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Figure 1

Figure 1: Figure 1

Abstract

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STUDIES IN THE FIELD OF BORON COMPOUNDS

SYNTHESIS AND PROPERTIES OF CYCLOPENTADIENYL COMPOUNDS OF BORON

(Presented by Academician A. V. Topchiev on 8 VI 1960)

After the discovery of ferrocene ([1]), dicyclopentadienyl derivatives of many transition elements were synthesized, and tricyclopentadienyl compounds were obtained for elements of group III of the periodic system. There is no information in the literature on cyclopentadienyl compounds of boron.

A convenient method for obtaining tricyclopentadienylboron is the reaction of bromocyclopentadienylmagnesium with boron trifluoride etherate in the presence of a threefold excess of the former. The yield is 72.5%. With a molar ratio $C_5H_5MgBr : BF_3 = 1 : 1$, cyclopentadienylboron difluoride was obtained (yield 69.8%). The reactions were carried out in an ether medium under a stream of purified nitrogen. After addition of the etherate, the colorless or light-yellow ethereal solution was poured into a flask filled with nitrogen and left for several days. Colorless crystals gradually precipitated from the ethereal solution. Both compounds oxidize in air, cyclopentadienylboron difluoride almost instantly blackening and melting, and tricyclopentadienylboron gradually turning into a white powder.

Fig. 1. Spectrum of tricyclopentadienylboron *(1)* and of its polymer *(2)* in the ultraviolet region. $E = D/CB$; for the polymer it was determined at $C = 1$ wt.% and $B = 1$ cm.

With pyridine, tricyclopentadienylboron formed a white crystalline 1 : 1 complex.

Elementary analysis for boron was carried out by the method proposed by B. M. Mikhailov and T. A. Shchegoleva ([2]).

Tricyclopentadienylboron is poorly soluble in organic solvents, and from some of

Fig. 2. Photograph of a crystal of tricyclopentadienylboron

Figure 2: Fig. 2. Photograph of a crystal of tricyclopentadienylboron

them it gradually precipitates in the form of flakes of a light-yellow precipitate (from heptane, tetrahydrofuran, chloroform, isooctane).

The spectrum of tricyclopentadienylboron in the ultraviolet region* was recorded (Fig. 1), confirming the presence of cyclopentadienyl rings in this compound. Fig. 2 gives a photograph of a crystal of tricyclopentadienylboron.

In ethereal solutions of tricyclopentadienylboron and cyclopentadienylboron difluoride obtained from the experiment, on exposure to air a heavier lower layer separated out, which gradually hardened, forming a polymer. When attempts were made to remove the ether in vacuum, the concentrated ethereal solu-

The solutions of both compounds readily polymerize, forming hard, bright-yellow polymers, elemental analysis of which confirmed the presence of boron in them. The UV spectrum of the polymer of tricyclopentadienylboron in chloroform (Fig. 1) showed that polymerization proceeds through rupture of one of the double bonds, and the high oxygen content in the polymer undoubtedly indicates that oxygen takes part in the polymerization. This confirms the mechanism of oxidative polymerization of unsaturated organoboron compounds proposed by us [3].

We investigated the catalytic effect of tricyclopentadienylboron on the polymerization of styrene. The experiments were carried out in sealed ampoules, with air displaced from the gas phase by nitrogen.

Ampoules containing styrene were kept for 3, 6, and 9 h at 100°. Upon addition of 1 mole % of tricyclopentadienylboron, the latter exerted a significant inhibiting effect on the polymerization of styrene (Fig. 3) (the polymer yields decreased to 0; 10.76; 15.03% after 3, 6, and 9 h, respectively), while the relative viscosity of the polystyrene obtained decreased (Fig. 4).

Fig. 2. Photograph of a crystal of tricyclopentadienylboron

By the method proposed above, we carried out the preparation of tris-(dicyclopentadienyl)-boron from dicyclopentadienylmagnesium bromide and boron trifluoride etherate. The compound obtained is a crystalline, colorless product that oxidizes in air,

$$C_2H_5MgBr + C_{10}H_{12} \rightarrow C_{10}H_{11}MgBr + C_2H_6,$$

$$3C_{10}H_{11}MgBr + BF_3 \rightarrow (C_{10}H_{11})_3B + 3MgBrF.$$

* The spectrum was recorded by N. L. Galanina.

