on Chromaton N-AW) and employing an internal standard. The standard compounds were synthesized by the hydroalumination of the appropriate α -olefins with LiAlH₄ and either subsequent oxidation or iodination [5].

<u>Hydrometallation of α -Olefins Using DAMH.</u> To a freshly prepared solution of 10 mmoles of Et₂NMgH in 10 ml of THF were added 10 mmoles of the olefin and 0.2 mole of the catalyst, and the mixture was stirred at 60° for 4 h.

a) Preparation of Iodoalkanes. To the catalysate, cooled to -20° , was added in drops a THF solution of 20 mmoles of I₂ until a permanent color appeared. The reaction mixture was treated with satd. NH₄Cl solution, and the organic layer was separated, washed with Na₂S₂O₃ solution, dried over MgSO₄, and the residue was vacuum-distilled.

b) Preparation of Alkanols. A stream of dry O_2 was passed through a solution of the catalysate for 2 h at O° , the mixture was decomposed with water, the organic layer was separated, the aqueous layer was extracted with ether, and the extracts were combined with the organic layer, dried over MgSO₄, and evaporated.

CONCLUSIONS

Diethylaminomagnesium hydride in the presence of Cp₂TiCl₂ regioselectively hydromagnesates 1-alkenes to give diethylaminomagnesium alkyls.

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REACTION OF BOROTHALLATED CARBORANES WITH ZERO-VALENT MERCURY AND SULFUR

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Previously we reported the cleavage of the B-Tl bond in borothallated carboranes by elemental Se and Te [1, 2]. The reduction of phenylthallium dichlorides was also described, which leads to phenylmercury salts [3]. In order to study if the B-Tl bond in borothallated carboranes can be cleaved by Hg(0) we reacted some (carboran-9-yl)thallium bis(trifluoro-acetates) with Hg(0).

It proved that the B-T1 bond is actually cleaved, and as a result the corresponding carboranylmercury salts are formed in about 20% yield. An analysis of the reaction mixtures disclosed that they also contain small amounts (2%) of the symmetrical product, namely bis-(carboran-9-y1)mercury.

 $H_{2}C_{2}B_{10}H_{9}Tl(OCOCF_{3})_{2} \xrightarrow{Hg(0)}{DMF} H_{2}C_{2}B_{10}H_{9}HgOCOCF_{3} + (H_{2}C_{2}B_{10}H_{9})_{2}Hg$

It should be mentioned that for the B-T1 bond this reaction proceeds under considerably more drastic conditions than the analogous cleavage of the C-T1 bond in arylthallium salts

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[3]. The symmetrization apparently proceeds via the reaction of the mercury salt of the substituted carborane, obtained by cleavage of the B-Tl bond, with Hg(0), analogous to the action of cadmium amalgam [4] or LiAlH₄ [5]. Actually, a blank experiment disclosed that trace amounts of the bis(carborany1)mercury are formed under the given conditions. It is also not excluded that the solvating capacity of the solvent is responsible for the symmetrization, but it should be mentioned that carborany1mercury salts are stable toward symmetrizing agents of the complexing type, for example KI [4].

$$m-\mathrm{H}_{2}\mathrm{C}_{2}\mathrm{B}_{10}\mathrm{H}_{9}\mathrm{HgOCOCF}_{3} \xrightarrow{\mathrm{Hg(0)}}{\mathrm{DMF}} \rightarrow (m-\mathrm{H}_{2}\mathrm{C}_{2}\mathrm{B}_{10}\mathrm{H}_{9})_{2}\mathrm{Hg}$$

Another path for transfer of the carboranyl radical from the Tl atom to the Hg atom is the transmetallation of borothallated carboranes by Hg(II) salts. Thus, the reaction of (o-carboran-9-y1)thallium bis(trifluoroacetate) with HgCl₂ leads to carboranylmercury chlorides [6]. The analogous transmetallation with Hg(CN)₂ leads to the previously unknown (carboran-9-y1)mercury cyanides. The site of the Hg atom in the carborane nucleus was proved by treating the obtained cyanide with NaCl, and, as a result, the known (o-carboran-9-y1)mercury chloride was obtained [4].

 $\begin{array}{c} HC \longrightarrow CH & Hg(CN)_{2} \\ & & & \\ \hline \\ B_{10}H_{9}Tl(OCOCF_{3})_{2} \end{array} \xrightarrow{Hg(CN)_{2}} HC \longrightarrow CH & & \\ \hline \\ B_{10}H_{9}HgCN & & & \\ \hline \\ B_{10}H_{9}HgCN & & \\ \hline \\ \end{array}$

From an analysis of the above results, and also the data given in [1-3, 7], it may be assumed that cleavage of the B-T1 and Ar-T1 bonds by treatment with zero-valent metals and nonmetals is a common property for organothallium compounds in general, and for borothallated carboranes in particular. This assumption is confirmed by the fact that the B-T1 bond in the o- and m-carboranylthallium dichloride is cleaved by elemental sulfur, as a result of which a mixture of (carboran-9-y1) mercaptan and di(carboran-9-y1) disulfide is formed. The reduction of this mixture with LiAlH, leads in good yield to (carboran-9-y1) mercaptans.

