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A STUDY OF THE REACTION OF TIN(II) ACETYLACETONATE WITH MERCURIC DERIVATIVES OF CARBORANES

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Summary

With the use of oxidative insertion of tin(II) acetylacetonate (acac) into mercuric derivatives of carboranes, new types of polymetallic chainlike compounds were obtained in which the acac ligands occupy *cis* positions on the tetravalent hexacoordinated tin. In was found that in benzene the insertion of $Sn(acac)_2$ into unsymmetrical *B*-carboranylmercuric derivatives proceeds at the B–Hg bond, whereas in a benzene-tetrahydrofuran mixture it takes place at both the B–Hg and C–Hg bonds.

The carbenoid type of $Sn(acac)_2$ insertion, which leads, in the first step, to the formation of derivatives with a metal–metal bond (Sn–Hg, Sn–Tl), was observed in its reactions with organomercuric compounds [1] and with Hg and Tl derivatives of carboranes [2,3]. It turned out that this reaction can be applied to symmetrical *C*- and *B*-substituted carboranyl derivatives of mercury and unsymmetrical *B*-carboranyl derivatives of mercury and thallium, in which the reaction centres are C–Hg, B–Hg, B–Tl, Tl–Hal, and Hg–Hal bonds. The interaction of $Sn(acac)_2$ and symmetrical *C*- and *B*-mercurated carboranes at lowered temperatures leads to the formation of bimetallic derivatives (III, IV):

$$\underset{(I,\,II)}{R_2Hg} + Sn(acac)_2 \longrightarrow \underset{(III,\,IV)}{RSn(acac)_2HgR} \qquad (1)$$

Protons of the $Sn(acac)_2$ methyl groups are seen in the ^1H NMR spectra (see Table 1) as two singlets ($\delta(CH_3) = 1.186$ and 1.112 ppm), while methine group protons are centered at 4.898 and 4.927 ppm. After insertion of $Sn(acac)_2$, the

(Continued on p. 134)

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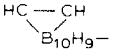
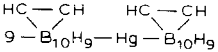
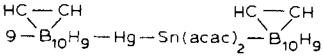
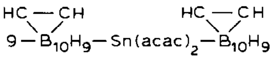
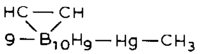
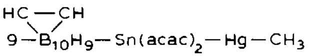
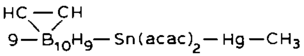
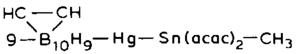
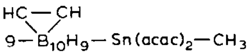
TABLE 1

^1H NMR SPECTRAL DATA OF PRODUCTS OF THE INSERTION OF $Sn(acac)_2$ INTO MERCURY CARBORANYL DERIVATIVES

No.	Compound	$Sn(acac)_2$		 $\delta(CH)$ (ppm)	E^a-CH_3 $\delta(CH_3)$ (ppm)
		$\delta(CH_3)$ (ppm)	$\delta(CH)$ (ppm)		
1	$Sn(acac)_2$	1.185 $(J(^{117}Sn-^1H) = 64.43$ Hz) $(J(^{119}Sn-^1H) = 62.72$ Hz) 1.112 $(J(^{117}Sn-^1H) = 61.37$ Hz) $(J(^{119}Sn-^1H) = 58\ 46$ Hz)	4.898 4.927		
2				2.142	
3		1.594 $(J(^{117}Sn-^1H) = 64.18$ Hz) $(J(^{119}Sn-^1H) = 61\ 34$ Hz) 1.608 $(J(^{117}Sn-^1H) = 60.26$ Hz) $(J(^{119}Sn-^1H) = 57.74$ Hz)	4.893 4.928	2.138	

