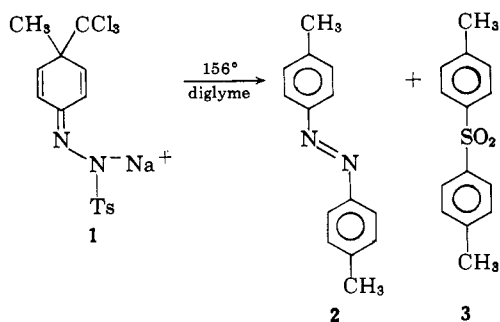
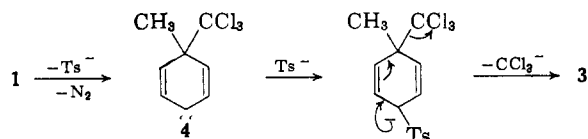


methyl-4-trichloromethyl-2,5-cyclohexadienone tosylhydrazone (**1**) in refluxing diglyme afforded, as the major products, *p*-azotoluene² (**2**) and *di-p*-tolyl sulfone³ (**3**), in 48 and 38% yields, respectively. The reaction products were identified by spectral evidence



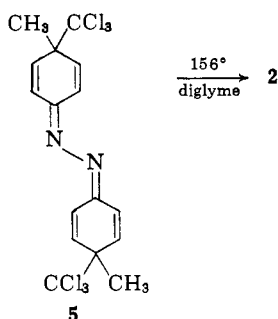
(infrared, ultraviolet, and n.m.r.) and by comparison of physical properties with those in the literature.

We suggest that sulfone **3** is formed by reaction of 4-methyl-4-trichloromethyl-2,5-cyclohexadienyliidene⁴ (**4**) with *p*-toluenesulfonate ion, followed by aromatization of the initial adduct by ejection of trichloromethyl anion. Sulfone formation has been noted in another



aprotic tosylhydrazone decomposition.⁵ Under our reaction conditions trichloromethyl anion is undoubtedly converted to dichlorocarbene. This may account for the complexity of the reaction mixture, which contains at least eleven products.

Our finding that 4-methyl-4-trichloromethyl-2,5-cyclohexadienone azine (**5**) is converted to azotoluene **2** in 82% yield under the original reaction conditions,



coupled with the well-documented formation of azines in the decomposition of diazo compounds,⁶ suggests that the azine **5** may be an intermediate in the conversion of **1** to **2**.

Tosylhydrazone⁷ **1**, m.p. 150–151°, was prepared in 81% yield by condensation of 4-methyl-4-trichloro-

- (1) Tosyl = Ts = *p*-toluenesulfonyl.
- (2) D. Vorländer and F. Meyer, *Ann.*, **320**, 122 (1902).
- (3) H. Meyer, *ibid.*, **433**, 327 (1923).
- (4) A large body of evidence suggests that carbenes are generated in the pyrolysis of tosylhydrazone salts in aprotic media. See, e.g., L. Friedman and H. Schechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959).
- (5) D. M. Lemal and A. J. Fry, *J. Org. Chem.*, **29**, 1673 (1964).
- (6) E.g., P. Yates and S. Danishefsky, *J. Am. Chem. Soc.*, **84**, 879 (1962).
- (7) Satisfactory microanalyses have been obtained for all new compounds.

methyl-2,5-cyclohexadienone⁸ with tosylhydrazine in pyridine. Condensation of the dienone with hydrazine hydrate in refluxing methanol afforded the orange azine⁷ **5**, m.p. 202.5–203.5° dec. (78% yield).

We are investigating the mechanisms of the thermal transformations reported herein, and are extending our studies to other cyclohexadienyliidenes.

Acknowledgments. Dr. Robert S. H. Liu, of the Central Research Department, E. I. duPont de Nemours and Company, kindly obtained the n.m.r. spectra of the compounds studied in this work. This research was supported from a National Science Foundation Institutional Grant to Wesleyan University.

(8) M. S. Newman and A. G. Pinkus, *J. Org. Chem.*, **19**, 978 (1954).

