

SYNTHESIS OF COMPOUNDS WITH POLYMETALLIC CHAINS INCLUDING BORON ATOMS OF A CARBORANE CAGE

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Summary

Compounds with B–Hg–Ge or Ge–Hg–B–B–Hg–Ge chains in which the boron atoms are members of a carborane cage have been prepared by treatment of the digermane $(C_6F_5)_3GeGeEt_3$, with *B*-mercurated derivatives of the carboranes $m-C_2H_2B_{10}H_9HgX$ ($X = Cl, OCOF_3$) and $m-C_2H_2B_{10}H_8(HgOCOF_3)_2$. Treatment of $HGe(C_6F_5)_2Ge(C_6F_5)_2H$ with methyl(*m*-carboran-9-yl)mercury resulted in a compound with a B–Hg–Ge–Ge–Hg–B chain containing two carborane cages at the ends of the chain. The compound prepared can take part in oxidative insertion of $Pt(PPh_3)_n$ ($n = 3,4$) to give the chains B–Hg–Pt–Ge, Ge–Pt–Hg–B–B–Hg–Ge and B–Hg–Pt–Ge–Ge–Pt–Hg–B.

Introduction

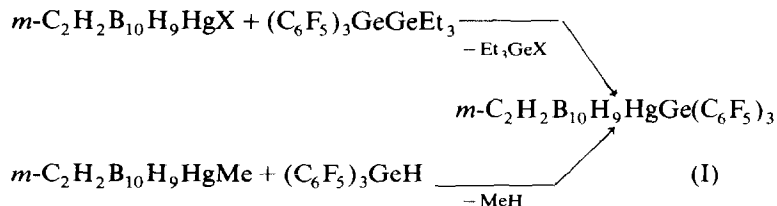
Previously, Vyazankin, Zakharkin and coworkers [1] have shown that the exchange reaction of *C*-mercurated carboranes of the type $o-RCB_{10}H_{10}CHgX$ ($X = Me, Ph, Cl$) with bis(triethylgermyl)mercury lead to stable germyl(carboranyl)mercury compounds. In these compounds Et_3GeHg fragments bond to the carborane cage through a carbon atom. A great variety of *B*-mercurated carboranes became available after realization of the mercuration of carboranes [2,3]. Their reactivity is equal in many cases to alkyls mercury. This allowed use these compounds for the synthesis of other *B*-metallated carboranes in which the boron atom bonds by a σ -bond to atoms of *p*-block [4,5], transition [6] and rare earth [7] metals. Compounds with polynuclear fragments containing the $C_2H_2B_{10}H_9$ -framework, for example $RCB_{10}H_9[TiSn(acac)_2Br_2]CR$, have also been prepared [8].

In this paper we report the synthesis of carboranyl derivatives containing longer heteroelemental chains on the boron atom. As ligands for these compounds penta-

fluorophenylgermyl groups were chosen since they are known to increase the stability of polynuclear fragments [9].

Results and discussion

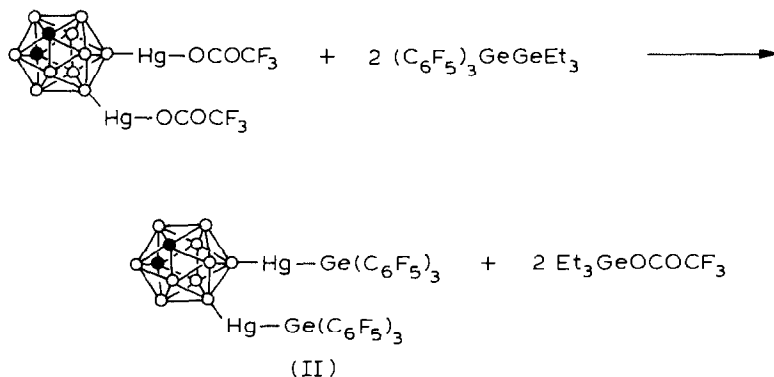
Carborane containing a $\text{HgGe}(\text{C}_6\text{F}_5)_3$ group at the B(9) atom was prepared by two methods. The first one is the reaction of digermene, $(\text{C}_6\text{F}_5)_3\text{GeGeEt}_3$, with $m\text{-C}_2\text{H}_2\text{B}_{10}\text{H}_9\text{HgX}$ ($\text{X} = \text{Cl}, \text{OCOCF}_3$), and the second, the hydride method, is one of the most convenient methods of forming a covalent metal-metal bond.



