium aluminum hydride to the diol **2a**,<sup>9</sup> which on treatment with *p*-toluenesulfonyl



(1) See R. C. Helgeson and D. J. Cram, *J. Am. Chem. Soc.*, **88**, 509 (1966), and earlier papers in the series. For a review, see B. H. Smith, "Bridged Aromatic Compounds," Academic Press Inc., New York, N. Y., 1964.

(2) C. J. Brown and A. C. Farthing, *Nature*, **164**, 915 (1949); C. J. Brown, *J. Chem. Soc.*, 3265 (1953).

(3) (a) D. J. Cram and H. Steinberg, *J. Am. Chem. Soc.*, **73**, 5691 (1951); (b) D. J. Cram, C. K. Dalton, and G. R. Knox, *ibid.*, **85**, 1088 (1963).

(4) H. E. Winberg, F. S. Fawcett, W. E. Mochel, and C. W. Theobald, *ibid.*, **82**, 1428 (1960); H. E. Winberg and F. S. Fawcett, *Org. Syn.*, **42**, 83 (1962).

(5) L. A. Errede and J. P. Cassidy, *J. Am. Chem. Soc.*, **82**, 3653 (1960); L. A. Errede, R. S. Gregorian, and J. M. Hoyt, *ibid.*, **82**, 5218 (1960); L. A. Errede, *ibid.*, **83**, 949 (1961).

(6) (a) D. T. Longone and C. L. Warren, *ibid.*, **84**, 1507 (1962); (b) D. T. Longone and F. P. Boettcher, *ibid.*, **85**, 3436 (1963); (c) D. T. Longone and M. T. Reetz, *Chem. Commun.*, 46 (1967).

(7) J. H. Golden (*J. Chem. Soc.*, 3741 (1961)) has reported that tetrabenzo[2.2]paracyclophane (the 9,10-dianthracene analog of **4** and **8**) is formed in 40-63% yield by treatment of 9,10-di(chloromethyl)anthracene and 9,10-di(bromomethyl)anthracene with sodium iodide, but the application of this method to the synthesis of simpler members has not been described.

(8) Substance **1** is readily prepared from naphthalene by successive treatment with sodium and carbon dioxide, followed by esterification (T. M. Lyssy, *J. Org. Chem.*, **27**, 5 (1962)).

(9) S. Hsi-Kwei Jiang, *Hua Hsueh Hsueh Pao*, **23**, 351 (1957) (*Chem. Abstr.*, **52**, 15481 (1958)).