as CbCh (660)[5] to distinguish it from another uncharacterized chlorophyll recently isolated from a different strain of presumably the same organism.[6,7]

In common with other chlorophylls CbCh contains magnesium,[8] an alcohol group which is removed by strong acids,[2] and a conjugated carbonyl group. Removal of magnesium by dilute acid yields Cb"Ph." Absorption data[9,10] from ether solutions of samples purified by column chromatography are (a) CbCh: λ_{max} 660 mμ (ϵ 95,400), 625 (15,900), 431 (143,000), 411 (72,100), 389 (45,400); (b) Cb"Ph": λ_{max} 666 mμ (ϵ 61,700), 608 (5,540), 546 (14,500), 516 (7,250), 483 (2,440), 426 (shoulder, *ca.* 55,200), 409 (114,000), 350–390 (shoulder, *ca.* 71,000). The product from strong acid hydrolysis is extractable from ether by alkali; its ether solution possesses a visible spectrum identical to that of Cb"Ph." The conjugated carbonyl group is indicated by the shift of the "red" maximum from 666 to 650 mμ on borohydride reduction of Cb"Ph." The reduced product is oxidized by chromic acid in benzene–acetic acid to one with the visible spectrum of Cb"Ph." A small amount of the alcohol obtained by alkaline hydrolysis of Cb"Ph" was isolated. Comparison of the infrared spectrum with that of phytol obtained from pheophytin a indicates that the two alcohols may be different.

It could be argued that Ring V is oxidized, *i.e.*, "allomerized," during extraction of the bacterial cells with methanol.[2,11] This is unlikely because extraction under acid conditions, which are known to prevent "allomerization," also yields Cb"Ph."

Chromic acid oxidation followed by purification of the products by gas–liquid partition chromatography[12] yields three imides, two of which, namely, methylethylmaleimide and dihydrohematinic acid imide also can be obtained from pheophorbide *a*.[13,14] The third has been identified by analysis, m.p. and nuclear magnetic resonance spectrum as methyl-*n*-propylmaleimide.[15] The isolation of the latter imide alone differentiates CbCh from other chlorophylls; moreover, this is the first recorded instance of its isolation from a naturally occurring porphyrin.

The above results, together with the fact that 2-acetylchlorophyll *a* absorbs maximally at 676 mμ,[16] appear to dispose of the possibility that "Bacterioviridin," the pigment of green sulfur bacteria, obtained by Metzner,[17] is 2-acetylchlorophyll *a*.[18]

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(5) Abbreviations used are: CbCh (660) for Chlorobium chlorophyll (660) and Cb"Ph" for Chlorobium "pheophytin." (660) is the wave length in mμ of the "red" absorption maximum of an ether solution. Cb"Ph" is used because it is not known whether phytol is present in the molecule or not.

(6) I. R. Kaplan and H. Silberman, *Arch. Biochem. Biophys.*, **80**, 114 (1959).

(7) That there exist at least two different "Chlorobium chlorophylls" was pointed out to the authors by Drs. J. H. C. Smith and R. Stanier.

(8) J. H. C. Smith and A. Benitez, "Modern Methods of Plant Analysis," Vol. 4, Springer-Verlag, Berlin, 1955, p. 161.

(9) Extinction coefficients were calculated on the assumption of a 1:1 ratio between magnesium and CbCh.

(10) Visible absorption curves obtained with partially purified samples have been published: (2) E. Katz and E. C. Wassink, *Enzymologia*, **7**, 97 (1939); (b) see reference 4; (c) T. W. Goodwin, *Biochim. Biophys. Acta*, **18**, 309 (1955).

(11) A. S. Holt, *Can. J. Biochem. Physiol.*, **36**, 439 (1958).

(12) H. V. Morley, F. P. Cooper and A. S. Holt, *Chemistry and Industry*, 1018 (1959).

(13) H. Fischer and S. Brietner, *Ann.*, **522**, 151 (1936).

(14) G. E. Ficken, R. B. Johns and R. P. Linstead, *J. Chem. Soc.*, 2272 (1956).

(15) H. Fischer and H. Orth, "Chemie des Pyrrols," Vol. 1, Akademische Verlagsgesellschaft m.b.H., Leipzig, 1934, p. 299.

(16) A. S. Holt and E. E. Jacobs, *Am. J. Botany*, **41**, 718 (1954).

(17) P. Metzner, *Ber.*, **40**, 125 (1922).