4		1.592 ($J(^{117}Sn-^{1}H) = 126.40$ Hz) ($J(^{119}Sn-^{1}H) = 123.58$ Hz)	4.896		
5				2.235	0.119 ($J(^{199}Hg-^{1}H) = 132.80$ Hz)
6		1.546 ($J(^{117}Sn-^{1}H) = 130.66$ Hz) ($J(^{119}Sn-^{1}H) = 128.18$ Hz)	4.987	2.239	0.108 ($J(^{199}Hg-^{1}H) = 126.20$ Hz
		1.593 ($J(^{117}Sn-^{1}H) = 136.46$ Hz) ($J(^{119}Sn-^{1}H) = 134.07$ Hz)	5.036		
7		1.556	4.973	2.239	0.109 ($J(^{199}Hg-^{1}H) = 126.82$ Hz
		1.498	4.983		
		1.454	5.017		0.553 ($J(^{117}Sn-^{1}H) = 143.49$ Hz) ($J(^{119}Sn-^{1}H) = 140.65$ Hz)
8		1.499 ($J(^{117}Sn-^{1}H) = 68.39$ Hz) ($J(^{119}Sn-^{1}H) = 65.94$ Hz)	4.883	2.139	0.099 ($J(^{117}Sn-^{1}H) = 127.20$ Hz) ($J(^{119}Sn-^{1}H) = 124.42$ Hz)

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[a] E = Hg, Sn.

acetylacetonate ligands in the ^{1}H NMR spectra are also seen as two singlets ($\delta(CH_3) = 1.594$ and 1.608 ppm); the methine protons being centered at 4.893 and 4.928 ppm. The ^{1}H NMR spectrum of bis(*o*-carboran-9-yl)bis(acetylacetonate)tin (IV) in benzene is presented in Fig. 1. The splitting of signals of methyl and methine protons of the acetylacetonate ligands points to their *cis* location around the tin atom.

When the reaction mixture is kept at room temperature, a slow (4 h) demercuration of the bimetallic compound takes place in benzene, while in THF-C_6H_6 demercuration proceeds rapidly (0.5–1 h).

$$\underset{\text{(IV)}}{9\text{-}o\text{-}H_2C_2B_{10}H_9Sn(acac)_2\text{–}Hg\text{–}B_{10}H_9C_2H_2} \xrightarrow[-Hg]{} \underset{\text{(V)}}{(9\text{-}o\text{-}C_2H_2B_{10}H_9)_2Sn(acac)_2} \quad (2)$$

During demercuration, the positions of signals of the methyl and methine protons of the acetylacetonate ligands are almost unchanged (in compound V, for example, $\delta(CH_3) = 1.592$ and 1.612, $\delta(CH) = 4.896$ and 4.922 ppm), which indicates that the configuration of the acetylacetonate ligands on tin atom is retained. To compare with the demercuration products (V) obtained by reaction 2, we performed an independent synthesis from $(9\text{-}o\text{-}C_2H_2B_{10}H_9)_2SnCl_2$ [4] and Na(acac):

$$(9\text{-}o\text{-}C_2H_2B_{10}H_9)_2SnCl_2 + 2Na(acac) \rightarrow (9\text{-}o\text{-}C_2H_2B_{10}H_9)_2Sn(acac)_2 + 2\ NaCl \quad (3)$$

According to ^{1}H NMR data, the acetylacetonate ligands were located in *cis* positions on the tin atom after the exchange ($\delta(CH_3) = 1.594$ and 1.604, $\delta(CH) = 4.896$ and 4.922 ppm).

The reaction of $Sn(acac)_2$ with *B*-carboranylmercury halides also leads to bimetallic derivatives:

$$9\text{-}o\text{-}C_2H_2B_{10}H_9HgHal + Sn(acac)_2 \rightarrow 9\text{-}o\text{-}C_2H_2B_{10}H_9\text{–}Hg\text{–}Sn(acac)_2Hal \quad (4)$$

However, addition of a second mole of $Sn(acac)_2$ to the reaction mixture does not lead to the formation of the product of double insertion, which has been observed earlier [3] for symmetrical *B*-mercury *o*-carboranes.

