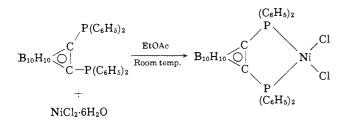
Complex formation occurred readily for this d⁸ system, but no reaction was observed between these ligands and the chloride and nitrate salts of divalent cobalt, iron, zinc, or trivalent iron and chromium. With copper chloride 4-hydrate a sluggish, ill-defined reaction occurred but the initial product appeared unstable. When Pt(II) and Pd(II) were substituted for the Ni(II), stable complexes were formed. However, these products have not as yet been characterized.

The room temperature reaction of the unbrominated phosphino-o-carborane with nickel chloride 6-hydrate yielded an isolable intermediate analysis of which showed a 1:1 complex. *Anal.* Calcd. for [Ni(B₁₀-



 $C_{26}H_{30}P_2$)Cl₂]: C, 48.65; H, 4.71; Cl, 11.04. Found: C, 48.61; H, 4.88; Cl, 11.0.

On refluxing in ethyl acetate this compound was converted to the 2:1 complex.

 $2[((C_{\mathfrak{g}}H_{\mathfrak{s}})_{\mathfrak{s}}P_{2}C_{2}B_{10}H_{10})NiCl_{2}] \xrightarrow{\text{EtOAc}}_{\text{Room temp.}} \\ [((C_{\mathfrak{g}}H_{\mathfrak{s}})_{\mathfrak{s}}P_{2}C_{2}B_{10}H_{10})]_{2}NiCl_{2} + NiCl_{2}$

Utilizing similar conditions for the reactions of the other three derivatives (those containing one, two, and three bromine atoms, respectively) the 1:1 complex could not be isolated.

In addition to obtaining infrared and ultraviolet spectra, magnetic moments were obtained at room temperature by the Gouy method using ferrous ammonium sulfate 6-hydrate and nickel(II) chloride 6hydrate as standards. Diamagnetic corrections were made for the ligands and anions. Molar conductances were measured using an Industrial Instruments, Inc., Model RC-16B conductivity bridge and a cell with a constant of 0.500 cm.⁻¹. The measurements were made at 25°, and with a bridge frequency of 1000 c.p.s. These results are listed in Table I.

Assignment of a square-planar configuration to the 2:1 complexes is based on the diamagnetism and diunivalent conductance which is exhibited in all cases. An examination of the electronic spectra of these complexes lends further support to the assignment of square-planar configurations. The transitions associated with octahedral configurations (${}^{3}A_{2g} \rightarrow {}^{3}T_{2g}$: ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(F)$: ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(P)$) are not to be found. However, the observed spectra are complicated by the onset of a strong band in the 500-m μ region which is probably of the charge-transfer variety. Further work is necessary before definite assignments can be made.

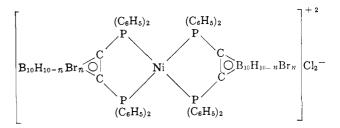
Alteration of the electronegativity of the borane nucleus by bromine substitution was clearly demonstrated in the reaction of the complexes with ethylenediamine. In acetone at room temperature the unsubstituted phosphinocarborane apparently underwent instantaneous ligand exchange producing a colorless solution and a pale blue. water-soluble solid.

Table I	
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Complex	Absor mµ	ption ^a E	l Conduc- tivity ^a	Magnetic mo- ments
$\begin{bmatrix} (C_6H_5)_2P - C & C - P(C_6H_5)_2 \\ B_{10}H_{10} \end{bmatrix}$ NiCl ₂	,			
B ₁₀ H ₁₀	• • •			
$\begin{bmatrix} (C_6H_5)_2P - C - C - P(C_6H_5)_2 \\ B_{10}H_{10} \end{bmatrix}$ NiCl	2		130.0	~ 0
$\begin{bmatrix} (C_6H_5)_2P-C & C-P(C_6H_5)_2 \\ B_{10}H_9Br \end{bmatrix}_2 $ NiCl	2 470	2600	131.5	~ 0
$\begin{bmatrix} (C_6H_5)_2P-C - C-P(C_6H_5)_2 \\ B_{10}H_8Br_2 \end{bmatrix}_2$ NiC	2 470	1640%	135.0	~0
$(C_6H_5)_2P-C - C - P(C_6H_5)_2$				
$\begin{bmatrix} (C_6H_5)_2P - C - C - P(C_6H_5)_2 \\ B_{10}H_7Br_3 \end{bmatrix}_2 NiCl$	2 470	3200		,
^a In DMF (10 ⁻⁴ m.). ^b 10 ⁻³	т.	·		

The monobromo derivative underwent a similar reaction but at an observably slower rate. The reaction of the dibromo compound was unique. Precipitation of a brownish solid occurred immediately. This product is very insoluble, high melting, and stable to oxidation and hydrolysis. The material is probably polymeric, involving, rather than displacement of the phosphorus ligands, coordination along the axis perpendicular to the plane of the Ni-P bonds. This is at present only speculation.