(18) H. Fischer, R. Lambrecht and H. Mittenzwei, *Z. physiol. Chem.*, **253**, 1 (1938).

(19) N.R.C. Postdoctoral Fellow, 1957–1959.

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RECEIVED NOVEMBER 14, 1959

THE CHEMISTRY OF BORAZINE. III. B-SILYL BORAZINES

Sir:

We are able to report the first preparation of compounds containing a boron–silicon bond. These compounds were prepared by the reaction of B-trichloro-N-trimethylborazine and B-trichloro-N-triphenylborazine with triphenylsilylpotassium.

A 10% excess (over the amount required for trisubstitution of the haloborazine) of a triphenylsilylpotassium suspension was used. This suspension was prepared[1] by cleaving hexaphenyldisilane with a 1:5 sodium–potassium alloy in anhydrous ether, excess alloy being removed by amalgamation. The ethereal triphenylsilylpotassium, prepared under an atmosphere of dry nitrogen, was added to an ethereal suspension of the B-trichloro-N-trimethyl- or B-trichloro-N-triphenylborazine in the dry box, and the reaction proceeded quite rapidly and smoothly as judged by the disappearance of the green color of the triphenylsilylpotassium suspension. The B-tris-(triphenylsilyl)-N-trimethyl- and B-tris-(triphenylsilyl)-N-triphenylborazines were the only ether-soluble products, and were isolated from the filtrate obtained from the reaction by evaporation of the ether; the former was obtained as a yellowish highly viscous oil, and the latter as an off-white waxy solid melting at 55–58°. The yields were 78 and 90%, respectively.

Both compounds are decomposed readily by heating with 20% aqueous sulfuric acid and the resulting solution was analyzed for B, N and Cl using standard methods. The silicon analysis was obtained by heating the compounds with concentrated sulfuric acid and gravimetrically estimating the silica produced. Carbon analysis was carried out by decomposing the compound with fuming nitric acid at 250° and measuring the amount of carbon dioxide produced in an apparatus designed by Schlesinger.[2]

Both compounds are soluble in carbon tetrachloride, diethyl ether and benzene; the N-phenyl compound was crystallized from benzene.

Anal. Calcd. for $B_3[Si(C_6H_5)_3]_3N_3(CH_3)_3$: B, 3.62; C, 76.25; Cl, 0.00; N, 4.62; Si, 9.39;

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(1) H. Gilman and T. C. Wu, *J. Org. Chem.*, **18**, 753 (1953).

(2) H. I. Schlesinger and A. O. Walker, THIS JOURNAL, **57**, 622 (1935).

mol. wt., 897.8. Found: B, 3.51; C, 77.04; Cl, 0.00; N, 4.85; Si, 9.19; mol. wt., 881.2. Calcd. for $B_3[Si(C_6H_5)_3]_3N_3(C_6H_5)_3$: B, 2.99; C, 79.76; Cl, 0.00; N, 3.88; Si, 7.77; mol. wt., 1084. Found: B, 3.02; C, 79.70; Cl, 0.00; N, 3.98; Si, 7.50; mol. wt., 1052.

In addition to the method of synthesis and analysis, the assignment of a substituted borazine structure to these compounds is supported by the molecular weights, determined cryoscopically in benzene, and by certain features of their infrared spectra in carbon tetrachloride. The salient features are: bands in the 7μ region characteristic of the borazine ring[3]

N-Trimethyl compound:	6.94 (s)	7.02 (ms)	7.27 (s)
N-Triphenyl compound:	6.68 (ms)	7.00 (s)	7.35 (vs)

Both compounds have absorption at 14.4 μ which is due to a monosubstituted phenyl group.[4] Also, the C–H band at about 3.5 μ is diffuse and seems to be characteristic of the triphenylsilyl group.[5]

Both compounds react with moist air, but do not take up dry oxygen at room temperature or at 160°. Reaction with bromine proceeds readily in carbon tetrachloride and at room temperature, producing triphenylbromosilane as the only soluble product (identified by infrared spectrum and bromine analysis) and a precipitate which does not exhibit the borazine ring frequency in a KBr pellet infrared spectrum. This suggests that ring cleavage had occurred.

[3] W. C. Price, R. P. B. Fraser, T. S. Robinson and H. C. Longuet-Higgins, *Disc. Faraday Soc.*, **9**, 131 (1950).

[4] H. M. Randall, "Infrared Determination of Organic Structures," D. Van Nostrand Co., New York, N. Y., 1949.