Albert J. Fry

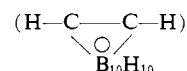
Hall Laboratory of Chemistry, Wesleyan University
Middletown, Connecticut 06457

Received January 19, 1965

Complexes of Bisphosphinocarboranes with Nickel(II) Chloride

Sir:

Considerable interest has been aroused by recent reports on the synthesis and reactions of *o*-carborane¹



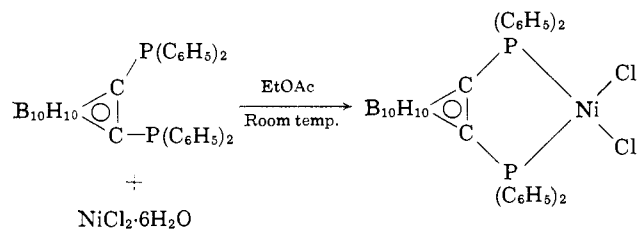
which consists of an icosahedron, the apices of which are ten boron and two carbon atoms, the latter being in nearest proximity and *ortho* to each other.² Of particular interest are the bisphosphino derivatives^{3,4} which should be structurally analogous to the *cis* forms of ethylenediamines and ethylenediphosphines and to the *o*-phenylenediphosphines and -diarsines. They lend themselves to a detailed study of ligand-metal bonding since varying the substituents on the borane portion of the molecule should affect the electronic environment of the phosphorus atoms and thus the stability of the complexes.

The reaction of nickel(II) chloride 6-hydrate with bisdiphenylphosphino-*o*-carborane³ as well as with the corresponding derivatives containing one, two, and three bromine atoms attached to the carborane nucleus⁴ in methanol and/or ethyl acetate produced complexes containing two molecules of bisphosphine and one of nickel(II) chloride. *Anal.* [Ni(B₁₀C₂₆H₃₀P₂)₂]Cl₂ as red crystals. Calcd. for C₅₂H₆₀B₂₀Cl₂NiP₄: C, 54.1; H, 5.20; Cl, 6.10; P, 10.7. Found: C, 53.1; H, 5.26; Cl, 6.14; P, 10.0. [Ni(B₁₀C₂₆H₂₉BrP₂)₂]Cl₂ as red crystals. Calcd. for C₅₂H₅₈B₂₀Br₂Cl₂NiP₄: C, 47.5; H, 4.41; Br, 12.16; Cl, 5.42. Found: C, 46.7; H, 4.42; Br, 12.15; Cl, 5.07. [Ni(B₁₀C₂₆H₂₈Br₂P₂)₂]Cl₂ as orange crystals. Calcd. for C₅₂H₅₆B₂₀Br₄Cl₂NiP₄: Br, 21.40; Cl, 4.80. Found: Br, 21.4; Cl, 4.88. [Ni(B₁₀C₂₆H₂₇Br₃P₂)₂]Cl₂ as orange crystals. Calcd. for C₅₂H₅₄B₂₀Br₃Cl₂NiP₄: Br, 27.30; Cl, 4.04. Found: Br, 28.30; Cl, 4.07.

- (1) A comprehensive listing of relevant references appears as ref. 1 of F. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **86**, 4222 (1964).
- (2) J. A. Potenza and W. N. Lipscomb, *ibid.*, **86**, 1874 (1964).
- (3) R. P. Alexander and H. Schroeder, *Inorg. Chem.*, **2**, 1107 (1963).
- (4) H. D. Smith, T. A. Knowles, and H. Schroeder, *ibid.*, **4**, 107 (1965).

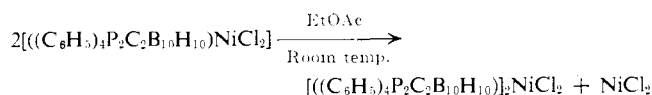
Complex formation occurred readily for this d^8 system, but no reaction was observed between these ligands and the chloride and nitrate salts of divalent cobalt, iron, zinc, or trivalent iron and chromium. With copper chloride 4-hydrate a sluggish, ill-defined reaction occurred but the initial product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



$\text{C}_{26}\text{H}_{30}\text{P}_2\text{Cl}_2$: 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 1.

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 (${}^3A_{2g} \rightarrow {}^3T_{2g}$; ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{F})$; ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{P})$) 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.

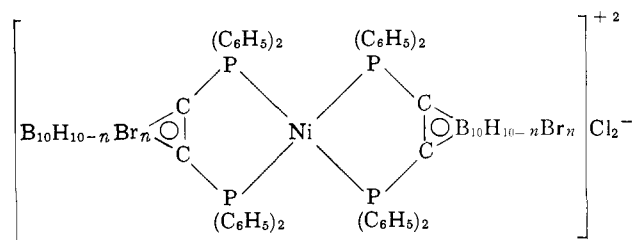
Table I

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



Acknowledgment. The author is indebted to Drs. M. A. Robinson and H. A. Schroeder for technical assistance and to Dr. T. L. Heying for help in preparing the manuscript. The work was sponsored by the Office of Naval Research.

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:

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