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ICOSAHEDRAL GERMACARBORANES AND SOME σ-BONDED METAL DERIVATIVES

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Summary

The syntheses, characterization and properties of 1,2-$B_{10}H_{10}$CHGeR (R = CH_3 and C_2H_5), 1,2-$B_{10}H_{10}CHGe^-$ and 1,2-$B_{10}H_{10}CHGeM(CO)_5^-$ (M = Cr, Mo and W) are described.

Introduction

We have reported in a preliminary communication [1] the syntheses of icosahedral heteroatom boranes which contain both a carbon and germanium atom in the cage and which are isoelectronic with $B_{12}H_{12}^{2-}$. Since that time the related germaborane molecules $B_9C_2H_{11}Ge$ [2] and $(CH_3)_2GeB_{10}H_{12}$ [3] have been reported. In this paper are given the full details concerning the preparation and characterization of our germacarboranes. We also report the syntheses of some metal carbonyl derivatives obtained from the 1,2-$B_{10}H_{10}CHGe^-$ ion.

Experimental

General comments

Elemental analyses were performed by either Schwarzkopf Microanalytical Laboratories, Woodside, New York or the Microanalytical Laboratory, University of Illinois. The infrared spectra were measured as KBr disks on a Perkin—Elmer 521 instrument. Low-resolution mass spectra were obtained with an Atlas CH-4 instrument. High resolution mass spectra were obtained with an AEI-MS-9 instrument. Boron (^{11}B) NMR spectra at 70.6 MHz were obtained with a Varian HR-220 spectrometer. 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 [4].

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Reported melting points were obtained in sealed capillaries and are uncorrected. All reactions were carried out under an atmosphere of prepurified nitrogen.

1,2-$B_{10}H_{10}CHGeCH_3$ (I)

The air-sensitive compound $Na_3B_{10}H_{10}CH(THF)_2$ was prepared from $B_{10}H_{12}CN(CH_3)_3$ (10 g, 0.052 mole) in a 500 ml, three-necked flask fitted with an overhead stirrer, nitrogen inlet, and reflux condenser as described previously [5]. To this slurry, maintained at 0°, was added dropwise over a 3 h period, 6 ml (0.052 mole) of germanium tetrachloride. The mixture was warmed to room temperature and stirred for 3 more hours. The solution was evaporated to dryness and 100 ml of fresh tetrahydrofuran (THF) added. Methyl iodide (19 ml, 0.2 mole) was added to the solution and the mixture was refluxed for 17 h. The solvent was removed in vacuo and the residues were extracted with five 200 ml portions of hot cyclohexane. The extract was evaporated to dryness and the residue sublimed at 120° (0.05 mm). Crystallization of the sublimed product from cyclohexane gave 3.08 g (26.9%) of (I) (m.p. 230-231°). The ^1H NMR spectrum ($CDCl_3$) contained a broad singlet (1H) at 7.45τ and a sharp singlet (3H) at 7.95τ assigned to the carborane CH and methyl group respectively. The ^{13}C NMR spectrum (CH_2Cl_2) contained resonances at —31.9 and +0.3 ppm (TMS = 0 ppm) assigned to the carborane and methyl carbon atoms respectively. The mass spectrum of (I) cut off at *m/e* 224 corresponding to the $[^{11}B_{10}{}^1H_{14}{}^{12}C_2{}^{76}Ge]^+$ parent ion.

1,2-$B_{10}H_{10}CHGeC_2H_5$ (II)

This compound was prepared in 7% yield by the same procedure described above for the synthesis of 1,2-$B_{10}H_{10}CHGeCH_3$. The analytical sample of (II) was purified by crystallization from methylene chloride/heptane, m.p. 156-157°. The proton NMR spectrum (acetone-d_6): quartet (J 7Hz) at 7.25, broad singlet at 7.35, triplet (J 7Hz) at 8.40τ assigned to ethyl CH_2, carborane CH and ethyl CH_3 protons respectively.