[5] The authors found that the infrared spectrum of hexaphenyldisilane had this same flattening effect.

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RECEIVED DECEMBER 11, 1959

THE SYNTHESIS AND STRUCTURE OF BIS-(CYCLOPENTADIENYLNICKEL)-ACETYLENE

Sir:

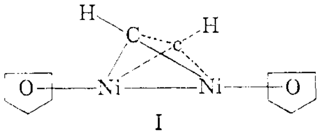
The first synthesis of an acetylene complex of nickel is herein reported, bis-(cyclopentadienylnickel)-acetylene being a product of the reaction between nickelocene and acetylene. Alkyne metal complexes in which the alkyne as such is bonded via its π electron system have been reported with the cobalt[1] and iron carbonyls[2] and various derivatives of platinum.[3,4] Recently certain alkyne nickel complexes have been reported as the products of reaction between alkynes and dicyclopentadienyldinickel dicarbonyl.[5] The isolation of bis-(cyclopentadienylnickel)-acetylene through a different route represents the first member of this novel series of nickel alkyne complexes.

Bis-(cyclopentadienylnickel)-acetylene was prepared by contacting 18 g. of nickelocene dissolved in tetrahydrofuran with acetylene at 180 p.s.i. and 80° for 15 hours. The reaction mixture was filtered and the solvent was removed at reduced pressure. Fractional vacuum sublimation of the dark green residue resulted in a recovery of 5.5 g. (30%) of unreacted nickelocene and the isolation of a less volatile dark green crystalline solid which crystallized from petroleum ether at −60° as light green lustrous plates m.p. 143–144° (dec.).

Anal. Calcd. for $(C_6H_6Ni)_2$; C, 52.7; H, 4.39; Ni, 42.9. Found: C, 52.3; H, 4.49; Ni, 42.6.

A Signer molecular weight determination of 290 supported the above written empirical formula. The total yield of product was 6.3 g. (48%).

The product exhibits moderate solubility in saturated hydrocarbons but is very soluble in all other common organic solvents. Oxidatively, it appears to be more stable than nickelocene and it can be handled readily in air for short periods of time. The infrared spectrum of the material contains bands characteristic of a π bonded cyclopentadienyl metal grouping. Magnetic susceptibility measurements[6] indicate that the product is diamagnetic which suggests that nickel has attained rare gas electronic structure. On the basis of the above data, Structure I corresponding to bis-(cyclopentadienylnickel)-acetylene is proposed in which acetylene is bonded via four π electrons to a binuclear cyclopentadienyl nickel system. The exact orientation of the acetylene carbons relative to the binuclear nickel bonding is unknown. However, in view of the recent X-ray studies by Sly[7] with the binuclear cobalt carbonyl complex of diphenylacetylene, the bonds probably are at right angles. The proposed structure is in agreement with the structures of the alkyne nickel complexes as outlined by Tilney-Bassett and Mills.



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The extension of the above reaction to substituted alkynes will be discussed in forthcoming publications.

[1] H. W. Sternberg, H. Greenfield, R. A. Friedel, J. Wotiz, H. R. Markby and I. Wender, THIS JOURNAL, **76**, 1457 (1954); **78**, 120 (1956).

[2] W. Hubel and E. H. Braye, *J. Inorg. Nucl. Chem.*, **10**, 250 (1959).

[3] S. V. Bukhovets and K. A Molodava, *Zhur. Neorg. Khim.*, **2**, 776 (1957); S. V. Bukhovets and N. K. Pukhova, *ibid.*, **3**, 1714 (1958).

[4] J. Chatt, C. A. Rowe and A. A. Williams, *Proc. Chem. Soc.*, 208 (1957); J. Chatt, L. A. Duncanson and R. G. Guy, *Chem. and Ind.*, 430 (1959).

[5] J. F. Tilney-Bassett and O. S. Mills, THIS JOURNAL, **81**, 4757 (1959).

[6] We are indebted to Dr. Stanley Kirschner of Wayne State University for carrying out the magnetic measurements.

[7] W. G. Sly, THIS JOURNAL, **81**, 18 (1959).

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SYNTHESIS OF THE LUPININE SYSTEM PATTERNED AFTER THE BIOGENETIC SCHEME OF SCHÖPF AND ROBINSON

Sir:

Consideration of structural relationships leads to the inference that the simple lupin alkaloids (III) arise in nature by Mannich cyclization of the amine dialdehyde I, formed in the plant by