

CARBORANYL DERIVATIVES OF NONTRANSITION METALS

V I BREGADZE

*A N Nesmeyanov Institute of Organo-Element Compounds,
USSR Academy of Sciences, Moscow, USSR*

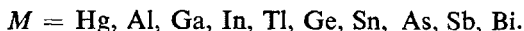
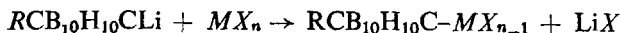
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This work describes the synthesis of unknown types of carboranyl derivatives of nontransition metals and compares the properties of carborane derivatives with carbon-nontransition metal bond on one hand, and boron-metal bond, on the other.

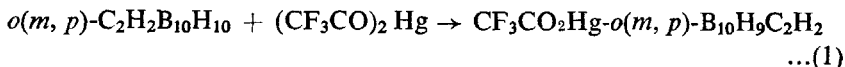
Key Words : Carboranyl Derivatives; Carbon-nontransition Metal Bond; Nontransition Metals; Boron-metal Bond

INTRODUCTION

THE derivatives of carborane containing a σ -bond between a carbon atom and an atom of nontransition metal were obtained by interaction of lithiumcarboranes with nontransition metal halides or organometallic derivatives with metal-halogen bond :



The existence of the new type of the carborane compounds with B-M σ -bond was revealed after realization of the mercuration of *o*-, *m*- and *p*-carboranes*¹⁻³ :



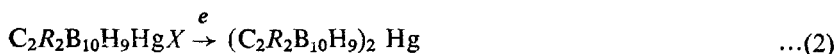
B-Mercurated carboranes obtained were used in the synthesis of many other carboranes with B-M bond.

The mercuration of the carboranes was carried out only by the action of a strong mercuration agent, mercury trifluoroacetate in trifluoroacetic acid, which have been used by Brown and Wirkkala for mercuration of arenes deactivated to the electrophilic substitution.⁴ The mercuration of *ortho*- and *meta*-carboranes proceeds easily at room temperature. The *ortho*-isomer even reacts exothermically. On the other hand, the mercuration of *para*-isomer requires boiling of the reaction mixture. The mercuration of *o*- and *m*-carboranes proceeds mostly at the boron atom of the carborane icosahedron at position 9 (in *p*-carborane all positions are equal). Later, Zakharkin and Pisareva found that the mercuration of *o*- and *m*-carboranes gives 85-99 per cent of B(9)-mercured carborane.⁵ The

o-, *m*- and *p*-carborane—the trivial name of 1,2-, 1,7- and 1,12-dicarba-closo dodecaborane(12), respectively.

detailed description of the mercuration of the carboranes, the synthesis of the salts and unsymmetric B-carboranylmercury compounds have been reported at the Fourth International Meeting on Boron Chemistry.⁶

The carboranylmercury salts do not undergo symmetrization in the presence of the complexing agents (KI, NaI, KCN, Na₂S₂O₃, NH₃). It has been found that symmetrization can be carried out only by reducing agents such as naphthalene, anion-radical and cadmium amalgam.³ The B-carboranylmercury salts were also symmetrized under the action of LiAlH₄⁷ and Na₂SnO₂.⁸ Preparative electrochemical symmetrization of the C- and B-carboranylmercury salts was carried out too :⁹



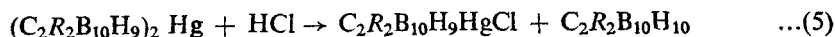
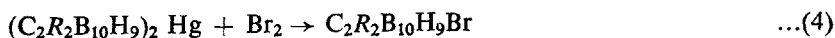
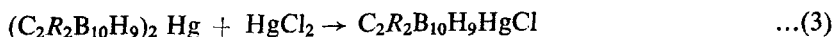
The electrolysis processes were run in a galvanostatic regime (300mA, 50–150V) without separating the cathode and anode spaces. With a Cu/Hg cathode, bis(B-carboran-9-yl) mercury was obtained exclusively whereas with a Pt cathode 7–8 per cent of bis(B-carboran-9-yl) was obtained along with the symmetrical mercuric compound. This results from one-electron reduction of the B-carboranylmercury salts, giving the B-carboranyl radical.⁹

The properties of the different types of B-mercurated carboranes have been studied and compared with those of C-carboranylmercury compounds, which have been shown earlier to have the properties unusual for classical organomercury compounds.¹⁰ Thus, in contrast to usual organomercury compounds, the *o*-carboranyl derivatives of mercury with Hg–C(carborane) bond have a high thermal stability (up to 300 °C). They remain unchanged after refluxing with such electrophiles as HCl, HgCl₂ (in ethanol) and Br₂ (in benzene). However, the action of the nucleophilic agents (BuLi, LiAlH₄) on these compounds results in fission of Hg–C(carborane) bond even-at room temperature.

It was interesting to compare such unusual properties of C-mercurated carboranes with those of carboranes derivatives containing mercury substituents at the B(9) atom which holds a position opposite to C-atoms of *o*-carborane cage.

Contrary to the compounds with Hg–C(carborane) bond, compounds with Hg–B(carborane) bond react easily with electrophiles and do not react with nucleophiles.

