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New B-substituted derivatives of *m*-carborane, *p*-carborane, and cobalt bis(1,2-dicarbollide) anion

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Abstract

The Pd-catalyzed cross-coupling reactions of B–I bond in *m*- and *p*-carboranes and cobalt bis(1,2-dicarbollide) anion with organomagnesium and organozinc compounds were studied. Carboranyl derivatives of furan, thiophene, indole, pyridine and quinoline were synthesized. 2-Pyridylethynyl and 3-quinolylethynyl derivatives of *p*-carborane were prepared by Pd-catalyzed cross-coupling reactions using corresponding alkynes or their magnesium derivatives.

Keywords: *m*-Carborane; *p*-Carborane; Cobalt bis(1,2-dicarbollide) anion; Cross-coupling reactions; Palladium catalysis

1. Introduction

The geometrical and electronic properties of polyhedral boron hydrides have attracted a great deal of attention in the context of design and construction of promising novel molecular and supramolecular materials [1–5]. Of particular interest are electronic interactions between carboranes, which are considered to be three-dimensional aromatic systems [6], and exopolyhedral π-substituents of a different nature. Another field of potential application of carboranes is medicine. At present, there are several approaches to the medical application of carboranes [7]. The leading application is in boron neutron capture therapy (BNCT), one of the most interesting and promising methods for cancer treatment [8]. Due to some chemical features of carboranes they also may act as hydrophobic pharmacophores in biologically active molecules [9].

Design and synthesis of novel carborane-based materials require development of effective methods of synthesis of carborane derivatives. Synthesis of carborane derivatives containing various types of π-substituents (e.g., vinyl, alkynyl, aryl, and heteroaryl substituents) attached to carbon atoms of the carborane cage is well documented [3,10–18]. Carborane derivatives containing π-substituents attached to boron atoms of the carborane cage are probably even more interesting due to the great diversity of substitution positions with different electronic effects. Unfortunately, synthesis of such derivatives is much less studied.

The B-arylation, B-heteroarylation, and B-alkynylarylation via cross-coupling reactions of carboranes containing B–I bond with organometallic compound RM catalyzed by Pd complexes are promising ways of synthesis of such types of compounds. However, activation of the B–I bond in carboranes is fairly difficult. To

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date, all attempts to fix products of the oxidative addition of the carborane B–I bond to Pd(0) complexes have failed [19]. Nevertheless, it was shown that cross-coupling reactions of B–I carboranes with active organometallic compounds [20,21a,b], terminal alkynes [21], arylboronic acids [22], as well as carboranylation of styrenes (i.e., the boron analogue of Heck reaction) [23] result in the corresponding derivatives with B–C bond. These results provide evidence that the equilibrium in the reaction with B–Pd(L_2)–I complex participation could be shifted to reaction products if the active partners and proper ligands are found.

The aim of this work was to study cross-coupling reactions of 9-iodo-1,7-dicarba-*closo*-dodecaborane (9-I-*m*-carborane), 2-iodo-1,12-dicarba-*closo*-dodecaborane (2-I-*p*-carborane), and iodo cobalt bis(dicarbollide) [8-I-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]$^-$ with organometallic derivatives of various nitrogen-, oxygen-, and sulfur-containing heterocycles.

2. Results and discussion

In spite of the fact that at present time many examples of successful B-arylation of carboranes in palladium-catalized reactions of iodocarboranes with a different types of nucleophilic aryl derivatives are reported, only individual attempts of introduction of a heteroaryl fragment to boron of carboranyl nucleus were carried out. In this work, we have studied a possibility to obtain the heteroaryl derivatives of the carboranes in Pd-catalyzed B–C cross-coupling reactions with participation of variety organozinc heterocycles. The choice of zinc organometallics as the reagents was caused on the one hand by their high activity in cross-coupling reactions, on the other hand by their tolerance to π-deficient heterocycles. Also two ways of obtaining heterocyclic ethynyl B-derivatives of *p*-carborane, Sonogashira-type and Kumada-type reactions, have been considered.

2.1. Reaction of 2-I-p-carborane and 9-I-m-carborane with organozinc compounds

The reaction of thien-2-ylzinc chloride and bis(thien-2-yl)zinc with 2-I-*p*-carborane was carried out in tetrahydrofuran (THF) or dioxane under catalysis by $Pd(PPh_3)_4$ or $PdCl_2(PPh_3)_2$ at 60 or 100 °C, to give the cross-coupling product in high yield (Table 1, entries 1 and 2).

$$IC_2B_{10}H_{11} + R_nM \rightarrow RC_2B_{10}H_{11}$$

Unfortunately, the reaction was accompanied by the formation of homo-coupling product R_2. Therefore, in order to reach a quantitative yield of B-thienyl- as well as B-furyl-*p*-carborane (Table 1, entry 6), an excess of organometallic compound should be used, although it is difficult to separate the reaction products from Het_2. Under the same conditions, 9-I-*m*-carborane reacts equally well with bis(thien-2-yl)zinc to give the corresponding 9-(thien-2-yl)-*m*-carborane in a quantitative yield (Table 1, entry 3). However, the reaction with thienylzinc containing electron-withdrawing 1,3-dioxalilyc group at position 5 of thiophen, bis[5-(1,3-dioxalylthien-2-yl)zinc, gives only 57% of the product (Table 1, entry 4). In contrast to 2-thienylzinc chloride, 2-thiazolylzinc chloride does not react with 2-I-*p*-carborane and 9-I-*m*-carborane, either under catalysis by Pd with Ph_3P ligand, or using complexes $PdCl_2$(dppb) as a catalyst, which was effective in the cross-coupling reaction with $ArB(OH)_2$ [22].

The same reactions with Zn-derivatives of nitrogen-containing heterocycles are more difficult to achieve since they require more severe conditions as well as 1,4-bis(diphenylphosphino)butane (dppb) as a ligand (see Table 1, entries 7–13).

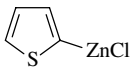
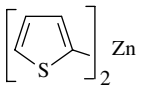
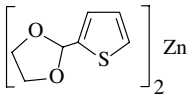
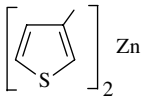
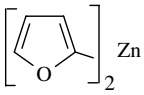
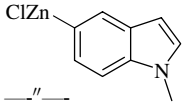
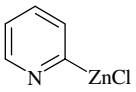
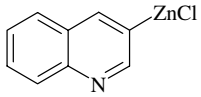
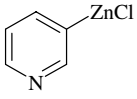
The B-carboranyl fragment could be introduced at position 5 of indole in 64% yield under the reaction of 5-indolylzinc chloride with 2-I-*p*-carborane. The reaction is not selective, and due to the formation of homo-coupling products, 36% of nonreacted 2-I-*p*-carborane was recovered (Table 1, entry 7). Also 9-I-*m*-carborane gave 65% yield of the cross-coupling product in the reaction with 5-indolylzinc chloride in dioxane and only 30% yield in the reaction in THF (Table 1, entries 8 and 9).

