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σ-BONDED COMPLEXES OF SUBSTITUTED PHOSPHA- AND ARSACARBORANES AND THEIR π-OLLYL DERIVATIVES

DON C. BEER AND LEE J. TODD
Department of Chemistry, Indiana University, Bloomington, Indiana 47401 (U.S.A.)*

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SUMMARY

The photochemical reaction of $(1,7\text{-}B_9H_9CHE)_2Fe^{2-}$ (E = P or As) with Group VI metal carbonyls leads to the formation of complexes with the general formula, $[1,7\text{-}B_9H_9CHE\text{-}M(CO)_5]_2Fe^{2-}$. It is proposed that each heteroatom carborane ligand is π-bonded to the iron atom and σ-bonded through either the phosphorus or arsenic atom to a Group VI metal carbonyl. The preparation and characterization of a neutral phosphacarborane σ-complex is described.

INTRODUCTION

Recently we reported[1] that 7,8- and $7,9\text{-}B_9H_{10}CHE^-$ (E = P or As) under photochemical conditions reacted with Group VI metal carbonyls to form 1/1 σ complexes of the general formula $[B_9H_{10}CHE\text{–}M(CO)_5]^-$. Deprotonation of 7,8- or $7,9\text{-}B_9H_{10}CHE^-$ with sodium hydride in tetrahydrofuran and reaction with iron(II) chloride produces π-complexes[2] of the form $(B_9H_9CHE)_2Fe^{2-}$. The phosphacarborane complexes react with two equivalents of methyl iodide[2] to form $(B_9H_9CHPCH_3)_2Fe$. This demonstrates the Lewis base character of the phosphorus atoms in this type of complex. This paper describes the preparation and properties of σ-bonded complexes of $(1,7\text{-}B_9H_9CHE)_2Fe^{2-}$ with Group VI metal carbonyls**. In addition the first neutral σ complexes of certain of these carboranes have been characterized.

EXPERIMENTAL

General comments

Boron (^{11}B) NMR spectra at 70.6 MHz were obtained with a Varian HR-220 spectrometer. Spectral integrals were obtained with a Lasico optical plainimeter. All spectra were externally referenced to $BF_3 \cdot O(C_2H_5)_2$. Proton NMR spectra were obtained with a Varian HA-100 spectrometer. The ^{13}C NMR spectra were carried out on a high-resolution carbon-13 Fourier transform NMR spectrometer consisting

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* Contribution No. 2000.
** The numbering systems employed in this article follow the recently adopted nomenclature rules[5].

mainly of a Varian high-resolution 14.1-kG electromagnet, a "home-built" NMR apparatus operating at 15.08 MHz, a Fabri-tek 1074 signal averager, and a PDP-8/I computer. The apparatus included an external ^{19}F lock and noise-modulated proton decoupling.

Carbon, hydrogen, nitrogen, boron and metal analyses were performed by either the University of Illinois Microanalytical Laboratory or by Schwarzkopf Microanalytical Laboratories, Woodside, New York. Infrared spectra were recorded as KBr disks or as acetonitrile solutions (carbonyl stretching region) using a Perkin–Elmer 621 instrument. For KBr spectra, the intensities are reported as vs, very strong; s, strong; m, medium; or w, weak.

Low resolution mass spectra were obtained with an Atlas CH-7 instrument. High resolution mass spectra were run on an AEI MS-9 instrument.

Osmometric molecular weights were determined in acetone solutions by Schwarzkopf Microanalytical Laboratories. Reported melting points were done in sealed capillaries and are uncorrected. All reactions were carried out under an atmosphere of prepurified nitrogen.

Starting materials

The tetramethylammonium salt of $7,8\text{-}B_9H_{10}CHP^-$ was prepared by the method of Todd, Little and Silverstein[3]. The tetramethylammonium salt of $7,9\text{-}B_9H_{10}CHAs^-$ was prepared by the method briefly described by Todd and co-workers[4]. The tetramethylammonium salts of $(1,7\text{-}B_9H_9CHP)_2Fe^{2-}$ and $(1,7\text{-}B_9H_9CHAs)_2Fe^{2-}$ were prepared by a previously reported method[2]. Chromium hexacarbonyl was purchased from Strem Chemicals, Danvers, Massachusetts. Molybdenum hexacarbonyl was purchased from Climax Molybdenum Company, New York. Tungsten hexacarbonylwas purchased from Pressure Chemical Company, Pittsburgh, Pennsylvania. 3-Bromopyridine was received from Reilly Tar and Chemical Corporation, Indianapolis, Indiana. Benzene was dried by distillation from sodium metal. Tetrahydrofuran was freshly distilled from lithium aluminum hydride.