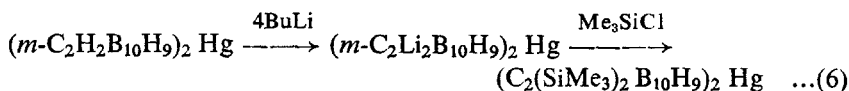
Thus, the symmetrical B-carboranylmercury compounds react with HgCl₂ (in acetone), Br₂ (in CCl₄) and water/acetone solution of HCl at room temperature :³



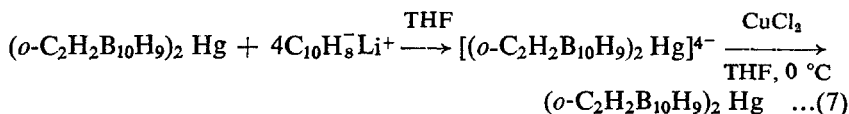
These reactions show that B-carboranyl derivatives of mercury differ sharply from analogous C-carboranylmercury compounds in their reactivity relative to

the electrophilic agents. The properties of B-carboranyl derivatives of mercury are more similar to those of aliphatic organomercuric compounds. The chemical behaviour of B-carboranylmercury compounds is in agreement with the quantitative data obtained under investigation of these compounds by ^{79}Br , ^{127}I NQR and polarographic methods.⁶

However, the most interesting feature of B-carboranylmercury compounds is the stability of the B-Hg bond towards nucleophilic reagents. Contrary to C-Hg bond in C-carboranyl derivatives of mercury, B-Hg bond in symmetrical B(9)-carboranyl derivatives of mercury is not split by BuLi and LiAlH_4 in refluxing THF. In the case of C-unsubstituted bis(*o*(*m*-carboran-9-yl)mercury, the C-H bond was metallated with BuLi to give C-Li derivatives. Thus, the interaction of bis(*m*-carboran-9-yl)mercury with four equivalents of BuLi followed by the addition of for equivalents of $(\text{CH}_3)_3\text{SiCl}$ gives bis(1,7-di(trimethylsilyl)-*m*-carboran-9-yl)mercury:¹¹



The action of the stable anion-radicals on the symmetrical B-carboranylmercury compounds has been studied. Bis(*m*-carboran-9-yl)mercury does not react with naphthalene anion-radical. However, bis(*o*-carboran-9-yl)mercury was shown to react with naphthalene lithium at -50°C in THF. The deep coloured solution of naphthalene anion-radical discolours till the addition of four equivalents of anion-radical to one equivalent of bis(*o*-carboran-9-yl)mercury. The electron-transfer from anion-radical molecule to carboranylmercury molecule affording tetra-anion of B-mercurated carborane seems to take place. The absence of the initial compound in the reaction mixture was confirmed by thin layer chromatography method. Even the action of excess naphthalene anion-radical solution does not break the B-Hg bond. The oxidation of tetraanion obtained with CuCl_2 suspension in THF at 0°C leads to the initial bis(*o*-carboran-9-yl)mercury:¹¹

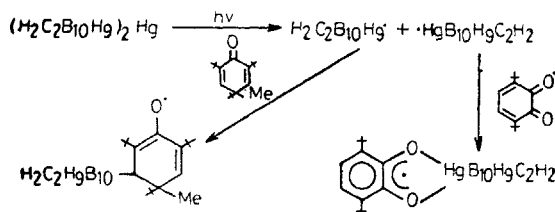


As mentioned previously, the symmetrical C-carboranyl derivatives of mercury have a high thermal stability. The photodecomposition of these compounds have not been described either. By contrast, the B-carboranyl derivatives of mercury undergo thermal and photodecomposition.

Zakhaykin and Pisareva⁸ have shown that the thermolysis of bis(carboran-9-yl)mercuric derivatives in sealed glass ampoules above 300°C gives mercury, carboranes, oligocarboranes and small amount of dicarboranyles which apparently are formed by recombination of the free carboranyl radicals. An increased yield of a dicarboranyl was obtained in the decomposition of bis(*m*-carboran-9-yl)

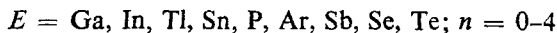
mercury in HMPA at 100 °C in the presence of the catalyst, $(\text{Ph}_3\text{P})_3\text{RhCl}$. Nevertheless, the pyrolysis of *o(m)*-carboran-9-yl-mercury chlorides, even in the presence of a catalyst, gives carboranes, their chloro-derivatives and metallic mercury, but not dicarboranyls.

We found that the formation of the B-carboranyl radicals occurs under the photodecomposition of bis(B-carboranyl)mercury compounds in solution. It has been proved by the EPR method for *o*-carboran-9-yl-, *m*-carboran-9-yl- and *p*-carboran-2-yl-derivatives. Depending on the type of a trap used, spectra of adducts derived from either B-centered or Hg-centered radicals have been recorded :¹²



SCHEME 1

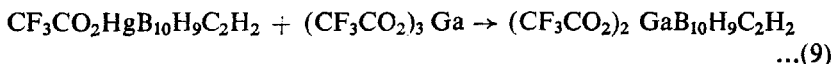
Interaction of the B-carboranylmercuric salts or symmetrical B-carboranyl derivatives of mercury with main groups III-V elements salts or non-metals of group VI leads to the B-carboranyl derivatives of groups III-VI elements :¹³



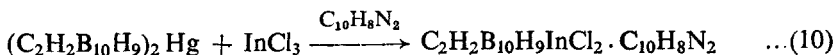
Zakharkin and Pisareva have prepared stable derivatives of carboranes with B-Pt σ -bond by the interaction of *o(m)*-carboran-9-yl-mercury chlorides with $(\text{Ph}_3\text{P})_3$.¹⁴

Below we'll discuss the properties of carboranyl derivatives of nontransition elements consecutively from III till VI groups elements.

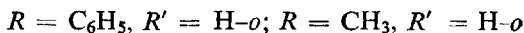
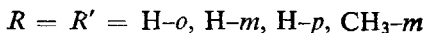
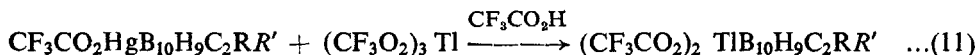
The B-carboranyl derivatives of gallium have been prepared by the interaction of B-carboranylmercury trifluoroacetate with tris(trifluoroacetate)gallium.¹⁵



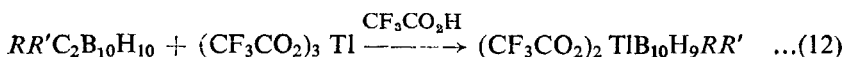
Heating of bis(*m*-carboran-9-yl)mercury with indium trichloride in tetrahydrofuran/dioxane mixture leads to *m*-carboran-9-yl-indium dichloride which was isolated in the form of α, α' -bipyridyl complex :



