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COMPLEXES OF $B_9H_{10}CHP^-$ AND $B_9H_{10}CHAs^-$ WITH GROUP VI METAL CARBONYLS

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SUMMARY

The photochemical reaction of $(CH_3)_4N[B_9H_{10}CHE]$ (E = P or As) with group VI metal carbonyls lead to the formation of complexes of the general formula, $(CH_3)_4N[B_9H_{10}CHE\cdot M(CO)_5]$. Available evidence suggests that the phosphorus or arsenic atom of the ligand is σ-bonded to the metal carbonyl in these new derivatives.

INTRODUCTION

The phosphorus atom in the cage molecule, 1,2-$B_{10}H_{10}CHP$ was considered to be much like the phosphorus atom of triphenylphosphine. However, attempts to involve the phosphorus lone pair electrons of this molecule in chemical bonding (*e.g.* quaternization with methyl iodide) have not been successful[1]. Treatment of 1,2-$B_{10}H_{10}CHP$ with piperidine results in removal of one boron atom from the cage structure to form the 7,8-$B_9H_{10}CHP^-$ ion***. One of the two equivalent boron atoms adjacent to both the carbon and phosphorus atoms in the icosahedral cage is the atom removed in this base reaction. The 7,8-$B_9H_{10}CHP^-$ ion reacts readily with methyl iodide to form the neutral compound, 7,8-$B_9H_{10}CHPCH_3$[3], demonstrating the increased Lewis basicity of this phosphacarborane.

Treatment of 7,8-$B_9H_{10}CHP^-$ with sodium hydride in tetrahydrofuran and then iron(II) chloride results in the formation of $(7,8\text{-}B_9H_9CHP)_2Fe^{2-}$. In this complex the phosphacarborane ligands are π-bonded to the metal[3]. In addition, this type of ligand should be able to σ-bond to transition metals employing the phosphorus atom lone pair electrons in the manner of triarylphosphines. This paper concerns the preparation and characterization of 1/1 sigma complexes of 7,8-$B_9H_{10}CHP^-$ and related ligands with chromium, molybdenum and tungsten carbonyls.

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*** The numbering systems employed in this article follow the new nomenclature rules which recently appeared[2].

EXPERIMENTAL

General comments

Boron analyses were performed by Schwartzkopf Microanalytical Laboratories, Woodside, New York. Carbon, hydrogen, nitrogen and metal analyses were performed by either the microanalytical laboratory, University of Illinois or by Midwest Microanalytical Laboratories, Indianapolis, Indiana. 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 s, strong; m, medium; or w, weak. Proton NMR spectra were obtained with a Varian A-60 spectrometer. Boron (^{11}B) NMR spectra were obtained using a Varian HA-100 spectrometer operating at 32.1 MHz. Spectral integrals were obtained with an optical planimeter. All spectra were externally referenced to $B(OCH_3)_3$. Addition of -18.15 ppm to the $B(OCH_3)_3$ chemical shift data converts these values to the $BF_3\cdot(C_2H_5)_2O$ standard.

Phosphorus (^{31}P) NMR spectra were obtained at 24.28 MHz using a modified Varian DA-60IL spectrometer utilizing a probe able to accept 13 mm tubes. The field of the DA-60IL spectrometer was locked to an external sample of hexafluorobenzene using a second V4311 transmitter-receiver unit which was tuned to 56.446 MHz. The R.F. frequency for detecting the ^{31}P nuclei was provided by a Hewlett–Packard 5100B frequency synthesizer which was swept (2000 Hz) with a Barry Research linear digitized programmer (LSC-7). A Varian (C-1024) time averaging computer was used for accumulating the spectra. The LSC-7 was triggered directly from the C-1024 unit.

Osmometric molecular weights were determined using a Mechrolab 301A osmometer. Conductometric data were obtained using a Wheatstone bridge and a Beckman CEL-3A fill type cell with a cell constant of 1.89×10^{-1} cm^{-1}. All reactions were carried out under an atmosphere of prepurified nitrogen.

