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σ-BONDED COMPLEXES OF SOME HETEROATOM BORANES WITH IRON AND MOLYBDENUM DERIVATIVES

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Summary

Reaction of the cationic complexes $[(\pi\text{-}C_5H_5)Fe(CO)_2(\text{cyclohexene})]^+$ and $[(\pi\text{-}C_7H_7)Mo(CO)_3]^+$ with $[1,2\text{-}GeCHB_{10}H_{10}]^-$ forms the neutral complexes $(\pi\text{-}C_5H_5)Fe(CO)_2GeCHB_{10}H_{10}$ and $(\pi\text{-}C_7H_7)Mo(CO)_2GeCHB_{10}H_{10}$. Similar transition metal complexes were obtained with the heteroatom borane anions, $[7,8\text{-}B_9H_{10}CHP]^-$, $[7,8\text{-}B_9H_{10}As_2]^-$, $[B_{10}H_{12}P]^-$ and $[B_{10}H_{12}As]^-$.
It is proposed that each heteroatom borane is σ-bonded to either the iron or molybdenum atom by means of a germanium, phosphorus or arsenic atom.

Introduction

A variety of phospha- and arsa-carboranes [e.g. 7,8- and $[7,9\text{-}B_9H_{10}CHE]^-$ and $[(1,7\text{-}B_9H_9CHE)_2Fe]^{2-}$ (E = P or As)] have been found to form 1/1 σ complexes with chromium, molybdenum, tungsten, manganese and iron carbonyls [1,2,3].

We have now found that metal carbonyl cation derivatives readily react with a variety of heteroatom borane anions to form 1/1 σ bonded complexes. This paper describes our initial results in what appears to be a general reaction of considerable scope.

Experimental

General comments

Boron (^{11}B) NMR (at 70.6 MHz) and ^1H NMR spectra were obtained with a Varian HR-220 spectrometer. The boron spectra were externally referenced to $BF_3 \cdot O(C_2H_5)_2$. The ^{13}C NMR spectra were obtained with a Varian XL-100-15 spectrometer operating in the pulsed Fourier transform mode at 25.1 MHz. The ^{13}C chemical shifts were measured relative to internal CH_2Cl_2 and then re-

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ported relative to tetramethylsilane. The chemical shift conversion factor used in this study is $\delta(TMS) = \delta(CH_2Cl_2) - 53.89$ ppm.

Carbon and hydrogen analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, New York. Infrared spectra were recorded as KBr disks using a Perkin-Elmer 621 instrument. Low resolution mass spectra were obtained with an Atlas CH-7 instrument. All reactions were carried out under an atmosphere of prepurified nitrogen.

Starting materials

Dicarbonyl(cyclohexene)cyclopentadienyliron hexafluorophosphate was prepared by the method of Fischer and Moser [4]. Tricarbonylcycloheptatrienylmolybdenum tetrafluoroborate was obtained by the method of King [5]. $K[7,8\text{-}B_9H_{10}CHP]$ and $(CH_3)_4N[1,2\text{-}GeCHB_{10}H_{10}]$ were obtained by previously reported methods [3,6]. Tetramethylammonium salts of $[B_{10}H_{12}P]^-$, $[B_{10}H_{12}As]^-$ and $[7,8\text{-}B_9H_{10}As_2]^-$ were generously supplied by Dr. John Little, Department of Chemistry, University of Mississippi.

$(\pi\text{-}C_5H_5)Fe(CO)_2AsB_{10}H_{12}$

$[(\pi\text{-}C_5H_5)Fe(CO)_2(\text{cyclohexene})]PF_6$ (0.07 g, 0.17 mmole) and $(CH_3)_4N\text{-}[B_{10}H_{12}As]$ (0.05 g, 0.19 mmole) were mixed in 15 ml of acetone and stirred at room temperature for two hours and then refluxed for three hours. The solution was evaporated to dryness, dissolved in 2 ml of acetone and placed on a preparative silica gel TLC plate. Elution with methylene chloride gave a fast-moving yellow band which was extracted from the TLC plate with acetone. The acetone solution was evaporated to dryness and the crude solid was crystallized from CH_2Cl_2/heptane to give 0.03 g (45% yield) of $(\pi\text{-}C_5H_5)Fe(CO)_2AsB_{10}H_{12}$ (III) (yellow needles). The elemental analysis of this compound is given in Table 1. The low voltage mass spectrum cuts off at *m/e* 375 corresponding to