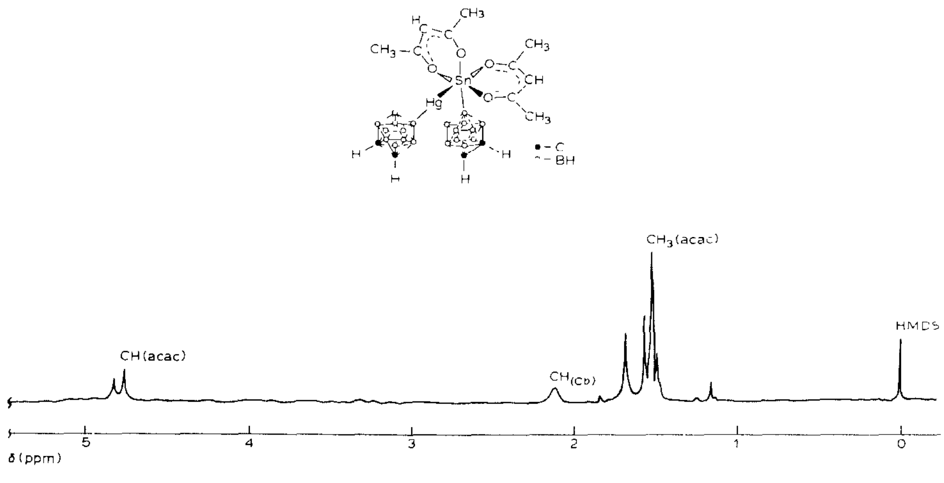
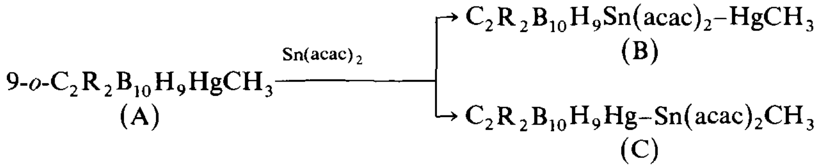


Fig. 1. ^{1}H NMR spectrum of bis(*o*-carboran-9-yl)bis(acetylacetonato)stannane.

To study the insertion of $Sn(acac)_2$ into a compound containing both the C–Hg and B–Hg bonds, the reaction of 9-methylmercury-*o*-carborane and 9-methylmercury-1,2-dimethyl-*o*-carborane with $Sn(acac)_2$ in benzene was carried out. The reaction may give rise to two products (B and C).



$$9\text{-}o\text{-}C_2R_2B_{10}H_9HgCH_3\ \text{(A)} \xrightarrow{Sn(acac)_2} \begin{cases} C_2R_2B_{10}H_9Sn(acac)_2\text{-}HgCH_3\ \text{(B)} \\ C_2R_2B_{10}H_9Hg\text{-}Sn(acac)_2CH_3\ \text{(C)} \end{cases} \qquad (5)$$

$(R = H, CH_3)$

Addition of equal quantities of $Sn(acac)_2$ to $9\text{-}o\text{-}CH_3HgB_{10}H_9C_2R_2$ ($\delta(CH_3) = 0.119$, $\delta(CH) = 2.235$ ppm $J(^{199}Hg\text{-}^1H) = 132.80$ Hz) causes an appearance in the ^1H NMR spectrum of proton signals from the methyl group directly bonded to the mercury atom ($\delta(CH_3) = 0.108$ ppm, $J(^{199}Hg\text{-}^1H) = 126.20$ Hz), along with signals from methyl and methine protons of the acetylacetonate ligands of the insertion products ($\delta(CH_3) = 1.546$ and 1.593, $\delta(CH) = 4.987$ and 5.036 ppm). The carborane nucleus protons are seen as a broadened signal centered at 2.239 ppm (CH). These data demonstrate that the insertion of $Sn(acac)_2$ into mercury *B*-carboranyl derivatives of the type $9\text{-}o\text{-}C_2R_2B_{10}H_9HgCH_3$ proceeds in benzene mainly at the B–Hg bond, with the acetylacetonate ligands situated, after the insertion, in *cis*-positions on the tin atom. In the ^1H NMR spectrum of demercuration product obtained by

