Journal of Organometallic Chemistry, 55 (1973) 363–369
© Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

σ-BONDED COMPLEXES OF THE 7,8- AND 7,9-$B_9H_{10}CHP^-$ IONS WITH IRON AND MANGANESE CARBONYLS

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

(Received November 13th, 1972)

SUMMARY

The photochemical reaction of 7,8-$B_9H_{10}CHP^-$ and 7,9-$B_9H_{10}CHP^-$ with $Fe(CO)_5$ and $Mn_2(CO)_{10}$ leads to the formation of complexes in which the phosphacarborane ligand has replaced a carbonyl group, forming σ-bonded transition metal complexes. Available evidence indicates that the phosphorus atom in the carborane ligand is bonded directly to the metal atom in these complexes.

INTRODUCTION

Recently, we reported[1] that 7,8- and 7,9-$B_9H_{10}CHE^-$ (E = P or As) under photochemical conditions reacted with Group VI metal carbonyls to form 1/1 σ complexes of the general formula $B_9H_{10}CHE{-}M(CO)_5^-$. The formation of σ-bonded complexes of $(1,7\text{-}B_9H_9CHE)_2Fe^{2-}$ with Group VI metal carbonyls has also been demonstrated[2]. This paper describes the preparation and properties of σ-bonded complexes of 7,8- and 7,9-$B_9H_{10}CHP^-$ with iron and manganese carbonyls.

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 ^{11}B spectra were externally referenced to $BF_3 \cdot O(C_2H_5)_2$. Proton NMR spectra were obtained with a Varian HA-100 or HR-220 spectrometer. The carbon-13 NMR spectra were obtained with a Fourier Transform Pulsed NMR spectrometer operating at 15.08 MHz as described previously[3].

Carbon, hydrogen, nitrogen, boron and metal analyses were performed 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.

Osmometric molecular weights were determined in acetone solutions by

---

* Contribution No. 2162.

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 or argon.

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]. Iron pentacarbonyl was purchased from General Aniline and Film Corporation and vacuum distilled before use. Dimanganese decacarbonyl was purchased from Ventron Corporation, Beverly, Massachusetts. Tetrahydrofuran was freshly distilled from lithium aluminum hydride.

Trimethylammonium salt of 7,8-$B_9H_{10}CHP^-$

The crude tetramethylammonium salt of the $B_9H_{10}CHP^-$ ion was dissolved in a 80/20 mixture of acetonitrile/water and slowly passed through a five-fold excess exchange capacity of sodium ion exchange resin. After removal of solvent the resulting white hygroscopic material was dissolved in a minimum of water, and a saturated aqueous solution of trimethylamine hydrochloride was added until precipitation was complete. Recrystallization was readily accomplished from acetone/water to give an 80% yield of purified product.

Potassium salt of 7,8-$B_9H_{10}CHP^-$

Into a 50 ml flask were placed 2.0 g (9.40 mmol) of $[(CH_3)_3NH][7,8\text{-}B_9H_{10}\text{-}CHP]$ and 1.6 g (28.2 mmol) of potassium hydroxide dissolved in 15 ml of water. The resulting solution was heated to 70° for 3–4 h (or until trimethylamine could no longer be detected in the exhaust gas). After cooling, gaseous CO_2 was bubbled through the system for two hours with stirring. The precipitated K_2CO_3 was separated by filtration and washed with 20 ml of ether. The aqueous filtrate was evaporated to dryness, and the residual solid was extracted with three 30 ml portions of ether. The combined ether extracts were placed in a distillation apparatus and distilled using benzene as a carrier. As the aqueous ether phase was azeotroped away, a white product crystallized on the sides of the flask. When the solution was concentrated to approximately 10 ml of benzene, the white crystalline product was separated by filtration to give 1.3 g (yield 70%) of the potassium salt, $K[7,8\text{-}B_9H_{10}CHP]$.

