

Carboranyl derivatives of nontransition metals

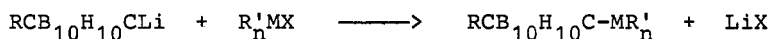
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Abstract - The synthesis of the unknown types of carboranyl derivatives of nontransition metals was carried out. The properties of carborane derivatives with the carbon-nontransition metal σ -bond, on the one hand, and the boron-metal bond, on the other, were compared. Boron-carboranyl derivatives of non-transition metals were shown to react with different reagents similar to organometallic compounds.

INTRODUCTION

Previously, carboranyl derivatives of nontransition metals with the C-M σ -bond have been prepared by the action of C-lithiumcarboranes on compounds with metal-halogen bond (refs. 1,2).

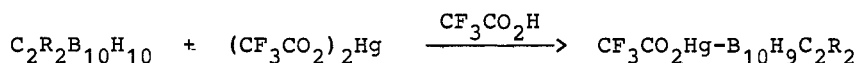


These compounds have been shown to have the properties unusual for the classical organometallic compounds. The o-carboranyl derivatives of mercury with the Hg-C(carborane) bond have a high thermal stability (up to 300°C) and remain unchanged after refluxing in acetone with electrophiles. But the action of nucleophilic agents on these compounds results in the cleavage of the Hg-C(carborane) bond even at room temperature (ref. 1). The same properties are also typical of bis(carboranyl)thallium halides with the Tl-C bond (ref.2).

The subject of this work is the synthesis of carboranes with the boron-non-transition metal bond, which is uncommon in chemistry, and the investigation of their properties in comparison with the properties of carborane derivatives with C-M σ -bond and other organometallic compounds.

CARBORANYL DERIVATIVES OF MERCURY

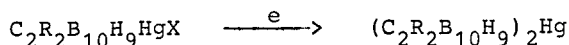
The preparative synthesis of carboranes containing the boron-nontransition metal bond became possible through the direct mercuration of o-, m- and p-carboranes (the trivial name of 1,2-, 1,7- and 1,12-dicarbocloso-dodecaborane(12), respectively) by the action of a strong mercurating agent, mercury trifluoroacetate in trifluoroacetic acid (refs. 3,4).



The mercuration of both unsubstituted and C,C'-disubstituted o- and m-carboranes occurs mainly in the 9 position of the carborane nucleus (however up to 15% of the 8-substituted derivative was isolated in the case of o-carborane (ref. 5). p-Carborane, in which all of the boron atoms are equivalent, is mercurated in the 2 position.

The carboranylmercury salts do not undergo symmetrization in the presence of the complexing agents (KI, NaI, KCN, $\text{Na}_2\text{S}_2\text{O}_3$, NH_3). Symmetrization can be carried out only by reducing agents such as naphthalene anion-radical and metal amalgams (ref. 4). Convenient methods for the symmetrization of B-mercuricboranes salts are based on the treatment with lithium aluminium hydride (ref. 6) and sodium stannite (ref. 7). The preparative electrochemical

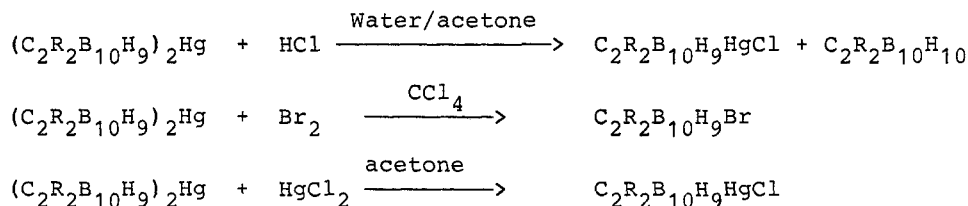
symmetrization of the C- and B-carboranylmercury salts has also been demonstrated (ref. 8).



Recently the symmetrization of B-carboranylmercury salts by zerovalent lanthanides (Ln = La, Sm and Yb) was carried out (ref. 9).

