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Preliminary communication

THE SYNTHESIS OF THE CARBORANYL DERIVATIVES OF MAIN GROUPS IV—VI ELEMENTS WITH BORON—ELEMENT BONDS

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Summary

B-Mercurated carbonares have been shown to be convenient initial compounds for the synthesis of carboranyl derivatives of Groups IV—VI elements with B—E bonds where E = Sn, As, Sb, S.

We have recently reported [1] the direct mercuration of carboranes at the B(9) position under the action of mercury trifluoroacetate and the synthesis of the various *B*-mercurated *ortho*-, *meta*- and *para*-carboranes [2]. *B*-Mercurated carboranes are convenient initial compounds for the synthesis of carboranyl derivatives with boron—element bonds due to transfer of the carboranyl group from the mercury atom to the atom of other main group elements. We have earlier carried out such reactions for the preparation of *B*-substituted carboranylthallium compounds [3], and we report here the synthesis of unknown types of carboranyl derivatives of Main Groups IV—VI elements with B—E bonds by the transfer of the *B*-mercurated carboranyl group from the mercury atom to Groups IV—VI element atoms.

Compounds with B—Sn bonds have been prepared by action of $SnCl_2$ on bis(*o*(*m*)-carboranyl(9))mercury (eq. 1). *B*-Metallated carboranyl derivatives

$$(C_2H_2B_{10}H_9\text{-}9)_2Hg + SnCl_2 \longrightarrow (C_2H_2B_{10}H_9\text{-}9)_2SnCl_2 + Hg \qquad (1)$$

of arsenic and antimony have been prepared by interaction of equimolecular amounts of bis(*o*(*m*)-carboranyl(9))mercury with arsenic and antimony chlorides (eq. 2).

$$(C_2H_2B_{10}H_9\text{-}9)_2Hg + MCl_3 \longrightarrow (C_2H_2B_{10}H_9\text{-}9)MCl_2 + (C_2H_2B_{10}H_9\text{-}9)HgCl \qquad (2)$$

(M = As, Sb)

The position of substitution in these compounds has been determined by fission of the B—M bond with bromine to give the known bromocarboranes.

Heating of bis(*m*-carboranyl(9))mercury with sulphur in an ampoule at

350°C for 30 min leads to the preparation of the corresponding carboranyl disulphide (eq. 3). These compounds do not react in dimethyl formamide up

$$(m\text{-}C_2H_2B_{10}H_9)_2Hg + S \longrightarrow (m\text{-}C_2H_2B_{10}H_9)_2S_2 + Hg \qquad (3)$$

to 115°C. Adding tetrabutylammonium iodide to the mixture causes the insertion of a sulphur atom into the B—Hg bond (eq. 4).

$$(m\text{-}C_2H_2B_{10}H_9)_2Hg + S \xrightarrow[\text{DMF}]{I^-} m\text{-}C_2H_2B_{10}H_9\text{—}S\text{—}Hg\text{—}B_{10}H_9C_2H_2 \qquad (4)$$

Acidic hydrolysis of the S—Hg bond in this compound leads to B(9))-substituted mercaptane as described by Plešek and Heřmánek [4].

TABLE 1

CARBORANYL DERIVATIVES OF GROUPS IV—VI ELEMENTS WITH B—ELEMENT BONDS

Compounds	M.p. (°C)	Yield (%)	Analysis (Found (calcd.) (%))					m/e
			C	H	B	Cl	E	
$(m\text{-}C_2H_2B_{10}H_9)_2SnCl_2$	223—225[a]	70	10.4	4.5	45.4	14.2		
			(10.1)	(4.7)	(45.4)	(14.9)	(24.9)	477
$o\text{-}C_2H_2B_{10}H_9AsCl_2$	77—79[b]	50	8.2	3.6	37.7	24.6	26.0	288
			(8.3)	(3.8)	(37.4)	(24.5)	(25.9)	
$m\text{-}C_2H_2B_{10}H_9AsCl_2$	80—81[b]	55	8.0	3.5	37.3	24.4	25.8	288
			(8.3)	(3.8)	(37.4)	(24.5)	(25.9)	
$m\text{-}C_2H_2B_{10}H_9SbCl_2$	95—96[b]	50	7.1	3.3	31.3			366
			(7.2)	(3.3)	(32.2)	(21.1)	(36.2)	
$(m\text{-}C_2H_2B_{10}H_9)_2S_2$	278—280[c]	30	14.1	6.2			17.5	350
			(13.7)	(6.3)	(61.7)		(18.3)	
$m\text{-}C_2H_2B_{10}H_9S$ $m\text{-}C_2H_2B_{10}H_9Hg$	323—324[d]	40	9.9	4.4	41.5	38.3[e]	6.0	519
			(9.3)	(4.3)	(41.6)	(38.6)	(6.2)	

[a] Crystallized from benzene. [b] Crystallized from heptane. [c] Crystallized from benzene/hexane. [d] Crystallized from toluene. [e] Analysis of Hg.

Table 1 contains the physical data for the compounds obtained.

It is concluded that *B*-mercurated carboranes may prove to be convenient initial compounds for the synthesis of various *B*-metallated carboranes.

References

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