($\text{X} = \text{Cl}, \text{OCOCF}_3$)

High yields of I ($\sim 70\%$) and Et_3GeX (or MeH) indicate that digermene (or hydrogermane) reacts only with the Hg-X (or Hg-C) bond without attacking the B-H bond.

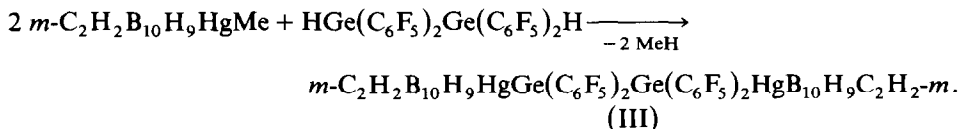
Under the same conditions (THF, 50°C , 1 h) B(9),B(10)-dimercurated m -carborane reacts with digermene to give compound II in which two $\text{HgGe}(\text{C}_6\text{F}_5)_3$ fragments are joined to a carborane cage.



It must be noted that the method of germylation of HgX_2 and RHgX with digermenes was discovered previously when reactivity of pentafluorophenyldigermenes was studied [10,11].

Geminal dimercurygermyl fragments, $-\text{HgGeHg}-$, are known to be unstable [12,13] in contrast to the stable derivatives of digermene, $-\text{Hg-GeR}_2\text{-GeR}_2\text{-Hg}-$, [13]. Such fragments turn out to be stable when two terminal carboranyl substituents link through a boron atom. 1,2-Bis(m -carboran-9-ylmercuro)-1,1,2,2-tetrakis(pentafluorophenyl)digermene (III) was prepared by treatment of 1,2-dihydrodigermene with

two equivalents of $m\text{-C}_2\text{H}_2\text{B}_{10}\text{H}_9\text{HgMe}$.



All carboranylgermylmercury compounds I, II, III (Table 1) are air stable, crystalline substances with melting points above 200°C . Their IR spectra contain absorption bands of $\text{C}_6\text{F}_5\text{Ge}$ [14] and carborane groups.

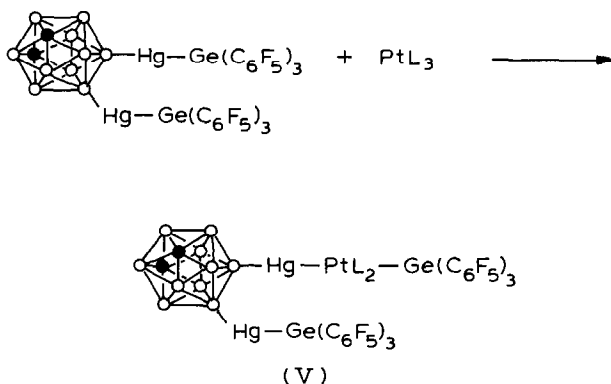
Similarly to other germylmercury compounds, the *B*-carboranylgermylmercury compound I readily adds a PtL_2 ($\text{L} = \text{PPh}_3$) fragment when treated with triphenylphosphine complexes of Pt^0 . The formation of two isomers with B-Hg-Pt-Ge or B-Pt-Hg-Ge fragments is possible. According to liquid chromatography data, the reaction product is a single compound, therefore it contains only one possible fragment. In our opinion the insertion of platinum is accomplished at the Ge-Hg bond, as it is the more polar bond:



$n = 3, 4$; $\text{L} = \text{PPh}_3$

It should be remarked that the interaction of PtL_3 with $9\text{-ClHg}m\text{-B}_{10}\text{H}_9\text{C}_2\text{H}_2$ is followed by demercuration of the products [6].

Interaction of tris(triphenylphosphine)platinum with compound II results in insertion of only one PtL_2 group, in spite of the presence of two B-Hg-Ge fragments in the initial carborane.



