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Preliminary communication

CARBORANES WITH B—Tl BONDS

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Summary

The transfer of the carboranyl group mercurated at the B(9) position from the mercury atom to the thallium atom has been carried out, and identical compounds have been prepared by the direct thallation of carboranes with thallium(III) trifluoroacetate.

We have recently [1] described the direct mercuration of carboranes under the action of mercury trifluoroacetate. The derivatives of *o*-, *m*- and *p*-carboranes with B—Hg bonds have been prepared [2, 3]. The synthesis of B-mercurated carboranes has led us to the preparation of the various derivatives of carboranes with B—M bonds due to transfer of the carboranyl group from the mercury atom to the atom of the other metal.

For the first time the transfer of the carboranyl group from the mercury atom to other elements has been carried out for C-mercurated carboranes [4]. The reduction of bis(phenylcarbonyl)mercury by the action of naphthalene anion-radical solution followed by the addition of $(CH_3)_3SiCl$ has led to tetrasubstituted silane with a Si—C (carborane) bond.

The subject of this paper is the transfer of the B-mercurated carboranyl group from the mercury atom to the thallium atom.

We have carried out such a transfer under the interaction of bis(*o*(*m*)-carboranyl)mercury mercurated at the B(9) position with thallium trifluoroacetate in ether:

$$(C_2H_2B_{10}H_9\text{-}9)_2Hg + (CF_3CO_2)_3Tl \rightarrow 9\text{-}(CF_3CO_2)_2Tl{-}B_{10}H_9C_2H_2$$

The same products have been obtained using trifluoroacetates of B-mercurated *ortho*- and *meta*-carboranes as the initial compounds in boiling trifluoroacetic acid:

$$9\text{-}CF_3CO_2Hg{-}B_{10}H_9C_2H_2 + (CF_3CO_2)_3Tl \rightarrow 9\text{-}(CF_3CO_2)_2Tl{-}B_{10}H_9C_2H_2$$

We have also carried out the direct thallation of *ortho*- and *meta*-carboranes by treatment of carborane with thallium trifluoroacetate in trifluoroacetic acid:

$$o(m)\text{-}C_2H_2B_{10}H_{10} + (CF_3CO_2)_3Tl \rightarrow (CF_3CO_2)_2Tl\text{-}o(m)\text{-}B_{10}H_9C_2H_2$$

These compounds are identical to derivatives prepared by means of the carboranyl group transfer from the mercury to the thallium atom. Table 1 contains physical data for the compounds obtained.

TABLE 1

B-SUBSTITUTED CARBORANYLTHALLIUM COMPOUNDS

Compounds	M.p. (°C)	Analysis: Found (calcd.) (%)				
		C	H	B	F	Tl
9-$(CF_3CO_2)_2Tl$—o-$B_{10}H_9C_2H_2$	199—200[a]	12.4 (12.6)	2.0 (1.9)	18.8 (18.8)	19.5 (19.9)	35.6 (35.6)
9-$(CF_3CO_2)_2Tl$—m-$B_{10}H_9C_2H_2$	205—206[a]	12.6 (12.6)	2.0 (1.9)	19.0 (18.8)	20.3 (19.9)	

[a] Crystallized from trifluoroacetic acid.

Carboranylthallium derivatives may be the convenient initial compounds for the synthesis of the various carboranes with B—M bonds. The first example of such synthesis is the transfer of the carboranyl group from the thallium to the mercury atom, which has been carried out by the action of $HgCl_2$ on *o*-carboranylthallium bis(trifluoroacetate) to give (*o*-carboranyl-9)mercury chloride described earlier [1].

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