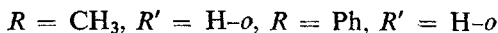
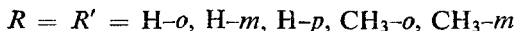
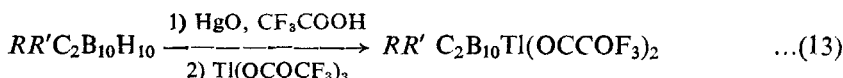
B-Thallated carboranes have been also obtained in good yields by the interaction of the B-mercurated carboranes with thallium(III) trifluoroacetate :¹⁶



We found that, similar to the thallation of arenes,^{17,18} the thallation of carboranes occurs but in more severe conditions than mercuration. The direct thallation of the unsubstituted *o*-, *m*-carboranes and phenyl-*o*-carborane with thallium(III) trifluoroacetate in boiling trifluoroacetic acid during 8–10 hours gives B-thallated carborane only in low yields (3–5 per cent). Satisfactory yields (45–50 per cent) of the thallated products were obtained only in the case of carborane activated by electron-donating substituents :¹⁹



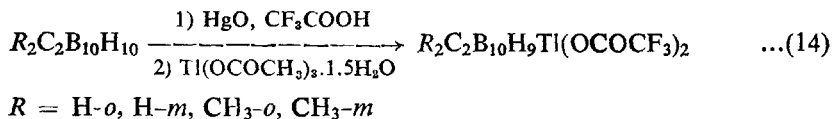
The thallation of *p*-carborane does not occur in these conditions. We succeeded in thallating *p*-carborane¹⁹ using only thallium(III) trifluoromethanesulfonate in trifluoroacetic acid which is stronger thallating reagent than thallium(III) trifluoroacetate. It was used by Deacon and Tunaley²⁰ for thallation of arenes deactivated to electrophilic substitution such as polyfluorobenzenes. However, the most convenient method of preparing B-thallated carboranes consists in the interaction of the initial carborane with mercuric oxide in trifluoroacetic acid, followed by treatment of the reaction mixture with thallium(III) trifluoroacetate :¹⁹



Actually, this “one-pot” reaction combines two processes : the mercuration of carboranes according to eq. 1 and the transfer of the carboranyl group from the mercury atom to the thallium atom, as presented in eq. 11. However, in contrast to reactions (1) and (11), this procedure allows the stage of isolation and purification of the intermediate B-mercurated carborane compound to be avoided without significant influence on the yields of the final products. The B-thallated carboranes prepared by procedure (13) precipitate from the reaction mixture and their purification is not practically required.

Al-Assawi and Roberts²¹ have shown that the rate constants of the thallation of aromatic substrates with thallium(III) acetate sesquihydrates ($\text{Ti}(\text{OCOCH}_3)_3 \cdot 1.5\text{H}_2\text{O}$) do not differ from those of the thallation of the same substrates with thallium(III) trifluoroacetate in trifluoroacetic acid. We found that the thallation had taken place under treatment of dimethyl-*o*-carborane with thallium(III) acetate sesquihydrate in trifluoroacetic acid, but the yield of the

thallated product was essentially lower than that of the same product when thallium(III) trifluoroacetate in trifluoroacetic acid was used. In addition, considerable amounts of the product of carborane nucleus B-H bond oxidation, 9-dihydroxycarborane, and unreacted dimethyl-*o*-carborane were found in the reaction mixture. However, $\text{Tl}(\text{OCOCH}_3)_3 \cdot 1.5\text{H}_2\text{O}$ is a convenient thallating agent in the method of carborane thallation with equimolecular amounts of HgO . In this method, sesquihydrate is even more convenient than trifluoroacetate since it is readily prepared from Tl_2O_3 and aqueous acetic acid. There is practically no difference in the yield of B-thallated carboranes when thallium(III) acetate sesquihydrate is used instead of trifluoroacetate:



Thus, the best agent for the direct thallation of carboranes was shown to be thallium(III) trifluoroacetate, and the most convenient method of obtaining B-thallated carboranes consists in the interaction of the initial carborane with mercuric oxide in trifluoroacetic acid, followed by treatment of the reaction mixture with thallium(III) trifluoroacetate or thallium(III) acetate sesquihydrate.

The position of thallation of carboranes was confirmed by X-ray analyses of bis(trifluoroacetato)-1,7-dimethyl-*m*-carboranyl(α, α' -bipyridyl)-thallium. This is

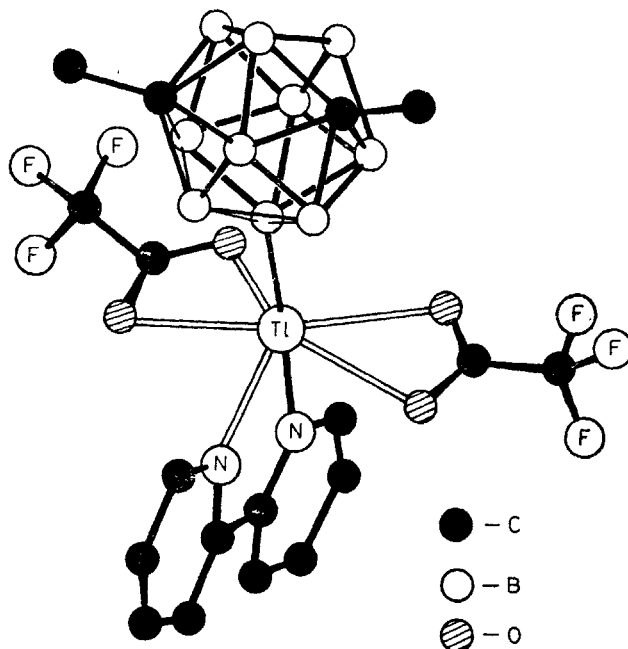


FIG 1 The structure of bis(trifluoroacetato)-1,7-dimethyl-*m*-carboranyl(α, α' -bipyridyl)-thallium

the first compound with σ -bond between a nontransition metal and a boron atom of the carborane cage to be studied structurally (Fig. 1).²²