Reaction of $[(CH_3)_4N]_2[Fe(1,7\text{-}B_9H_9CHP)_2]$ *with* $W(CO)_6$

In a typical experiment, $[(CH_3)_4N]_2[Fe(1,7\text{-}B_9H_9CHP)_2]$ (0.50 g, 0.984 mmole) and $W(CO)_6$ (0.692 g, 1.96 mmole) were placed in a Vycor Schlenk tube with 40 ml of dry tetrahydrofuran. The stirred solution was irradiated with a 550 W high pressure, Hanovia mercury vapor lamp for 11 h, the resulting red solution filtered and the solvent removed in *vacuo*. Next the material was placed in a sublimer and heated at 75° for 3 h to remove any unreacted $W(CO)_6$. The crude tetramethylammonium salt was then dissolved in a 50/50 mixture of acetonitrile/water and slowly passed through a five-fold excess exchange capacity of sodium ion exchange resin. After removal of solvent the gummy red material obtained was dissolved in a minimum of water and a saturated aqueous solution of tetrabutylammonium iodide added until precipitation was complete. The pink solids were filtered and dried in *vacuo* overnight.

The crude product was then dissolved in a mixed solvent system (acetone/ethanol 50/50) and the volume reduced by heating while additions of ethanol and a few drops of water were made. When the solution was sufficiently concentrated it was removed from the heat and allowed to cool slowly to form red-needle crystals.

The amount of product was 0.484 g, 40% yield. The complex melts at 207–209° without decomposition.

The infrared spectrum contains absorptions at λ_{max} 3031 m, 3005 m (sh), 2943 m, 2607 s, 2127 s, 2009 s, 1948 vs (br), 1915 vs, 1494 m, 1413 m, 1287 w, 1177 w, 1132 m, 1062 m, 1022 m, 911 w, 784 w, 767 w, 641 w, 624 m, 609 m, 555 w, 477 w, 441 w, and 407 m cm^{-1}. The proton NMR spectrum (acetone-d_6) exhibits four sets of multiplets with complex splitting patterns centered at τ 6.60 (2H), 8.17 (2H), 8.56 (2H) and 8.98 (3H) ppm. The ^{11}B NMR spectrum at 70.6 MHz in acetone consists of a downfield doublet centered at -0.62 ppm of area 2 (J 133 Hz) and a broad resonance of area 7 with peaks at 10.08 and 15.50 ppm.

$[(C_4H_9)_4N]_2[Fe(1,7\text{-}B_9H_9CHAs\cdot Cr(CO)_5)_2]$

The method of preparation of this complex is identical to that of $[(C_4H_9)_4N]_2$-$[Fe(1,7\text{-}B_9H_9CHP\cdot W(CO)_5)_2]$. The infrared spectrum exhibits absorptions at λ_{max} 2957 m, 2937 m (sh), 2871 m, 2509 s, 2317 w, 2055 s, 1985 m, 1931 vs, 1881 s, 1466 m, 1382 m, 1161 w, 1092 m, 1029 m, 988 m, 877 m, 753 w (sh), 734 m, 653 m, 631 m (sh) and 449 m cm^{-1}.

The proton NMR spectrum (acetone-d_6) exhibits four sets of multiplets with complex splitting patterns centered at τ 6.60 (2 H), 8.16 (2 H), 8.55 (2 H), and 8.98 (3 H) ppm.

The ^{11}B NMR spectrum at 70.6 MHz in acetone consists of a downfield doublet at 3.33 ppm of area 2 (J 160 Hz) and a broad resonance of area 7 with peaks at 11.04 and 20.44 ppm.

$[(CH_3)_4N]_2[Fe(1,7\text{-}B_9H_9CHP\cdot Mo(CO)_5)_2]$

The method of preparation of this complex and the following compound is identical to that of $[(C_4H_9)_4N]_2[Fe(1,7\text{-}B_9H_9CHP\cdot W(CO)_5)_2]$ except that the tetramethylammonium salt is purified by recrystallization from acetone/methanol/H_2O solvent system. The infrared spectrum exhibits absorptions at λ_{max} 3003 w, 2595 s, 2133 s, 2027 s, 1949 vs (br), 1516 s, 1481 m, 1317 w, 1129 m, 1069 m, 1025 m, 976 m, 940 m (sh), 770 w, 635 m, 618 m, 559 w, 478 w, 431 m and 399 m cm^{-1}. The proton NMR spectrum (acetone-d_6) contains two singlets at τ 6.95 (12 H) and 7.79 (1 H).