Substitution of iodine in 9-I-*m*-carborane and 2-I-*p*-carborane with pyridyl and quinolyl moieties is fairly problematic because their organozinc derivatives are very weak nucleophiles. Nevertheless use of dppb as a ligand leads in the case of *p*-carborane to a moderate yield of cross-coupling products (Table 1, entries 10 and 12). In the case of reaction of 2-pyridylzinc chloride with 2-I-*p*-carborane a 57% yield of 2-(pyridyl-2)-*p*-carborane was attained. By contrast, the less active 9-I-*m*-carborane reacted with 2-pyridylzinc chloride in a yield of 12% after 24 h (Table 1, entries 1011). With regard to the interaction of 2-quinolylzinc chloride even with 2-I-*p*-carborane, the yield of 9-(quinolyl-2)-*m*-carborane was very modest (37%) (Table 1, entry 12).

2.2. Palladium-catalyzed alkynylation of 2-I-p-carborane

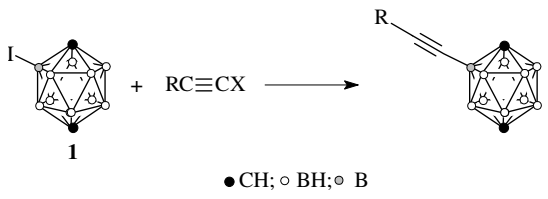
For introduction of *N*-heterocyclic fragments in the carborane cage, we used the modification of the Sonogashira reaction with participation of the B–I bond, although in this case these fragments are separated from the B atom by two carbon atoms. Substitution of iodine in 2-I-*p*-carborane with 2-pyridylethynyl and 3-quinolylethynyl moieties was carried out via two routes: using the Pd-catalyzed reaction of Mg derivatives (Iotsich

Table 1
Reaction of 2-I-*p*- and 9-I-*m*-carboranes with organozinc compounds R_nM

Entry[a]	$IC_2B_{10}H_{11}$	R_nM	Catalyst	Solvent	Time (h)	Ratio of boronated products[b] ($RC_2B_{10}H_{11}/IC_2B_{10}H_{11}$/s.p[c])
1	2-I-*p*-carborane		$PdCl_2(PPh_3)_2$	THF	4	100/0/0
2	2-I-*p*-carborane		$Pd(PPh_3)_4$	THF	5	100/0/0
3	9-I-*m*-carborane	—″—	$Pd(PPh_3)_4$	THF	5	100/0/0
4	9-I-*m*-carborane		$Pd(PPh_3)_4$	THF	5	57/37/6
5	2-I-*p*-carborane		$PdCl_2(PPh_3)_2$	Dioxane	12	97/3/0
6[d]	2-I-*p*-carborane		$PdCl_2(PPh_3)_2$	Dioxane	12	100/0/0
7	2-I-*p*-carborane		$PdCl_2$ (dppb)	Dioxane	3	64/36/0
8	9-I-*m*-carborane	—″—	$PdCl_2$ (dppb)	Dioxane	3	65/35/0
9	9-I-*m*-carborane	—″—	$PdCl_2$ (dppb)	THF	3	30/60/10
10	2-I-*p*-carborane		$PdCl_2$ (dppb)	Dioxane	21	57/43/0
11	9-I-*m*-carborane	—″—	$PdCl_2$ (dppb)	Dioxane	24	12/88/0
12	2-I-*p*-carborane		$PdCl_2$ (dppb)	Dioxane	24	37/63/0
13	9-I-*m*-carborane		$PdCl_2$ (dppb)	Dioxane	24	10/89/1

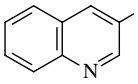
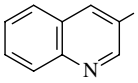
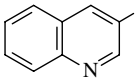
[a] General conditions: 1 equivalent of iodocarborane, 1.5 equivalents of organozinc reagent (the ratio was calculated per heteroaromatic group), 2 mol% catalyst, THF or dioxane (10 ml/mmol iodocarborane), reflux under argon.
[b] The ratios were determined by ^{11}B NMR.
[c] Unidentified side product.
[d] 2.5 equivalents of Fu_2Zn and 5 mol% of the catalyst were used.

complexes) and using free alkynes in the presence of catalytic amounts of CuI and $PdCl_2(PPh_3)_2$.



As in the case of organozinc compounds, excess of organomagnesium reagent was used to increase the yield of coupling products (Table 2, entries 1, 2). However, because 2-pyridylalkyne is strongly tarred under reaction conditions the quantitative yield was reached only in the case of 3-quinolylalkyne. The reactions of free alkynes were performed under the classic conditions of the Sonogashira reaction using pyrrolidine, both as a base and as a solvent. Under these conditions, a high yield (~80%) of product was reached for 3-quinolylalkyne (Table 2, entry 3), but for thermally less stable 2-pyridylalkyne the reaction was proceeded unselectively with a fairly moderate yield of product (Table 2, entry 5). In dimethylformamide (DMF) and benzene, the reaction became more

Table 2
Reactions of 2-I-*p*-carborane with heteroaryl derivatives of acetylene RC≡CX

Entry[a]	R	X	Method	RC≡CX / **1**	Time (h)	Ratio of boronated products[b] (RC≡CC$_2$ B$_{10}$ H$_{11}$/**1**/s.p)[c]
1		MgBr	A	1.2	20	30/70/0
2		MgBr	A	3	12	100/0/0
3		H	B	1.1	22	79/21/0
4		MgBr	A	3	8	15/85/0
5		H	B	2	14	36/30/34

[a] Method A: 2-I-*p*-carborane (0.2 mmol), 2-pyridyl- or 3-quinolylethynyl magnesium bromide, $PdCl_2(PPh_3)_2$ (4 mol%), CuI (4 mol%), dioxane (2 ml) reflux under argon. Method B: 2-I-*p*-carborane (0.2 mmol), ethynyl-N-heteroarene, $PdCl_2(PPh_3)_2$ (4 mol%), CuI (4 mol%), pyrrolidine (3 ml) reflux under argon.
[b] The ratios were determined by ^{11}B NMR.
[c] Unidentified side product.

selective in respect of 2-I-*p*-carborane, but the yield was still low.

2.3. Synthesis of cobalt bis(1,2-dicarbollide) derivatives

Cobalt bis(1,2-dicarbollide) anion [3,3′-Co(1,2-$C_2B_9H_{11})_2]^-$ is another polyhedral boron compound which have nice perspectives of application in various fields from extraction of radionuclides from wastes and synthesis of new materials to nuclide medicine [24]. It should be noted that the cross-coupling reactions of its iodo derivatives are significantly less studied than the reactions of iodo derivatives of *p*- and *m*-carboranes. Until recently, only reaction of its hexaiodo derivative [8,8′,9,9′,12,12′-I_6-3,3′-Co(1,2-$C_2B_9H_8)_2]^-$ with MeMgBr under $PdCl_2(PPh_3)_2$ catalysis resulting in the hexamethyl derivative [8,8′,9,9′,12,12′-Me_6-3,3′-Co(1,2-$C_2B_9H_8)_2]^-$ was described [25]. Later the reaction of the diodo derivative [9,9′-I_2-3,3′-Co(1,2-$C_2B_9H_{10})_2]^-$ with organomagnesium and organozinc reagents was shown to give the corresponding derivatives with alkyl and aryl substituents at positions 9 and 9′ of the cobaltacarborane cage [26]. Similarly, the Pd-catalyzed reactions of methyl- and ethylmagnesium bromides with the [8,8′-I_2-3,3′-Co(1,2-$C_2B_9H_{10})_2]^-$ isomer gave the corresponding derivatives containing alkyl substituents at positions 8 and 8′ adjacent to Co atom, [8,8′-R_2-3,3′-Co(1,2-$C_2B_9H_{10})_2]^-$ [27]. Quite recently, when this paper was in preparation (see preliminary report [28]), the Pd-catalyzed cross-coupling reactions of the monoiodo derivative [8-I-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11})]^-$ with various alkyl- and arylmagnesium reagents were reported [29].

