

**Carbametallc Boron Hydride Derivatives.**  
**II. Apparent Analogs of  $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_3$**   
**and  $\pi\text{-C}_5\text{H}_5\text{Re}(\text{CO})_3$**

Sir:

In a previous communication<sup>1</sup> we reported the preparation of ionic species which may be ferrocene and ferricinium ion analogs in which the  $\text{C}_5\text{H}_5^-$  ring systems were replaced by two  $\text{B}_9\text{C}_2\text{H}_{11}^{-2}$  (I) ions. I is believed to have the geometry of an eleven-particle icosahedral fragment with six electrons in three bonding molecular orbitals formed at the open face.<sup>1</sup> We now wish to report the synthesis of stable anions which appear to be analogous to  $\pi$ -cyclopentadienylmanganese tricarbonyl<sup>2,3</sup> and the corresponding rhenium compound.<sup>4,5</sup> A proposed structure presented in Figure 1

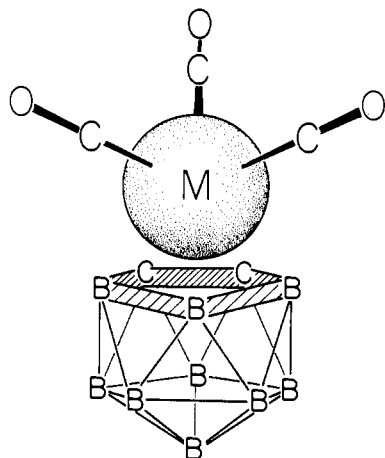
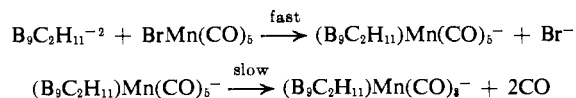


Figure 1. A possible structure for  $(\text{B}_9\text{C}_2\text{H}_{11})\text{Mn}(\text{CO})_3^-$  and  $(\text{B}_9\text{C}_2\text{H}_{11})\text{Re}(\text{CO})_3^-$  (H atoms have been omitted).

is consistent with the formulation of these anions as  $(\text{B}_9\text{C}_2\text{H}_{11})\text{Mn}(\text{CO})_3^-$  (II) and  $(\text{B}_9\text{C}_2\text{H}_{11})\text{Re}(\text{CO})_3^-$  (III). Both II and III were prepared from the corresponding bromometal pentacarbonyl<sup>6,7</sup> and the sodium salt of I<sup>1</sup> in tetrahydrofuran solution at the reflux temperature. In both systems sodium bromide (90% yield) precipitated immediately after mixing the reagents, and 2 moles of CO was evolved during a 2-hr. period. These results suggest the initial formation of unstable  $(\text{B}_9\text{C}_2\text{-$



$\text{H}_{11})\text{Mn}(\text{CO})_5^-$  and  $(\text{B}_9\text{C}_2\text{H}_{11})\text{Re}(\text{CO})_5^-$  intermediates. Yields of II and III were of the order of 80–90% when isolated as their  $\text{Cs}^+$  or  $(\text{CH}_3)_4\text{N}^+$  salts. The cesium salts could be recrystallized without change from water.

*Anal.* Calcd. for  $(\text{B}_9\text{C}_2\text{H}_{11})\text{Mn}(\text{CO})_3\text{Cs}$ : B, 24.06; C, 14.85; H, 2.74; Mn, 13.59; Cs, 32.87; equiv.

(1) M. F. Hawthorne, D. C. Young, and P. A. Wegner, *J. Am. Chem. Soc.*, **87**, 1818 (1965).

(2) T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).

(3) E. O. Fischer and R. Jira, *Z. Naturforsch.*, **9b**, 618 (1954).

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

(7) W. Hieber and H. Fuchs, *Z. anorg. allgem. Chem.*, **248**, 256 (1941).

wt., 404. Found: B, 24.15; C, 14.72; H, 3.17; Mn, 13.2; Cs, 32.88; equiv. wt., 410.8.<sup>8</sup>

*Anal.* Calcd. for  $(\text{B}_9\text{C}_2\text{H}_{11})\text{Re}(\text{CO})_3\text{Cs}$ : B, 18.17; C, 11.21; H, 2.07; Re, 34.77; Cs, 24.82; equiv. wt., 536. Found: B, 18.00; C, 11.70; H, 2.15; Re, 35.27; Cs, 24.05; equiv. wt., 547.9.<sup>8</sup> The <sup>11</sup>B n.m.r. spectra of II and III were essentially identical and extended over 30 p.p.m. They have not been interpreted except that a gross similarity to  $\text{B}_9\text{C}_2\text{H}_{12}^-$  was noted. The infrared spectra of II and III contained B–H stretching bands near 2550  $\text{cm}^{-1}$  and carbonyl stretching bands between 2150 and 1850  $\text{cm}^{-1}$ . Electronic spectra were determined in methanol [ $\lambda_{\text{max}}$  m $\mu$  ( $\epsilon$ ): II, 212 (33,300) and 346 (2500); III, 210 (24,000) and 272 (2900)]. Degradation of II with concentrated aqueous hydroxide ion in the presence of air at 100° for 6 hr. produced  $\text{MnO}_2$  (85%) and the  $\text{B}_9\text{C}_2\text{H}_{12}^-$  ion.

Further synthetic and structural studies are in progress.

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(8) Equivalent weights were determined with an accuracy of  $\pm 3\%$  by passing a 50-mg. sample of the compound through an acidified cation-exchange column (Ion-X Resin, Dowex type, 50–100 mesh) and titrating the liberated acid with standard base. The titration curves obtained in each case were those of a strong monobasic acid.

(9) Alfred P. Sloan Research Fellow.

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**The Phthalocyanine of Gold<sup>1</sup>**

Sir:

Gold phthalocyanine has been prepared by the action of gold monobromide<sup>2a</sup> on molten 1,3-diiminoisodoline,<sup>2b</sup> in the absence of solvent.

Phthalocyanines with two monovalent transition metal atoms, analogous to the alkali metal derivatives, are unknown.<sup>3</sup> The compounds of gold(III) so far examined had been found to be diamagnetic, four-coordinated, and square-planar.<sup>4</sup> These properties are incompatible with bonding to a *divalent*, four-coordinating, and square-planar ligand such as phthalocyanine. However, in 1959 Vånngård and Åkerström<sup>5</sup> detected divalent gold by electron spin resonance in a long-lived intermediate in the oxidation of aurous dialkyl dithiocarbamate; this intermediate could not, apparently, be isolated.

An approximately 0.001 *M* solution of gold phthalocyanine in 1-chloronaphthalene was examined by electron spin resonance at 77°K., as previously de-

(1) This investigation was supported in part by Research Grant GM 5144 from the Division of General Medical Sciences, Public Health Service, National Institutes of Health.

(2) (a) City Chemical Corp., New York, N. Y. (b) Sample furnished by E. I. du Pont de Nemours and Co.; synthesis described by J. A. Elvidge and R. P. Linstead, *J. Chem. Soc.*, 5000 (1952).

(3) F. H. Moser and A. L. Thomas, "Phthalocyanine Compounds," Reinhold Publishing Corp., New York, N. Y., 1963.

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(5) T. Vånngård and S. Åkerström, *Nature*, **184**, 183 (1959).