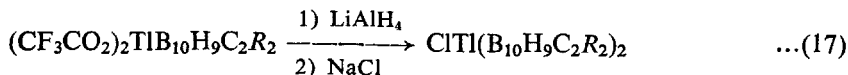
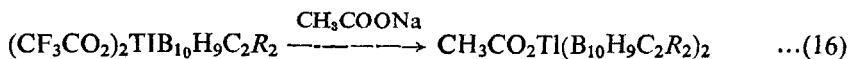
In this compound the thallium atom is linked to the boron atom of the carborane cage at position 9. The thallium atom has a pentagonalpyramidal configuration with short axial bonds Tl-B (2.06(2) Å) and Tl-N (2.16(1) Å) subtending almost a straight line, which is characteristic of organothallium compounds with two Tl-C bonds. The Tl-B distance is considerably less than the sum of Tl and B covalent radii. The second nitrogen atom of bipyridyl and the four oxygen atoms of the trifluoroacetate groups occupy the equatorial positions. The axial Tl-N bond (2.16(1) Å) is considerably less than the equatorial Tl-N bond (2.440(9) Å).

We have compared the properties of B-carboranyl derivatives of Tl and Hg. Unlike B(9)-Hg bond, B(9)-Tl bond is stable under the action of HCl and Br₂. But similar to the B-Hg bond in the B-mercurated carboranes, the B-Tl bond in the B-thallated carboranes is stable towards nucleophilic reagents. It provides a very convenient entry into derivatives with two different radicals on Tl atom which would otherwise be difficult to access:²³



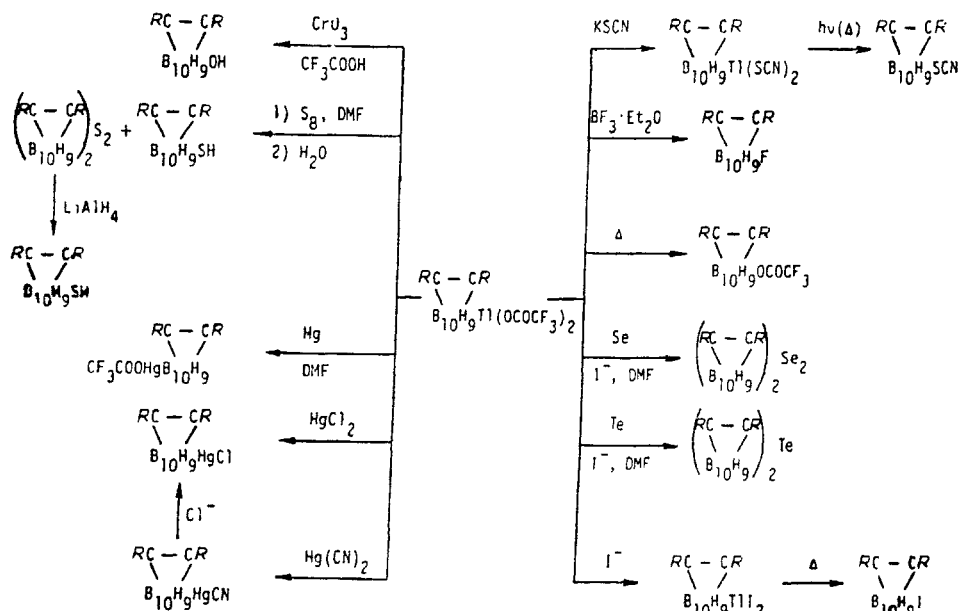
$R = \text{Alkyl, Aryl, C-carboranyl}; M = \text{Li, MgX}; X = \text{Cl, Br, I}$

We have obtained bis(B-carboranyl) thallium salts by the action of symmetrizing agents such as sodium acetate in boiling water or lithium aluminium hydride in ether on carbonylthallium-bis (trifluoroacetates).²⁴



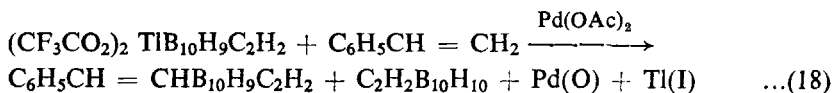
One of the most important features of organothallium compounds is their use in organic synthesis, for example, for the selective preparation of arene derivatives. We have obtained carboranes with substituents in the 9 position of the icosahedron by the reactions of the B-Tl bond in B-thallated carboranes. These reactions mainly occur under radical conditions (pyrolysis, photolysis) as well as under the action of oxidants, zerovalent metals and non-metals. The new 9-fluore-, 9-thiocyano-, 9-trifluoroacetoxy-, 9-cyanomercuro-carboranes, bis(carboran-9-yl) diselenides, bis(carboran-9-yl) tellurides, and 9-iodo-, 9-hydroxy-, 9-trifluoroacetoxymercuro-, 9-mercapto-carboranes, bis(carboran-9-yl) disulfides, which have been reported previously, were synthesised (Scheme 2).^{23,25,26}

We have also studied the possibility of carboranyllating olefins and of the formation of biscarboranyls using combinations of B-thallated carboranes (or carboranes and thallium salts) with catalytic quantities of palladium(II) salts. The interaction of (*o*-carboran-9-yl) thallium trifluoroacetate with Pd(OAc)₂ in the