$(CH_3)_4N[1,2\text{-}B_{10}H_{10}CHGe]$ (III)

A solution of 1,2-$B_{10}H_{10}CHGeCH_3$ (0.60 g, 0.027 mole) in 10 ml of piperidine and 10 ml of benzene was heated at reflux for 19 h. The solution was evaporated to dryness under vacuum and the solid residues were extracted with acetone/water. Addition of a saturated aqueous solution of tetramethylammonium chloride to the acetone/water extract precipitated the product. The crude product was crystallized from acetone/methanol to give 0.25 g (33% yield) of $(CH_3)_4N[B_{10}H_{10}CHGe]$. The ^1H NMR spectrum (dimethyl-d_6 sulfoxide) contains two singlets at 6.88τ (12H) and 8.0τ (1H, broad) assigned to the tetramethylammonium and carborane CH protons respectively.

$(CH_3)_4N[1,2\text{-}B_{10}H_{10}CHGeCr(CO)_5]$ (IV)

In a Vycor Schlenk tube were placed $(CH_3)_4N[1,2\text{-}B_{10}H_{10}CHGe]$ (0.81 g, 0.0029 mole), $Cr(CO)_6$ (0.64 g, 0.0029 mole), and 80 ml of dry THF. The stirred solution was irradiated with a 550 watt high pressure, Hanovia mercury vapor lamp for 18 h. The solvent was removed in vacuo at room temperature. The solid residue was washed with three 75 ml portions of benzene to remove unreact-

TABLE 1

ELEMENTAL ANALYSES OF GERMACARBORANE DERIVATIVES

Compound	Found (calcd) (%)		
	C	H	N
$1,2\text{-}B_{10}H_{10}CHGeCH_3$ (I)[a]	10.91	6.61	
	(10.96)	(6.44)	
$1,2\text{-}B_{10}H_{10}CHGeC_2H_5$ (II)	15.41	7.09	
	(15.45)	(6.92)	
$(CH_3)_4N[1,2\text{-}B_{10}H_{10}CHGe]$ (III)[b]	21.49	8.61	5.48
	(21.58)	(8.33)	(5.03)
$(CH_3)_4N[1,2\text{-}B_{10}H_{10}CHGeCr(CO)_5]$ (IV)[c]	25.37	4.87	3.31
	(25.55)	(4.94)	(2.98)
$(CH_3)_4N[1,2\text{-}B_{10}H_{10}CHGeMo(CO)_5]$ (V)	23.57	4.76	3.03
	(23.36)	(4.52)	(2.72)
$(CH_3)_4N[1,2\text{-}B_{10}H_{10}CHGeW(CO)_5]$ (VI)	20.16	3.93	2.53
	(19.95)	(3.86)	(2.33)

[a] Boron calcd. 49.42%, found 49.34%. [b] Boron calcd. 38.91%, found 38.48%. [c] Chromium calcd. 11.06%, found 10.70%.

ed $Cr(CO)_6$. The remaining solid was crystallized from acetone/methanol/H_2O to give 0.429 g (29% yield) of $(CH_3)_4N[1,2\text{-}B_{10}H_{10}CHGeCr(CO)_5]$ as colorless plates. The complexes $(CH_3)_4N[1,2\text{-}B_{10}H_{10}CHGeMo(CO)_5]$ (V) and $(CH_3)_4N\text{-}[1,2\text{-}B_{10}H_{10}CHGeW(CO)_5]$ (VI) were prepared and purified by the procedure given above.

Results and discussion

Icosahedral germacarboranes

Reaction of $Na_3B_{10}H_{10}CH(THF)_2$ with CH_3GeCl_3 in THF solution formed $1,2\text{-}B_{10}H_{10}CHGeCH_3$ (I) in very low yield (2%) as well as $(CH_3)_4N[1,2\text{-}B_{10}H_{10}\text{-}CHGe]$ (III). The chemical analyses and infrared spectral data of (I) and the other new compounds reported here are given in Tables 1 and 2. These data as well as the proton and ^{13}C NMR and mass spectral data given in the experimental