Although a more detailed study of the complexes reported is necessary before an unequivocable assignment of structures can be made, based on the information reported above it is logical to assume that these 2:1 complexes can be represented as



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Hampton D. Smith, Jr. Chemicals Division, Olin Mathieson Chemical Corporation New Haven, Connecticut Received January 20, 1965

Carbametallic Boron Hydride Derivatives. I. Apparent Analogs of Ferrocene and Ferricinium Ion Sir:

r:

We wish to report the synthesis of very stable ionic species which exhibit many of the properties of π -

bonded organometallic compounds and which may contain a single Fe^{II-III} simultaneously bonded to the open faces of two $B_9C_2H_{11}^{-2}$ icosahedral fragments. Compounds of this type present a novel marriage of carboranes with transition metal derivatives.

The synthesis of $Fe(B_9C_2H_{11})^{-2}$ (I) and $Fe(B_9C_2 H_{11}_{2^{-1}}$ (II) was implemented by the preparation of a new ion, $B_9C_2H_{11}^{-2}$ (III). C-Substituted derivatives were obtained from the corresponding derivatives of III. The $B_9C_2H_{12}^-$ ion¹ (IV), which appears to have the geometry of an eleven-particle icosahedral fragment, was readily converted to III by the abstraction of a proton with sodium metal or sodium hydride in tetrahydrofuran. Hydrolysis of III regenerated IV in quantitative yield. The hypothetical $B_{11}H_{11}^{-4}$ ion, isoelectronic with III, may be formally generated from icosahedral $B_{12}H_{12}^{-2}$ by the removal of a BH^{+2} unit. This delocalized model of $B_{11}H_{11}^{-4}$ would resemble the $C_5H_5^-$ ion in that the five equivalent atomic orbitals directed toward the empty apex would form a set of three bonding molecular orbitals which contain a total of six electrons.

The reaction of FeCl₂ with III and its C-substituted derivatives produced the corresponding I derivative. Air oxidation of the reaction mixture allowed the isolation of II and its C-substituted derivatives in yields as high as 85%. The salts of unsubstituted II are red $[\lambda_{max} (\epsilon): 272 (21,200), 296 (18,000), 444 (585), and sh.$ 520 (400)] and stable to acids, bases, and high temperatures (>300°). Anal. Calcd. for $Fe(B_9C_2H_{11})_2$ -N(CH₃)₄: C, 24.40; B, 49.30; H, 8.64; N, 3.56; Fe, 14.18; equiv. wt., 394; mol. wt., 394. Found: C, 24.56; B, 49.00; H, 8.73; N, 3.65; Fe, 14.39; equiv. wt., 406; mol. wt., 402. Degradation of C,C'-dimethyl II with aqueous hydroxide ion at the reflux temperature produces C,C'-dimethyl IV (95%) and 97.5% of the theoretical Fe as hydrous oxide. I is diamagnetic and II is paramagnetic. Polarography of II gives a one-electron reduction to produce I. Reduction of II with sodium amalgam in aqueous acetonitrile produces I in quantitative yield. The ¹H n.m.r. spectrum of I [bis N⁺(CH₃)₄ salt] contained a carborane proton resonance (intensity 1) at τ 6.52 and a methyl proton resonance (intensity 6) at τ 6.83. The ¹¹B n.m.r. spectrum of I extended over 30 p.p.m. and exhibited structure which could not be conclusively interpreted. Since II is paramagnetic, no useful ¹H n.m.r. spectra could be obtained. The ¹¹B n.m.r. spectrum of II was unique when compared with the spectra of known compounds since it extended over approximately 560 p.p.m., was well resolved, and gave no evidence of ${}^{11}B-{}^{1}H$ coupling.² A broad singlet (intensity 2) was observed at highest field with II, but separated into two singlets in the case of C-phenyl II. This may be taken as evidence that the two boron atoms responsible for this resonance are at the same time very near iron and the two carbon atoms. The remainder of the spectrum consisted of two welldefined peaks (intensity 1) and an unresolved set of at least two and more likely three resonances of total intensity 5. A true "sandwich" structure would require a third boron atom to be in close proximity to