The ^{11}B NMR spectrum at 70.6 MHz in acetone exhibits a downfield doublet at -0.55 ppm of area 2 (J 132 Hz) and a broad resonance of area 7 with peaks at 9.95 and 15.90 ppm.

$[(CH_3)_4N]_2[Fe(1,7\text{-}B_9H_9CHP\cdot Cr(CO)_5)_2]$

The infrared spectrum contains absorptions at λ_{max} 3009 m, 2987 m (sh), 2921 w, 2587 s, 2101 s, 2001 m, 1947 vs, 1918 s, 1489 m, 1403 m, 1179 w, 1052 w, 1012 m, 899 vw, 755 w, 679 m, 654 m (sh) and 474 m cm^{-1}. The proton NMR spectrum (acetone-d_6) contains two singlets at τ 6.90 (12 H) and τ 7.78 (1 H).

The ^{11}B NMR spectrum at 70.6 MHz in acetone exhibits a downfield doublet at 0.13 ppm of area 2 (J 127 Hz) and a broad resonance of area 7 with peaks at 10.78 and 16.05 ppm.

$7,8\text{-}B_9H_9(3\text{-}bromopyridine)CHP$

A solution of 0.715 g (4.4 mmole) of anhydrous ferric chloride in 30 ml of molecular sieve dried benzene and 1.69 ml of 3-bromopyridine was added dropwise from a pressure-equalized addition funnel over a period of 1 h to a refluxing solution of 0.50 g (2.2 mmol) of $[(CH_3)_4N][7,8\text{-}B_9H_{10}CHP]$ in 75 ml of dried benzene with 0.86 ml of 3-bromopyridine. The solution turned a bright yellow color upon addition of the ferric chloride and a solid precipitate formed. The reaction mixture was cooled and filtered and the precipitate washed with 100 ml of hot benzene. The combined filtrates were then placed in a 1000 ml separatory funnel and washed with 300 ml portions of distilled water until the aqueous phase was neutral.

After removal of the solvent in *vacuo*, the crude yellow reaction product was applied to a 2.25 cm × 50 cm liquid phase chromatographic column packed with 100–200 mesh silica gel and eluted with benzene. The first yellow band was collected and solvent removed. The product was further purified by recrystallization from benzene/hexane to give 0.206 g (30% yield). The compound melts at 205–209° with decomposition.

The infrared spectrum exhibits absorptions at λ_{max} 3107 m, 3067 w, 2523 w, 1617 m, 1557 m, 1475 m, 1434 s, 1401 m (sh), 1321 w, 1254 m, 1198 m, 1159 s, 1146 m (sh), 1115 m, 1067 w, 1029 m, 987 m, 969 m (sh), 904 m, 867 m, 834 w, 802 m, 756 m, 707 m (sh), 697 m, 677 m, 647 m, 605 m, 575 w, 466 w, and 411 w cm^{-1}. The proton NMR spectrum (acetone-d_6) consists of a distorted doublet at τ 1.10 (2 H), a quadruplet at 1.28 (1 H), and a quadruplet at 2.00 (1 H) and a broad singlet at 8.24 (1 H) ppm.

7,9-B_9H_9(3-bromopyridine)CHAs

The method of preparation of this compound is similar to that of 7,8-B_9H_9(3-bromopyridine)CHP. The infrared spectrum exhibits at λ_{max} 3050 m, 2522 s, 1601 m, 1452 m, 1417 m, 1275 m, 1251 w, 1158 m, 1110 m, 1079 m (sh), 1040 m, 1009 w, 958 w, 921 w, 833 m, 800 m, and 767 m cm^{-1}. The compound melts at 205–207° with decomposition.

The low voltage mass spectrum cuts off at *m/e* 355 corresponding to the $(^{11}B_9{}^1H_{14}{}^{12}C_6{}^{14}N^{81}Br^{75}As)^+$ parent ion.

