

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 communication¹ we reported the preparation of ionic species which may be ferrocene and ferricinium ion analogs in which the C_5H_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.¹ We now wish to report the synthesis of stable anions which appear to be analogous to π -cyclopentadienylmanganese tricarbonyl^{2,3} and the corresponding rhenium compound.^{4,5} A proposed structure presented in Figure 1

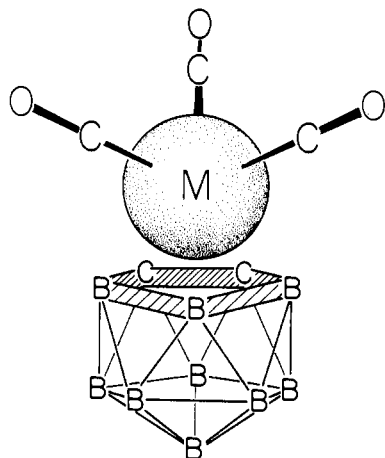
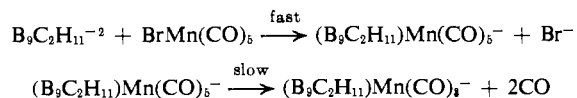


Figure 1. A possible structure for $(\text{B}_9\text{C}_2\text{H}_{11})\text{Mn}(\text{CO})_3^-$ and $(\text{B}_9\text{C}_2\text{H}_{11})\text{Re}(\text{CO})_3^-$ (H atoms have been omitted).

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^{6,7} and the sodium salt of I¹ 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 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.

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wt., 404. Found: B, 24.15; C, 14.72; H, 3.17; Mn, 13.2; Cs, 32.88; equiv. wt., 410.8.⁸

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., 547.9.⁸ The ¹¹B 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 cm^{-1} and carbonyl stretching bands between 2150 and 1850 cm^{-1} . Electronic spectra were determined in methanol [λ_{max} m μ (ϵ): 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 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.

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The Phthalocyanine of Gold¹

Sir:

Gold phthalocyanine has been prepared by the action of gold monobromide^{2a} on molten 1,3-diiminoisodoline,^{2b} in the absence of solvent.

Phthalocyanines with two monovalent transition metal atoms, analogous to the alkali metal derivatives, are unknown.³ The compounds of gold(III) so far examined had been found to be diamagnetic, four-coordinated, and square-planar.⁴ These properties are incompatible with bonding to a divalent, four-coordinating, and square-planar ligand such as phthalocyanine. However, in 1959 Vånngård and Åkerström⁵ 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.

(4) (a) P. Pascal, "Nouveau Traité de Chimie Minérale," Vol. III, Maisson et Cie, Paris, 1957; (b) H. Kuhn, *J. Chem. Phys.*, **16**, 727 (1948).

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

scribed in our investigations of copper and silver porphyrin and phthalocyanine.⁶ Gold was detected in the divalent state.

The paramagnetic resonance spectrum obtained shows hyperfine splitting for both gold ($I = 3/2$) and the four isoindole nitrogens of the phthalocyanine. The perpendicular side to the spectrum is shown in Figure 1 and from it we calculate $g_{\perp} = 1.996 (\pm 0.001)$; the gold hyperfine splitting parameter B is $6.1 \times 10^{-3} \text{ cm.}^{-1}$, and the nitrogen hyperfine splitting D , $1.58 \times 10^{-3} \text{ cm.}^{-1}$. g_0 is approximately 2.065 (± 0.005), in comparison with 2.042 for copper and 2.093 for silver phthalocyanine,⁷ while Vännegård and Åkerström calculate 2.040, 2.046, and 2.019 as the g_0 values for gold, copper, and silver dialkyl dithiocarbamates, respectively. The perpendicular nitrogen hyperfine constant is $1.78 \times 10^{-3} \text{ cm.}^{-1}$ for copper phthalocyanine and $2.32 \times 10^{-3} \text{ cm.}^{-1}$ for silver. Solution spectra could not be obtained at room temperature.