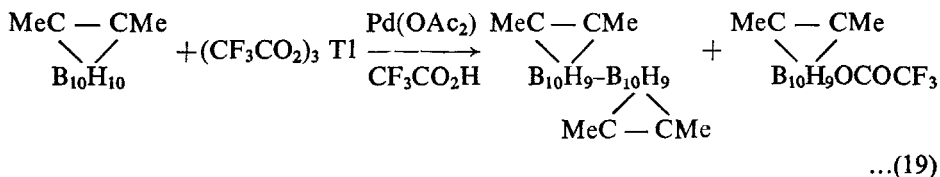


Scheme 2

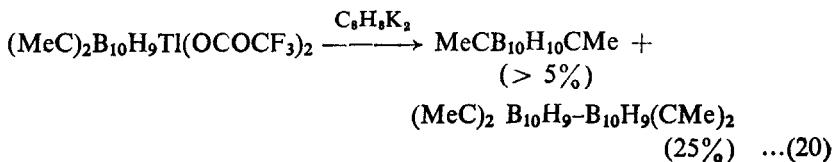
presence of styrene gives (*o*-carboran-9-yl) styrene, *o*-carborane, metallic palladium and thallium salts.²⁷



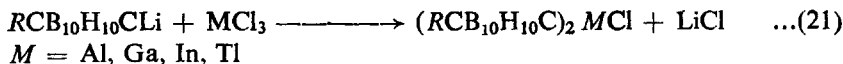
The interaction of 1,2-dimethyl-*o*-carborane with thallium(III) trifluoroacetate in the presence of palladium(II) acetate gives bis(1,2-dimethyl-*o*-carboran-9-yl) in 35 per cent yield²⁸.



Bis(1,7-dimethyl-*m*-carboran-9-yl) is formed under the conditions of homogeneous reduction of bis(trifluoroacetato) (1,7-dimethyl-*m*-carboran-9-yl) thallium with cyclooctatetraene dipotassium salt.²⁹

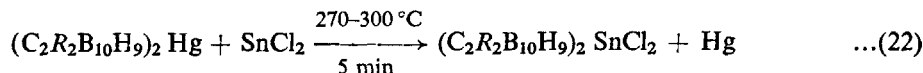


We compared the properties of the B-carboranyl derivatives of the III group metals with those of the C-carboranyl derivatives, which were obtained by the interaction of C-carboranyl lithium with metal chlorides.^{15,30}

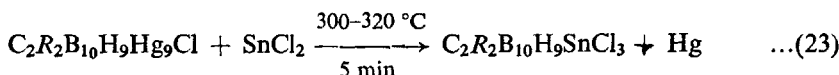


It was shown that, contrary to the dramatic differences in the properties of the B- and C-carboranyl derivatives of mercury, the properties of the B-carboranyl derivatives of the III group metals do not differ greatly from those of C-carboranyl analogues. Thus bis(B-carboranyl) thallium salts do not react with HCl and halogens, similarly to analogous carborane compounds with C-Tl bond.³⁰ But unlike bis(C-carboranyl) thallium salts, bis(B-carboranyl) thallium salts do not form complexes with α, α' -bipyridyl and *o*-phenantroline, due to the difference in the electronic effects of the C- and B-carboranyl groups.²⁴ Both the B-carboranyl and C-carboranyl derivatives of gallium and indium are oxidized and hydrolysed in air. But they are stable in the presence of the ligands coordinated with the metal atoms.

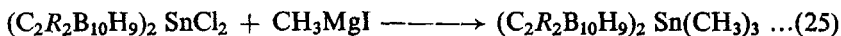
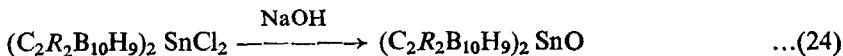
Bis (*o(m)*-carboran-9-yl) tin dichlorides were obtained in a good yield by the interaction of bis (*o(m)*-carboran-9-yl) mercury with an excess of fused stannous chloride at 270–300 °C³¹:



Under similar conditions *o*- and *m*-carboranylmercury chlorides give *o*- and *m*-carboranyltin trichlorides³¹:



Contrary to C(carborane)-Sn bond,¹⁰ the B-Sn bond in carboranyltin chlorides is stable towards nucleophilic reagents, which makes it possible to replace chlorine atoms by the hydroxy group under the action of an alkali in aqueous-etherial medium and by alkyl groups under the action of Grignard reagents³¹



The interaction of carboranyl (methyl) stannanes with an equimolar amounts of HCl gives methane. Carborane is absent in the reaction mixture showing initial rupture of the Sn-CH₃ bond and the stability of the B-Sn bond. Iodine also reacts with the initial rupture of the Sn-CH₃ bond, and only an excess of the halogen causes B-Sn bond rupture.

The effect of B-substituted carboranyl groups on the electron environment of the tin nucleus was studied by gamma resonance spectroscopy method. The influence of the 9-carboranyl group (Table I, compounds 2-4, 8-15) was shown to be close to that of an alkyl group (compounds 1, 5, 6) and differ greatly from that of C-carboranyl group (compound 7).³¹