[7,8-B_9H_9(3-bromopyridine)CHP]$Cr(CO)_5$

The method of preparation of this complex was similar to that of $[(C_4H_9)_4N]_2\text{-}\{Fe[B_9H_9CHP\cdot W(CO)_5]_2\}$ except that the crude material obtained from the photochemical reaction was dissolved in methylene chloride and chromatographed on a 20 cm × 20 cm silica gel TLC plate. The yellow component that separated from a blue band was collected and extracted from the silica gel with benzene. The benzene solution was evaporated in *vacuo* at 40° yielding yellow feathery crystals. Further purification was readily accomplished by recrystallization from benzene/hexane. A yield of 42% or 0.340 g was recorded. The complex melts at 206–208° without decomposition. The infrared spectrum contains absorptions at λ_{max} 3119 m, 2579 m (sh), 2539 s, 2069 s, 2000 s, 1924 vs (br), 1607 m, 1557 w, 1467 m, 1432 m, 1400 m (sh), 1194 m, 1174 m, 1155 m, 1122 m, 1082 m, 1054 m, 1019 m, 974 m, 881 w, 855 m, 825 m, 765 m, 727 m, 690 m (sh), 671 m (sh), 645 s, 599 m, 575 m, 519 w and 447 m cm^{-1}. The proton NMR spectrum (acetone-d_6) consists of three multiplets centered at τ 0.94 (1 H), 1.49 (2 H) and 1.88 (1 H) ppm.

The low mass spectrum cuts off at *m/e* 503 corresponding to the $(^{11}B_9{}^1H_{14}\text{-}{}^{12}C_{11}{}^{14}N^{16}O_5{}^{31}P^{81}Br^{52}Cr)^+$ parent ion.

RESULTS AND DISCUSSION

An attempt to remove a proton from $[7,9\text{-}B_9H_{10}CHP\cdot Cr(CO)_5]^-$ and to π-bond the dianion with iron(II) chloride was not successful. A tetrahydrofuran solution of $[(CH_3)_4N]_2$ $[(1,7\text{-}B_9H_9CHP)_2Fe]$ and $W(CO)_6$ in a 1/2 mole ratio respectively was irradiated with a high pressure mercury vapor lamp for 11 h. The product was difficult to purify as the tetramethylammonium salt. It was converted to the tetrabutylammonium salt which was crystallized from acetone/ethanol to give deep red needles in 40% yield. The analytical data for $[(C_4H_9)_4N]_2[1,7\text{-}B_9H_9CHP\cdot W(CO)_5]_2Fe$ and the other new compounds described in this article are given in Table 1. Further evidence concerning the molecular formula was obtained from an osmometer molecular weight determination (acetone solution). Mol. wt. found: 1.493. Mol. wt. $[(C_4H_9)_4N]_2[1,7\text{-}B_9H_9CHP\cdot W(CO)_5]_2Fe$: calcd.: 1.489.

TABLE 1

ANALYTICAL DATA OF σ-BONDED COMPLEXES

Compound	Analysis, found (calcd.) (%)					
	C	H	B	Fe	M[a]	N
$[Fe(1,7\text{-}B_9H_9CHP\cdot Cr(CO)_5)_2]$ $[N(CH_3)_4]_2$	27.74	5.17	22.03	7.40	10.90	3.44
	(27.02)	(5.00)	(21.89)	(6.28)	(11.70)	(3.15)
$[Fe(1,7\text{-}B_9H_9CHP\cdot Mo(CO)_5)_2]$ $[N(CH_3)_4]_2$	26.26	4.94	19.46	5.65	20.19	3.01
	(25.59)	(4.55)	(19.92)	(5.72)	(19.64)	(2.87)
$[Fe(1,7\text{-}B_9H_9CHP\cdot W(CO)_5)_2]$ $[N(n\text{-}C_4H_9)_4]_2$	35.30	6.04	13.40	3.51	25.00	2.04
	(35.48)	(6.23)	(13.07)	(3.75)	(24.69)	(1.88)
$[Fe(1,7\text{-}B_9H_9CHAs\cdot Cr(CO)_5)_2]$ $[N(n\text{-}C_4H_9)_4]_2$	40.07	8.18	15.20	4.93		2.65
	(40.23)	(7.06)	(14.82)	(4.25)		(2.13)
$7,8\text{-}B_9H_9(C_5H_4NBr)CHP$	24.31	4.57				4.60
	(23.37)	(4.58)				(4.54)
$7,9\text{-}B_9H_9(C_5H_4Br)CHAs$	20.37	4.40				3.46
	(20.45)	(4.01)				(3.88)
$7,8\text{-}B_9H_9(C_5H_4NBr)CHP\cdot Cr(CO)_5$	26.24	3.09	19.78		10.06	3.01
	(26.40)	(2.82)	(19.44)		(10.39)	(2.80)

[a] Chromium, molybdenum, or tungsten.