Taking into account that design of new compounds for BNCT requires introduction of only one functional substituent in cobalt bis(dicarbollide) system [30] agents we focused our efforts on functionalization of cobalt bis(dicarbollide) via Pd-catalyzed cross-coupling the monoiodo derivative (Et_4N)[8-I-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (**2**) with organo magnesium (4-methoxyphenyl magnesium bromide) and organozinc (diethylzinc, di(2-thienyl)zinc) reagents. The experiment results are presented in Tables 3 and 4.

Besides Pd catalyst the reaction with organomagnesium compound requires the presence of catalytic amounts of CuI. According to [20c], it suppresses the formation of homo-coupling byproduct. However, even in the presence of CuI some amount of the homo-coupling product was usually formed and nonreacted cobaltacarborane was partially recovered (the result was the same as for *m*- and *p*-carboranes). Using $PdCl_2(PPh_3)_2$ as catalyst the yield of the goal product does not exceed 63% (Table 3, entry 2).

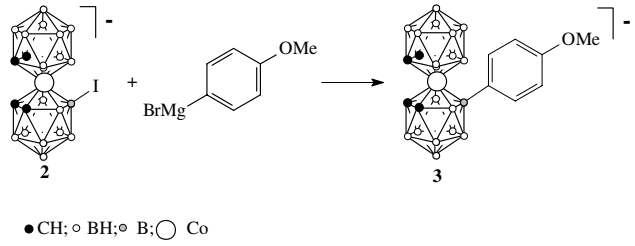
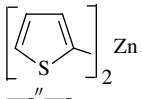


Table 3
Reactions of $(Et_4N)[8\text{-I-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$ with *p*-anisylmagnesium bromide

Entry[a]	Catalyst (mol%)	ArMgBr/**2**	Time (h)	Ratio of products – cobalt bis(dicarbollide) anion derivatives[b] (**3**/**2**/s.p.[c])
1[d]	$PdCl_2(PPh_3)_2$ (2)	2.3	15	5/94/1
2	$PdCl_2(PPh_3)_2$ (2)	2.4	28	63/34/3
3	$PdCl_2$ (dppf) (2)	2.5	20	16/72/12
4	$Pd(dba)_2$ (5); PFu_3 (11)	2.6	24	23/71/6
5	$Pd(dba)_2$ (2); P(*o*-Tol)$_3$ (2)	2.5	20	26/74/0
6	$Pd(dba)_2$ (2); PCy_3 (4)	2.5	20	45/47/8
7	$Pd(dba)_2$ (2); PCy_3 (4)	7.5	22	76/22/2
8	$PdCl_2(PPh_3)_2$ (2)	7.5	22	95/5/0
9	$Pd(dba)_2$ (3); PFu_3 (7)	7.5	22	100/0/0
10	$PdCl_2(PPh_3)_2$ (2)	8	4	100/0/0

[a] General conditions: $(Et_4N)[8\text{-I-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$ (0.2 mmol), anisylmagnesium bromide (0.5 M in Et_2O), catalyst, CuI (5 mol%), dioxane (5 ml), reflux under argon.
[b] The ratios were determined by ^1H NMR.
[c] Unidentified side product.
[d] Reaction was performed in THF.

Table 4
Reactions of $(Et_4N)[8\text{-I-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$ with diethyl- and dithienylzinc

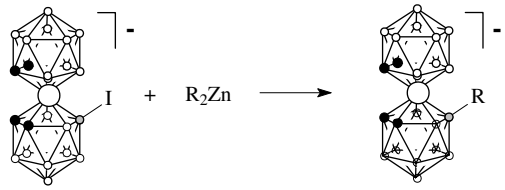
Entry[a]	R_2 Zn	Catalyst (mol%)	R_2 Zn	Time (h)	Ratio of products – cobalt bis(dicarbollide) anion derivatives[b] (**3**/**2**/s.p.[c])
1	Et_2 Zn	$PdCl_2(PPh_3)_2$ (2)	1	22	12/78/10
2	—″—	$Pd(dba)_2$ (2); PFu_3 (4)	1	22	54/29/17
3	—″—	$PdCl_2(PPh_3)_2$ (2)	3	22	100/0/0
4	—″—	$PdCl_2(PPh_3)_2$ (2) CuI (5)	3	22	89/11/0
5		$PdCl_2(PPh_3)_2$ (2)	4	15	80/20/0
6	—″—	$Pd(dba)_2$ (2); PFu_3 (4)	4	15	75/35/0
7	—″—	$Pd(dba)_2$ (2); P(*o*-Tol)$_3$ (5)	3	15	58/38/4
8	—″—	$Pd(dba)_2$ (2); PCy_3 (5)	3	15	100/0/0

[a] General conditions: $(Et_4N)[8\text{-I-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$ (0.2 mmol), diethylzinc (1 M in THF) or dithienylzinc (0.2 M in THF), catalyst, dioxane (5 ml), reflux under argon.
[b] The ratios were determined by ^1H NMR.
[c] Unidentified side product.

Our attempts to increase the goal product yield varLying catalysts with monodentate (P(*o*-Tol)$_3$, PCy_3, PFu_3 [tris(2-furyl)phosphine]) and bidentate [dppb, dppf (1,1′-diphenylphosphinoferrocene)] ligands were not successful (Table 3, entries 3-6). Using $NiCl_2(PPh_3)_2$ as catalyst was not efficient at all.

Since the low yield of the cross-coupling product is the result of consumption of RMgX in the homo-coupling reaction to increase the goal product yield we increased the organomagnesium:cobaltacarborane ratio to 7–8. As the result, quantitative yield of the goal product was obtained using $Pd(dba)_2/PFu_3$ (dba = dibenzylidenacetone) or $PdCl_2(PPh_3)_2$ catalysts (Table 3, entries 9 and 10). Shortened reaction time was an additional effect of using large excess of RMgX.

