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Preliminary communication

INTERACTION OF THE LITHIUM DERIVATIVES OF CARBORANES WITH LANTHANIDES CHLORIDES

V.I. BREGADZE*, N.A. KOVAL'CHUK, N.N. GODOVIKOV,
A.N. Nesmeyanov Institute of Organo-Element Compounds, Academy of Sciences of the U.S.S.R., Vavilov St. 28, Moscow (U.S.S.R.)
G.Z. SULEIMANOV and I.P. BELETSKAYA
L. Ya. Karpov Institute of Physical Chemistry, Moscow (U.S.S.R.)

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Summary

Carboranyl derivatives of lanthanides have been prepared by interaction of the lithium derivatives of carboranes with the salts $LnCl_3 \cdot n$THF (Ln = La, Tm, Yb). The influence of the ratio of the reagents, the type of metal and the nature of solvents on these reactions has been studied.

We have recently reported [1] that the interaction of C- and B-mercurated carboranes with activated metals of the lanthanides group leads to carboranyl derivatives of di- and tri-valent lanthanides with C—Ln and B—Ln bonds. We have now prepared C-substituted carboranyl derivatives of lanthanides by reaction of the lithium derivatives of methyl- and phenyl-carboranes with lanthanides chlorides of the type $LnCl_3 \cdot 3$THF (Ln = La, Tm, Yb).

It is known that the synthesis of most of the organic derivatives of the lanthanides is based on the reaction of RLi with LnX_3. These reactions are usually carried out in ether or THF. However, mono- or di-substituted derivatives of lanthanides prepared thus formed with RLi in some cases ate-complexes of the type $R_{3-n}LnX_n \cdot LiR \cdot m$THF ($n = 1, 2$; $m = 2$—4). The formation of such ate-complexes depends on the type of organic group, the lanthanides and the nature of the solvent [2]. We isolated such ate-complexes from the reaction mixture of methyl- or phenyl-carboranyllithium with thulium or ytterbium chlorides in benzene-ether-THF at 20°C:

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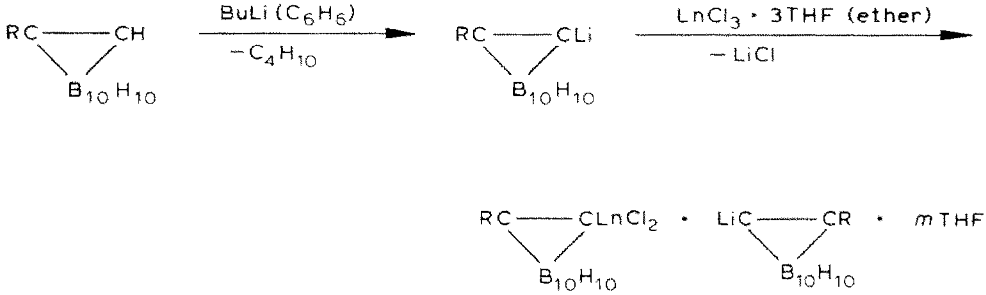
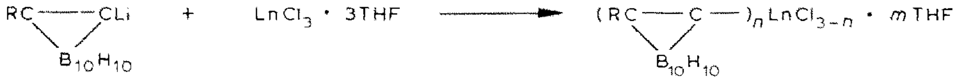


(R = CH_3, C_6H_5 ; Ln = Tm, Yb ; m = 2-5)

The compounds prepared were characterized by hydrolysis and by reactions with $HgCl_2$ and HCl.

The reactions of lithium derivatives of carboranes with lanthanides chlorides in a benzene-THF mixture lead to mono-, di- or tri-substituted derivatives depending on the reagents:



(Ln = La, Tm, Yb ; n = 1-3 ; m = 1-5)

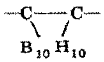
If this reaction is carried out with thulium chloride in benzene-ether-THF mixture the substitution stops at the stage of di-substituted product, even with ratio $RLi/TmCl_3 \cdot 3THF = 3/1$.

TABLE 1

CARBORANYL DERIVATIVES OF LANTHANIDES

Compounds[a]	Yield (%)	M.p. (°C)	Analysis (Found (calcd.) (%))			
			C	H	B	Cl
Me-carb-$LaCl_2$	36	133—135	10.6 (9.8)	4.7 (3.6)		
(Ph-carb-)$_3$La · THF	39	260 (dec.)	38.7 (38.7)	7.3 (6.6)		
(Ph-carb-)$_2$TmCl · 5THF	43	78—80	44.2 (43.1)	7.9 (7.0)	22.5 (21.5)	2.6 (3.6)
(Ph-carb-)$_3$Tm · 2THF	34	275 (dec.)	39.4 (39.5)	7.2 (6.5)	32.4 (33.3)	
Me-carb-$TmCl_2$ · 4THF	51	86—88	33.5 (33.1)	8.2 (7.1)		
Ph-carb-$TmCl_2$· · Li-carb-Ph · 5THF	75	106—108	46.6 (45.4)	8.8 (7.4)		4.8 (5.6)
Me-carb-$YbCl_2$ · · Li-carb-Me · 2THF	78	113—115	22.4 (23.7)	6.2 (5.9)		
(Me-carb)$_3$Yb · THF	26	280 (dec.)	19.9 (21.7)	6.5 (6.6)		

[a] carb =



According to element analysis, all carboranyl derivatives of lanthanides prepared contain 1 to 5 THF molecules per molecule of carboranyllanthanides. An attempt at elimination of THF from the complexes resulted usually in their decomposition. In this case THF molecules appear to stabilize the C—Ln bond. Table 1 contains the physical data for the compounds obtained.

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