$[(CH_3)_4N][7,8\text{-}B_9H_{10}CHP\text{–}Fe(CO)_4]$

$K[7,8\text{-}B_9H_{10}CHP]$ and $Fe(CO)_5$ (a two fold excess) in tetrahydrofuran were photolyzed for 4 h. During the course of the reaction the solution changed in color from yellow to rusty-red. The solvent and unreacted $Fe(CO)_5$ were removed using a vacuum system (10^{-3} mmHg) and condensed in a liquid nitrogen trap. The recovered yellow powder was dissolved in H_2O and filtered. An aqueous solution of tetramethylammonium chloride was added until precipitation was complete. The solid was filtered and recrystallized in an aspirator vacuum from methylene chloride/chloroform to obtain 0.46 g (yield 70%) of feathery yellow needle crystals. The complex decomposed without melting at 174–176°.

The infrared spectrum contains absorption maxima at 2525 s, 2041 vs, 1972 vs, 1952 vs, 1929 vs, 1481 s, 1025 w, 1010 m, 987 w, 942 m, 649 m, 617 s and 467 w cm^{-1}.

Reaction of $[(CH_3)_4N][7,8\text{-}B_9H_{10}CHP]$ *with* $Mn_2(CO)_{10}$

$[(CH_3)_4N][7,8\text{-}B_9H_{10}CHP]$ (0.250 g, 1.10 mmol) and $Mn_2(CO)_{10}$ (0.429 g, 1.10 mmol) were placed in a Vycor Schlenk tube with 50 ml of dry tetrahydrofuran. The mixture was irradiated with a 550 W high pressure Hanovia mercury vapor lamp for 13 h. The resulting yellow-orange solution was rotary evaporated to dryness, and the residue was washed three times with 25 ml portions of hexane. The crude yellow product was then dissolved in a minimum of ethyl acetate and filtered. The addition of hexane to the filtrate resulted in the precipitation of a yellow amorphous powder. This material was dissolved in a 50/50 mixture of acetone/methanol, and the volume of the solvent was reduced without heating. A few drops of water were added as the material concentrated. When the first crystals were observed, the solution was placed in an ice bath then transferred to a $-10°$ refrigerator. After about 20 min at this temperature the solution was filtered to obtain a crop of yellow needle crystals. A second crop was obtained by further reduction of the volume of solvent and subsequent cooling. The yield of $[(CH_3)_4N][7,8\text{-}B_9H_{10}CHP\text{–}Mn_2(CO)_9]$ was 52%.

The infrared spectrum (KBr) contains absorption maxima at 2530 s, 2082 vs, 2010 vs, 1964 vs, 1932 vs, 1920 vs, 1478 s, 1020 w, 1005 w, 937 m, 630 s, 540 w, 477 w, 460 m, and 393 w cm^{-1}. The proton NMR spectrum (acetone-d_6) contains two singlets at τ 6.60 (12 H) and 8.35 (1 H). The 70.6 MHz ^{11}B NMR spectrum of $(CH_3)_4N$-$[7,8\text{-}B_9H_{10}CHP\text{–}Mn_2(CO)_9]$ in acetone exhibited doublets at [chemical shifts in ppm relative to $BF_3\cdot O(C_2H_5)_2$ (relative intensity), coupling constant (Hz)]: -1.74 (1 B), 145; $+5.6$ (1 B), 140; $+8.3$ (1 B); $+11.1$ (1 B), 150; $+13.5$ (1 B), 150; $+24.2$ (3 B); $+31.03$ (1 B), 150.

$[(CH_3)_4N]_2[7,9\text{-}B_9H_{10}CHP\text{–}Mn(CO)_4]_2$

The method of preparation of this complex was similar to that of $[(CH_3)_4N]$-$[7,8\text{-}B_9H_{10}CHP\text{–}Mn_2(CO)_9]$ except that the tetramethylammonium salt was purified by recrystallization from a methylene chloride/acetone/chloroform solvent system. The complex softened at 200° and decomposed at 307–310°. The infrared spectrum exhibits absorption maxima at 2535 s, 2043 s, 1975 vs, 1940 vs, 1908 vs, 1479 s, 1080 w, 1060 w, 978 w, 940 m, 740 w, 640 m and 624 s cm^{-1}. The proton NMR spectrum (acetone-d_6) contains two singlets at τ 6.57 (12 H) and 7.10 (1 H).