Similarly, the reaction of **2** with organozinc compounds also needs the excess of organometallics. In the reaction with Et_2Zn in the presence of $PdCl_2(PPh_3)_2$ in dioxane, the yield of $(Et_4N)[8\text{-Et-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$ was increased from 12% to quantitative yield with an increase in the Et_2Zn/**2** ratio from 1 to 3 (Table 4, entries 1 and 3). It should be noted that the use of PFu_3 ligand in this reaction gives better results than the use of the PPh_3 ligand (Table 4, entry 2). In contrast to the reaction with RMgX, the addition of CuI reduces the yield (Table 4, entry 4).



2 **4**

In the reaction of **2** with dithienylzinc, the three- to four-fold excess of organozinc reagent leads to 8-thienyl derivative of cobaltacarborane in close to quantitative yield. The most active catalytic system in this case was found to be $Pd(dba)_2/PCy_3$ (entry 8).

3. Experimental

All experiments were performed under argon atmosphere. Isolation of products was performed in air. Tetrahydrofuran and 1,4-dioxane were freshly distilled from sodium benzophenone. Zinc chloride was freshly dried before use for 4 h at 150 °C and <0.1 mm Hg. Flash chromatography was carried out on Merck Silica Gel 60 (4360 mesh), and Merck Silica 60 F_{254} was used for thin-layer chromatography (TLC). The TLC plates were developed with palladium chloride in acidified (hydrochloric acid) methanol solution. Unless otherwise stated, ^{1}H and ^{11}B NMR spectra were recorded in $CDCl_3$ with Bruker AMX-400 and Varian XL-400 spectrometers at 400 and 128.3 MHz, respectively. ^{11}B NMR spectra were acquired with $BF_3 \cdot Et_2O$ as external standard at 0 ppm. Mass spectra were recorded on a Finnigan SSQ 7000. Elemental analyses were performed in the Microanalytical Laboratory of INEOS, in Moscow, Russia.

3.1. Preparation of organozinc reagents

Method A: *n*-BuLi (1.7 M in hexane, 0.59 ml, 1.0 mmol) was slowly added at −80 °C to solution of 1.0 mmol heteroaryl bromide (2-bromothiophene, 5-bromo-1-methylindole) or 2-(1′,3′-dioxol-2′-yl)thiophene in 2 ml THF. The reaction mixture was stirred at −80 °C for 30 min, solution of 68 mg (0.5 mmol) anhydrous $ZnCl_2$ in 0.5 ml THF was slowly added, and the reaction mixture was allowed to warm to room temperature (rt).

Method B: *t*-BuLi (1.7 M in pentane, 0.59 ml, 1.0 mmol) was slowly added at −100 °C to a solution of 1.0 mmol heteroaryl bromide (3-bromothiophene, 2-bromopyridine, 3-bromopyridine, or 3-bromoquinoline) in 2 ml Et_2O. The reaction mixture was stirred at −100 °C for 30 min, a solution of 68 mg (0.5 mmol) anhydrous $ZnCl_2$ in THF was slowly added, and the reaction mixture was allowed to warm to r.t.

Method C: a solution of 68 mg (1.0 mmol) furane in 1 ml THF was treated with *n*-BuLi (1.7 M in hexane, 0.59 ml, 1.0 mmol) at −50 °C. The reaction mixture was stirred at r.t. for 1 h, a solution of 68 mg (0.5 mmol) anhydrous $ZnCl_2$ in 0.5 ml THF was added.

3.2. Reactions of 2-I-p- and 9-I-m-carboranes with organozinc reagents (Table 1)

A solution of 54 mg (0.2 mmol) iodocarborane (2-I-*p*-carborane or 9-I-*m*-carborane) and 0.004 mmol, 2 mol% of catalyst ($PdCl_2(PPh_3)_2$ or $PdCl_2$dppb) in 2 ml of an appropriate solvent was treated with freshly prepared solution of 1.5 eq. organozinc reagent in 1 ml THF. The mixture was stirred under reflux for an appropriate time. After cooling to r.t., the reaction mixture was quenched with 0.1 ml NH_4Cl, diluted with CH_2Cl_2, filtered through a pad of Celite, and concentrated under reduced pressure. The reaction mixtures were analyzed by ^{11}B NMR.

3.3. 2-(2′-Furyl)-1,12-dicarba-closo-dodecaborane

A solution of 670 mg (4.0 mmol) 2-furylzinc chloride in 5 ml THF, freshly prepared as described above, was added to a solution of 540 mg (2.0 mmol) 2-I-*p*-carborane and 28 mg (0.04 mmol, 2 mol%) $PdCl_2(PPh_3)_2$ in 30 ml dioxane. The mixture was refluxed for 15 h. 0.1 ml of water was when added to quench the excess of organozinc reagent. Solution was filtered and evaporated in vacuo. Water was added to the dark brown residue and extracted with dichloromethane (3×20 ml). The combined organic layers were dried over anhydrous $MgSO_4$. Purification of the crude product by flash chromatography with light petroleum as the eluent gave 320 mg (76% yield) of 2-(2′-furyl)-*p*-carborane as a white solid. The sample for elemental analysis was obtained by recrystallization from hexane at −30 °C.

^{1}H NMR (ppm): 1.5–3.0 (9H, br. m, BH,), 2.88 (1H, br. s, CH_{carb}), 3.06 (1H, br. s, CH_{carb}), 6.35 (1H, dd, J = 1.9, 3.4 Hz), 6.60 (1H, d, J = 3.4 Hz), 7.51 (1H, d, J = 1.9 Hz). ^{11}B NMR (ppm): −9.1 (1B, s, Ar–B), −13.8 (2B, d), −14.7 (6B, d), −16.8 (1B, d). MS (*m*/*z*): 207–212 (210, M, 100%). Anal. Calc. for $C_6H_{14}B_{10}O$ (210.29); C, 34.27; H, 6.71; B, 51.41. Found: C, 34.28; H, 6.71; B, 51.40%.

3.4. 2-(2′-Thienyl)-1,12-dicarba-closo-dodecaborane

A mixture of 130 mg (0.8 mmol) freshly prepared 2-thienylzinc chloride, 108 mg (0.4 mmol) 2-I-*p*-carborane, and 5.6 mg (0.008 mmol, 2 mol%) $PdCl_2(PPh_3)_2$ in 10 ml THF was refluxed for 5 h. Work-up and purification as described above gave the mixture of 2-(2′-thienyl)-*p*-carborane and 2,2′-dithienyl in the ratio 3:1 (by ^{1}H NMR spectrum) as colorless oil (110 mg). Purification by column chromatography or by bulb-to-bulb distillation did not gave pure sample of product.

^{1}H NMR (ppm): 1.5–3.0 (9H, br. m, BH), 2.89 (1H, br. s, CH_{carb}), 3.05 (1H, br. s, CH_{carb}), 7.07 (1H, dd, J = 3.4, 5.0 Hz), 7.24 (1H, d, J = 3.4 Hz), 7.42 (1H, d, J = 5.0 Hz). ^{11}B NMR (ppm): −7.1 (1B, s, Ar–B), −13.5 (2B, d), −14.5 (4B, d), −15.3 (2B, d), −17.4 (1B, d). MS (*m*/*z*): 223–229 (226, M, 100%).