TABLE 1

CHEMICAL ANALYSES

Compound		Analysis found (calcd.) (%)	
		C	H
$(\pi\text{-}C_5H_5)Fe(CO)_2GeCHB_{10}H_{10}$	(I)	25.3 (25.4)	4.21 (4.33)
$(\pi\text{-}C_5H_5)Fe(CO)_2PB_{10}H_{12}$	(II)	25.2 (25.6)	5.11 (5.18)
$(\pi\text{-}C_5H_5)Fe(CO)_2AsB_{10}H_{12}$	(III)	23.0 (22.6)	5.23 (4.57)
$(\pi\text{-}C_5H_5)Fe(CO)_2PCHB_9H_{10}$	(IV)	29.2 (29.3)	5.01 (4.87)
$(\pi\text{-}C_5H_5)Fe(CO)_2As_2B_9H_{10}$	(V)	20.4 (19.3)	3.66 (3.90)
$(\pi\text{-}C_7H_7)Mo(CO)_2GeCHB_{10}H_{10}$	(VI)	26.9 (26.9)	4.00 (4.03)
$(\pi\text{-}C_7H_7)Mo(CO)_2PCHB_9H_{10}$	(VII)	30.7 (30.4)	4.78 (4.56)
$(\pi\text{-}C_7H_7)Mo(CO)_2PB_{10}H_{12}$	(VIII)	27.2 (27.4)	4.66 (4.82)

TABLE 2

^{11}B NMR SPECTRA (70.6 MHz)

Compound	Solvent	Chemical shift[a] (Relative intensity)
(I)	CH_2Cl_2	+3.6(1), +9.6(1), +11.0(4), +12.8(2), +14.1(2)
(II)	CH_2Cl_2	—3.4(1), +8.3(2), +10.5(2), +16.5(2), +24.1(3)
(III)	$(CH_3)_2CO$	—4.8(1), +6.5(4), +14.6(2), +22.6(3)
(IV)	CH_2Cl_2	—1.0(1), +6.9(1), +9.0(1), +12.0(1), +14.9(1), +25.6(3), +32.5(1)
(V)	CH_2Cl_2	—10.0(1), —8.1(1), +4.4(1), +6.1(1), +8.0(1), +16.4(3), +28.7(1)
(VI)	$(CH_3)_2CO$	+4.1(1), +7.3(1), +10.0(4), +13.0(2), +13.9(2)
(VII)	CH_2Cl_2	—0.9(1), +6.9(1), +9.2(1), +12.2(1), +14.3(1), +24.6(3), +35.6(1)
(VIII)	CH_2Cl_2	—4.1(1), +7.4(2), +10.8(2), +16.4(2), +22.9(1), +24.7(2)

[a] ppm vs. $BF_3 \cdot O(C_2H_5)_2$. All signals doublets with J(B—H) 150 ± 15 Hz.

the $[^{12}C_7{}^1H_{17}{}^{11}B_{10}{}^{16}O_2{}^{57}Fe_1{}^{75}As_1]^+$ parent ion. The infrared spectral data are given in Table 4. The ^{1}H and ^{11}B NMR spectral data are presented in Tables 2 and 3. This synthesis represents the general method used to prepare all the new complexes described in this article.

Results and discussion

(π-C_5H_5)Fe(CO)$_2$(ligand) complexes

There have been several reports concerning the formation of (π-C_5H_5)Fe(CO)$_2$(carborane) complexes using (π-C_5H_5)Fe(CO)$_2$I as a starting material.

TABLE 3

^{1}H NMR SPECTRA

Compound	Chemical shift τ(ppm)[a]	Assignment
(I)	4.34, singlet	C_5H_5 group
	7.40, singlet	Carborane CH
(II)	4.39, doublet [J(^{31}P—H) 2.8 Hz]	C_5H_5 group
	14.1, singlet (broad)	Bridge hydrogens
(III)	4.46, singlet	C_5H_5 group
	14.2, singlet (broad)	Bridge hydrogens
(IV)	4.28, doublet [J(^{31}P—H) 2.9 Hz]	C_5H_5 group
	8.41, doublet [J(^{31}P—H) 20 Hz]	Carborane CH
(V)	4.44, singlet	C_5H_5 group
	14.2	Bridge hydrogen
(VI)	3.89, singlet	C_7H_7 group
	7.26, singlet (broad)	Carborane CH
(VII)	4.07, doublet [J(^{31}P—H) 3 Hz]	C_7H_7 group
	9.2, doublet [J(^{31}P—H) 17 Hz]	Carborane CH
(VIII)	4.50, doublet [J(^{31}P—H) 2.8 Hz]	C_7H_7 group

[a] Acetone-d_6 solvent.