TABLE 2

INFRARED SPECTRA OF THE GERMACARBORANE DERIVATIVES

Compound	Infrared spectra[a] (cm^{-1})
I	2980 w, 2550 s, 1380 m, 1225 m, 1035 s, 990 s, 919 m, 885 m, 832 m, 739 m, 727 m, 685 w
II	2890 w, 2550 s, 1440 m, 1365 m, 1210 m, 1040 m, 990 m, 915 w, 887 w, 730 m, 712 m
III	2900 w, 2500 s, 1470 m, 1045 w, 1000 m, 948 m, 722 w
IV	2560 s, 2060 m, 1920 s, 1480 m, 1090 w, 1045 w, 1005 m, 948 m, 678 m
V	2900 w, 2530 s, 2075 m, 1985 m, 1925 s, 1480 m, 1090 w, 1045 w, 1005 m, 945 m
VI	2900 w, 2550 s, 2070 m, 1920 s, 1480 m, 1085 w, 1045 w, 1005 m, 947 m.

[a] KBr disks.

TABLE 3

70.6 MHz ^{11}B NMR SPECTRA OF GERMACARBORANE DERIVATIVES

Compound[a]	Chemical Shift[b] (relative intensity) [J(B—H) (Hz)][c]
I	+5.9 (1)[148], +10.9 (1), +14.0 (6), +14.9 (2)
II	+5.6 (1)[142], +8.6(1),, +13.7 (6), +15.3 (2)
III	+3.7 (2), +6.7 (2), +8.2 (2), +12.7 (4)
IV	+4.1 (1)[142], +8.0 (1), +10 (4), +13.1 (2), +13.7 (2)
V	+4.2 (1), +7.3 (1), +9.7 (4), +13.2 (4)
VI	+4.5 (1), +7.3 (1), +10.2 (4), +13.3 (4)

[a] Acetone solvent. [b] Ppm vs. $BF_3 \cdot O(C_2H_5)_2$. [c] All signals are doublets with J(B—H) 150 ± 15 Hz. Due to the overlap of signals, measurement of accurate values of some coupling constants is not possible.

are consistent with the formulation proposed for (I). It is a sublimable solid which can be stored in air for several months with negligible decomposition, and like 1,2-$B_{10}H_{10}C_2H_2$, it appears to have a very large melting point depression constant. Small amounts of impurity which can not be detected by infrared, NMR or elemental analyses significantly lower the melting point of (I). Earlier [1] we reported the melting point as 216-217°. Further purification has raised the melting point to 230-231°. The ^{11}B NMR spectrum of (I) (see Table 3) contains two doublets of unit area at lowest field which must be due to the two unique boron atoms which are farthest away from the carbon and germanium atoms (antipodal) in the cage structure. This same feature is observed in the ^{11}B NMR spectra of other icosahedral carborane molecules such as 1,2-$B_{10}H_{10}C_2H_2$ [6] and 1,2-$B_{10}H_{10}$CHP [5]. The formation of 1,2-$B_{10}H_{10}CHGe^-$ in the reaction described above was initially an unexpected result. Subsequently it was found that treatment of (I) with piperidine at reflux generated 1,2-$B_{10}H_{10}CHGe^-$ which was isolated and characterized as the tetramethylammonium salt (III). This demonstrated that basic reagents could easily demethylate (I) to form 1,2-$B_{10}H_{10}CHGe^-$. In addition, the 7-$B_{10}H_{12}CH^-$ ion [7] was isolated from the reaction products and characterized by its 70.6 MHz ^{11}B NMR spectrum. Thus it appears that basic reagents can slowly abstract the germanium atom from the germacarborane cage. The 1,2-$B_{10}H_{10}CHGe^-$ ion can be readily alkylated. Thus reflux of (III) with excess methyl iodide in THF solution reforms 1,2-$B_{10}H_{10}CHGeCH_3$ in 75% yield.

The synthesis used initially to prepare 1,2-$B_{10}H_{10}CHGeCH_3$ gives very low and irregular yields. Recently, we have developed a simplified method which forms (I) in 27% yield. The improved procedure, which is given in detail in the experimental section, involves reaction of $Na_3B_{10}H_{10}CH(THF)_2$ with $GeCl_4$ and subsequent methylation with methyl iodide. Employing this new procedure, 1,2-$B_{10}H_{10}CHGeC_2H_5$ (II) was also obtained and characterized.