Starting materials

The tetramethylammonium salts of 7,8- and 7,9-$B_9H_{10}CHP^-$ were prepared by the method of Todd, Little and Silverstein[4]. The tetramethylammonium salts of 7,8- and 7,9-$B_9H_{10}CHAs^-$ were prepared by the method briefly described by Todd and coworkers[5]. Chromium hexacarbonyl was purchased from Strem Chemicals, Danvers, Massachusetts. Molybdenum hexacarbonyl was purchased from Climax Molybdenum Company, New York, New York. Tungsten hexacarbonyl was purchased from Pressure Chemical Company, Pittsburgh, Pennsylvania. Tetrahydrofuran was freshly distilled from lithium aluminum hydride.

Reaction of $(CH_3)_4N(7,8\text{-}B_9H_{10}CHP)$ with $Mo(CO)_6$

In a typical experiment, $(CH_3)_4N(7,8\text{-}B_9H_{10}CHP)$ (0.50 g, 0.0021 mole) and $Mo(CO)_6$ (0.46 g, 0.0021 mole) were placed in a Vycor Schlenk tube with 50 ml of dry tetrahydrofuran. The stirred solution was irradiated with a 550 watt high pressure, Hanovia mercury vapor lamp for 12 h. The solvent was removed *in vacuo* at room temperature and the solid products dissolved in 10-15 ml of acetone and then filtered. The solution volume was reduced by slow evaporation at approximately 40° and small portions of methanol were added to the mixture to reduce the solubility of the complex. When the first crystals were observed, 1–2 ml of water was added and the solution heated to approximately 55° to redissolve all solids. Upon cooling white platelets were formed and removed by filtration. A second crop of crystals could be obtained by adding more water. The combined weight of $(CH_3)_4N[7,8\text{-}B_9H_{10}CHP\cdot Mo(CO)_5]$ was 0.336 g (35% yield). The complex decomposed without melting above 130°.

The infrared spectrum contains absorptions at λ_{max} 3030(w), 2530(s), 2079(s), 1950(vs, broad), 1485(s), 1415(w), 1030(w), 1020(m), 990(w), 825(w), 750(w), 730(w), 650(w), 610(s), 585(s) and 475(m) cm^{-1}.

The proton NMR spectrum (acetone-d_6) contains two singlets at τ 6.58 (12 H) and τ 7.18 (1 H).

The osmometric molecular weight in acetone was 236; calcd: 2×231.

$(CH_3)_4N[7,8\text{-}B_9H_{10}CHP\cdot W(CO)_5]$

The method of preparation of this complex and the following compounds is identical to that of $(CH_3)_4N[7,8\text{-}B_9H_{10}CHP\cdot Mo(CO)_5]$. The infrared spectrum exhibits absorptions at λ_{max} 3020(w), 2520(s), 2073(s), 1900(vs, broad), 1480(s), 1445(w), 1415(w), 1055(w), 1025(m), 1015(m), 985(w), 945(m), 820(w), 759(w), 730(w), 650(m), 595(s), 565(s), 495(w), 465(m), 430(m), 420(w, sh) and 370(s) cm^{-1}. The proton NMR spectrum (acetone-d_6) exhibits two singlets at τ 6.6 (12 H) and τ 7.1 (1 H).

$(C_4H_9)_4N[7,8\text{-}B_9H_{10}CHP\cdot Cr(CO)_5]$

The infrared spectrum exhibits absorptions at λ_{max} 3000(w, sh), 2960(m), 2940(m, sh), 2765(m), 2530(s), 2069(s), 1900(vs, broad), 1470(s), 1445(m, sh), 1380(m), 1355(w), 1300(w), 1160(m), 1130(w), 1065(m), 1025(m), 1010(m), 980(w), 915(w), 875 (m), 825(w), 735(m), 675(s), 645(s), 595(w), 500(w), 460(m), 435(w) and 350(w) cm^{-1}.

$(CH_3)_4N[7,9\text{-}B_9H_{10}CHP\cdot Mo(CO)_5]$

The infrared spectrum contains absorptions at λ_{max} 3020(w), 2540(s), 2077(s), 1900(vs, broad), 1480(s), 1415(w), 1090(w), 1070(m), 985(m), 945(s), 705(s), 680(s) and 540(s) cm^{-1}. The proton NMR spectrum (acetone-d_6) contains two singlets at τ 6.60 (12 H) and τ 7.15 (1 H).