Employing the same procedure, the complexes $[1,7\text{-}B_9H_9CHP\cdot M(CO)_5]_2Fe^{2-}$ (where M=Cr or Mo) and $[1,7\text{-}B_9H_9CHAs\cdot Cr(CO)_5]_2Fe^{2-}$ have been prepared and characterized. The complexes of the type $[B_9H_{10}CHP\cdot W(CO)_5]^-$ are not stable in solution above 55°[1]. The phosphacarborane three-metal complexes described here are more stable thermally since they can be crystallized from acetone/ethanol mixtures at reflux without decomposition. In contrast, the arsenic derivative, $[1,7\text{-}B_9H_9CHAs\cdot Cr(CO)_5]_2Fe^{2-}$ was less stable and was crystallized at about room temperature. All the new complexes can be stored at room temperature under nitrogen for at least two months with negligible decomposition.

The infrared spectra of the metal carbonyl stretching region (acetonitrile solution) for the new complexes is given in Table 2. These spectra are very similar to those reported previously[1] for complexes like $[7,9\text{-}B_9H_{10}CHP\cdot W(CO)_5]^-$. The

TABLE 2

INFRARED SPECTRAL DATA IN THE CARBONYL REGION

Compound	CO stretching frequency (cm^{-1})			
	$A_1^{(2)}$	B_1	E	$A_1^{(1)}$
$[Fe(1,7\text{-}B_9H_9CHP\cdot W(CO)_5)_2][N(n\text{-}C_4H_9)_4]_2$	2072 m	1977 w	1930 vs	1896 vs
$[Fe(1,7\text{-}B_9H_9CHAs\cdot Cr(CO)_5)_2][N(n\text{-}C_4H_9)_4]_2$	2065 m	1976 w	1941 vs	1902 s
$[Fe(1,7\text{-}B_9H_9CHP\cdot Mo(CO)_5)_2][N(CH_3)_4]_2$	2075 m	1984 w	1946 vs	1903 s
$[Fe(1,7\text{-}B_9H_9CHP\cdot$	2051 m	1976 w	1939 vs	1906 s
$7,8\text{-}B_9H_9$(3-bromopyridine)-$CHP\cdot Cr(CO)_5$	2067 m	1983 w	1945 vs	1924

stretching frequency of the CO [$A_1^{(1)}$] *trans* to the phosphacarborane ligand is at 1906–1896 cm^{-1} in these complexes. This is very near to the position of the $A_1^{(1)}$ band of (amine)M(CO)$_5$ compounds (1905–1895 cm^{-1}).

The NMR spectra of $[(CH_3)_4N]_2[1,7\text{-}B_9H_9CHP\cdot M(CO)_5]_2Fe$ (M=Cr or Mo) consist of a sharp singlet at τ 6.9 (12 H) and a broad singlet at τ 7.8 ppm (1 H) assigned to the tetramethylammonium and carborane CH protons respectively. The ^{11}B NMR spectra of the three-metal complexes contain many badly overlapping resonances even at 70.6 MHz and gave no useful structural information. The ^{13}C NMR spectrum of $[(CH_3)_4N][7,9\text{-}B_9H_{10}CHP\cdot Mo(CO)_5]$ in acetonitrile solution contained two doublets at –7.43 ppm* (area 1) and at –4.78 ppm (area 4) which can be assigned to the *trans* and *cis* carbonyl carbon resonances respectively. The phosphorus–carbon spin coupling to the *trans* carbonyl carbon is larger [$J(^{13}C\text{–}^{31}P)$ 26 Hz] than the coupling to the *cis* carbonyl carbon [$J(^{13}C\text{–}^{31}P)$ 8 Hz]. Similar results have been observed for the ^{13}C NMR of $Ph_3P\cdot Mo(CO)_5$.[7] Evidence that the Cr(CO)$_5$ groups are directly bonded to the phosphorus atoms in $[(CH_3)_4N]_2Fe[1,7\text{-}B_9H_9CHP\cdot Cr(CO)_5]_2$ is obtained from its ^{13}C NMR spectrum in acetonitrile solution. The *cis* carbonyl resonance appears as a doublet at -25.1 ppm [$J(^{13}C\text{–}^{31}P)$ 12 Hz]. The *trans* carbonyl resonance was a weak signal at -31.5 ppm and no spin coupling could be observed.

