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Preliminary communication

SYNTHESIS OF CARBORANYL DERIVATIVES OF DI- AND TRI-VALENT LANTHANIDES

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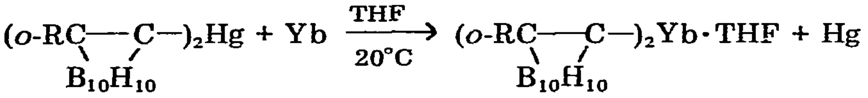
Summary

It has been shown that the interaction of *C*- and *B*-mercurocarboranes with lanthanides (La, Tm, Yb) in THF at 20°C give carboranyl derivatives of lanthanides in which the lanthanides are linked with the carborane nuclei via C—Ln or B—Ln bonds.

In continuation of investigations on the synthesis of new derivatives of lanthanides [1] we have studied the reaction of *C*- and *B*-mercurocarboranes with Ln^0, where Ln = La, Tm, Yb.

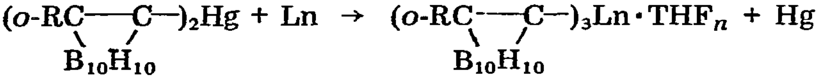
It is known that ytterbium(0) reacts with R_2Hg to give stable organic derivatives in the divalent state [2,3]. Investigations of the reaction of symmetrical *C*-mercuro derivatives of methyl- and phenylcarboranes with ytterbium(0) showed that these compounds react in THF at 20°C to give *C*-carboranyl derivatives of ytterbium(II) in 30—50% yield (eq. 1).



$$(o\text{-}R\underbrace{C{-}C}_{B_{10}H_{10}}{-})_2Hg + Yb \xrightarrow[20^{\circ}C]{THF} (o\text{-}R\underbrace{C{-}C}_{B_{10}H_{10}}{-})_2Yb\cdot THF + Hg \qquad (1)$$

(R = CH_3, C_6H_5)

Under similar reaction conditions *C*-mercuro derivatives of carboranes react with lanthanum(0) or thulium(0) to form carboranyl derivatives of trivalent lanthanum or thulium (eq. 2).



$$(o\text{-}R\underbrace{C{-}C}_{B_{10}H_{10}}{-})_2Hg + Ln \rightarrow (o\text{-}R\underbrace{C{-}C}_{B_{10}H_{10}}{-})_3Ln\cdot THF_n + Hg \qquad (2)$$

(R = CH_3, C_6H_5; Ln = La, Tm; n = 1—3)

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B-Mercuro derivatives of carboranes undergo the same reaction to give in the case of Yb carboranyl derivatives of ytterbium(II) linked with the carborane nucleus via a boron atom. However, this reaction takes place with large excess (5—6 times) of activated Yb only (eq. 3)

$$(o\text{-}C_2H_2B_{10}H_9)_2Hg + m\,Yb \rightarrow (o\text{-}C_2H_2B_{10}H_9)_2Yb\cdot THF + Hg/Yb \qquad (3)$$

$(m = 5,6)$

With smaller quantities of Yb the reaction proceeds very slowly and leads to a mixture of products which are difficult to separate. We found also that unsymmetrical *B*-mercurocarboranyl derivatives react with thulium to give carboranyl derivatives of thulium with B—Tm bond (eq. 4), but is it also possible that the formation of B—Tm—C derivative is followed by disproportionation.

$$C_2H_2B_{10}H_9{-}Hg{-}CH_3 + Tm \rightarrow (C_2H_2B_{10}H_9)_3Tm\cdot THF + Hg \qquad (4)$$

Table 1 contains the physical data for the compounds obtained.

TABLE 1

CARBORANYL DERIVATIVES OF LANTHANIDES

Compounds[a]	Decomposition point (°C)	Yield (%)	Analysis (Found (calcd.) (%))	
			C	H
$(C_6H_5CB_{10}H_{10}C)_3La\cdot THF$	260	32	38.7 (38.7)	7.4 (6.1)
$(C_6H_5CB_{10}H_{10}C)_3Tm\cdot 3THF$	275	39	42.6 (41.8)	5.2 (6.8)
$(CH_3CB_{10}H_{10}C)_3Tm\cdot 3THF$	280	45	28.3 (29.3)	7.8 (7.4)
$(C_6H_5CB_{10}H_{10}C)_2Yb\cdot 2THF$	262	29	34.7 (33.8)	5.6 (5.4)
$(CH_3CB_{10}H_{10}C)_2Yb\cdot 2THF$	287	47	22.0 (22.9)	4.7 (5.7)
$(C_2H_2B_{10}H_9)_3Tm\cdot THF$	265	34	18.8 (17.9)	5.0 (5.9)
$(C_2H_2B_{10}H_9)_2Yb\cdot THF$	290	22	17.7 (18.4)	6.0 (5.7)

[a] The *ortho*-isomer of carborane was used.

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