RESULTS AND DISCUSSION

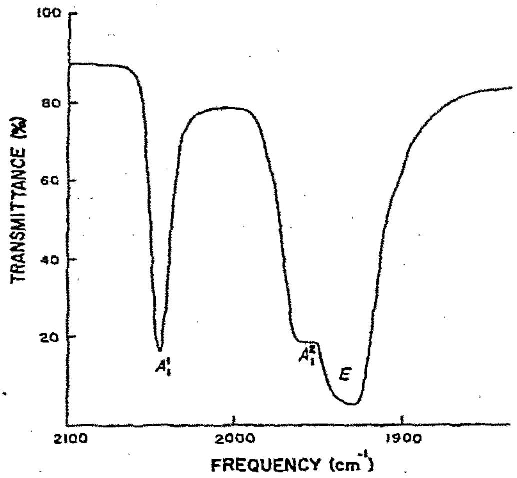
Photolysis of $Fe(CO)_5$ and the potassium salt of $7,8\text{-}B_9H_{10}CHP^-$ in tetrahydrofuran gave high yields ($\approx 70\%$) of $7,8\text{-}B_9H_{10}CHP\text{–}Fe(CO)_4^-$. The yellow crystalline compound is relatively unstable in air and begins to darken within a few hours of exposure. The salt, however, can be stored under argon for several weeks with negligible decomposition. The elemental analysis data of this complex and the other new compounds reported in the article are given in Table 1.

The infrared spectrum (acetonitrile solution) (Fig. 1) of the carbonyl stretching region was similar to that of a series of mono-substituted iron carbonyl complexes, of the type $LFe(CO)_4$, studied by Cotton[5], in which a square pyramidal structure was rejected in favor of the C_{3v} form on the grounds of selection rules. Assignment of the IR-active bands was made following the method of Bigorgne[6]: the high intensity low frequency band to the E mode, the higher of the two A_1 modes due to the equatori-

TABLE 1

ANALYTICAL DATA OF σ-BONDED COMPLEXES

Compound	*Analysis, found (calcd.) (%)*				
	C	*H*	*B*	*Fe or Mn*	*N*
$[(CH_3)_4N][7,8\text{-}B_9H_{10}CHP\text{–}Fe(CO)_4]$	27.32	5.68	24.85	13.99	3.58
	(27.47)	(5.90)	(24.73)	(14.20)	(3.56)
$[(CH_3)_4N][7,8\text{-}B_9H_{10}CHP\text{–}Mn_2(CO)_9]$	28.78	3.85	16.19	18.88	2.68
	(28.63)	(3.92)	(16.57)	(18.71)	(2.38)
$[(CH_3)_4N]_2[7,9\text{-}B_9H_{10}CHP\text{–}Mn(CO)_4]_2$	27.42	5.89		13.28	3.22
	(27.55)	(5.87)		(13.99)	(3.57)



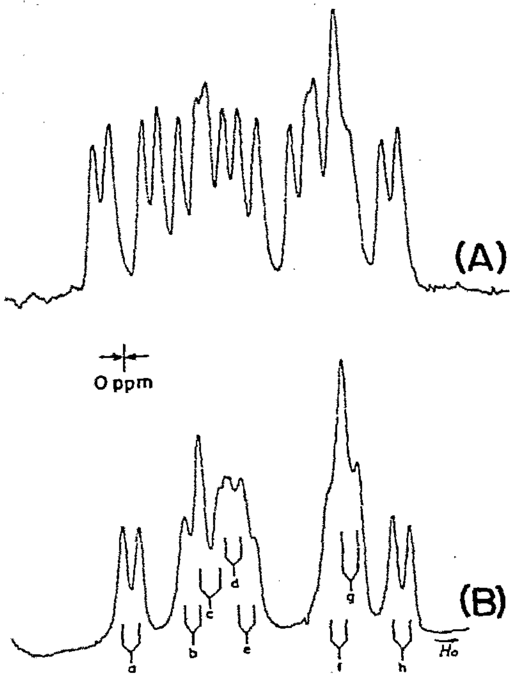


Fig. 1. The infrared spectrum (acetonitrile solution) of $[(CH_3)_4N][7,8\text{-}B_9H_{10}CHP\text{–}Fe(CO)_4]$ in the carbonyl stretching region. Absorption maxima occur at 2045 (A_1^1), 1954 (A_1^2), and 1926 (E) cm^{-1}.