TABLE 4

IR SPECTRA

Compound	Wave number (cm^{-1})
(I)	3047 w, 2875 vw, 2802 vw, 2558 (sh), 2540 vs, 2515 (sh), 2500 (sh), 2035 vs, 1997 vs, 1614 vw, 1410 s, 1134 vw, 1091 vw, 1041 w, 980 s, 860 s, 737 w, 717 w
(II)	3103 w, 2564 vs, 2045 vs, 1991 vs, 1422 w, 1094 w, 1020 s, 952 (sh), 864 s, 704 w
(III)	3117 w, 2519 vs, 2503 (sh), 2040 vs, 1986 vs, 1613 w, 1411 w, 1083 w, 1017 w, 980 w, 861 w, 800 vw
(IV)	3064 s, 2880 vw, 2833 vs, 2523 vs, 2045 vs, 1995 vs, 1612 w, 1420 s, 1030 w, 1013 s, 989 w, 866 s, 819 vw, 748 vw, 734 vw
(V)	3107 w, 2967 w, 2533 vs, 2040 vs, 1990 vs, 1615 vw, 1419 w, 1072 w, 1004 w, 983 w, 872 w, 731 w
(VI)	3090 w, 2934 vw, 2539 vs, 2500 (sh), 2017 vs, 1970 vs, 1608 w, 1428 s, 1246 w, 1090 w, 1042 w, 999 s, 882 w, 860 vw, 804 vs, 733 w, 722 w
(VII)	3020 w, 2873 vw, 2807 vw, 2560 vs, 2014 vs, 1966 vs, 1622 vw, 1422 vw, 1030 (sh), 1012 s, 1003 w, 804 s
(VIII)	3058 w, 2533 vs, 2023 vs, 1970 vs, 1953 vs, 1922 (sh), 1432 s, 1248 vw, 1232 vw, 1030 s, 1010 s, 958 (sh), 946 w, 862 w, 801 s.

Treatment of the iodide with 1-lithio-2-methyl-1,2-$C_2B_{10}H_{10}$ or 1-lithio-10-methyl-1,10-$C_2B_8H_{10}$ afforded 1-[(π-C_5H_5)Fe(CO)$_2$]-2-methyl-1,2-$C_2B_{10}H_{10}$ or 1-[(π-C_5H_5)Fe(CO)$_2$]-10-methyl-1,10-$C_2B_8H_8$ respectively [7]. In these cases it is proposed that the carborane is attached to the complex by an iron—carbon σ bond. Treatment of the [2,3-$C_2B_4H_7$]$^-$ ion with (π-C_5H_5)Fe(CO)$_2$I produced (π-C_5H_5)Fe(CO)$_2C_2B_4H_7$ [8]. Based on ^{1}H and ^{11}B NMR data, there does not appear to be either a carbon—iron or boron—iron σ-bond in this complex. Therefore it is proposed that this carborane is attached to the iron atom by a B—Fe—B three-center two-electron bridge bond.

Our attemps to bring about a reaction of (π-C_5H_5)Fe(CO)$_2$I with heteroatom borane anions had not been successful. We therefore sought a complex with a better leaving group than the iodide ion. Accordingly, dicarbonyl(cyclohexene)cyclopentadienyliron hexafluorophosphate was allowed to react with the *closo*-anion, [1,2-$GeCHB_{10}H_{10}$]$^-$ to form yellow (π-C_5H_5)Fe(CO)$_2$-$GeCHB_{10}H_{10}$ (I) in 45% yield. The low voltage mass spectrum of (I) cuts off at *m/e* 387 corresponding to the $[^{12}C_8{}^1H_{16}{}^{11}B_{10}{}^{16}O_2{}^{76}Ge_1{}^{57}Fe_1]^+$ parent ion. Elemental analysis (Table 1) support this formula. The ^{1}H NMR spectrum of (I) contains a singlet at τ4.34 ppm (5H) and broad singlet at τ7.40 ppm (1H) assigned to the cyclopentadienyl and carborane CH protons respectively. The ^{11}B NMR spectrum (see Table 2) of (I) exhibits considerable overlap of the doublet resonances as is also the case for the ^{11}B NMR spectrum of the [1,2-$GeCHB_{10}H_{10}$]$^-$ ion. We propose that the germacarborane is attached to the iron atom via an iron—germanium σ-bond and has a structure similar to 1-(π-C_5H_5)Fe(CO)$_2$-2-methyl-1,2-$C_2B_{10}H_{10}$ reported earlier [7].

The *nido*-heteroatom borane anions, [$B_{10}H_{12}P$]$^-$, [$B_{10}H_{12}As$]$^-$, [7,8-$B_9H_{10}CHP$]$^-$ and [7,8-$B_9H_{10}As_2$]$^-$, were also found to react readily with [(π-C_5H_5)Fe(CO)$_2$ (cyclohexene)]PF_6 to afford the yellow derivatives (π-C_5H_5)Fe(CO)$_2PB_{10}H_{12}$ (II), (π-C_5H_5)Fe(CO)$_2AsB_{10}H_{12}$ (III), (π-C_5H_5)Fe-(CO)$_2PCHB_9H_{10}$ (IV), and (π-C_5H_5)Fe(CO)$_2As_2B_9H_{10}$ (V). The elemental analyses, mass spectral, ^{1}H NMR, ^{11}B NMR and infrared data are presented in

Tables 1—4. The synthesis of the $[B_{10}H_{12}P]^-$ ion was not reported earlier by Little and Wong [9] because they had difficulty in obtained a good elemental analysis. The synthesis and characterization of (II) confirms the composition of the $[B_{10}H_{12}P]^-$ ion.