3.5. 2-(3′-Thienyl)-1,12-dicarba-closo-dodecaborane

A mixture of 72 mg (0.44 mmol) freshly prepared 3-thienylzinc chloride, 59.4 mg (0.22 mmol) 2-I-*p*-carborane, and 3.1 mg (0.0044 mmol, 2 mol%) $PdCl_2(PPh_3)_2$ in 5 ml diethyl ether–dioxane (1:4) was refluxed for 12 h. Work-up and purification as described above gave

the mixture of 2-(3′-thienyl)-*p*-carborane and 3,3′-dithienyl in the ratio 4:1 (by ^{1}H NMR spectrum) as white solid (55 mg).

^{1}H NMR (ppm): 1.5–3.0 (9H, br. m, BH), 2.87 (1H, br. s, CH_{carb}), 2.98 (1H, br. s, CH_{carb}), 7.16 (1H, dd, J=1.5, 4.8 Hz), 7.28 (1H, dd, J=2.5, 4.8 Hz), 7.39 (1H, dd, J=1.5, 2.5 Hz). ^{11}B NMR (ppm): −6.9 (1B, s, Ar–B), −13.6 (2B, d), −14.5 (4B, d), −15.3 (2B, d), −17.5 (1B, d). MS (*m*/*z*): 223–229 (226, M, 100%).

3.6. 2-(1′-Methylindol-5′-yl)-1,12-dicarba-closo-dodecaborane

A mixture of 950 mg (4.52 mmol) freshly prepared 1-methylindol-5-yl-zinc chloride, 405 mg (1.5 mmol) 2-I-*p*-carborane, and 18 mg (0.03 mmol, 2 mol%) $PdCl_2$(dppb) in 28 ml THF-dioxane (2:5) was refluxed for 6 h. Work-up and purification as described above gave 330 mg (81% yield) of 2-(1′-methylindol-5′-yl)-*p*-carborane as white crystals. The sample for elemental analysis was obtained by recrystallization from hexane.

^{1}H NMR (ppm): 1.5–3.0 (9H, br. m, BH), 2.90 (1H, br. s, CH_{carb}), 3.11 (1H, br. s, CH_{carb}), 3.78 (3H, s), 6.46 (1H, d, J=3.5 Hz), 7.03 (1H, d, J=3.5 Hz), 7.27 (1H, d, J=8.4 Hz), 7.41 (1H, d, J=8.4 Hz), 7.83 (1H, s). ^{11}B NMR (ppm): −3.6 (1B, s, Ar–B), −13.4 (2B, d), −14.6 (4B, d), −15.3 (2B, d), −18.1 (1B, d). MS (*m*/*z*): 270–275 (273, M, 100%). Anal. Calc. for $C_{11}H_{19}B_{10}N$ (273.39); C, 48.33; H, 7.01; B, 39.54. Found: C, 48.78; H, 7.36; B, 39.9%.

3.7. 2-(2′-Pyridyl)-1,12-dicarba-closo-dodecaborane

A mixture of 710 mg (4.5 mmol) freshly prepared 2-pyridylzinc chloride, 405 mg (1.5 mmol) 2-I-*p*-carborane, and 36 mg (0.06 mmol, 4 mol%) $PdCl_2$(dppb) in 30 ml diethyl ether–dioxane (1:2) was refluxed for 6 h. Work-up and purification as described above gave 160 mg (48% yield) of 2-(2′-pyridyl)-*p*-carborane as white crystals. The sample for elemental analysis was obtained by sublimation at 65 °C and 0.05 mm Hg.

^{1}H NMR (ppm): 1.5–3.2 (9H, br. m, BH), 2.87 (1H, br. s, CH_{carb}), 3.58 (1H, br. s, CH_{carb}), 7.21 (1H, m), 7.62 (1H, m), 7.72 (1H, m), 8.59 (1H, m). ^{11}B NMR (ppm): −6.6 (1B, s, Ar–B), −13.0 (2B, d), −14.7 (6B, d), −16.8 (1B, d). MS (*m*/*z*): 217–223 (221, M, 100%). Anal. Calc. for $C_7H_{15}B_{10}N$ (221.31); C, 37.99; H, 6.83; B, 48.85. Found: C, 37.70; H, 6.88; B, 48.87%.

3.8. 2-(3′-Quinolyl)-1,12-dicarba-closo-dodecaborane

A mixture of 62 mg (0.3 mmol) freshly prepared 3-quinolylzinc chloride, 54 mg (0.2 mmol) 2-I-*p*-carborane, and 2.4 mg (0.004 mmol, 2 mol%) $PdCl_2$dppb in 3 ml diethyl ether–dioxane (1:2) was refluxed for 24 h. Work-up and purification as described above gave 10 mg (18% yield) of 2-(3′-quinolyl)-*p*-carborane as white solid.

^{1}H NMR (ppm): 1.5–3.2 (9H, br. m, BH), 2.86 (1H, br. s, CH_{carb}), 3.45 (1H, br. s, CH_{carb}), 7.58 (1H, m), 7.69 (1H, m), 7.75 (1H, m), 8.05 (1H, m), 8.34 (1H, m), 8.86 (1H, m). ^{11}B NMR (ppm): −6.4 (1B, s, Ar–B), −11.2 (1B, d), −12.7 (2B, d), −15.4 (5B, d), −17.2 (1B, d). MS (*m*/*z*): 267–273 (271, M, 100%).

3.9. 9-(5′-(1″,3″-dioxol-2″-yl)thien-2′-yl)-1,7-dicarba-closo-dodecaborane

A mixture of 78 mg (0.5 mmol) freshly prepared 5-(1′, 3′-dioxol-2′-yl)thien-2-ylzinc chloride, 108 mg (0.4 mmol) 9-I-*m*-carborane, and 9.2 mg (0.008 mmol, 2 mol%) $Pd(PPh_3)_4$ in 3 ml THF–dioxane (1:2) was refluxed for 5 h. Work-up and purification as described above gave 60 mg (50% yield) of the 9-(5′-(1″, 3″-dioxol-2″-yl)thien-2′-yl)-*m*-carborane as white solid.

^{1}H NMR (ppm): 1.5–3.2 (9H, br. m, BH), 2.98 (2H, br. s, CH_{carb}), 4.06 (4H, m), 6.06 (1H, s), 6.98 (1H, m), 7.08 (1H, m). ^{11}B NMR (ppm): −2.7 (1B, s, Ar–B), −6.4 (2B, d), −9.6 (1B, d), −13.0 (2B, d), −13.9 (2B, d), −17.5 (1B, d), −19.7 (1B, d). MS (*m*/*z*): 250–256 (254, M − CH_3CHO, 100%).

3.10. 9-(1′-Methylindol-5′-yl)-1,7-dicarba-closo-dodecaborane

A mixture of 950 mg (4.52 mmol) freshly prepared 1-methylindol-5-yl-zinc chloride, 405 mg (1.5 mmol) 9-I-*m*-carborane, and 18 mg (0.03 mmol, 2 mol%) $PdCl_2$(dppb) in 28 ml THF–dioxane (2:5) was refluxed for 6 h. Work-up and purification as described above gave 310 mg (76% yield) of 9-(1′-methylindol-5′-yl)-*m*-carborane as white crystals. The sample for elemental analysis was obtained by recrystallization from hexane.