Fig. 2. (A). The 70.6 MHz ^{11}B NMR spectrum of $[(CH_3)_4N][7,8\text{-}B_9H_{10}CHP]$ in methylene chloride. (B). The 70.6 MHz ^{11}B NMR spectrum of $[(CH_3)_4][7,8\text{-}B_9H_{10}CHP\text{–}Fe(CO)_4]$ in methylene chloride. Chemical shifts [ppm relative to external $BF_3 \cdot O(C_2H_5)_2$], (number of boron atoms) and coupling constants (Hz) are: (a) +0.7 (1 B), 140; (b) +7.9 (1 B), ~140; (c) +9.9 (1 B), ≈160; (d) +12.7 (1 B), ≈140; (e) +14.3 (1 B), ≈140; (f) +25.1 (1 B), ≈130; (g) +26.6 (2 B), ≈140; and (h) +32.7 (1 B), 140.

al symmetric stretch (A_1^1) and the remaining band due to the axial CO stretching mode (A_1^2). These data suggest a trigonal bipyramidal structure in which the phosphacarborane ligand is axially substituted.

The proton NMR spectrum of $[(CH_3)_4N][7,8\text{-}B_9H_{10}CHP\text{–}Fe(CO)_4]$ consisted of a sharp singlet at τ 6.58 (12 H) and a broad singlet at τ 6.26 (1 H) assigned to the tetramethylammonium and carborane CH protons, respectively. The ^{11}B NMR spectrum (70.6 MHz) of the free carbaphosphaborane ligand* and the corresponding metal carbonyl complex are given in Fig. 2.

σ-Coordination through the phosphorus atom would not be expected to seriously change the electronic environment of the boron cage and, therefore, the boron NMR spectrum of free and complexed phosphacarborane should bear some similarity. The ^{11}B NMR spectrum of the iron complex (Fig. 2B) is interpreted in terms of eight doublets representing nine different borons (two of which are accidentally degenerate) which are slightly shifted from the resonance positions of the free ligand.

The ^{13}C NMR spectrum** of $[(CH_3)_4N][7,8\text{-}B_9H_{10}CHP\text{–}Fe(CO)_4]$ in methylene chloride solution contained a doublet at -213.33 ppm, $J(^{13}C\text{–}^{31}P)$ 22 Hz assigned to the carbonyl carbons. The presence of one doublet suggests that the three carbonyl groups in the equatorial positions and the single carbonyl group in the axial position are undergoing rapid exchange in methylene chloride at room temperature, and that on the relatively slow NMR time scale an average environment is detected***. The observed $^{13}C\text{–}^{31}P$ spin coupling, however, does indicate the close proximity of the phosphorus atom to the carbonyl carbon atoms and gives support to the proposal that the $B_9H_{10}CHP^-$ ligand is σ-bonded via the phosphorus atom to the iron atom.

The reaction of $7,8\text{-}B_9H_{10}CHP^-$ with dimanganese decacarbonyl resulted in substitution with retention of the metal–metal bond, producing $7,8\text{-}B_9H_{10}CHP\text{–}Mn_2(CO)_9^-$ in moderate yield. The molecular formula was further confirmed by determination of the osmometric molecular weight in acetone (calcd. 587, found 614).

