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Dimethyloxonium and Methoxy Derivatives of *nido*-Carborane and Metal Complexes Thereof

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Received: 27 February 2019; Accepted: 22 March 2019; Published: 27 March 2019

Abstract: 9-Dimethyloxonium, 10-dimethyloxonium, 9-methoxy and 10-methoxy derivatives of *nido*-carborane (9-Me_2O-7,8-$C_2B_9H_{11}$, 10-Me_2O-7,8-$C_2B_9H_{11}$, [9-MeO-7,8-$C_2B_9H_{11}$]$^-$, and [10-MeO-7,8-$C_2B_9H_{11}$]$^-$, respectively) were prepared by the reaction of the parent *nido*-carborane [7,8-$C_2B_9H_{12}$]$^-$ with mercury(II) chloride in a mixture of benzene and dimethoxymethane. Reactions of the 9 and 10-dimethyloxonium derivatives with triethylamine, pyridine, and 3-methyl-6-nitro-1*H*-indazole result in their N-methylation with the formation of the corresponding salts with 9 and 10-methoxy-*nido*-carborane anions. The reaction of the symmetrical methoxy derivative [10-MeO-7,8-$C_2B_9H_{11}$]$^-$ with anhydrous $FeCl_2$ in tetrahydrofuran in the presence of *t*-BuOK results in the corresponding paramagnetic iron bis(dicarbollide) complex [8,8′-$(MeO)_2$-3,3′-Fe(1,2-$C_2B_9H_{10})_2$]$^-$, whereas the similar reactions of the asymmetrical methoxy derivative [9-MeO-7,8-$C_2B_9H_{11}$]$^-$ with $FeCl_2$ and $CoCl_2$ presumably produce the 4,7′-isomers [4,7′-$(MeO)_2$-3,3′-M(1,2-$C_2B_9H_{10})_2$]$^-$ (M = Fe, Co) rather than a mixture of *rac*-4,7′- and *meso*-4,4′-isomers.

Keywords: *nido*-carborane; iron bis(dicarbollide); cobalt bis(dicarbollide); dimethyloxonium derivatives; methoxy derivatives; synthesis; properties

1. Introduction

Cyclic oxonium derivatives of polyhedral boron hydrides are well studied due to their use as convenient starting compounds for the preparation of various functional derivatives [1,2]. In particular, this approach was used for synthesis of various derivatives of *nido*-carborane, including boron-containing biomolecules [3–5] and crown ethers [6,7]. At the same time, in the literature there are only a few examples of acyclic oxonium derivatives of polyhedral boron hydrides [8–14], and to the best of our knowledge, there are no examples of dimethyloxonium derivatives.

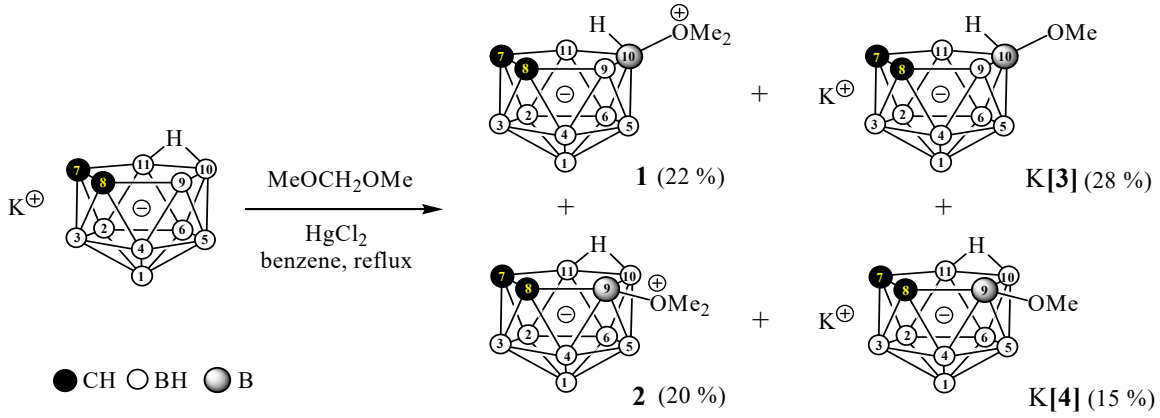
In this contribution we describe synthesis of dimethyloxonium derivatives of *nido*-carborane [9-Me_2O-7,8-$C_2B_9H_{11}$] and [10-Me_2O-7,8-$C_2B_9H_{11}$], their demethylation reactions to the corresponding methoxy derivatives [9-MeO-7,8-$C_2B_9H_{11}$]$^-$ and [10-MeO-7,8-$C_2B_9H_{11}$]$^-$ as well as the formation of ferra- and cobaltacarborane complexes thereof.