$(CH_3)_4N[7,9\text{-}B_9H_{10}CHP\cdot W(CO)_5]$

The infrared spectrum contains absorptions at λ_{max} 3020(w), 2540(s), 2073(s), 1900(vs, broad), 1480(s), 1410(m), 1080(m), 1060(m), 1020(w), 1000(w), 980(m), 940(s), 860(w), 800(w), 745(m), 590(s), 565(s), 510(m, sh), 460(m), 440(m), 400(m) and 365(s) cm^{-1}. The proton NMR spectrum (acetone-d_6) contains two singlets at τ 6.56 (12 H) and τ 7.15 (1 H).

$(CH_3)_4N[7,9\text{-}B_9H_{10}CHP\cdot Cr(CO)_5]$

The infrared spectrum contains absorptions at λ_{max} 3020(w), 2535(s), 2067(s), 1900(vs, broad), 1480(s), 1410(m), 1085(m), 1060(m), 1020(w), 980(m), 940(s), 915(w, sh), 860(w), 740(m), 675(s), 640(s), 535(m), 450(s), 380(w) and 350 (w) cm^{-1}. The proton NMR spectrum (acetone-d_6) contains two singlets at τ 6.60 (12 H) and τ 7.15 (1 H).

$(CH_3)_4N[7,8\text{-}B_9H_{10}CHAs\cdot Mo(CO)_5]$

The infrared spectrum contains absorptions at λ_{max} 3020(w), 2520(s), 2079(s), 1950(vs, broad), 1480(s), 1415(w), 1110(w), 1060(m), 1025(m), 1005(m), 980(m, sh), 945(s), 930(w, sh), 740(w), 600(s), 545(s), 435(w), 380(m), 360(s) and 310(m) cm^{-1}. The proton NMR spectrum (acetone-d_6) contains two singlets at τ 6.60 (12 H) and τ 7.15 (1 H).

$(CH_3)_4N[7,9\text{-}B_9H_{10}CHAs\cdot Mo(CO)_5]$

The infrared spectrum contains absorptions at λ_{max} 3020(w), 2530(s), 2073(s), 1900(vs, broad), 1480(s), 1415(w), 1090(m), 1060(m), 1020(w), 980(m), 940(w), 740(w), 605(s), 580(s), 380(w) and 360(s) cm^{-1}. The proton NMR spectrum (acetone-d_6) contains two singlets at τ 6.60 (12 H) and τ 7.15 (1 H).

$(CH_3)_4[7,9\text{-}B_9H_{10}CHAs\cdot W(CO)_5]$

The infrared spectrum contains absorptions at λ_{max} 3020(w), 2535(s), 2073(s), 1900(vs, broad), 1480(s), 1445(w), 1415(w), 1085(m), 1065(m), 1020(w), 985(m), 940(s), 750(w), 675(s), 640(s), 535(m), 450(s), 380(w) and 350(w) cm^{-1}. The proton NMR spectrum (acetone-d_6) contains two singlets at τ 6.60 (12 H) and τ 7.15 (1 H).

$(CH_3)_4N[7,9\text{-}B_9H_{10}CHAs\cdot Cr(CO)_5]$

The infrared spectrum contains absorptions at λ_{max} 3020(w), 2535(s), 2064(s), 1900(vs, broad), 1480(s), 1445(w), 1415(w), 1085(m), 1065(m), 1020(w), 985(m), 940(s), 750(w), 675(s), 640(s), 535(m), 450(s), 380(w) and 350(w) cm^{-1}. The proton NMR spectrum (acetone-d_6) contains two singlets at τ 6.60 (12 H) and τ 7.15 (1 H).

RESULTS AND DISCUSSION

A tetrahydrofuran solution of $(CH_3)_4N[7,8\text{-}B_9H_{10}CHP]$ and $Mo(CO)_6$ in a 1/1 mole ratio was irradiated with a high pressure mercury-vapor lamp for 10 h. The crude product could be crystallized as thin plates from acetone/water if care was taken not to heat the compound over 55°. The analytical data for $(CH_3)_4N[7,8\text{-}B_9H_{10}\text{-}CHP\cdot Mo(CO)_5]$ and the other complexes described in this article are given in Table 1.