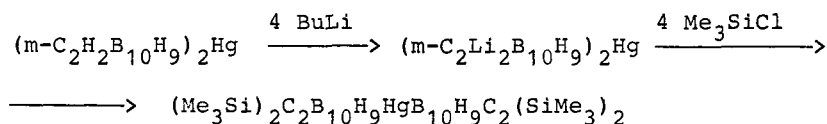
The molecular structure of bis(p-carboran-2-yl)mercury was determined by gas electron diffraction. The length of a relatively rare chemical bond Hg-B is $2.16 \pm 0.02 \text{ \AA}$ (ref. 10). The Hg-C distance in bis(p-carboran-1-yl)mercury determined by the same method is $2.084 \pm 0.013 \text{ \AA}$ (ref. 11).

In contrast to the behaviour of the C-carboranyl analogues (ref. 1), the symmetrical B-carboranylmercury compounds readily react even at room temperature with such electrophilic reagents as hydrogen chloride, bromine and mercuric chloride (ref. 4).

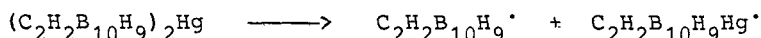


These reactions show that the reactivity of the B-carboranyl derivatives of mercury is broadly similar to that of aliphatic and aromatic organomercuric compounds.

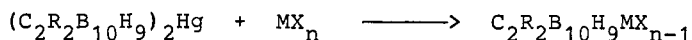
The most interesting feature of B-carboranylmercury compounds is the stability of the Hg-B bond towards nucleophilic reagents, hydrides and organometallic compounds. Contrary to Hg-C bond in C-carboranyl derivatives of mercury, B-Hg bond in the symmetrical B(9)-carboranylmercury compounds is not split by butyllithium and lithium aluminium hydride in refluxing THF. This makes it possible to tetralithiate bis(o(m)-carboran-9-yl)mercury with BuLi by replacing all four hydrogen atoms on the carborane carbon atoms by lithium. The addition of four equivalents of trimethylchlorosilane to tetralithiated bis(m-carboran-9-yl)mercury gives the corresponding tetrasilyl derivative (ref.12).



As mentioned previously the C-carboranylmercury compounds have a high thermal stability. The photodecomposition of these compounds have not been described either. By contrast, the B-carboranylmercury compounds undergo thermal and photodecomposition (refs. 7,12). The formation of the B-carboranyl radicals in the photodecomposition of bis(B-o(m,p)-carboranyl)mercury in solution has been proved by the EPR method. Depending on the type of a trap used spectra of adducts derived from either B-centered or Hg-centered radicals have been recorded (ref. 12).



Similarly to organomercury compounds the B-mercurated carboranes turned out to be key compounds in the synthesis of B-carboranyl derivatives of other nontransition metals (refs. 13, 14).

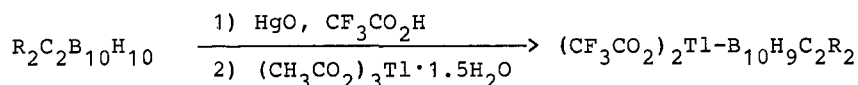


M = Ga, In, Tl, Sn, As, Sb

CARBORANYL DERIVATIVES OF THALLIUM

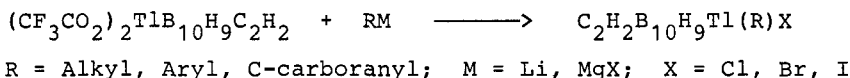
The thallation of carboranes occurs but in more severe conditions than mercuration. The B-thallated carboranes were obtained in satisfactory yields (45-50%) only when carboranes activated by electron-donating substituents were treated with thallium(III) trifluoroacetate in trifluoroacetic acid. However, the most convenient method for the preparation of B-thallated carboranes

consists in the interaction of the starting carborane with mercuric oxide in trifluoroacetic acid followed by treatment of the reaction mixture with thallium(III) trifluoroacetate or sesquihydrate of thallium(III) acetate (ref. 15).