^{1}H NMR (ppm): 1.5–3.0 (9H, br. m, BH), 3.00 (2H, br. s, CH_{carb}), 3.76 (3H, s), 6.44 (1H, d, J=3.0 Hz), 6.99 (1H, d, J=3.0 Hz), 7.24 (1H, d, J=8.2 Hz), 7.39 (1H, d, J=8.2 Hz), 7.79 (1H, s). ^{11}B NMR (ppm): −1.5 (1B, s, Ar–B), −6.5 (2B, d), −9.6 (1B, d), −13.1 (2B, d), −14.0 (2B, d), −17.6 (1B, d), −20.6 (1B, d). MS (*m*/*z*): 270–275 (273, M, 100%). Anal. Calc. for $C_{11}H_{19}B_{10}N$ (273.39); C, 48.33; H, 7.01; B, 39.54. Found: C, 48.32; H, 7.09; B, 39.52%.

3.11. 9-(2′-Pyridyl)-1,7-dicarba-closo-dodecaborane

A mixture of 190 mg (1.2 mmol) freshly prepared 2-pyridylzinc chloride, 190 mg (1.2 mmol) 108 mg (0.4 mmol) 9-I-*m*-carborane, and 4.8 mg (0.008 mmol, 2 mol%) $PdCl_2$(dppb) in 7 ml diethyl ether–dioxane (2:5) was refluxed for 24 h. Work-up and purification as described above gave 20 mg (23% yield) of 9-(2′-pyridyl)-*m*-carborane as white solid.

^{1}H NMR (ppm): 1.4–3.0 (9H, br. m, BH), 3.06 (2H, br. s, CH_{carb}), 7.19 (1H, m), 7.57 (1H, m), 7.60 (1H, m), 8.66 (1H, m). ^{11}B NMR (ppm): −1.4 (1B, s, Ar–B), −6.4 (2B, d), −9.7 (1B, d), −12.9 (2B, d), −13.6 (2B, d), −17.2 (1B, d), −18.9 (1B, d). MS (*m/z*): 217–223 (221, M, 100%). Anal. Calc. for $C_7H_{15}B_{10}N$ (221.31); C, 37.99; H, 6.83; B, 48.85. Found: C, 37.69; H, 6.85; B, 48.90%.

3.12. 9-(3′-Pyridyl)-1,7-dicarba-closo-dodecaborane

A mixture of 190 mg (1.2 mmol) freshly prepared 3-pyridylzinc chloride, 108 mg (0.4 mmol) 9-I-*m*-carborane, and 4.8 mg (0.008 mmol, 2 mol%) $PdCl_2$(dppb) in 7 ml diethyl ether–dioxane (2:5) was refluxed for 24 h. Work-up and purification as described above gave 24 mg (27% yield) of 9-(3′-pyridyl)-*m*-carborane as white solid.

^{1}H NMR (ppm): 1.6–3.2 (9H, br. m, BH), 3.05 (2H, br. s, CH_{carb}), 7.16 (1H, m), 7.76 (1H, m), 8.47 (1H, m), 8.67 (1H, m). ^{11}B NMR (ppm): −1.2 (1B, s, Ar–B), −6.5 (2B, d), −9.6 (1B, d), −13.1 (2B, d), −13.6 (2B, d), −17.3 (1B, d), −19.2 (1B, d). MS (*m/z*): 217–223 (221, M, 100%). Anal. Calc. for $C_7H_{15}B_{10}N$ (221.31); C, 37.99; H, 6.83; B, 48.85. Found: C, 37.75; H, 6.93; B, 48.78%.

3.13. Reactions of 2-I-p-carborane with heteroaryl derivatives of acetylene (Table 2)

Method A: a solution of 54 mg (0.2 mmol) 2-I-*p*-carborane, 5.6 mg (0.008 mmol, 4 mol%) $PdCl_2(PPh_3)_2$), and 1.52 mg (0.008 mmol, 4 mol%) CuI in 2 ml dioxane was added to suspension of 1 eq. 2-pyridyl- or 3-quinolylethynyl magnesium bromide in 2 ml dioxane, freshly prepared by addition of ethylmagnesium bromide (1.7 M in diethyl ether) to an appropriate (heteroaryl)ethyne in dioxane. The mixture was stirred under reflux for an appropriate time. After cooling to r.t., the reaction mixture was quenched with NH_4Cl (0.1 ml), diluted with CH_2Cl_2, filtered through a pad of Celite, and concentrated under reduced pressure. The reaction mixtures were analyzed by ^{11}B NMR.

Method B: a solution of 54 mg 2-I-*p*-carborane, ethynyl-*N*-heteroarene (1 eq. for 3-quinolylacetylene and 2 eq. for 2-pyridylacetylene), catalyst (4 mol%), and (0.008 mmol, 4 mol%) copper(I) iodide in pyrrolidine (3 ml) was heated to reflux. The resulting mixture was evaporated in vacuo, diluted with diethyl ether, filtered through a pad of Celite, and concentrated under reduced pressure. The reaction mixtures were analyzed by ^{11}B NMR.

3.14. 2-(2′-Pyridyl)ethynyl-1,12-dicarba-closo-dodecaborane

2-(2′-pyridyl)ehynyl-*p*-carborane was prepared according to method B using 540 mg (2.0 mmol) of 2-iodo-*p*-carborane, 412.5 mg (4.0 mmol) 2-pyridylacetylene, 56.2 mg (0.08 mmol, 4 mol%) $PdCl_2(PPh_3)_2$, 15.4 mg (0.08 mmol, 4 mol%) CuI, and 20 ml pyrrolidine. The reaction mixture was heated under reflux for 10 h. Purification of the residue by flash chromatography with light petroleum as the eluent gave 112 mg (23% yield) of 2-(2-pyridyl)ehynyl-*p*-carborane as a pale yellow solid. The sample for elemental analysis was obtained by recrystallization from hexane.

^{1}H NMR (ppm): 1.5–3.0 (9H, br. m, BH), 2.81 (1H, br. s, CH_{carb}), 3.11 (1H, br. s, CH_{carb}), 7.22 (1H, m), 7.46 (1H, m), 7.63 (1H, m), 8.56 (1H, m). ^{11}B NMR (ppm): −13.4 (2B), −14.3 (3B), −15.0 (4B), −16.4 (1B). MS (*m/z*): 241–247 (245, M, 100%). Anal. Calc. for $C_9H_{15}B_{10}N$ (245.34); C, 44.06; H, 6.16; B, 44.07. Found: C, 44.06; H, 6.29; B, 43.98%.