TABLE I
Gamma resonance spectroscopy data of some organotin compounds

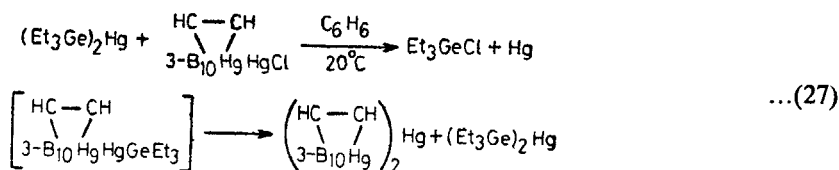
Compound	Isomeric shift* δ (mm/sec)	Quadrupole splitting Δ (mm/sec)
1 CH_3SnCl_3	-0.78	2.07
2 $o\text{-C}_2\text{H}_2\text{B}_{10}\text{H}_9\text{SnCl}_3$	-0.49	2.25
3 $m\text{-C}_2\text{H}_2\text{B}_{10}\text{H}_9\text{SnCl}_3$	-0.63	2.20
4 $m\text{-(CH}_3)_2\text{C}_2\text{B}_{10}\text{H}_9\text{SnCl}_3$	-0.63	2.21
5 $(\text{CH}_3)_2\text{SnCl}_2$	-0.55	3.60
6 $(\text{C}_3\text{H}_7)_2\text{SnCl}_2$	-0.40	3.60
7 $(\text{C}_6\text{H}_5\text{CB}_{10}\text{N}_{10}\text{C})_2\text{SnCl}_2$	-0.85	0.90
8 $(o\text{-C}_2\text{H}_2\text{B}_{10}\text{H}_9)_2\text{SnCl}_2$	-0.31	3.80
9 $(m\text{-C}_2\text{H}_2\text{B}_{10}\text{H}_9)_2\text{SnCl}_2$	-0.41	3.70
10 $(o\text{-(CH}_3)_2\text{C}_2\text{B}_{10}\text{H}_9)_2\text{SnCl}_2$	-0.35	3.50
11 $(m\text{-(CH}_3)_2\text{C}_2\text{B}_{10}\text{H}_9)_2\text{SnCl}_2$	-0.48	3.35
12 $(o\text{-C}_2\text{H}_2\text{B}_{10}\text{H}_9)_2\text{Sn}(\text{CH}_3)_2$	-0.75	-0.40
13 $(o\text{-(CH}_3)_2\text{C}_2\text{B}_{10}\text{H}_9)_2\text{Sn}(\text{CH}_3)_2$	-0.81	-0.30
14 $(o\text{-(CH}_3)_2\text{C}_2\text{B}_{10}\text{H}_9)\text{Sn}(\text{CH}_3)_3$	-0.68	-0.30
15 $(o\text{-C}_2\text{H}_2\text{B}_{10}\text{H}_9)_2\text{SnO}$	-0.53	3.48

*Relative to $\alpha\text{-Sn}$

The X-ray study of bis(1,2-dimethyl-*o*-carboranyl) dimethylstannane confirmed that the tin atom is linked to the boron atom of the carborane cage at the 9 position.³² Contrary to the B-thallated carboranes structurally investigated, the Sn-B distances (2.222(8) and 2.240(8)Å) are practically equal to the sum of Sn and B radii (2.21 Å).

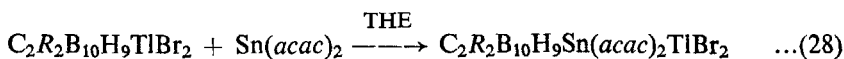
Thus the analysis of the properties of the B-carboranyl tin compounds has shown that, similarly to carboranylmercury compounds, B-carboranyl derivatives of tin differ sharply from C-carboranyl analogues.

An interesting area of synthetic application of the B-metallated carboranes involves the preparation of polyelemental chain compounds. The early attempt of Zakharkin, Vyazankin and co-workers³³ to obtain compounds of such type from B(3)-mercurated carborane and bis(triethylgermyl)mercury afforded only bis(*o*-carboran-3-yl)mercury which was thought to be formed as a result of disproportionation of the intermediate (*o*-carboran-3-yl)triethylgermylmercury :

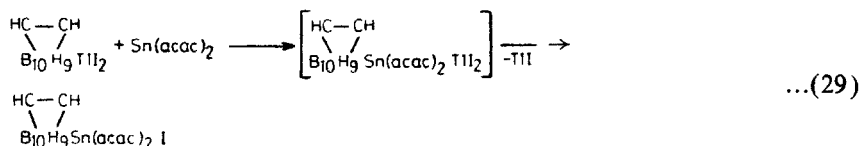


These authors also obtained the stable germyl (carboranyl) mercury compounds by exchange reaction of C-mercurated carboranes of the type *o*-RCB₁₀H₁₀CHgX (X = Me, Ph, Cl) with bis(triethylgermyl)mercury. In these compounds Et₃GeHg fragments bond to the carborane cage through a carbon atom.

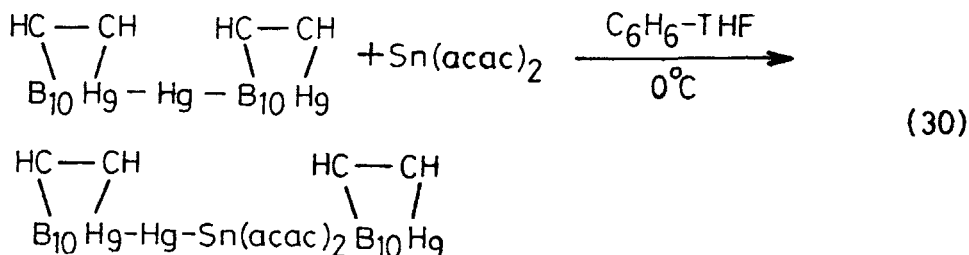
We obtained the first example of bimetallic B-carboranyl compounds by the action of Sn(*acac*)₂ on (*m*-carboran-9-yl) thallium dibromide.³⁴



Unlike the dibromides, B-carboranylthallium dichlorides do not react with Sn(*acac*)₂ even after heating for many hours. In contrast, (*o*-carboran-9-yl) thallium diiodide reacts with Sn(*acac*)₂ with the instant formation of thallium(I) iodide. It may therefore be suggested that the reaction proceeds *via* the intermediate formation of insertion product of Sn(*acac*)₂ followed by the elimination of TlI.¹³



The interaction of bis(*o*-carboran-9-yl) mercury with Sn(*acac*)₂ in a mixture of benzene and THF (10 : 1) at 0 °C leads to the formation of Sn-Hg bimetallic derivatives of carborane.^{35,36}



Protons of the Sn(*acac*)₂ methyl groups are seen in the ¹H NMR spectra as two singlets (δ(CH)₃ = 1.186 and 1.112ppm) while methine groups protons are centered at 4.898 and 4.927ppm. After insertion of Sn(*acac*)₂, the methyl protons of the acetylacetonate ligands in the ¹H NMR spectra also seen as two singlet (δ(CH₃) = 1.594 and 1.608ppm); the methine protons being centered at 4.893 and 4.928ppm. The ¹H NMR spectrum of (*o*-carborane-9-yl) (*o*-carboran-9-yl-mercuro) bis(acetylacetonato) stannane in benzene is presented in Fig. 2. The splitting of