The σ -covalency of the I-B group phthalocyanines, therefore, exhibits a maximum at silver, which shows the minimum stability in the series toward demetalation in concentrated sulfuric acid; copper phthalocyanine is by far the most stable of the three. Gold(II) phthalocyanine is the most soluble in 1-chloronaphthalene, and the samples for e.s.r. could be readily prepared without recourse to supersaturation, which is necessary to achieve proper resolution of the hyperfine spectrum of silver, and particularly of copper phthalocyanine, in this solvent.^{7b,8}

The reaction between gold monobromide (or finely divided metallic gold) and 1,3-diiminoisoindoline was accomplished by mixing the two components intimately, in a ratio of 1:2, and heating for 5 min. at a temperature between 240 and 250°. The reaction mixture was quickly cooled in an ice bath. The product was purified (but not completely separated from other organic components) by repeated extraction with benzene and acetone. Synthesis at temperatures above 280° often leads to the formation of some metal-free phthalocyanine, and gold phthalocyanine is not obtained beyond 300°.

The visible spectrum of gold(II) phthalocyanine shows absorption peaks at 662, 633, 601, and 348 $m\mu$, on an instrument which reproduces Whalley's values for copper phthalocyanine.⁹

It is of interest to note that a porphyrin of gold, the magnetic properties of which are different from those of gold phthalocyanine, has also been synthesized. Gold mesoporphyrin was prepared by the room temperature rearrangement of the mesoporphyrin-IX dimethyl ester-gold acid trichloride association complex¹⁰ (prepared in ethyl acetate-ethanol) in benzene. The Soret absorption band of this compound in methanol is at 384 $m\mu$ while the visible bands are at 508 and 541 $m\mu$; an ultraviolet shift with respect to silver mesoporphyrin comparable to that observed for platinum mesoporphyrin with regard to the palladium derivative.¹¹ These shifts have been interpreted in the past¹²

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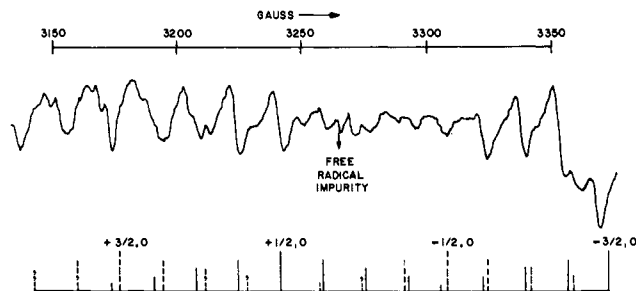


Figure 1. The perpendicular side of the electron spin resonance spectrum of gold phthalocyanine.

as an indication of stability, and, indeed, gold mesoporphyrin is undecomposed in concentrated sulfuric acid at room temperature. Its proton magnetic resonance spectrum in pyridine and chloroform is similar to that of copper mesoporphyrin but appears diamagnetic by the n.m.r. method of Fritz and Schwarzhau.¹³ A more complete report on this compound will appear in a forthcoming paper.

The stability of gold(II) phthalocyanine with respect to the silver(II) compound, apart from possible mechanistic differences, is in agreement with Linstead's correlation¹⁴ between the metallic radii and the resistance of the phthalocyanines to demetalation. Because of the lesser degree of covalency (as shown by spin resonance) and the lanthanide contraction, it may be supposed that the effective radius of the metal atom in the gold complex is closer than in silver phthalocyanine to the estimated "ideal" fit of 1.35 Å. The greater ionicity of the gold derivative in this series also agrees with the greater electronegativity of gold.¹⁵ This would help to explain why within the same subgroup of the periodic table the stabilities of porphyrin derivatives are in general less sensitive to variations in the metallic radii than those of the phthalocyanines.

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On the Configuration of a Lysine-vasopressin Dimer

Sir:

Wade, Winitz, and Greenstein¹ reported the formation of "parallel" dimer during the oxidation of cysteinyl-L-cysteine. Heaton, Rydon, and Schofield² assigned "antiparallel" cyclic structures to the polymers formed from the oxidation of L-cysteinyl-polyglycyl-L-cysteines. In view of recent reports on the preparation and

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(2) G. R. Heaton, P. N. Rydon, and J. A. Schofield, *J. Chem. Soc.*, 3157 (1956).