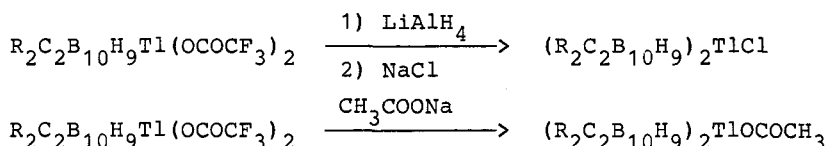
Complex of bis(trifluoroacetato)-1,7-dimethyl-m-carboranylthallium with α, α' -bipyridil is the first compound with a σ -bond between a nontransition metal and a boron atom of the carborane cage to be studied structurally (ref. 16). In this compound the thallium atom has a pentagonal-pyramidal configuration 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 second nitrogen atom of bipyridyl and the four oxygen atoms of the trifluoroacetate groups occupy the equatorial positions. The axial Tl-N bond is considerably less than the equatorial Tl-N bond (2.440(9) Å). The Tl-B distance is considerably less than the sum of Tl and B covalent radii (1.55 + 0.81 = 2.36 Å). This distance is less than the Tl-B distance (2.24(2) Å) in the stable anionic heteroligand complex recently studied $n-Bu_4N[m-C_2H_2B_{10}H_9TlCl_{2.35}I_{0.65}]$ (ref. 17).

Similarly to the B-Hg bond in the B-mercurated carboranes, the B-Tl bond in the B-thallated carboranes is stable towards nucleophilic reagents. This makes it possible to use the alkylation of carboranylthallium-bis(trifluoroacetates) for preparing derivatives with two different radicals on thallium atom: such derivatives being not so easily obtained in the chemistry of organothallium compounds (ref. 18).



The Tl-B bond in carboranyl derivatives readily undergoes homolytic dissociation on photolysis or thermolysis. The formation of the Tl-centered or B-centered radicals in toluene solution has been proved by the EPR method (ref. 19). The photodecomposition of B(9)-m-carboranyl derivatives of thallium and mercury in the presence of arenes results in the formation of 9-aryl-m-carboranes (ref. 20).

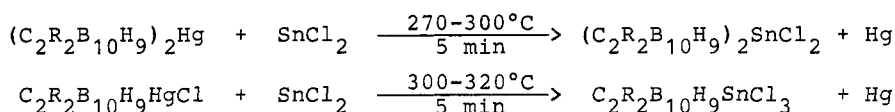
Bis(B-carboranyl)thallium salts have been obtained by the action of symmetrizing agents such as lithium aluminium hydride in ether or sodium acetate in boiling water on (B-carboranyl)thallium bis(trifluoroacetates) (ref. 21).



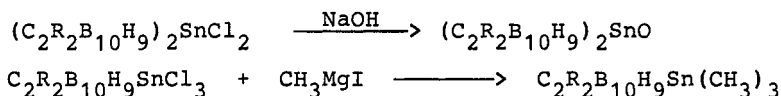
Contrary to the dramatic difference in the properties of the B- and C-carboranyl derivatives of mercury, the properties of the B-carboranyl derivatives of the III group metals do not differ greatly from those of C-carboranyl analogues. Thus bis(B-carboranyl)thallium salts do not react with HCl and halogens, similarly to analogous carborane compounds with Tl-C bond (ref. 2). 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 (ref. 21).

CARBORANYL DERIVATIVES OF TIN

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°C. Under similar conditions o- and m-carboranylmercury chlorides give carboranyl tin trichlorides (ref. 22).



Contrary to Sn-C(carborane) bond (ref. 1), the Sn-B bond in carboranyl tin 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 reagents (ref. 22).



Gamma resonance spectroscopy method has been used for studying the effect of B-carboranyl groups on the electron environment of the tin nucleus. The influence of the 9-carboranyl group was shown to be close to that of a methyl group and to differ greatly from that of C-carboranyl group (ref. 22).

Thus, the analysis of the properties of the B-carboranyl derivatives of Hg, Tl and Sn has shown that they differ sharply from the properties of the C-carboranyl analogues and similar to those of the corresponding organometallic compounds.

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