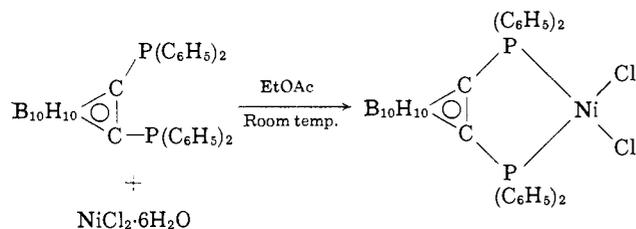


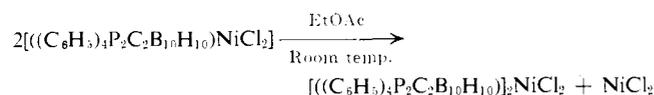
Complex formation occurred readily for this d^8 system, but no reaction was observed between these ligands and the chloride and nitrate salts of divalent cobalt, iron, zinc, or trivalent iron and chromium. With copper chloride 4-hydrate a sluggish, ill-defined reaction occurred but the initial product 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 $[\text{Ni}(\text{B}_{10}$ -



$\text{C}_{26}\text{H}_{30}\text{P}_2\text{Cl}_2$: 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.



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 6-hydrate 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 divalent 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 (${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$; ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$; ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$) are not to be found. However, the observed spectra are complicated by the onset of a strong band in the 500- 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.

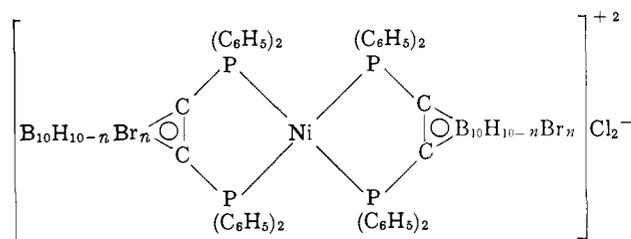
Table I

Complex	Absorption ^a		Conductivity ^a	Magnetic moments
	$m\mu$	E		
$[(\text{C}_6\text{H}_5)_2\text{P}-\text{C}(\text{C}_6\text{H}_5)_2-\text{C}(\text{C}_6\text{H}_5)_2-\text{P}(\text{C}_6\text{H}_5)_2] \text{NiCl}_2$ $\text{B}_{10}\text{H}_{10}$
$[(\text{C}_6\text{H}_5)_2\text{P}-\text{C}(\text{C}_6\text{H}_5)_2-\text{C}(\text{C}_6\text{H}_5)_2-\text{P}(\text{C}_6\text{H}_5)_2]_2 \text{NiCl}_2$ $\text{B}_{10}\text{H}_{10}$	130.0	~ 0
$[(\text{C}_6\text{H}_5)_2\text{P}-\text{C}(\text{C}_6\text{H}_5)_2-\text{C}(\text{C}_6\text{H}_5)_2-\text{P}(\text{C}_6\text{H}_5)_2]_2 \text{NiCl}_2$ $\text{B}_{10}\text{H}_9\text{Br}$	470	2600	131.5	~ 0
$[(\text{C}_6\text{H}_5)_2\text{P}-\text{C}(\text{C}_6\text{H}_5)_2-\text{C}(\text{C}_6\text{H}_5)_2-\text{P}(\text{C}_6\text{H}_5)_2]_2 \text{NiCl}_2$ $\text{B}_{10}\text{H}_8\text{Br}_2$	470	1640 ^b	135.0	~ 0
$[(\text{C}_6\text{H}_5)_2\text{P}-\text{C}(\text{C}_6\text{H}_5)_2-\text{C}(\text{C}_6\text{H}_5)_2-\text{P}(\text{C}_6\text{H}_5)_2]_2 \text{NiCl}_2$ $\text{B}_{10}\text{H}_7\text{Br}_3$	470	3200

^a In DMF (10^{-4} m). ^b 10^{-3} m .

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 unequivocal 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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New Haven, Connecticut
Received January 20, 1965

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

Sir:

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