We propose that the $1,7\text{-}B_9H_9CHP^{2-}$ anion functions simultaneously as a π-ligand to iron and as a σ-ligand to the Group VI metal. A proposed structure for the three-metal complexes is presented in Fig. 1.

In many boron hydride systems it is possible to formally replace a hydride ion on a boron atom with a neutral Lewis base. In the case of the phospha- and arsacarboranes this would give a neutral ligand. σ-Complexes of this type of ligand might be easier to characterize and more readily compared with the complexes of regular organophosphorus and organoarsenic ligands. Oxidation of $[(CH_3)_4N]$-$[7,8\text{-}B_9H_{10}CHP]$ with ferric chloride in benzene solution in the presence of 3-bromopyridine formed bright yellow $7,8\text{-}B_9H_9$(3-bromopyridine)CHP in 30%

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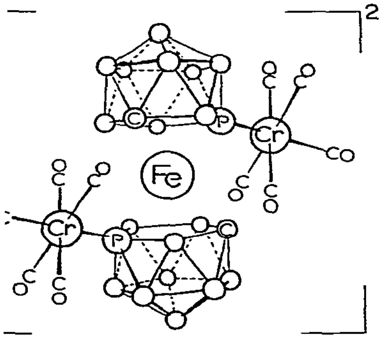
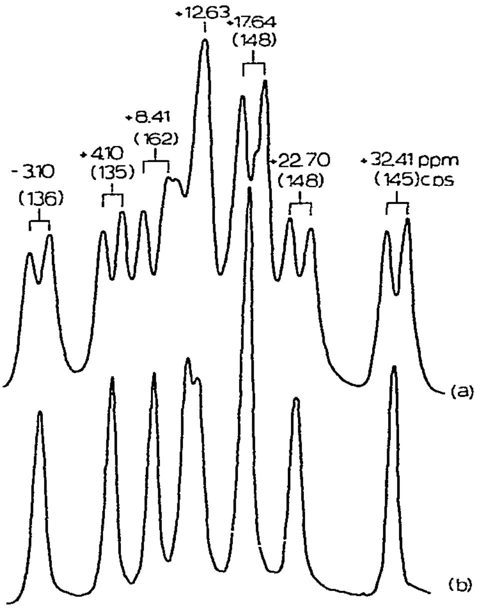
* The ^{13}C chemical shifts are relative to CS$_2$ (0 ppm).





1. Proposed structure of the $\{[1,7\text{-}B_9H_9CHP\cdot Cr(CO)_5]_2Fe\}^{2-}$ ion and related complexes.

2. The 70.6 MHz ^{11}B NMR spectrum of (a) 7,8-B_9H_9(3-bromopyridine)CHP and (b) proton de-
pled spectrum of the same sample in acetone solution externally referenced to $BF_3\cdot O(C_2H_5)_2$.

ld. Employing the same procedure, 7,9-B_9H_9 (bromopyridine) CHAs was also
epared. Similar “oxidative-substitution” reactions have been reported previously
th the isoelectronic 7,8-$B_9C_2H_{12}^-$ system[6]. The new phosphacarborane derivative
s characterized by elemental analysis (Table 1) and measurement of the mass
ectral parent ion peak at high resolution, calcd. for $^{11}B_9{}^{1}H_{14}{}^{12}C_6{}^{14}N^{81}B^{31}P^+$:
1.0864; found: 311.0815.

The ^{11}B NMR spectrum (70.6 MHz) of 7,8-B_9H_9(3-bromopyridine)CHP
presented in Fig. 2. In the proton decoupled spectrum eight of the nine possible
ron resonances are observed. In the ^{11}B NMR (70.6 MHz) of 7,8-$B_9H_{10}CHP^-$
nine of the boron resonances are observable and the span of chemical shifts is
arly the same as the pyridine substituted derivative. The pyridine substituted
ron resonance occurs at 12.6 ppm. This data suggests that a single isomer of
-B_9H_9(3-bromopyridine)CHP was isolated. The position of attachment of the
omopyridine to the carborane cage is not presently known.