2. Results and Discussion

Electrophile-induced nucleophilic substitution (EINS) reactions of *nido*-carboranes with a various nucleophiles are well known and widely used for their modification. Typical are $HgCl_2$-mediated reactions of *nido*-carborane with nucleophilic solvents resulting in the [10-L-7,8-$C_2B_9H_{11}$] (L = 1,4-dioxane [15], tetrahydrofuran [15,16], tetrahydropyran [17], alkylnitriles [18], and pyridine [16]) derivatives. It is assumed that initially formed mercuric derivatives [19,20] decompose at elevated temperatures to form quasi-borinium cations, which acts as the potent Lewis acids [21] react with nucleophilic solvent molecules. The corresponding acyclic oxonium derivatives of polyhedral boron hydrides are much less studied and limited mainly by diethoxy derivatives [8–14]. Since dimethyl ether is gaseous under normal conditions, working with it at elevated temperatures is possible only with the use of high-pressure vessels that is normally unacceptable in common laboratories.

The comparative analysis of ^{1}H NMR spectral data of a series of polyhedral boron hydride derivatives BL (L = SMe_2, 1,4-dioxane) and the corresponding MX_5L complexes (M = Nb, Ta; X = F, Cl) demonstrated their very close similarity that could be explained by comparable electronic effects of the metal and boron moieties in these compounds [22]. It is known that $NbCl_5$ is effective reagent for removal of the methoxy methyl ether protecting group in organic synthesis [23]. More detailed study of reactions of MX_5 (M = Nb, Ta; X = F, Cl) with acetals/ketals (1,1-dialkoxyalkanes) or trimethylformate revealed that the ethereal bonds can be broken by the MX_5 Lewis acids and the rate of the process is enhanced by the presence of the further vicinal ether function. The reaction pathway was found to include formation of the $MX_5(OMe_2)$ complexes, which were identified by NMR spectroscopy [24,25]. It prompted us to study reaction of *nido*-carborane with dimethoxymethane $MeOCH_2OMe$ in the presence of $HgCl_2$.

We found that the reaction of potassium 7,8-dicarba-*nido*-undecaborate K[7,8-$C_2B_9H_{12}$] with mercury(II) chloride in a mixture of dimethoxymethane and benzene results in the formation of mixture of symmetrically and asymmetrically substituted dimethyloxonium derivatives **1** and **2**, as well as the corresponding methoxy derivatives K[**3**] and K[**4**] (Scheme 1), that was separated by column chromatography on silica.



Scheme 1. Preparation of dimethyloxonium and methoxy derivatives of *nido*-carborane.

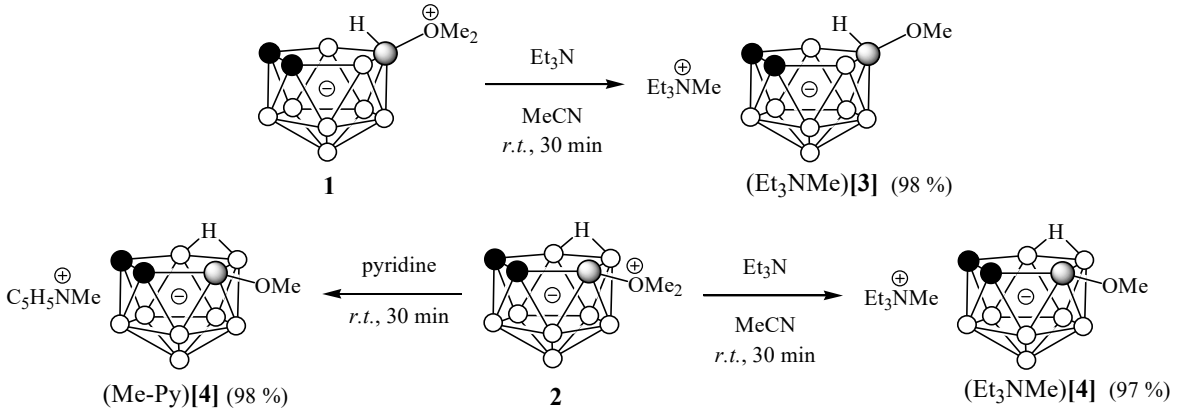
The ^{11}B{^{1}H} NMR spectrum of **1** displays characteristic 1:2:2:2:1:1 pattern with signals at −8.8, −12.4, −16.9, −21.8, −22.3 and −39.5 ppm, respectively, that agree well with the planar symmetry of B(10)-substituted *nido*-carborane cage. The signal corresponding to the B(10) atom is observed at −8.8 ppm that is close to the corresponding signals in other oxonium derivatives of *nido*-carborane [10-R_2O-7,8-$C_2B_9H_{11}$] [11,15,17]. The ^{1}H NMR spectrum of **1** contains signal of the dimethyloxonium group at 4.17 ppm, signal of the carborane CH groups at 1.94 ppm, broad signal of the BH groups in the range 2.6–0.1 ppm and signal of the *endo*-BH hydrogen at −2.6 ppm. The ^{13}C NMR spectrum of **1** contains signals of the dimethyloxonium group and the carborane CH groups at 73.4 ppm and

