Journal of Organometallic Chemistry, 233 (1982) C33—C34
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

SYNTHESIS OF CARBORANYL DERIVATIVES OF SELENIUM AND TELLURIUM

V.I. BREGADZE*, V.TS. KAMPEL, A.YA. USIATINSKY, O.B. PONOMAREVA and N.N. GODOVIKOV

A.N. Nesmeyanov Institute of Organo-Element Compounds, Academy of Sciences of the USSR, Vavilov St. 28, Moscow (U.S.S.R.)

(Received April 13th, 1982)

Summary

B-Mercurated and *B*-thalliated carboranes have been shown to react with selenium and tellurium to give carboranyl derivatives with B—Se and B—Te bonds.

We previously reported [1] that carboranes mercurated at the B(9) position of the carborane icosahedral react with sulphur giving either the corresponding carboranyl disulphides or compounds with sulphur atoms inserted into the B—Hg bond, depending on the reaction conditions. It has been shown that the substitution position is retained during these reactions and that carboranyl derivatives with B(9)—S bonds are formed.

We now report that selenium and tellurium can also be inserted into the B—Hg bond of *B*-mercurated carboranes (eq. 1).

$$(C_2H_2B_{10}H_9)_2Hg + E \longrightarrow C_2H_2B_{10}H_9\text{—}Hg\text{—}E\text{—}B_{10}H_9C_2H_2$$
$$(E = Se, Te) \qquad (1)$$

The reactions of bis(*o*(*m*)-carboranyl(9))mercury with selenium take place in boiling tetrahydrofuran, dimethoxyethane or dimethyl formamide during 10 hours. The yields of the main products of eq. 1 amount to 60%. In the case of tellurium the reactions proceed in the presence of catalytic amounts of tetrabutylammonium iodide. The compounds obtained are the first examples of carboranyl derivatives with the following chains of atoms: B—Hg—Se—B and B—Hg—Te—B. In these reactions substitution of mercury also takes place to a lesser extent and bis(carboranyl) diselenides are formed in less than 10% yield. The same compounds have been prepared in 30% yield fusing bis(*o*(*m*)-carboranyl-(9))mercury with selenium (eq. 2), but contrary to the case of selenium,

0022-328X/82/0000—0000/$02.75

bis(*m*-carboranyl)telluride has been prepared from tellurium under the same conditions.

$$(C_2H_2B_{10}H_9)_2Hg + E \xrightarrow{270-300^\circ} (C_2H_2B_{10}H_9)_2E_n \qquad (2)$$

$(E = Se,\ n = 2;\ E = Te,\ n = 1)$

TABLE 1

CARBORANYL DERIVATIVES OF SELENIUM AND TELLURIUM

Compounds	M.p. (°C)	Analysis (Found (calcd.) (%))				*m/e*
		C	H	B	Hg	
$(o\text{-}C_2H_2B_{10}H_9)_2HgSe$	273–274[a]	9.1	4.0	37.2	35.1	566
		(8.5)	(3.9)	(38.1)	(35.4)	
$(m\text{-}C_2H_2B_{10}H_9)_2HgSe$	224–226[a]			37.9	35.2	566
		(8.5)	(3.9)	(38.1)	(35.4)	
$(m\text{-}C_2H_2B_{10}H_9)_2HgTe$	141–142[b]	9.1	4.3	36.0	32.2	614
		(7.8)	(3.6)	(35.2)	(32.6)	
$(o\text{-}C_2H_2B_{10}H_9)_2Se_2$	290–291[c]	11.6	5.4	48.5		444
		(10.8)	(5.0)	(48.6)		
$(m\text{-}C_2H_2B_{10}H_9)_2Se_2$	262–263[c]	10.5	5.0	48.7		444
		(10.8)	(5.0)	(48.6)		
$(m\text{-}C_2H_2B_{10}H_9)_2Te$	248–250[b]	10.7	4.7	51.0		414
		(11.6)	(5.3)	(52.2)		

[a] Crystallized from benzene. [b] Crystallized from benzene/hexane. [c] Crystallized from toluene/heptane.

We have also studied the interaction of *B*-thalliated carboranes [2] with S, Se and Te. Recently it has been shown that diarylthallium bromide reacts with Se to give diaryl diselenide [3]. Compounds with B—Tl bonds turned out to react similarly. For instance, bis(*m*-carboranyl(9)) disulphide or bis(*m*-carboranyl(9)) diselenide are formed in the reaction of *B*-thalliated carboranes with sulphur or selenium in dimethyl formamide in the presence of tetrabutylammonium iodide. However, monotelluride has been isolated in the reaction of (*m*-carboranyl(9))-thallium bis(trifluoroacetate) with tellurium under the same conditions (eq. 3).

$$(CF_3CO_2)_2TlB_{10}H_9C_2H_2 + Te \xrightarrow[DMF]{I^-} (C_2H_2B_{10}H_9)_2Te \qquad (3)$$

Table 1 contains the physical data for the compounds obtained.

References

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