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Synthesis of 9-C_6H_5-3-(π-C_5H_5)-3,1,2-$CoC_2B_9H_{10}$ by cross-coupling reaction of 9-I-3-(π-C_5H_5)-3,1,2-$CoC_2B_9H_{10}$ with C_6H_5ZnCl catalyzed by palladium complexes

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The cross-coupling reaction of 9-I-3-(π-C_5H_5)-3,1,2-$CoC_2B_9H_{10}$ with organozinc compounds catalyzed by palladium complexes was used to synthesize the first representative of *B*-phenyl-substituted carboranes, 9-C_6H_5-3-(π-C_5H_5)-3,1,2-$CoC_2B_9H_{10}$.

Key word: π-cyclopentadienyl-3,1,2-dicarbollylcobalt, catalysis, cross-coupling.

No *B*-phenyl derivatives of π-cyclopentadienyl-3,1,2-dicarbollylcobalt have been prepared to date.[1] Recently,[2] the salt $[MePPh_3]^+[\pi\text{-}C_2B_9H_8(CH_3)_3]_2Co^-$ was synthesized by cross-coupling reaction of $[MePPh_3]^+[\pi\text{-}C_2B_9H_8I_3]_2Co^-$ with CH_3I catalyzed by palladium complexes[2] using the reaction we found in 1982,[3] *i.e.*, replacement of iodine atom with an organic group in *B*-iodocarboranes under the action of organomagnesium compounds in the presence of metallocomplex catalysts. This reaction cannot be used in the case of *B*-iodo-substituted derivatives of 3-(π-C_5H_5)-3,1,2-$CoC_2B_9H_{10}I$ since organomagnesium compounds react with the π-C_5H_5-group of 3-(π-C_5H_5)-3,1,2-$CoC_2B_9H_{11}$ to replace a hydrogen atom with the organic group.[4]

In this connection, we studied the cross-coupling reaction of 9-I-3-(π-C_5H_5)-3,1,2-$CoC_2B_9H_{10}$ (**1**) with organozinc compounds in the presence of $(Ph_3P)_4Pd$ taking C_6H_5ZnCl as an example. We found that this reaction occurs with the replacement of the iodine atom with the phenyl group and with the formation of 9-C_6H_5-3-(π-C_5H_5)-3,1,2-$CoC_2B_9H_{10}$ (**2**) in a high yield analogously to reactions with other *B*-iodocarboranes.[5] In this case, the π-C_5H_5 group does not enter into the substitution reaction under the action of C_6H_5ZnCl. The reaction occurs by the following scheme:

Scheme 1

$$\underset{\mathbf{1}}{9\text{-I-3-}(\pi\text{-}C_5H_5)\text{-}3,1,2\text{-}CoC_2B_9H_{10}} + C_6H_5ZnCl \xrightarrow[\text{THF}]{(Ph_3P)_4Pd^0}$$

$$\longrightarrow \underset{\mathbf{2}}{9\text{-}C_6H_5\text{-}3\text{-}(\pi\text{-}C_5H_5)\text{-}3,1,2\text{-}CoC_2B_9H_{10}}$$

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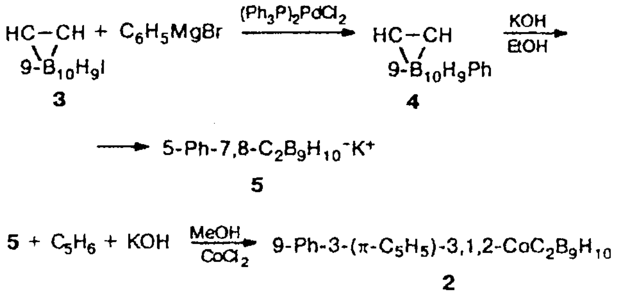
In such a simple way, we synthesized compound **2**, which is the first organoboron derivative of π-cyclopentadienyl-π-dicarbollylcobalt.