Reaction of chromium hexacarbonyl with 7,8-B_9H_9(3-bromopyridine)CHP
tetrahydrofuran solution with UV irradiation produced yellow 7,8-B_9H_9(3-
omopyridine)CHP·$Cr(CO)_5$ in 42% yield. The ^{11}B NMR spectrum of this neutral
rborane complex is presented in Fig. 3. The pyridine substituted boron resonance
at 10.1 ppm. Comparison of the proton decoupled spectra of the free and complexed
osphacarborane indicates that they are quite similar. σ-Coordination through the
osphorus atom would not be expected to seriously change the boron NMR spectrum
free and complexed phosphacarborane.

Graham has proposed a method for separating inductive effects operating

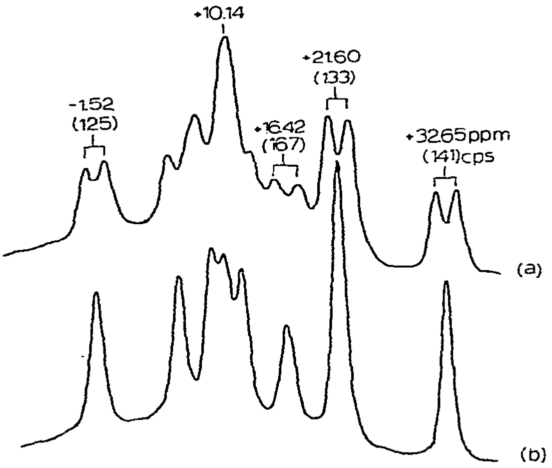


Fig. 3. The 70.6 MHz ^{11}B NMR spectrum of (a) 7,8-B_9H_9(3-bromopyridine)CHP·$Cr(CO)_5$ and (b) proton decoupled spectrum of the same sample in acetone solution externally referenced to $BF_3 \cdot O(C_2H_5)_2$.

through the metal–ligand σ-bond and the metal–ligand π-bond in $LM(CO)_5$ compounds. He has defined the σ and π effects of a ligand in these complexes in terms of the effect of the ligand on the CO force constants. A positive value of σ or π parameters implies that the ligand is acting as a σ or π acceptor, whereas a negative value of σ or π parameters implies the ligand is a σ or π donor relative to the reference ligand cyclohexylamine.

Table 3 contains calculated CO force constants and σ and π parameters for various $LM(CO)_5$ complexes (M=Cr and Mo) in which the ligand is a phosphine or a phosphacarborane. According to Graham's method the phosphacarborane ligands are weaker σ donors than cyclohexylamine. A negative value of the π parameter for the phosphacarborane ligands, including the neutral 7,8-B_9H_9(3-bromopyridine)-

TABLE 3

GRAHAM σ AND π PARAMETERS FOR SOME $LM(CO)_5$ COMPLEXES[a]

Ligand L	Force constants (mdyn/Å)				σ (mdyn/Å)	π (mdyn/Å)
	M	k_1	k_2	k_i		
$P(C_6H_5)_3$[9]	Cr	15.51	15.86		−0.27	+0.35
7,8-$B_9H_{10}CHP^-$	Cr	15.15	15.88	0.32	+0.15	−0.04
7,8-B_9H_9(3-bromopyridine)CHP	Cr	15.12	15.88	0.30	+0.18	−0.07
7,9-$B_9H_{10}CHP^-$	Cr	15.05	15.86	0.32	+0.21	−0.12
$[Fe(1,7\text{-}B_9H_9CHP)_2]^{2-}$	Cr	14.82	15.77	0.29	+0.26	−0.26
PF_3[8]	Mo	16.59	16.54	0.28	−0.09	+0.79
$P(OC_6H_5)_3$[8]	Mo	15.93	16.19	0.29	−0.13	+0.48
$P(C_6H_5)_3$[8]	Mo	15.49	15.96	0.30	−0.15	+0.27
7,9-$B_9H_{10}CHP^-$	Mo	15.03	15.98	0.34	+0.35	−0.21
$[Fe(1,7\text{-}B_9H_9CHP)_2]^{2-}$	Mo	14.77	15.90	0.30	+0.45	−0.39

[a] The reference compound is (cyclohexylamine)metal$(CO)_5$; σ=0, π=0.

CHP, implies that these ligands are π donors. In any event, this comparison suggests that the phosphacarboranes are an unusual type of phosphine ligand.

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