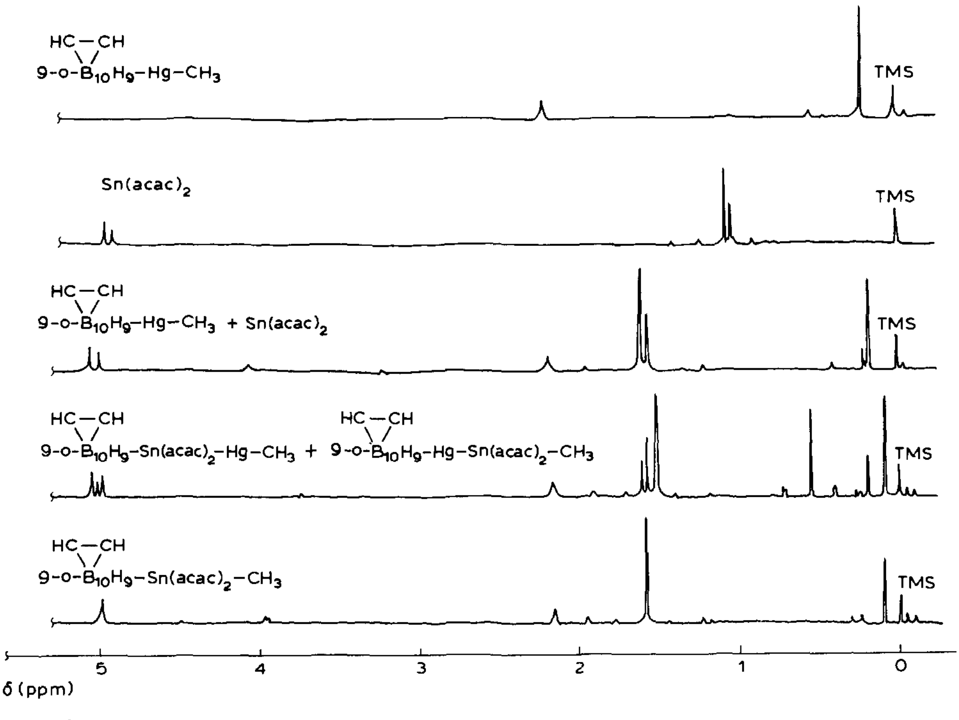


Fig. 2. ^1H NMR spectrum of product of insertion of $Sn(acac)_2$ into 9-methylmercury-*o*-carborane.

reaction 5 (see Fig. 2), proton signals of the methyl group directly connected to the tin atom are centered at 0.099 ppm and have satellites, which are conditioned by spin–spin interaction with tin isotopes ^{117}Sn and ^{119}Sn with coupling constants of 127.20 and 124.42 Hz, respectively. It should be noted that the acetylacetonate ligands on the tin atom have a translocation, which is evidenced by the equivalence of their methyl and methine protons ($\delta(CH_3) = 1.499$, $\delta(CH) = 4.883$ ppm).

The reaction in a C_6H_6-THF mixture with equal quantities of the reagents is accompanied with a gradual disappearance of compound A and the formation of products B and C, which is indicated by a smooth decrease in the intensity of the signal of methyl group protons on the mercury atom ($\delta(CH_3) = 0.119$ ppm, $J(^{199}Hg-^{1}H) = 132.80$ Hz) and by a rise in the signals centered at 0.108 ppm (CH_3, $J(^{199}Hg-^{1}H) = 126.82$ Hz) and at 0.553 ppm (CH_3, $J(^{117}Sn-^{1}H) = 143.49$ Hz and $J(^{119}Sn-^{1}H) = 140.68$ Hz). In this case, the acetylacetonate ligands on the tin atom also occupy the *cis* positions: $\delta(CH_3) = 1.556$, 1.498, 1.454 ppm (acac), $\delta(CH) =$ 4.973, 4.982, 5.017 ppm (acac).

The use of two equivalents of $Sn(acac)_2$ in the reaction under study results in a complication of the process and the assignment of signals in the ^{1}H NMR spectrum becomes somewhat ambiguous.

The compounds obtained in this work were purified by reprecipitation. Recrystallization from chlorinated and polar solvents causes decomposition of the substances. Compounds were characterized by elemental analysis and by IR spectra. The latter contain characteristic bands of B–H groups (2610–2630 cm^{-1}) and of the acetylacetonate ligand (1540–1680 cm^{-1}).

Experimental

Mercuric derivatives of *B*-substituted carboranes were obtained as described [5]. Tin(II) acetylacetonate was prepared according to a reported method [6]. All the reactions were carried out in an atmosphere of dry argon. ^{1}H NMR spectra were recorded on a Bruker WP-200-SY spectrometer (200.13 MHz) using TMS as internal reference.