Attempted thermal isomerization of (I) at 450° in a sealed tube resulted in nearly complete decomposition. Heating Cs($B_{10}H_{10}$CHGe) at 475° followed by alkylation with methyl iodide gave a low yield of 1,2-$B_{10}H_{10}CHGeCH_3$. No isomerized products were isolated in our experiments.

Metal carbonyl complexes

We have shown that those heteroatom borane anions which are strong

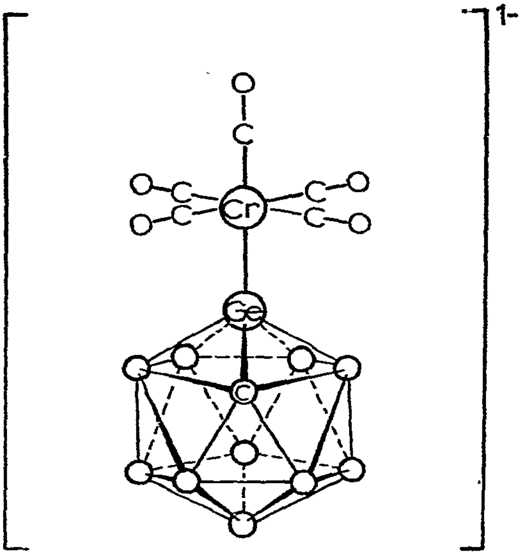

Fig. 1. Proposed Structure of the 1, 2-$B_{10}H_{10}CHGeCr(CO)_5^-$ ion.

enough Lewis bases to react with CH_3I to form neutral methylated products can also form σ-bonded complexes with metal carbonyls [8]. Photochemical irradiation of a tetrahydrofuran solution of $(CH_3)_4N(1,2\text{-}B_{10}H_{10}CHGe)$ and $Cr(CO)_6$ in a 1/1 mole ratio formed $(CH_3)_4N[1,2\text{-}B_{10}H_{10}CHGeCr(CO)_5]$ (IV). The corresponding molybdenum and tungsten complexes (V and VI) were formed by the same type of reaction.

We have recently reported the syntheses of $1,2\text{-}B_{10}H_{10}CHGeFe(CO)_2\text{-}(\pi\text{-}C_5H_5)$ and $B_{10}H_{10}CHGeMo(CO)_2(\pi\text{-}C_7H_7)$ by reaction of (III) with metal carbonyl cation reagents [9]. In all these complexes we propose that a germanium—metal σ bond is formed as illustrated in Fig. 1. Analogous σ-bonded metal complexes of $1,2\text{-}B_{10}H_{10}C_2H_2$ have been reported [e.g. $1\text{-}[(\pi\text{-}C_5H_5)Fe(CO)_2]\text{-}2\text{-}CH_3\text{-}1,2\text{-}(C_2B_{10}H_{10})$ and $1\text{-}[Mn(CO)_5]\text{-}2\text{-}CH_3\text{-}1,2\text{-}(C_2B_{10}H_{10})$ [10]. The ^{11}B NMR spectra of these metal complexes and the parent carborane have a very similar pattern. A similarity in ^{11}B NMR spectral pattern is also observed (see Table 3) in the spectra of $1,2\text{-}B_{10}H_{10}CHGeR$, $1,2\text{-}B_{10}H_{10}CHGeM(CO)_5^-$ and $1,2\text{-}B_{10}H_{10}\text{-}CHGeFe(CO)_2(\pi\text{-}C_5H_5)$ [9]. However, the ^{11}B NMR spectrum of $1,2\text{-}B_{10}H_{10}\text{-}CHGe^-$ is quite different from that of the substituted derivatives. In the substituted germacarboranes the lone pair electrons on germanium are involved in *exo*-cage bonding. In the case of $1,2\text{-}B_{10}H_{10}CHGe^-$ the available lone pair electrons on germanium are more accessible for interaction with cage orbital electrons and this is reflected in the different ^{11}B NMR spectrum of this anion.

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