The reason for such anomalous behaviour seems to be the steric hindrance which arises after insertion of the first PtL_2 group due to the neighbouring position of mercurated boron atom. This steric hindrance seems to prevent the second Hg-Ge bond from attacking the platinum complexes.

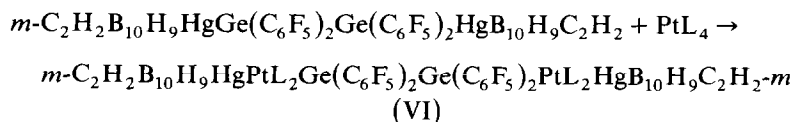
On the contrary, in the dicarboranyl compound III mercury atoms are separated

TABLE 1
 CARBORANES WITH *B*-SUBSTITUTED HETEROELEMENT CHAINS

No	Compound	M.p. (°C)	Yield (%)	Analysis (Found (calcd.) (%))		
				C	H	F
I	$m\text{-C}_2\text{H}_2\text{B}_{10}\text{H}_9\text{HgGe}(\text{C}_6\text{F}_5)_3$	210–212	67 ^a	26.14 (26.19)	1.25 (1.20)	31.22 (31.06)
II	$m\text{-C}_2\text{H}_2\text{B}_{10}\text{H}_8[\text{HgGe}(\text{C}_6\text{F}_5)_3]_2$	210–213	67	27.45 (26.99)	0.90 (0.60)	
III	$[m\text{-C}_2\text{H}_2\text{B}_{10}\text{H}_9\text{HgGe}(\text{C}_6\text{F}_5)_2]_2$	215–220	74	23.50 (22.40)	1.62 (1.47)	^b
IV	$m\text{-C}_2\text{H}_2\text{B}_{10}\text{H}_9\text{HgPt}(\text{PPh}_3)_2\text{Ge}(\text{C}_6\text{F}_5)_3$	184–187 ^c	75	41.72 (41.08)	2.46 (2.52)	17.40 (17.41)
V	$m\text{-C}_2\text{H}_2\text{B}_{10}\text{H}_8$ $\begin{array}{c} \diagup \text{HgGe}(\text{C}_6\text{F}_5)_3 \\ \diagdown \text{HgPt}(\text{PPh}_3)_2\text{Ge}(\text{C}_6\text{F}_5)_3 \end{array}$	137 ^c	71	36.82 (36.89)	2.20 (1.68)	^d
VI	$[m\text{-C}_2\text{H}_2\text{B}_{10}\text{H}_9\text{HgPt}(\text{PPh}_3)_2\text{Ge}(\text{C}_6\text{F}_5)_2]_2$	137–140	50	39.17 (40.85)	2.83 (2.81)	13.06 (12.92)

^a By reaction of $(\text{C}_6\text{F}_5)_3\text{GeGeEt}_3$ with $m\text{-C}_2\text{H}_2\text{B}_{10}\text{H}_9\text{HgCl}$. ^b Hg, 26.71(26.73); Ge, 9.12(9.67); B, 14.40(14.41)%. ^c Decomposition. ^d Hg, 17.30(16.64); Pt, 7.58(8.09)%.

by $\text{GeR}_2\text{-GeR}_2$ fragments, and this compound adds two equivalents of PtL_2 to give a six-membered chain containing $m\text{-C}_2\text{H}_2\text{B}_{10}\text{H}_9$ groups at the ends:



It was shown previously that insertion of PtL_2 into a Ge–Ge bond does not occur under comparable conditions [15]. Therefore, the sequence of heteroatoms of the chain in compound VI shown in the equation is the most probable.

Carboranylmercuryplatinum complexes IV–VI are isolated by precipitation with hexane from benzene solution as yellow microcrystalline powders. They are air stable and are well soluble in the usual organic solvents except alkanes. The relatively low yield of VI (Table 1) is due to considerable loss during isolation and purification. IR spectra of complexes contain, except bands of $\text{C}_6\text{F}_5\text{Ge}$ and carboranyl groups, absorption bands of coordinately bonded triphenylphosphine in the region $450\text{--}650\text{ cm}^{-1}$. In going from compound IV to compounds V and VI the intensity ratio of PPh_3 and $\text{C}_6\text{F}_5\text{Ge}$ bands changes symbatically with changing ratios of these groups in the complex.