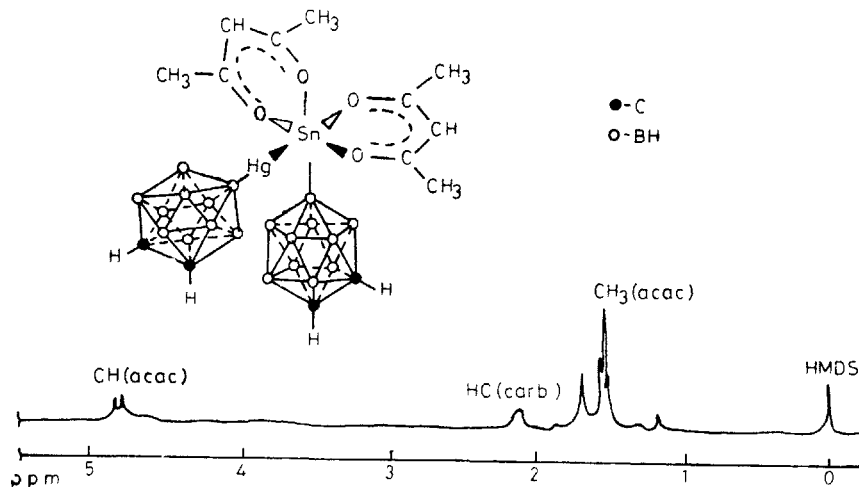
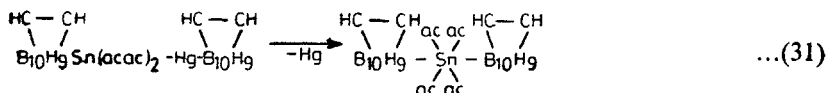
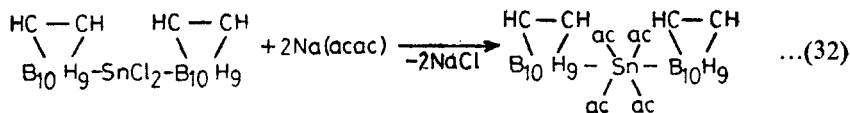


FIG 2 ^1H NMR spectrum of (*o*-carbon-9-yl) (*o*-carboran-9-ylmercurio)-bis (acetylacetonato) stannane.

signals of methyl and methine protons of the acetylacetonate ligands points to the existence of the isomer with *cis*-location of acetylacetonate ligands around the tin atom. When the reaction mixture is kept at room temperature, a slow (4h) demercuration of the bimetallic compound takes place in benzene, while in THF- C_6H_6 demercuration proceeds rapidly (0.5–1h):



During demercuration, the positions of signals of the methyl and methine protons of the acetylacetonate ligands are almost unchanged, which indicates that the configuration of the acetylacetonate ligands on tin atom is retained. To compare with the demercuration products obtained by reaction 31 we performed an independent synthesis from $(\text{C}_2\text{H}_2\text{B}_{10}\text{H}_9)_2 \text{SnCl}_2$ and $\text{Na}(\text{acac})$:

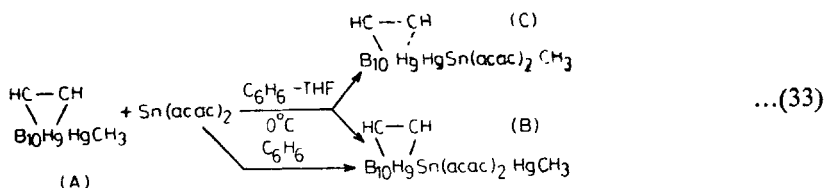


According to ^1H NMR data, the acetylacetonate ligands were located in *cis*-positions of the tin atom after the exchange.

If the insertion reaction is carried out using two molar equivalents of $\text{Sn}(\text{acac})_2$ the product represents the first example of the double insertion of $\text{Sn}(\text{acac})_2$ into Hg-element bonds.³⁵

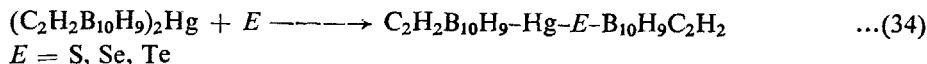
The reaction of $\text{Sn}(\text{acac})_2$ with B-carboranylmercury halides also leads to bimetallic derivatives.^{35,36}

To study the insertion of $\text{Sn}(\text{acac})_2$ into a compound containing both the C-Hg and B-Hg bonds, the reaction of 9-methylmercur-*o*-carborane and 9-methylmercur-1,2-dimethyl-*o*-carborane with $\text{Sn}(\text{acac})_2$ in benzene was carried out. The reaction may give rise to two products (B and C).⁴⁰



Addition of equal quantities of $\text{Sn}(\text{acac})_2$ to 9-*o*- $\text{CH}_3\text{HgB}_{10}\text{H}_9\text{C}_2\text{R}_2$ - ($\delta(\text{CH}_3) = 0.119$, $\delta(\text{CH}) = 2.235\text{ppm}$, $J(^{199}\text{Hg}-^1\text{H}) = (132.80\text{Hz})$, causes an appearance in the ^1H NMR spectrum of proton signals from the methyl group directly bonded to the mercury atom ($\delta(\text{CH}_3) = 0.108\text{ppm}$, $J(^{199}\text{Hg}-^1\text{H}) = 126.20\text{Hz}$), along with signals from methyl and methine protons of the acetylacetonate ligands of the insertion products ($\delta(\text{CH}_3) = 1.546$ and 1.593 , $\delta(\text{CH}) = 4.987$ and 5.036 ppm). These data demonstrate that the insertion of $\text{Sn}(\text{acac})_2$ into mercury B-carboranyl derivatives of the type 9-*o*- $\text{C}_2\text{R}_2\text{B}_{10}\text{H}_9\text{HgCH}_3$ proceeds in benzene mainly at the B-Hg bond with the acetylacetonate ligands situated, after the insertion, in *cis*-positions on the tin atom. The reaction in a C_6H_6 -THF mixture with equal quantities of the reagents is accompanied with a gradual disappearance of compound A and the formation of products B and C, which is indicated by a smooth decrease in the intensity of the signal of methyl group protons on the mercury atom ($\delta(\text{CH}_3) = 0.119\text{ppm}$, $J(^{199}\text{Hg}-^1\text{H}) = 132.80\text{Hz}$) and by a rise in the signals centered at 0.108ppm (^1H , $J(^{199}\text{Hg}-^1\text{H}) = 126.82\text{Hz}$) and at 0.553ppm (CH_3 , $J(^{117}\text{Sn}-^1\text{H}) = 143.49\text{Hz}$ and $J(^{119}\text{Sn}-^1\text{H}) = 140.68\text{Hz}$). In the case, the acetylacetonate ligands on the tin atom also occupy the *cis* positions: $\delta(\text{CH}_3) = 1.556$, 1.498 , 1.454ppm (*acac*), $\delta(\text{CH}) = 4.973$, 4.982 , 5.017ppm (*acac*).