There is no evidence in the ^{11}B NMR spectra of derivatives (II)-(V) of any singlet resonances which would be indicative of a boron—iron σ-bond. Some of these derivatives have the expected number of bridge hydrogens (see ^1H NMR data Table 3) suggesting that there are no B—Fe—B bridge bonds in the molecules. Also the carborane CH resonance is observed in the ^1H NMR spectrum of (IV). Therefore it is proposed that the heteroatom borane is σ-bonded to the iron atom via a phosphorus or arsenic atom in derivatives (II)-(V). In the ^1H NMR spectra of (II) and (IV) the cyclopentadienyl resonances appear as doublets with $J(^{31}P—H)$ coupling of 2.8 and 2.9 Hz respectively. The ^{13}C NMR spectrum of (II) in CH_2Cl_2 solution contained a doublet at —209.7 ppm $[J(^{13}C—^{31}P)$ 21.8 Hz] (area 2) and an apparent singlet at —86.4 ppm (area 5) which are assigned to the carbonyl and cyclopentadienyl resonances respectively. The presence of $^{31}P—^1H$ and $^{31}P—^{13}C$ spin coupling supports the proposal that the $(\pi\text{-}C_5H_5)Fe(CO)_2$ group is directly bonded to the phosporus atom of the $[B_{10}H_{12}P]^-$ ligand in (II). The proposed structure of this complex is illustrated in Fig. 1.

$(\pi\text{-}C_7H_7)Mo(CO)_2$(ligand) complexes

Treatment of the cation $[(\pi\text{-}C_7H_7)Mo(CO)_3]^+$ with a variety of anions leads to products which suggest attack of the anion either at the C_7H_7 ring or at the metal atom. Reaction of this cationic metal carbonyl with sodium borohydride or sodium diethylmalonate produced $(C_7H_8)Mo(CO)_3$ and $[C_7H_7CH(CO_2C_2H_5)_2]Mo(CO)_3$ respectively [10]. In contrast, reaction of the cation with $Na[Mn(CO)_5]$ [11] or sodium iodide [5] afforded the green complexes $(C_7H_7)Mo(CO)_2Mn(CO)_5$ and $(C_7H_7)Mo(CO)_2I$ respectively. Treatment of $[(\pi\text{-}C_7H_7)Mo(CO)_3]BF_4$ with $Cs[GeCHB_{10}H_{10}]$ at reflux in acetone for two hours produced red $(\pi\text{-}C_7H_7)Mo(CO)_2GeCHB_{10}H_{10}$ (VI) in 33% yield. The ^1H NMR spectrum (acetone-d_6) contained a singlet at τ 3.89 ppm (7H) and a broad

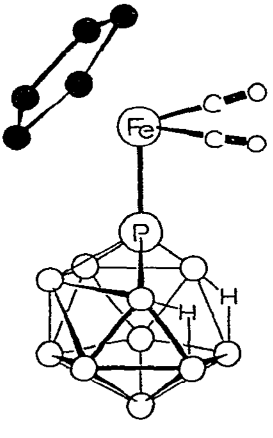

Fig. 1. Proposed structure for $(\pi\text{-}C_5H_5)Fe(CO)_2PB_{10}H_{12}$ (II).

singlet at τ 7.26 ppm (1H) corresponding to the cycloheptatrienyl and carborane CH resonances respectively. In a similar manner treatment of the molybdenum cation with $[7,8\text{-}B_9H_{10}CHP]^-$ and $[B_{10}H_{12}P]^-$ afforded $(\pi\text{-}C_7H_7)Mo(CO)_2\text{-}PCHB_9H_{10}$ (VII) and $(\pi\text{-}C_7H_7)Mo(CO)_2PB_{10}H_{12}$ (VIII). The ^1H NMR spectra of (VII) and (VIII) (acetone-d_6) contained doublets at τ 4.07 ppm [$J(^{31}P—^1H)$ 3 Hz] and τ 4.50 ppm [$J(^{31}P—H)$ 2.8 Hz] respectively attributed to the cycloheptatrienyl group. The ^{11}B NMR spectrum of each of these molybdenum complexes is quite similar to the spectrum of the corresponding $(\pi\text{-}C_5H_5)Fe(CO)_2$ ligand derivative described above. This evidence suggests that the heteroatom borane is σ-bonded to the molybdenum atom via a germanium or phosphorus atom.

All of these complexes irreversibly change color at approximately 200°. Possible thermal reactions as well as photochemical processes are being investigated.

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