Two different positions of substitution of the phosphacarborane ligand in this mono-substituted nonacarbonyldimanganese(0) compound are possible. Group theory predicts that five bands ($2E$ and $3A_1$) should be present in the carbonyl stretching region of the solution infrared spectrum for axial substitution, while the symmetry of the equatorially substituted molecule demands nine bands ($6A'$ and $3A''$)[7]. The observation of five bands (Fig. 3) in the solution IR spectrum of $7,8\text{-}B_9H_{10}CHP\text{–}Mn_2(CO)_9^-$ argues in favor of substitution at the axial position. In contrast, Fischer[8], recently reported the photochemical reaction between PH_3 and $Mn_2(CO)_{10}$ to give equatorially-substituted $(PH_3)Mn_2(CO)_9$. Because of steric factors it is not surprising that the bulky boron hydride ligand appears to bond at the least hindered (axial) site of the metal carbonyl. The ^{11}B NMR spectrum of this

---

* The chemical shift values (and coupling constants) of the nine doublets of $[(CH_3)_4N][7,8\text{-}B_9H_{10}\text{-}CHP]$ in acetone solution [ppm relative to external $BF_3 \cdot O(C_2H_5)_2$] are: -2.33 (135), $+3.47$ (135), $+7.95$ (155), $+11.13$ (145), $+15.07$ (160), $+21.15$ (145), $+24.15$ (160), $+26.20$ (140) and 31.50 (140). The spectrum and chemical shift data of this compound in methylene chloride and acetone solution are nearly identical.

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

*** A similar effect was observed in $Fe(CO)_5$. The ^{13}C NMR spectrum at room temperature of a neat liquid sample exhibited one sharp singlet at -211.24 ppm.

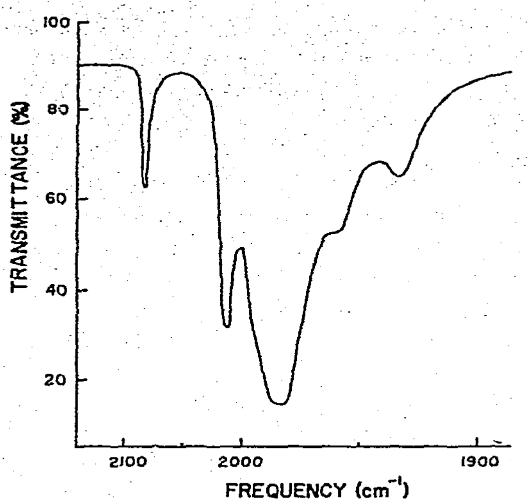


Fig. 3. The infrared spectrum (acetonitrile solution) of $[(CH_3)_4N][7,8\text{-}B_9H_{10}CHP\text{-}Mn_2(CO)_9]$ in the carbonyl stretching region. The following absorption maxima are observed: 2084, 2009, 1975, 1951, and 1929 cm^{-1}.