Experimental Part

Preparation of tricyclopentadienylboron $(C_5H_5)_3B$**.** Into a four-necked flask equipped with a stirrer, dropping funnel, condenser, and gas outlet were charged 15.2 g of magnesium turnings and 125 ml of absolute ether, and 54.5 g of ethyl bromide in 25 ml of ether was added. After completion of the reaction, 41.2 g of cyclopentadiene was added, and the reaction flask was left overnight. To the resulting cyclopentadienylmagnesium bromide, 7 g of freshly distilled boron trifluoride etherate in 25 ml of dry ether was added dropwise. The light-yellow ether layer that formed was decanted. Tricyclopentadienylboron has m.p. (in sealed capillaries) 138-139°.

Found, %: B 5.4
$(C_5H_5)_3B$. Calculated, %: B 5.26.

Fig. 3. Kinetics of the polymerization of styrene in the presence of tricyclopentadienylboron at 100°: 1 –without $B(C_5H_5)_3$, 2 –with addition of 1 mole % $B(C_5H_5)_3$

Preparation of cyclopentadienylmagnesium difluoride $C_5H_5MgBF_2$**.** Into a four-necked flask, the reagents were charged in the following ratio: 15.2 g of magnesium turnings, 125 ml of absolute ether, 54.5 g of ethyl bromide. After completion of the reaction, 41.2 g of cyclopentadiene was added, and the reaction mixture was left overnight. Then 23.5 g of freshly ⋯

distilled etherate. The ether layer was decanted; crystals of cyclopentadienylmagnesium difluoride gradually separated from it. M.p. 38–41°.

$C_5H_5BF_2$.	Found, %:	B 9.88
	Calculated, %:	B 9.5

Polymer of tricyclopentadienylboron was obtained by slow oxidation of an ethereal solution of tricyclopentadienylboron, dried in vacuum. M.p. 147-149°. Found, %: C 53.86; 53.97; H 6.18; 6.17; B 4.38 4.46.

Fig. 4. Dependence of the relative viscosity of polystyrene on concentration: 1 –without $B(C_5H_5)_3$, 2 –with addition of $B(C_5H_5)_3$.

If the ethereal solution is poured into heptane, light-yellow flakes of the polymer separate from the latter. After drying, the polymer had m.p. 151-152°. Found, %: C 47.37; H 6.36; B 3.88.

Complex of tricyclopentadienylboron with pyridine $(C_5H_5)_3B \cdot C_5H_5N$. Pyridine was added dropwise at 20° to an ethereal solution of tricyclopentadienylboron. The reaction proceeds with heating and precipitation of white flakes of the complex. Pyridine was added until precipitation of these flakes ceased. The complex was dried in vacuum. The melting point of the crystals was above 250°.

$(C_5H_5)_3B \cdot C_5H_5N$.	Found, %:	B 4.11
	Calculated, %:	B 3.8

Preparation of tris-(dicyclopentadienyl)-boron $B\,(C_{10}H_{11})_3$. Into a three-necked flask were charged 15.2 g of magnesium turnings and 150 ml of absolute ether. 54.5 g of ethyl bromide was gradually added. To the resulting Grignard reagent, 82.5 g of dicyclopentadiene was added dropwise and the mixture was left overnight. The reaction proceeded with slight heating and evolution of gas bubbles. Then 8 g of boron fluoride etherate in 25 ml of absolute ether was added dropwise, the reaction proceeding with considerable heating of the reaction mixture. The ethereal solution was decanted; crystals of tris-(dicyclopentadienyl)-boron gradually separated from it. M.p. 180–182° (in sealed capillaries).

$(C_{10}H_{11})_3$.	Found, %:	B 2.27
	Calculated, %:	B 2.67

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