

Preliminary communication

CARBORANYL DERIVATIVES OF LANTHANIDES OF THE TYPE $R\text{LnI}$

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Summary

Interaction of *C*-lithiumcarboranes with LnI_2 ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Yb}$) 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 $R\text{LnI}$ 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 $R\text{LnI}$.

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 $R\text{LnI}$.

It is known that alkyl and aryl iodides react with some lanthanides to give divalent derivatives $R\text{LnI}$ 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 $R\text{LnI}$ 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*-phenylcarboranyl lithium actively reacts with samarium, europium and ytterbium diiodides in THF at $-10-0^\circ\text{C}$. After action of trimethylchlorosilane on the reaction mixture 1-phenyl-2-trimethylsilyl-*o*-carborane was prepared in 80% yield (eq. 1).

from hexane to give 1-phenyl-2-trimethylsilyl-*o*-carborane (86% yield, m.p. 102–103°C. IR spectrum: $\nu(\text{B-H})$ 2595, $\nu(\text{CH}_3)$ 2850, 2935 cm^{-1} . (Found: C, 44.40; H, 8.00; B, 36.50. $\text{C}_{11}\text{H}_{24}\text{B}_{10}\text{Si}$ 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.

References

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