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Preliminary communication

CARBORANYL DERIVATIVES OF LANTHANIDES OF THE TYPE RLnI

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Summary

Interaction of *C*-lithiumcarboranes with LnI_2 (Ln = Sm, Eu, Yb) give compounds which react with trimethylchlorosilane or carboxylic acid chloroanhydride to give trimethylsilylcarboranes or carboranyl ketones. The carborane derivatives formed at the first stage can be assigned the composition RLnI similar to Grignard reagents. The compounds prepared by the reaction of *C*-iodocarboranes with Eu and Yb have similar properties and also can be assigned composition RLnI.

We have earlier prepared carbonyl derivatives of di- and tri-valent lanthanides by interaction of *B*-mercurated carboranes with lanthanides [1] and by the reaction of *C*-lithium carboranes with lanthanide halides [2]. We now report the synthesis of carboranyl derivatives of lanthanides of the type RLnI.

It is known that alkyl and aryl iodides react with some lanthanides to give divalent derivatives RLnI of Grignard reagent type [3].

We obtained carboranyllanthanide iodides in two routes either by interaction of *C*-lithium derivatives of carboranes with lanthanides diiodides or by the reaction of *C*-iodocarborane with lanthanides. The formation of carboranyllanthanide iodides RLnI was confirmed by interaction of the reaction mixture with trimethylchlorosilane which lead to trimethylsilyl derivatives of carborane, or, as in ref. 4, by interaction of the reaction mixture with carboxylic acid chloroanhydride which lead, in some cases, to carboranylketones. Thus *o*-phenylcarboranyllithium actively reacts with samarium, europium and ytterbium diiodides in THF at −10—0°C. After action of trimethylchlorosilane on the reaction mixture 1-phenyl-2-trimethylsilyl-*o*-carborane was prepared in 80% yield (eq. 1).

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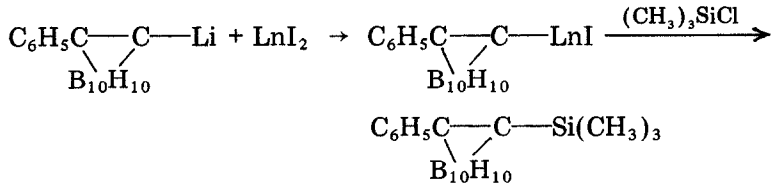
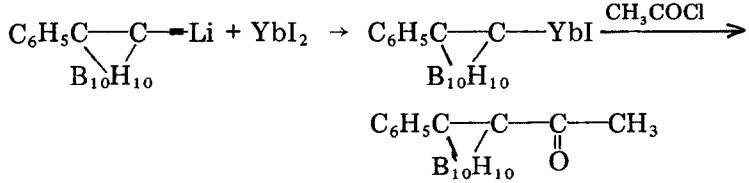


(1)

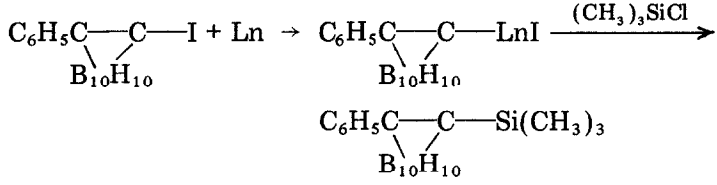
(Ln = Sm, Eu, Yb)

In the case of ytterbium addition of one equivalent of acetyl chloride to the reaction mixture results in formation of methylphenylcarboranyl ketone (eq. 2).



(2)

The oxidative addition of Ln^0, where Ln = Eu, Yb, to 1-phenyl-2-iodo-*o*-carborane takes place in THF at 20°C. This addition was confirmed by interaction of the reaction mixture with trimethylchlorosilane which resulted in the formation of 1-phenyl-2-trimethylsilyl-*o*-carborane in 86% yield (eq. 3).



(3)

(3)

(Ln = Eu, Yb)

Derivatives of divalent lanthanides also could be prepared by metallation of 1-phenyl-*o*-carborane with CH_3YbI at low temperature.

Experimental

Interaction of 1-phenyl-2-lithium-o-carborane with LnI_2. A solution of 0.72 g of $YbI_2 \cdot 4THF$ in THF was added at –10—0°C to a benzene solution of 1-phenyl-2-lithium-*o*-carborane prepared from 0.35 g of 1-phenyl-*o*-carborane. The reaction mixture was stirred at 0°C for 2—3 h. After the reaction stopped the yellow solution was decanted.

(a) 0.11 g of trimethylchlorosilane was added to the above solution, and the formation of a precipitate was observed. After 2 h the precipitate was filtered off and dried. The residue was recrystallized from hexane to give 1-phenyl-2-trimethylsilyl-*o*-carborane (80% yield, m.p. 103—104°C) (lit. [5], m.p. 105—106°C).

Similarly, 1-phenyl-2-trimethylsilyl-*o*-carborane was obtained after addition of trimethylchlorosilane to a solution prepared by reaction of 1-phenyl-2-lithium-*o*-carborane with diiodides of samarium and europium.

(b) At 0°C 0.08 g of acetyl chloride was added to a solution prepared from 1-phenyl-2-lithium-*o*-carborane and 0.72 g of $YbI_2 \cdot 4THF$. The reaction mixture was stirred for 6—8 h, then filtered, and dried. The residue was recrystallized

from hexane to give 1-phenyl-2-trimethylsilyl-*o*-carborane (86% yield, m.p. 102—103°C. IR spectrum: ν(B—H) 2595, $\nu(CH_3)$ 2850, 2935 cm^{-1}. (Found: C, 44.40; H, 8.00; B, 36.50. $C_{11}H_{24}B_{10}Si$ calcd.: C, 45.15; H, 8.27; B, 36.98%.

Similarly, 1-phenyl-2-trimethylsilyl-*o*-carborane was obtained after addition of trimethylchlorosilane to a solution prepared from 1-phenyl-2-iodo-*o*-carborane and metallic europium.

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