The conductivity of $(CH_3)_4N[7,8\text{-}B_9H_9CHP\cdot Mo(CO)_5]$ was determined in acetone solution over the concentration range 9.6×10^{-4} to 3.00×10^{-3} *M*. These data were compared with the conductivity of $(C_2H_5)_4N[ClO_4]$ over the same concentration range and a graph of the square root of the concentration versus the observed molar conductivity is given in Fig. 1. This study strongly suggests that the phosphacarborane complex is a 1/1 electrolyte. Further evidence concerning the molecular formula of this complex was obtained from an osmometric molecular weight determination (acetone solution), calcd. for $(CH_3)_4N[7,8\text{-}B_9H_{10}CHP\cdot Mo\text{-}(CO)_5]$: 2×231; found: 236.

Ten of the twelve possible derivatives of the type, $LM(CO_5)^-$ (where M=Cr, Mo or W and L=7,8- or 7,9-$B_9H_{10}CHP^-$ or 7,8- or 7,9-$B_9H_{10}CHAs^-$) have been characterized. All the complexes were prepared by the procedure described above. The chromium complexes appear to be the most heat sensitive in solution and were the most difficult to purify by crystallization. In the solid state, the complexes decompose

TABLE 1

ANALYTICAL DATA OF SUBSTITUTED METAL CARBONYL DERIVATIVES

Compound	Analyses, found (calcd.) (%)				
	C	H	N	B	M
$7,8\text{-}B_9H_{10}CHPCr(CO)_5^-$ [a]	45.66	8.80	2.33		
	(45.10)	(8.09)	(2.39)	(16.59)	(8.87)
$7,8\text{-}B_9H_{10}CHPMo(CO)_5^-$ [b]	26.28	5.30	3.35	21.15	19.71
	(26.02)	(5.02)	(3.03)	(21.08)	(20.79)
$7,8\text{-}B_9H_{10}CHPW(CO)_5^-$	22.14	4.46	2.05		
	(21.86)	(4.22)	(2.53)	(17.71)	(33.46)
$7,9\text{-}B_9H_{10}CHPCr(CO)_5^-$	29.10	5.81	3.98		
	(30.00)	(5.79)	(3.50)	(11.82)	(12.99)
$7,9\text{-}B_9H_{10}CHPMo(CO)_5^-$	26.04	5.26	3.29		19.97
	(26.02)	(5.02)	(3.03)	(21.08)	(20.79)
$7,9\text{-}B_9H_{10}CHPW(CO)_5^-$	21.92	4.46	2.42	16.96	
	(21.86)	(4.22)	(2.53)	(17.71)	(33.46)
$7,8\text{-}B_9H_{10}CHAsMo(CO)_5^-$	23.83	4.94	3.15		
	(23.83)	(4.61)	(2.78)	(19.25)	(19.00)
$7,9\text{-}B_9H_{10}CHAsCr(CO)_5^-$	25.19	5.38	2.90		
	(25.99)	(5.16)	(3.03)	(21.09)	(11.27)
$7,9\text{-}B_9H_{10}CHAsMo(CO)_5^-$	22.60	5.08	2.54		
	(23.83)	(4.61)	(2.78)	(19.25)	(19.00)
$7,9\text{-}B_9H_{10}CHAsW(CO)_5^-$	20.63	3.95	2.91		
	(20.24)	(3.91)	(2.36)	(16.44)	(31.99)

[a] Tetrabutylammonium salt. [b] This and subsequent complexes are tetramethylammonium salts.

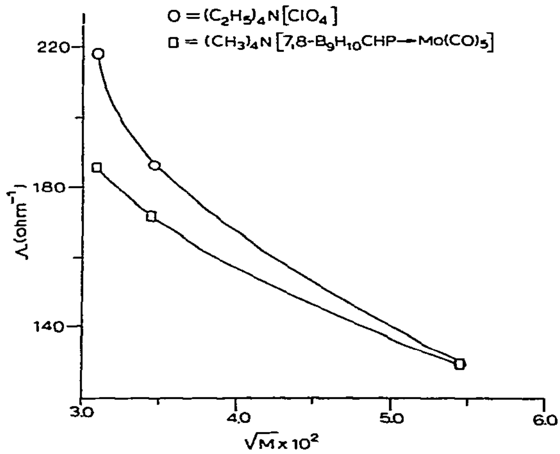


Fig. 1. Molar conductivity data in acetone solution for $(CH_3)_4N[7,8\text{-}B_9H_{10}CHP \cdot Mo(CO)_5]$ and $(C_2H_5)_4N[ClO_4]$.

above 110° but can be stored in air at room temperature for two to three weeks with negligable decomposition. After six months storage in air, extensive decomposition had occurred. An attempt to prepare the molybdenum carbonyl complex of $7,8\text{-}B_9H_{10}CHSb^-$ using the described procedure was unsuccessful.