3.15. 2-(3′-Quinolyl)ethynyl-1,12-dicarba-closo-dodecaborane

The 2-(3′-quinolyl)ethynyl-*p*-carborane was prepared according to method B using 540 mg (2.0 mmol) of 2-iodo-*p*-carborane, 612.7 mg (4.0 mmol) of 2-quinolylacetylene, 56.2 mg (0.08 mmol, 4 mol%) $PdCl_2(PPh_3)_2$, 15.4 mg (0.08 mmol, 4 mol%) CuI, and 20 ml pyrrolidine. The reaction mixture was heated under reflux for 12 h. Purification of the residue by flash chromatography with light petroleum as the eluent gave 360.4 mg (61% yield) of 2-(3-quinolyl)ehynyl-*p*-carborane as a white solid. The sample for elemental analysis was obtained by recrystallization from hexane.

^{1}H NMR (ppm): 1.5–3.2 (9H, br. m, BH), 2.85 (1H, br. s, CH_{carb}), 3.13 (1H, br. s, CH_{carb}), 7.55 (1H, m), 7.71 (1H, m), 7.76 (1H, m), 8.07 (1H, m), 8.27 (1H, m), 8.91 (1H, m). ^{11}B NMR (ppm): −13.3 (3B), −14.3 (3B), −15.0 (4B). MS (*m/z*): 291–297 (295, M, 100%). Anal. Calc. for $C_{13}H_{17}B_{10}N$ (295.40); C, 52.86; H, 5.80; B, 36.60. Found: C, 53.7; H, 6.12; B, 34.01%.

3.16. Reactions of NEt_4[8-I-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] with p-anisylmagnesium bromide (Table 3)

A suspension of 116 mg (0.2 mmol) (Et_4N)[8-I-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)], catalyst, and 1.9 mg (0.01 mmol, 5 mol%) CuI in 5 ml dioxane was treated with anisylmagnesium bromide (0.5 M in diethyl ether) at r.t. The mixture was stirred under reflux for an appropriate time. The resulting mixture was quenched with 0.1 ml aqueous NH_4Cl, diluted with methanol, filtered, and concentrated under reduced pressure. The reaction mixtures were analyzed by ^{1}H NMR.

3.17. $(Et_4N)[8\text{-}(4''\text{-}MeOC_6H_4)\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$

$(Et_4N)[8\text{-}(4''\text{–}MeOC_6H_4)\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$ was prepared according to the general procedure using 580 mg (1.0 mmol) of $(Et_4N)[8\text{-}I\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$, 16 ml of 0.5 M ether solution of anisylmagnesium bromide (8 mmol), 14 mg (0.02 mmol, 2 mol%) $PdCl_2(PPh_3)_2$, and 9.5 mg (0.05 mmol, 5 mol%) CuI. The reaction mixture was heated under reflux for 8 h and then was treated to work-up as described above. Purification of the residue by flash chromatography with $CHCl_3$ as the eluent (to remove nonpolar byproducts) and then with mixture $CHCl_3$-CH_3OH (10:1) gave 476 mg (85% yield) of the desired product as a red-brown solid. The sample for elemental analysis was obtained by recrystallization from ethanol.

^1H NMR (acetone-d_6, ppm): 1.37 (12H, t, 12H, Et_4N^+), 3.45 (8H, q, Et_4N^+), 3.71 (3H, s, OCH_3), 3.76 (2H, br. s, CH_{carb}), 4.59 (2H, br. s, CH_{carb}), 6.71 (2H, d, $J=8.3$ Hz, C_6H_4), 7.21 (2H, d, $J=8.3$ Hz, C_6H_4). ^{11}B NMR (acetone-d_6, ppm): 12.8 (1B, s), 4.8 (1B, d), 2.0 (1B, d), 1.3 (1B, d), −3.6 (2B, d), −5.2 (3B, d), −5.8 (1B, d), −7.0 (2B, d), −17.4 (2B, d), −18.8 (2B, d), −21.8 (1B, d), −23.2 (1B, d). Anal. Calc. for $C_{19}H_{48}B_{18}NOCo$ (560.13); C, 40.74; H, 8.64; B, 34.74; N, 2.50. Found: C, 42.34; H, 8.80; B, 34.72; N, 3.22%.

3.18. Reactions of $NEt_4[8\text{-}I\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$ with diethyl- and dithienylzinc (Table 4)

A suspension of 116 mg (0.2 mmol) $(Et_4N)[8\text{-}I\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$ and catalyst in 5 ml dioxane was treated with diethylzinc (1 M in THF) or dithienylzinc (0.5 M in THF) at r.t. The mixture was stirred under reflux for an appropriate time. The resulting mixture was quenched with 0.1 ml aqueous NH_4Cl, diluted with methanol, filtered, and concentrated under reduced pressure. The reaction mixtures were analyzed by ^1H NMR.

3.19. $(Et_4N)[8\text{-}Et\text{-}3,3'\text{-}Co(C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$

$(Et_4N)[8\text{-}Et\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$ was prepared according to the general procedure using 580 mg (1.0 mmol) of $(Et_4N)[8\text{-}I\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$, 3 ml of 1 M solution of diethylzinc (3 mmol) in THF, and 14 mg (0.02 mmol, 2 mol%) $PdCl_2(PPh_3)_2$. The reaction mixture was heated under reflux for 24 h and then was treated to work-up as described above Purification of the residue by flash chromatography with $CHCl_3$ as the eluent (to remove nonpolar byproducts) and then with mixture $CHCl_3$-CH_3OH (10:1) gave 390 mg (81% yield) of the desired product as a dark orange solid.

^1H NMR (acetone-d_6, ppm): 0.80 (3H, t, CH_2CH_3), 1.29 (2H, q, CH_2CH_3), 1.38 (12H, t, Et_4N^+), 3.46 (8H, q, Et_4N^+), 3.90 (2H, br. s, CH_{carb}), 4.12 (2H, br. s, CH_{carb}). ^{11}B NMR (acetone-d_6, ppm): 18.1 (1B, s), 7.0 (1B, d), 0.4 (2B, d), −5.6 (5B, d), −6.6 (3B, d), −17.4 (2B, d), −17.9 (2B, d), −22.7 (1B, d), −25.24 (1B, d).

3.20. $(Et_4N)[8\text{-}(2''\text{-}C_4H_3S)\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$

$(Et_4N)[8\text{-}(2''\text{-}C_4H_3S)\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$ was prepared according to the general procedure using 580 mg (1.0 mmol) of $(Et_4N)[8\text{-}I\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$, 6 ml of 0.5 M solution of dithienylzinc (3 mmol) in THF, 11.5 mg (0.02 mmol, 2 mol%) $Pd(dba)_2$, and 14 mg (0.05 mmol, 5 mol%) PCy_3. The reaction mixture was heated under reflux for 24 h. Work-up and purification as described above gave 410 mg (76% yield) of the desired product as a red-brown solid. The sample for elemental analysis was obtained by recrystallization from mixture ethanol–water.