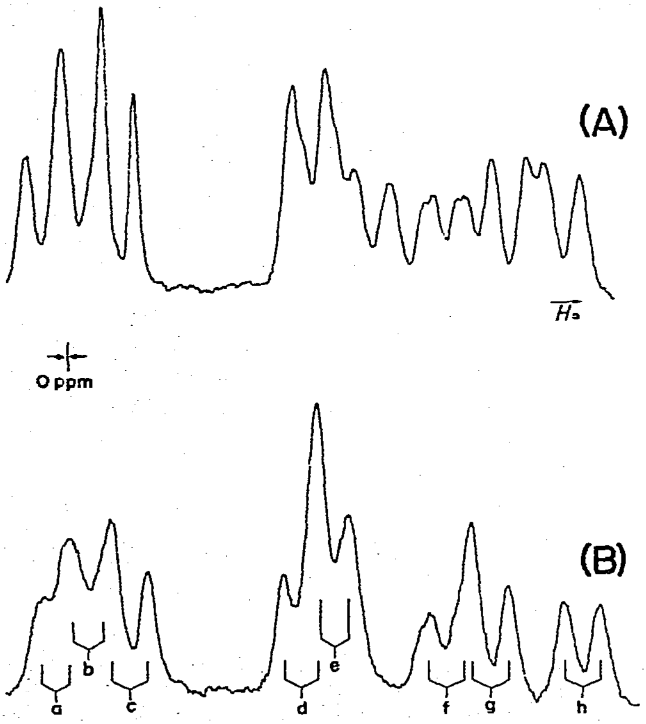


Fig. 4. (A). The 70.6 MHz ^{11}B NMR spectrum of $[(CH_3)_4N][7,9\text{-}B_9H_{10}CHP]$ in acetone.
(B). The 70.6 MHz ^{11}B NMR spectrum of $[(CH_3)_4N]_2[7,9\text{-}B_9H_{10}CHP\text{-}Mn(CO)_4]_2$ in acetone. Chemical shifts [ppm relative to external $BF_3 \cdot O(C_2H_5)_2$], number of borons and coupling constants (Hz) are: (a) −0.99 (1 B), ≈140; (b) +1.2 (1 B), ≈140; (c) +2.8 (1 B), ≈150; (d) +13.6 (1 B), ≈150; (e) +15.2 (2 B), ≈130; (f) +21.5 (1 B), ≈150; (g) +24.4 (1 B), ≈150; and (h) +30.03 (1 B), 140.

manganese complex has similar features and chemical shift values (see Experimental Section) to that of 7,8-$B_9H_{10}CHP–Fe(CO)_4^-$.

In contrast to the 7,8- anion, 7,9-$B_9H_{10}CHP^-$ reacted with $Mn_2(CO)_{10}$ under photolytic conditions to give a yellow-orange crystalline material that analyzed for $[(CH_3)_4]_2[$7,9-$B_9H_{10}CHP–Mn(CO)_4]_2$. Stiddard[9] has investigated the reactions of $Mn_2(CO)_{10}$ with various tertiary phosphines with photochemical initiation and has reported that this method leads predominantly to products of the type $[Mn(CO)_4L]_2$. Reaction of these manganese complexes with bromine resulted in uptake of two bromine atoms per molecule and the formation of $BrMn(CO)_4L$ in good yield. This suggested that one phosphine is attached to each metal atom in this type of complex. Application of simple group theory predicts only two infrared-active C–O stretching modes (E_1 and B_2). Although three strong and one weak bands are exhibited by the $[$7,9-$B_9H_{10}CHP–Mn(CO)_4]^{2-}$ complex, the asymmetry of the carborane ligand could easily account for the additional modes.

The ^{11}B NMR (70.6 MHz) spectrum of $[(CH_3)_4N]_2[$7,9-$B_9H_{10}CHP–Mn(CO)_4]_2$ (Fig. 4) covers about the same range of chemical shift values and is similar in character to that of the free ligand. The unshifted ^{11}B NMR spectrum of $[$7,9-$B_9H_{10}CHP–Mn(CO)_4]_2^{2-}$ suggests that this complex is diamagnetic.

The data described above are consistent with the postulate that the 7,8- and 7,9-$B_9H_{10}CHP^-$ ions function as 2-electron σ-ligands in Group VII and VIII metal carbonyl complexes.

REFERENCES

1 H. T. Silverstein, D. C. Beer and L. J. Todd, *J. Organometal. Chem.*, 21 (1970) 139.
2 D. C. Beer and L. J. Todd, *J. Organometal. Chem.*, 36 (1972) 77.
3 D. Doddrell and A. Allerhand, *Proc. Nat. Acad. Sci. U.S.*, 68 (1971) 1083.
4 L. J. Todd, J. L. Little and H. T. Silverstein, *Inorg. Chem.*, 8 (1969) 1698.
5 F. A. Cotton and R. V. Parish, *J. Chem. Soc.*, (1960) 1440.
6 A. Reckziegel and M. Bigorgne, *J. Organometal. Chem.*, 3 (1965) 341.
7 M. L. Ziegler, H. Haas and R. K. Sheline, *Chem. Ber.*, 98 (1965) 2454.
8 E. O. Fischer and W. A. Herrman, *Chem. Ber.*, 105 (1972) 286.
9 A. G. Osborne and M. H. B. Stiddard, *J. Chem. Soc.*, (1964) 634.