 $\begin{array}{c} H_2C_2B_{10}H_0TICl_2 \xrightarrow{1. S_{\bullet}, DMF} & \rightarrow H_2C_2B_{10}H_0SH + (H_2C_2B_{10}H_0)_2S_2 \\ & \downarrow LiAIH_4 \\ & H_2C_2B_{10}H_0SH \end{array}$

EXPERIMENTAL

Reaction of (o-Carboran-9-y1)thallium Bis(trifluoroacetate) (I) with Hg Metal. A solution of 2.8 g (5 mmoles) of (I) in 50 ml of DMF was stirred for 40 h with 5 ml of Hg under solvent reflux. Then the reaction mixture was cooled and poured into water. The aqueous solution was extracted with an ether-benzene mixture, the organic extract was separated, evaporated, and the residue was recrystallized from a benzene-hexane mixture to give 0.4 g (18%) of (o-carboran-9-y1)mercury trifluoroacetate, mp 160°C (cf. [4]). Column chromatog-raphy of the mother liquor on Al_2O_3 gave 0.02 g of bis(o-carboran-9-y1)mercury, mp 332° (cf. [4]). In a similar manner, from (m-carboran-9-y1)thallium bis(trifluoroacetate) we obtained (m-carboran-9-y1)mercury trifluoroacetate in 20% yield, mp 117° (cf. [4]).

(m-Carboran-9-y1)mercury Chloride. A solution of 2.8 g (5 mmoles) of (m-carboran-9-y1)thallium bis(trifluoroacetate) in 50 ml of DMF was stirred with 5 ml of Hg for 40 h under reflux. Then it was poured into water, extracted with an ether-benzene mixture, and the organic extract was separated and evaporated. The solid residue was dissolved in acetone and poured into aqueous NaCl solution. The obtained precipitate was separated, dried, and recrystallized from m-xylene to give 0.3 g (15%) of (m-carboran-9-y1)mercury chloride, mp 266° (cf. [4]).

<u>(o-Carboran-9-y1)mercury Cyanide</u>. A solution of 2.8 g (5 mmoles) of (I) and 1.8 g (7 mmoles) of $Hg(CN)_2$ in 50 ml of DMF was stirred under reflux for 3 h. Then the reaction mixture was poured into water, the aqueous solution was extracted with an ether-benzene mixture, and the organic extract was separated, dried, and evaporated. The solid residue was recrystallized from benzene to give 1.1 g (60%) of (o-carboran-9-y1)mercury cyanide, mp 219-220°. Found: C 10.2; H 3.0; B 29.2; Hg 54.4; N 3.8%. C₃H₁₁B₁₀NHg. Calculated: C 9.8; H 2.9; B 29.3; Hg 54.2; N 3.7%.

(o-Carboran-9-yl)mercury Chloride. A solution of 0.6 g of (o-carboran-9-yl)mercury cyanide in 20 ml of acetone was poured into aqueous NaCl solution. The obtained precipitate was separated, dried, and recrystallized from m-xylene to give 0.4 g (66%) of (o-carboran-9-yl)mercury chloride, mp 263° (cf. [4]).

(m-Carboran-9-y1) Mercaptan. To a solution of 4.18 g (0.01 mole) of (m-carboran-9-y1)thallium dichloride in 50 ml of DMF was added 0.32 g of elemental sulfur and the mixture was stirred under reflux for 6 h. Then the reaction mixture was poured into water and extracted with an ether-benzene mixture. Based on the GLC data, the organic extract is a mixture of (m-carboran-9-y1) mercaptan and di(m-carboran-9-y1) disulfide. The organic layer was separated, dried, the solvent was distilled off, and the residue was dissolved in 50 ml of THF and added dropwise to a suspension of LiAlH₄ (0.5 g) in 25 ml of THF. The reaction mixture was stirred for 2 h at approximately 20° and then heated for 2 h, after which it was decomposed in succession with MeOH and water, poured into water, and extracted with benzene. The benzene extract was separated, dried, the benzene was removed and the residue was recrystallized from hexane to give 1 g (60%) of (m-carboran-9-y1)mercaptan, mp 177° (cf. [8]). In a similar manner, from (o-carboran-9-y1)thallium dichloride we obtained (o-carboran-9-y1) mercaptan in 50% yield, mp 200° (cf. [8]).

CONCLUSIONS

1. The B-Tl bond in borothallated carboranes is cleaved by Hg metal, which leads to carboranylmercury salts.

2. The reduction of the reaction products of (B-carboranyl)thallium with elemental sulfur by LiAlH₄ gave (B-carboranyl) mercaptans.

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