The infrared spectra (acetonitrile solution) of the metal carbonyl stretching region for the compounds are reported in Table 2. The spectrum of $(CH_3)_4N[7,9\text{-}$

TABLE 2

INFRARED SPECTRAL DATA IN THE CARBONYL REGION

Compound	CO stretching frequency[a] (cm^{-1})			
	$A_1^{(2)}$	B_1	E	$A_1^{(1)}$
$7,8\text{-}B_9H_{10}CHPCr(CO)_5^-$ [b]	2069 m	1983 vw	1943 vs	1925 s
$7,8\text{-}B_9H_{10}CHPMo(CO)_5^-$ [c]	2079 m	1983 vw	1950 vs	1927 s
$7,8\text{-}B_9H_{10}CHPW(CO)_5^-$	2073 m	1989 vw	1941 vs	1920 s
$7.9\text{-}B_9H_{10}CHPCr(CO)_5^-$	2067 m	1982 vw	1942 vs	1919 s
$7,9\text{-}B_9H_{10}CHPMo(CO)_5^-$	2077 m	1989 vw	1946 vs	1917 s
$7,9\text{-}B_9H_{10}CHPW(CO)_5^-$	2073 m	1983 vw	1939 vs	1911 s
$7,8\text{-}B_9H_{10}CHAsMo(CO)_5^-$	2079 m		1950 vs	1902 s
$7,9\text{-}B_9H_{10}CHAsCr(CO)_5^-$	2064 m	1986 vw	1953 vs	1912 s
$7,9\text{-}B_9H_{10}CHAsMo(CO)_5^-$	2073 m	1993 vw	1947 vs	1907 s
$7,9\text{-}B_9H_{10}CHAsW(CO)_5^-$	2073 m	1988 vw	1937 vs	1905 s

[a] m, medium; vw, very weak; s, strong; vs, very strong. [b] Tetrabutylammonium salt. [c] This and subsequent complexes are tetramethylammonium salts.

$B_9H_{10}CHP \cdot W(CO)_5]$, a typical example, is given in Fig. 2. Employing the local symmetry approximation, a compound of the $LM(CO)_5^-$ type (C_{4v} point symmetry) has four stretching modes in the carbonyl region. Based on the relative band positions and intensities and application of the secular equations of Cotton and Kraihanzel[6], we have made the following assignments of the carbonyl bands. Reading from lowest frequency one observes the $A_1^{(1)}$, E, B_1 and $A_1^{(2)}$ bands respectively. The stretching frequency of the CO ($A_1^{(1)}$) *trans* to the phosphacarborane ligand is at 1927–1911 cm^{-1} which is intermediate between the position of the $A_1^{(1)}$ band of (amine)$M(CO)_5$ compounds (1905–1895 cm^{-1})[7] and the $A_1^{(1)}$ band of (phosphine)$M(CO)_5$ complexes

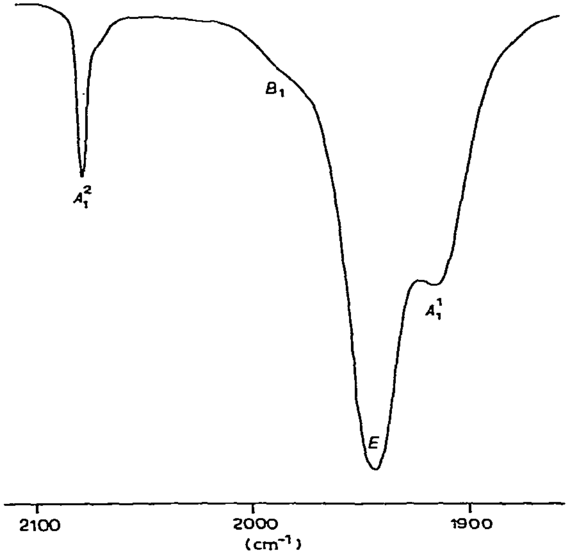


Fig. 2. The infrared spectrum (acetonitrile solution) of $(CH_3)_4N[7,9\text{-}B_9H_{10}CHP \cdot W(CO)_5]$ in the carbonyl stretching region.