Elemental sulphur, selenium and tellurium are inserted into the B-Hg bonds of boronmercurated carboranes in THF, dimethoxyethane or DMF to form (in ~ 60 yield) compounds containing the atom chains (B-Hg-S-B, B-Hg-Se-B and B-Hg-Te-B).^{13,26}

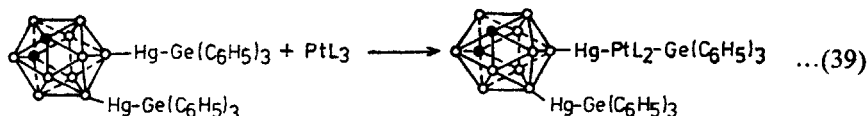


Mercury separates in the course of the reaction, demercuration products being formed in slight amount (to 10 per cent). The same products are obtained in 30 per cent yield when the reaction is run under severe conditions (fusing at 270 - 300°C), sulphur and selenium forming disulphides and diselenides, respectively, and tellurium giving the monotelluride.

The investigation of polymetallic chain compounds including boron atoms of the carborane unit resulted in the synthesis of carborane derivatives containing up to 8 atoms of the element E in the chain.³⁷

It should be remarked that the interaction of PtL_3 with 9-CIHg-*m*-B₁₀H₉C₂H₂ is followed by demercuration of the products.¹⁴

The interaction of tris(triphenylphosphine) platinum with carborane containing two B-Hg-Ge fragments results in the insertion of only one PtL_2 group:



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 the second mercurated boron atom. This steric hindrance seems to prevent the second Hg-Ge bond from attacking the platinum complexes.

The ¹⁹⁹Hg, ³¹P and ¹⁹F NMR spectra data confirm the structure of the PtL_2 insertion products and point to the *cis*-location of the triphenylphosphine ligands around the platinum atom (Fig. 3).

The dicarboranyl compound with mercury atoms separated by GeR₂-GeR₂ fragment adds two equivalents of PtL_2 to give a six-membered chain containing *m*-C₂H₂B₁₀H₉ groups at the ends:

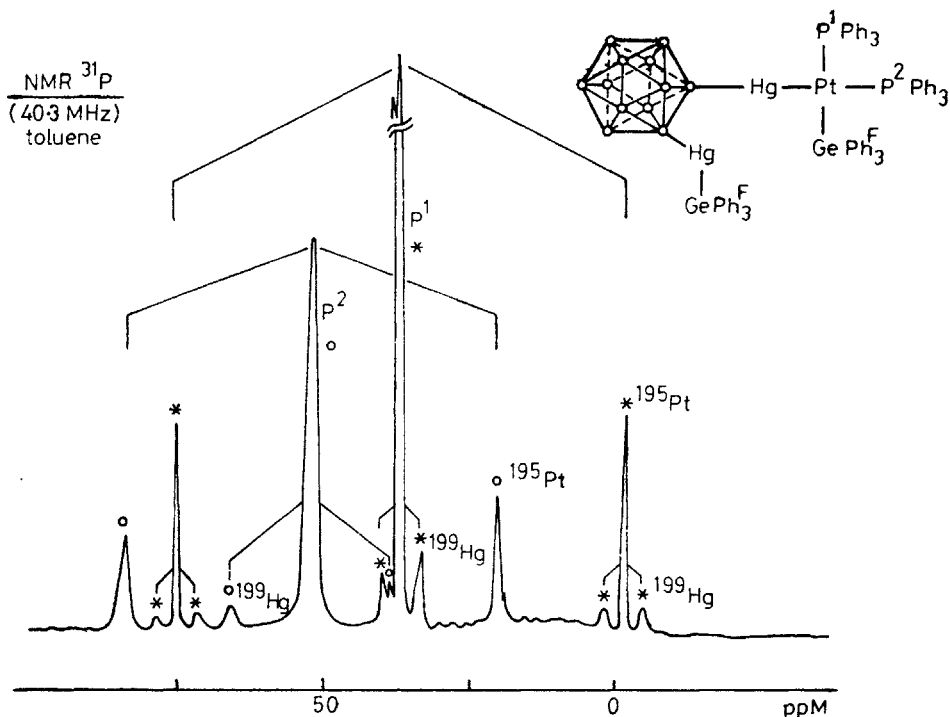
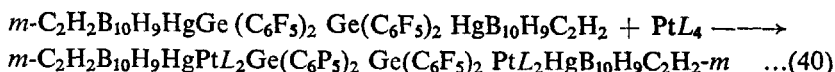


FIG 3 ³¹P NMR spectrum of $(C_6F_5)_2 GeHg(B_{10}H_9C_2H_2) HgPt(PPh_3)_2 Ge(C_6F_5)_2$



Such compounds are undoubtedly only the first examples of a great variety of polyelemental chains which can be obtained using these new reactions of the boronmetallated carboranes.

In general, it should be noted that the B-metallated carboranes with boron-non-transition bonds B-M have in many cases characteristic parallel to those of organometallic compounds with C-M bonds.

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