The structure of compound **2** was confirmed by elemental analysis and independent synthesis according to the following scheme:

Scheme 2



9-Phenyl-*o*-carborane (**4**) obtained under the action of PhMgBr on 9-iodo-*o*-carborane (**3**) in the presence of $(Ph_3P)_2PdCl_2$ according to the procedure[3] was cleaved with an alcohol solution of KOH to anion **5**; the latter was isolated as the tetraethylammonium salt. Complex **2** identical to that obtained above was synthesized in the reaction of anion **5** with cyclopentadiene and $CoCl_2$ in a fair yield following a procedure reported in Ref. 6. It should be noted that we are the first who applied this procedure to *B*-organyl-7,8-dicarbaundecaborate salts.

Further, we plan to show that the cross-coupling reaction using organozinc compounds can be used as a general procedure for synthesizing various compounds of the *B*-organyl-$3\text{-}(\pi\text{-}C_5H_5)\text{-}3,1,2\text{-}CoC_2B_9H_{10}$ type.

Experimental

The starting 9-iodo-*o*-carborane[7] and 9-phenyl-*o*-carborane[3] were synthesized following known procedures. Column chromatography was performed using L 100/160 silica gel.

9-Iodo-3-π-cyclopentadienyl-3,1,2-dicarbollylcobalt (1). A mixture of KOH (5.6 g, 0.1 mol) and compound **3** (2.7 g, 0.01 mol) in 20 mL of abs. methanol was refluxed for 2 h. The mixture was cooled to 0 °C and a cooled mixture of $CoCl_2 \cdot 6H_2O$ (5.9 g, 0.025 mol) in 15 mL of methanol and cyclopentadiene (1.32 g, 0.02 mol) was added. The mixture was stirred under an argon atmosphere for 1.5 h at 45—50 °C, cooled to 20 °C, and poured into water. The residue was filtered off and washed with water, and then with diluted hydrochloric acid. The residue was dissolved in acetone, then water was added and acetone was evaporated *in vacuo*, and the crystals precipitated were filtered off and dried *in vacuo* over P_2O_5. The crystals were purified by recrystallization from a toluene—hexane mixture and column chromatography (benzene) to give compound **1** (1.7 g, 45%), m.p. 176 °C. Found (%): C, 22.00; H, 4.34; B, 24.90; Co, 15.28. $C_7H_{15}B_9CoI$. Calculated (%): C, 21.97; H, 3.95; B, 25.46; Co, 15.41.

9-Phenyl-3-π-cyclopentadienyl-3,1,2-dicarbollylcobalt (2). C_6H_5MgCl (0.03 mol) in 25 mL of THF was added to a solution of $ZnCl_2$ (4 g, 0.03 mol) in 25 mL of THF at 20 °C. The mixture was stirred under an argon atmosphere for 30 min and compound **1** (3.82 g, 0.01 mol) and $(Ph_3P)_4Pd$ (0.2 g, 0.0002 mol) in 15 mL of THF were added. The obtained solution was refluxed for 40 h. The reaction mass was treated with 10% hydrochloric acid and extracted with ether. The organic layer was dried over Na_2SO_4. The solvent was removed, and the residue was purified by recrystallization from heptane and column chromatography (benzene) to give compound **2** (1.16 g, 35 %), m.p. 215 °C. Found (%): C, 47.47; H, 6.41; B, 28.78. $C_{13}H_{20}B_9Co$. Calculated (%): C, 46.97; H, 6.06; B, 29.28.

Potassium salt of 5-phenyl-7,8-dicarbaundecaborate (5). A mixture of compound **4** (2.2 g, 0.01 mol) and KOH (1.7 g, 0.03 mol) in 20 mL of MeOH was refluxed until starting compound **4** disappeared. The potassium salt was identified by synthesizing a tetraethylammonium salt, m.p. 120 °C (from water). Found (%): C, 55.66; H, 10.31; B, 28.57; N, 4.15. $C_{16}H_{36}B_9N$. Calculated (%): C, 56.34; H, 10.67; B, 28.65; N, 4.11.

9-Phenyl-3-π-cyclopentadienyl-3,1,2-dicarbollylcobalt (2). The solution of potassium salt **5** obtained in the preceding run was treated with $CoCl_2 \cdot 6H_2O$ (5.9 g, 0.25 mol) in 15 mL of MeOH and cyclopentadiene (1.32 g, 0.02 mol), analogously to the synthesis of compound **1** described above, to give compound **2** (2 g, 60%, m.p. 214 °C) identical to that obtained from compound **1** and PhZnCl.

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