^1H NMR (acetone-d_6, ppm): 1.36 (12H, t, Et_4N^+), 3.45 (8H, q, Et_4N^+), 3.93 (2H, br. s, CH_{carb}), 4.61 (2H, br. s, CH_{carb}), 6.76 (1H, d, $J=3.2$ Hz), 6.87 (1H, dd, $J=3.2$, 4.6 Hz), 7.21 (1H, d, $J=4.6$ Hz). ^{11}B NMR (acetone-d_6, ppm): 8.7 (1B, s), 4.8 (1B, d), 1.8 (2B, d), −3.2 (2B, d), −5.41 (4B, d), −6.7 (2B, d), −17.2 (2B, d), −18.9 (2B, d), −21.5 (1B, d), −22.6 (1B, d). Anal. Calc. for $C_{16}H_{44}B_{18}NSCo$ (536.13); C, 35.85; H, 8.27; B, 36.30; S, 5.98; Co, 10.99. Found: C, 35.97; H, 8.25; B, 36.26; S, 5.94; Co, 10.88%.

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References

[1] D.M. Murphy, D.M.P. Mingos, J.M. Forward, J. Mater. Chem. 3 (1993) 139.
[2] W. Jiang, D.E. Harwell, M.D. Mortimer, C.B. Knobler, M.F. Hawthorne, Inorg. Chem. 35 (1996) 4355.
[3] U. Schöberl, T.E. Magnera, R.M. Harrison, F. Fleischer, J.L. Pflug, P.F.H. Schwab, X. Meng, D. Lipiak, B.C. Noll, V.S. Allured, T. Rudalevige, S. Lee, J. Michl, J. Am. Chem. Soc. 119 (1997) 3907.
[4] P. Kaszynski, A.G. Douglas, J. Organomet. Chem. 581 (1999) 28.
[5] D.G. Allis, J.T. Spenser, J. Organomet. Chem. 614 (2000) 309.
[6] R.B. King, Chem. Rev. 101 (2001) 1119.
[7] J.F. Valliant, K.J. Guenther, A.S. King, Coord. Chem. Rev. 232 (2002) 173.

[8] M.F. Hawthorne, Angew. Chem. Int. Ed. Engl. 32 (1993) 950.
[9] Y. Endo, T. Iijima, Y. Yamakoshi, H. Fukasawa, C. Miyaura, M. Inada, A. Kubo, A. Itai, Chem. Biol. 8 (2001) 341.
[10] V.I. Bregadze, Chem. Rev. 92 (1992) 209.
[11] R. Coult, M.A. Fox, W.R. Gill, P.L. Herbertson, J.A.H. MacBride, K. Wade, J. Organomet. Chem. 462 (1993) 19.
[12] W.R. Gill, P.L. Herbertson, J.A.H. MacBride, K. Wade, J. Organomet. Chem. 507 (1996) 249.
[13] M.A. Fox, J.A. MacBride, R.J. Peace, K. Wade, J. Chem. Soc., Dalton Trans. (1998) 401.
[14] Y. Endo, T. Iijima, Y. Yamakoshi, A. Kubo, A. Itai, Bioorg. Med. Chem. Lett. 9 (1999) 3313.
[15] Y. Endo, T. Iijima, Y. Yamakoshi, M. Yamaguchi, H. Fukasawa, K. Shudo, J. Med. Chem. 42 (1999) 1501.
[16] Y. Endo, T. Iijima, T. Yoshimi, Y. Yamakoshi, Bioorg. Med. Chem. Lett. 9 (1999) 3387.
[17] A.S. Batsanov, M.A. Fox, J.A.K. Howard, J.A.H. MacBride, K. Wade, J. Organomet. Chem. 610 (2000) 20.
[18] P. Kaszynski, S. Pakhomov, V.G. Young, Collect. Czech. Chem. Commun. 67 (2002) 1061.
[19] W.J. Marshall Jr., R.J. Young, V.V. Grushin, Organometallics 20 (2001) 523.
[20] (a) J. Li, C.F. Logan, M. Jones Jr., Inorg. Chem. 30 (1991) 4866;
(b) L.I. Zakharkin, V.A. Ol'shevskaya, Russ. J. Gen. Chem. 57 (1987) 317;
(c) Z. Zheng, W. Jiang, A.A. Zinn, C.B. Knobler, M.F. Hawthorne, Inorg. Chem. 34 (1995) 2095;
(d) L.I. Zakharkin, A.I. Kovredov, V.A. Ol'shevskaya, Z.S. Shaugumbekova, J. Organomet. Chem. 226 (1982) 217;
(e) A.I. Kovredov, Z.S. Shaugumbekova, P.V. Petrovskii, L.I. Zakharkin, Russ. J. Gen. Chem. 59 (1989) 537;
(f) L.I. Zakharkin, A.I. Kovredov, V.A. Ol'shevskaya, Bull. Acad. Sci. USSR Div. Chem. Sci. (1981) 1775;
(g) D.M. Murphy, D.M.P. Mingos, J.M. Forward, J. Mater. Chem. 3 (1993) 67;
(h) M.J. Bayer, A. Herzog, M. Diaz, G.A. Harakas, H. Lee, C.B. Knobler, M.F. Hawthorne, Chem. Eur. J. 9 (2003) 2732.
[21] (a) W. Jiang, C.B. Knobler, C.E. Curtis, M.D. Mortimer, M.F. Hawthorne, Inorg. Chem. 34 (1995) 3491;
(b) L.I. Zakharkin, V.A. Ol'shevskaya, Synth. React. Inorg. Met.-Org. Chem. 21 (1991) 1041;
(c) W. Jiang, D.E. Harwell, M.D. Mortimer, C.B. Knobler, M.F. Hawthorne, Inorg. Chem. 35 (1996) 4355.
[22] L. Eriksson, I.P. Beletskaya, V.I. Bregadze, I.B. Sivaev, S. Sjöberg, J. Organomet. Chem. 657 (2002) 267.
[23] L. Eriksson, K.J. Winberg, R.T. Claro, S. Sjöberg, J. Org. Chem. 68 (2003) 3569.
[24] I.B. Sivaev, V.I. Bregadze, Collect. Czech. Chem. Commun. 64 (1999) 783.
[25] M.D. Mortimer, C.B. Knobler, M.F. Hawthorne, Inorg. Chem. 35 (1996) 5750.
[26] L.I. Zakharkin, V.A. Ol'shevskaya, E.V. Balagurova, P.V. Petrovskii, Russ. J. Gen. Chem. 70 (2000) 590.
[27] I. Rojo, F. Teixidor, R. Kivekäs, R. Sillanpää, C. Viñas, Organometallics 22 (2003) 4642.
[28] V.I. Bregadze, I.P. Beletskaya, V.A. Ivushkin, I.B. Sivaev, G.G. Zhigareva, S. Sjöberg, in: Abstract XV FECHEM Conference on Organomet. Chem., Zurich (Switzerland), 10–15 August 2003, OP34.
[29] I. Rojo, F. Teixidor, C. Viñas, R. Kivekäs, R. Sillanpää, Chem. Eur. J. 9 (2003) 4311.
[30] I.B. Sivaev, Z.A. Starikova, S. Sjöberg, V.I. Bregadze, J. Organomet. Chem. 649 (2002) 1.