Experimental

All syntheses were carried out in argon atmosphere, and isolation and purification of products in air. The liquid-adsorption analysis was carried out on a Tsvet-304 liquid chromatograph equipped with a UV detector (254 nm). A $19 \times 0.4\text{ cm}$ column filled with Silasorb-600 was used, and a n-hexane/ether (20/1) mixture was used as eluent. IR spectra were obtained on a UR-20 spectrometer.

m-C₂H₂B₁₀H₉HgGe(C₆F₅)₃(I)

a) A solution of 0.35 g of *m-C₂H₂B₁₀H₉HgCl* in 5 ml of THF was added to a solution of 0.65 g of (C₆F₅)₃GeGeEt₃ in 5 ml of THF. The mixture was heated to 50°C for 1 h. After THF had been removed, the residue was recrystallized from hexane to give 0.56 g (67%) of compound I, m.p. 210–212°C. In hexane 0.16 g (89%) of Et₃GeCl was found by GLC. Similarly, a reaction of *m-C₂H₂B₁₀H₉OCOCF₃* with (C₆F₅)₃GeGeEt₃ was carried out. The yield of compound I is 64%.

b) A reaction mixture of 0.36 g of *m-C₂H₂B₁₀H₉HgMe* and 0.57 g of (C₆F₅)₃GeH in 10 ml of THF was heated for 3 h at 90–100°C. 20 ml (89%) of methane was evolved. After substitution of THF by hexane the residue was recrystallized from hexane to give 0.6 g (65%) of I, m.p. 210–213°C.

m-C₂H₂B₁₀H₈[HgGe(C₆F₅)₃]₂(II)

A mixture of 0.8 g of (C₆F₅)₃GeGeEt₃ and 0.42 g of *m-C₂H₂B₁₀H₈(HgOCOCF₃)₂* in 10 ml THF was heated for 1 h at 50°C. THF was substituted by hexane. A crystalline precipitate was obtained and washed with hexane to remove Et₃GeOCOCF₃. After recrystallization from toluene, 0.62 g (67%) of compound II was obtained, m.p. 210–214°C. In the hexane solution 0.24 g (83%) of Et₃GeOCOCF₃ was found by GLC.

[m-C₂H₂B₁₀H₉HgGe(C₆F₅)₂]₂(III)

A solution of 1.29 g of 1,2-dihydro-1,1,2,2-tetrakis(pentafluorophenyl)digermane and 1.135 g of *m-C₂H₂B₁₀H₉HgMe* in 5 ml of toluene was heated in the vessel equipped with a condenser and connected with a gas burette. The temperature of the bath was gradually increased up to 160°C during 2.5 h. The mixture was kept at this temperature for 0.5 h. During heating steady evolution of methane (60 ml, 86%) was observed. The hot solution was decanted from the mercury precipitated (0.049 g, 8%) and cooled. The precipitate was filtered, washed with toluene and dried in a vacuum: 1.32 g (74%) of III (m.p. 215–220°C) was obtained. The recrystallization of III from toluene did not change the melting point.

m-C₂H₂B₁₀H₉HgPt(PPh₃)₂Ge(C₆F₅)₃(IV)

A solution of 0.169 g of compound I in 5 ml of benzene was added to a solution of 0.181 g of Pt(PPh₃)₃ in 10 ml of benzene at 20°C. The solution was allowed to stand for 10 h and then passed through a layer of C-3 silica gel of 2 cm thickness. The solvent was removed by condensation in a vacuum at 20°C and hexane (15 ml) was added to the viscous liquid residue. After treatment of viscous liquid with a glass rod the microcrystalline bright yellow precipitate thus formed was washed with hexane (2 × 5 ml) and dried at 30°C in a vacuum: 0.23 g (75%) of compound IV was obtained, m.p. 184–187°C (with decomposition).

Similarly, complexes V and VI were prepared. The absence of impurities was checked by liquid-adsorption chromatography. PtL₄ was used for the preparation of VI.

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