iron, but the ¹¹B n.m.r. resonance associated with this boron atom has not been clearly observed although it may reside amidst the unresolved array of intensity 5. The chemical evidence now available suggests that each $B_9C_2H_{11}^{-2}$ unit contributes six electrons for bonding to Fe^{+2} in I, and the two $B_9C_2H_{11}^{-2}$ units thus complete the krypton shell about iron. The novel "sandwich" structure which would allow a single iron atom to complete two carborane icosahedra cannot be ruled out with the evidence now at hand. Further synthetic and structural studies are in progress.

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(3) Alfred P. Sloan Research Fellow.

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Azodicarbonitrile

Sir

We have prepared the elusive azodicarbonitrile $(1)^1$ in 54% yield by the pyrolysis of cyanogen azide.² At 200° in the vapor phase the synthesis is believed to involve cyanonitrene (2) as an intermediate.³

$$N_{3}CN \xrightarrow{200^{\circ}} NCN + N_{2}$$

$$2$$

$$N_{3}CN + NCN \longrightarrow NCN = NCN + N_{2}$$

$$1$$

Azodicarbonitrile is a crystalline, orange-red, volatile solid, m.p. 35.5-37°. Anal. Calcd. for 1: N, 70.0. Found: N, 69.5, 70.2, 69.5; mol. wt., 80 (mass spectrometer); $\lambda_{\text{max}}^{\text{CH}_{a}\text{CN}}$ 240 (ϵ 7830), 445 m μ (ϵ 18); λ_{max} 4.51 μ . Vapor pressure measurements and gas-liquid chromatography indicate both *cis* and *trans* isomers are present; however, they have not been separated. Vapor phase decomposition of 1 at 100° is slow; however, crystalline 1 detonates when mechanically shocked or heated in a closed vessel. Because of the hazardous nature of pure cyanogen azide, 1 has been synthesized on a limited scale. Azodicarbonitrile is soluble without reaction in benzene, acetonitrile, ethyl acetate, 1,1,2trichloro-1,2,2-trifluoroethane, and nitromethane. It is decomposed by methanol, water, or ether.

Azodicarbonitrile reacts instantly as a dienophile with 2,3-dimethylbutadiene to give 1,2-dimethyl-4,5dicyano-4,5-diazacyclohexene (3), m.p. 79° (Anal. Calcd. for 3: C, 59.2; H, 6.2: N, 34.6. Found: C, 59.0; H, 6.3; N, 34.5), and with cyclopentadiene to give 5,6-dicyano-5,6-diazabicyclo[2.2.1]heptene (4), m.p. 68-69° (Anal. Calcd. for 4: C, 57.5: H, 4.1: N, 38.4. Found: C, 57.2, 57.7; H, 4.2, 4.3; N, 37.3). The anthracene adduct, 1,2,3,4-tetrahydro-1,4-o-benzenophthalazine-2,3-dicarbonitrile (5), m.p. 180-181.5°,

⁽¹⁾ R. A. Wiesboeck and M. F. Hawthorne, J. Am. Chem. Soc., 86, 1642 (1964).

⁽²⁾ W. N. Lipscomb and A. Kaczmarczyk, Proc. Natl. Acad. Sci. U. S., 47, 1796 (1961), have observed the loss of ¹¹B-¹H coupling in ¹¹B n.m.r. spectra obtained in the presence of Fe¹¹¹.

^{(1) (}a) H. Wieland and H. Hess, Ber., 42, 4175 (1909), attempted dehydration of $NH_2CON=NCN=NOH$ without positive results; (b) bold for the parguin, *ibid.*, 46, 2000 (1913), dehydrated azodicarbonamide with P_2O_5 and obtained H_2O , N_2 , HOCN, and HCN. (2) F. D. Marsh and M. E. Hermes, J. Am. Chem. Soc., 86, 4506

^{(1964).}

^{(3) (}a) A. G. Anastassiou, H. E. Simmons, and F. D. Marsh, ibid., 87, in press; (b) F. D. Marsh, ibid., 87, in press; (c) G. J. Pontrelli and A. G. Anastassiou, J. Chem. Phys., 41, in press.