(1950–1934 cm^{-1})[8]. This suggests that the phosphacarborane ligands may have weaker π-acceptor ability than trialkylphosphines.

All the proton NMR spectra of these complexes consist of a sharp singlet at τ 6.6 (12 H) and a broad singlet at τ 7.2 assigned to the tetramethyl ammonium and carborane CH protons respectively.

In most cases, the ^{11}B NMR spectrum (32.1 MHz) of the free ligand and the corresponding metal carbonyl complex are quite similar (see Fig. 3). σ-Coordination through the phosphorus or arsenic atom would not be expected to seriously change the electronic environment of the boron cage and therefore the boron spectra of the ligand and the complex should be similar. Further interpretation of these complex boron spectra was not attempted.

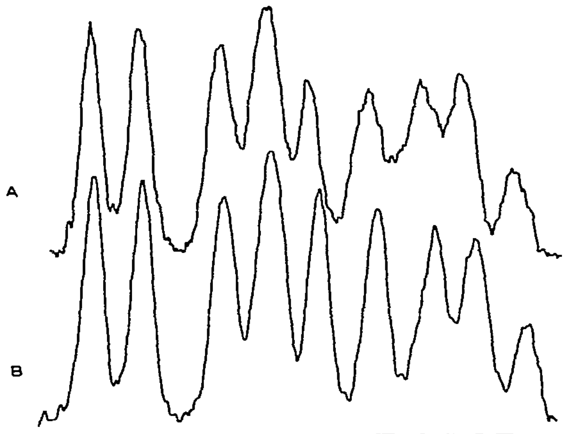
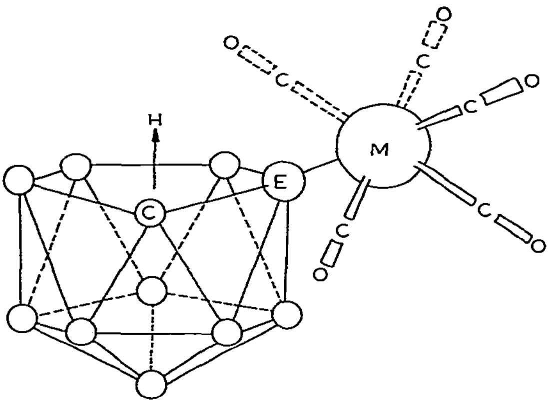


Fig. 3. The ^{11}B NMR spectra (32 MHz) of (a) 7,8-$B_9H_{10}CHAs \cdot Mo(CO)_5^-$ and (b) 7,8-$B_9H_{10}CHAs^-$ in acetone solution externally referenced to $BF_3 \cdot O(C_2H_5)_2$.

The ^{31}P NMR spectrum (24.3 MHz) of $(CH_3)_3NH$(7,8-$B_9H_{10}CHP$) (acetone solution) contained a very broad peak centered at +48.2 ppm (85% H_3PO_4 = 0 ppm). The ^{31}P chemical shifts of $R_3PM(CO)_5$ complexes studied by Grim, Wheatland and McFarlane[8] were always found at much lower field than the free ligand resonance. In contrast, the broad ^{31}P signal of $(CH_3)_4N$[7,8-$B_9H_{10}CHP \cdot W(CO)_5$] (acetone solution) was centered at +56.7 ppm. The change in the phosphorus NMR between the free phosphacarborane anion and the metal carbonyl complex suggests that there is a direct interaction between the phosphorus and tungsten atoms in this complex. However, the reason for the direction of change in chemical shifts is not at present known.

The data described above are consistent with the postulate that the $B_9H_{10}CHP^-$ and $B_9H_{10}CHAs^-$ ions are functioning as 2-electron σ-ligands in the Group VI metal carbonyl complexes reported here. A proposed structure for these metal carbonyl anions is presented in Fig. 4. Thus it has now been demonstrated that these heteratom carboranes can function as either σ- or π-bonding ligands to metals. It remains to be shown that this type of ligand can function simultaneously as both a σ- and



E = P, As
M = Cr, Mo, W

Fig. 4. Proposed structure of the 7,8-$B_9H_{10}CHE \cdot M(CO)_5^-$ complexes.

π-bonding ligand to different metal atoms. This aspect is at present being actively investigated.

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