Insertion of $Sn(acac)_2$ into bis(o-carboran-9-yl) mercury (II)

To a solution of 0.25 g of I in a mixture of 20 ml of C_6H_6 and 2 ml of C_4H_8O was added 0.18 g of twice distilled $Sn(acac)_2$. The reaction mixture was kept for 3 h at 0°C, then 5 ml of hexane was added and the mixture was allowed to stay for 24 h at 0°C. The mixture was filtered, the filtrate was evaporated, and the oil-like product was washed with a benzene-hexane mixture (1 : 10) until it was solid. The compound thus obtained does not contain II (TLC). Filtration of the precipitate with subsequent washing with hexane gave 0.29 g (72%) of IV, m.p. 171–173°C (decomp.). Found: C, 19.80; H, 4.50. $C_{14}H_{36}B_{20}HgSnO_4$ calcd.: C, 20.90; H, 4.50%. The presence of Sn and Hg in compound IV was established by X-ray-fluorescence. IR spectrum (KBr): 1552, 1668 (acac), 2614 cm^{-1} (B–H).

Preparation of bis(o-carboran-9-yl)bis(acetylacetonate)stannane (V) from bimetallic compound IV

A solution of 0.3 g of IV in 50 ml of C_6H_6 was stirred at room temperature to complete separation of mercury (4–5 h). The precipitate was filtered and the filtrate was evaporated. Crystallization of the residue from a benzene-hexane mixture (1 : 1) afforded 0.12 g (60%) of V, m.p. 176–178°C. Found: C, 27.39; H, 5.63. $C_{14}H_{36}B_{20}O_4Sn$ calcd.: C, 27.85; H, 5.96%. IR spectrum (KBr): 1539, 1668 (acac), 2618 cm^{-1} (B–H).

Reaction of bis(o-carboran-9-yl)dichlorostannane with sodium acetylacetonate

To a solution of 0.48 g of bis(*o*-carboran-9-yl)dichlorostannane in 25 ml of THF was added 0.23 g of sodium acetylacetonate, the reaction mixture was stirred at 28°C for 10 h, whereupon the precipitate was filtered off and the filtrate was evaporated to dryness. The residue was washed with distilled water and dried over P_2O_5. Crystallization from hexane furnished 87% of V, m.p. 176–178°C. Found: C, 26.77; H, 5.48. $C_{14}H_{36}B_{20}O_4Sn$ calcd.: C, 27.85; H, 5.96%. IR spectrum (KBr): 1539, 1667 (acac), 2618 cm^{-1} (B–H).

Insertion of Sn(acac)$_2$ into 9-methylmercury-o-carborane (VI)

To a solution of 0.35 g VI in 25 ml of benzene was added 0.32 g of $Sn(acac)_2$. The reaction mixture was stirred with cooling for 2–3 h, then the precipitate was filtered off and the filtrate was evaporated to dryness. The residue was washed with hexane to yield 0.37 g (55.5%) of VII, m.p. 124–126°C (decomp.). Found: C, 23.45; H, 4.22; B, 15.34; Hg, 29.36. $C_{13}H_{28}B_{10}HgO_4Sn$ calcd.: C, 23.09; H, 4.04; B, 16.01; Hg, 29.89%. IR spectrum (KBr): 1545, 1658 (acac), 2624 cm^{-1} (B–H).

Insertion of Sn(acac)$_2$ into (o-carboran-9-yl)mercurychloride

To a solution of 0.25 g of (*o*-carboran-9-yl)mercurychloride in 22 ml of a benzene-THF mixture (10 : 1) was added 0.41 g of $Sn(acac)_2$. The reaction mixture was kept at 0°C for 72 h. After addition of 5 ml of hexane, the reaction mixture was kept at 0°C for 18 h. The precipitate was filtered off and dried in vacuum to give 0.21 g (60%) of (*o*-carboran-9-yl)bis(acetylacetonato)stannane chloride, m.p. 186–188°C (decomp.). Found: C, 19.2; H, 3.1; Cl, 5.8. $C_{12}H_{25}B_{10}ClHgO_4Sn$ calcd.: C, 20.7; H, 3.6; Cl, 5.1%. IR spectrum (KBr): 1542, 1655 (acac), 2625 cm^{-1} (B–H).

Preparation of (o-carboran-9-yl)methylbis(acetylacetonato)stannane (VIII) from bimetallic compound VII

To a solution of 0.35 g of VII in 50 ml benzene was added 0.32 g of freshly distilled $Sn(acac)_2$. The reaction mixture was kept at room temperature for 96 h for complete separation of mercury. The precipitate was filtered off and the filtrate was evaporated to dryness. The residue was extracted with hot hexane, and the product was crystallized from this solvent to yield 75% of VIII, m.p. 192–193°C.

Acknowledgement

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