43.1 ppm, respectively. Taking into account the strong electron-donating effect of the boron cage, the signals of the dimethyloxonum group are very close to those of the trimethyloxonium cation Me_3O^+ (4.68 and 78.8 ppm, respectively) [26].

The $^{11}B\{^1H\}$ NMR spectrum of **2** contains nine non-equivalent signals at 8.3, −12.9, −13.8, −19.1, −21.9, −22.8, −25.3, −34.0, and −39.9 ppm, which is consistent with asymmetry of B(9)-substituted *nido*-carborane cage. The signal corresponding to the B(9) is observed at 8.3 ppm, which is close to the corresponding signal in the diethyloxonium derivative [9-Et_2O-7,8-$C_2B_9H_{11}$] [11]. The ^1H NMR spectrum of **2** contains signal of the dimethyloxonium group at 4.12 ppm, signals of the carborane CH groups at 1.94 and 2.02 ppm, broad signal of the BH groups in the range 2.6–0.1 ppm and signal of the bridging BHB hydrogen at −2.5 ppm. It is worth noting that, unlike the analogous dimethylsulfonium derivative [9-Me_2S-7,8-$C_2B_9H_{11}$] where the methyl groups are not equivalent [27] due to interaction of a sulfur lone pair with the B9-B10 antibonding orbital of the *nido*-carborane cage [28], both methyl groups in **2** are equivalent indicating free rotation around the B-O bond and low inversion barrier at the oxygen atom. The ^{13}C NMR spectrum of **2** contains signals of the dimethyloxonium group at 72.0 ppm and the carborane CH groups at 41.5 and 34.4 ppm.

In the ^1H NMR spectra of K[**3**] and K[**4**] the signals of methoxy groups are shifted to high field in comparison with **1** and **2** up to 3.22 and 3.17 ppm, respectively, and appear as 1:1:1:1 quartets due to long-range B–H coupling ($^3J_{B,H}$ = 3.7–3.8 Hz). Such coupling has also been previously observed for some organoboron compounds [29–32], methylsulfanyl derivatives of the *closo*-dodecaborate anion [33,34] and *B*-methysulfanyl derivatives of cobalt bis(dicarbollide) anion [35].

The dimethyloxonium derivatives of *nido*-carborane can be easily demethylated to the corresponding methoxy derivatives with triethylamine or pyridine within 30 min at ambient temperature (Scheme 2). These results demonstrated that the dimethyloxonium derivatives **1** and **2** are active methylating agents.



Scheme 2. Demethylation of dimethyloxonium derivatives of *nido*-carborane.

This prompted us to study reactions of **1** and **2** with 3-methyl-6-nitro-1*H*-indazole. This compound is a starting material for the manufacture of pazopanib hydrochloride (Figure 1). Pazopanib hydrochloride is tyrosine kinase inhibitor and is used clinically as angiogenesis modulating and antineoplastic agent [36]. The first stage of its manufacture includes *N*-methylation of 3-methyl-6-nitro-1*H*-indazole. This process is critical stage since desirable 2,3-dimethyl-6-nitro-2*H*-indazole (**5**) is always contaminated with isomeric 1,3-dimethyl-6-nitro-1*H*-indazole (**6**). Several papers have reported optional reagents and conditions for preparation of **5** [37–39], however, laborious recrystallizations have been still required to purify **5** from isomeric **6**.

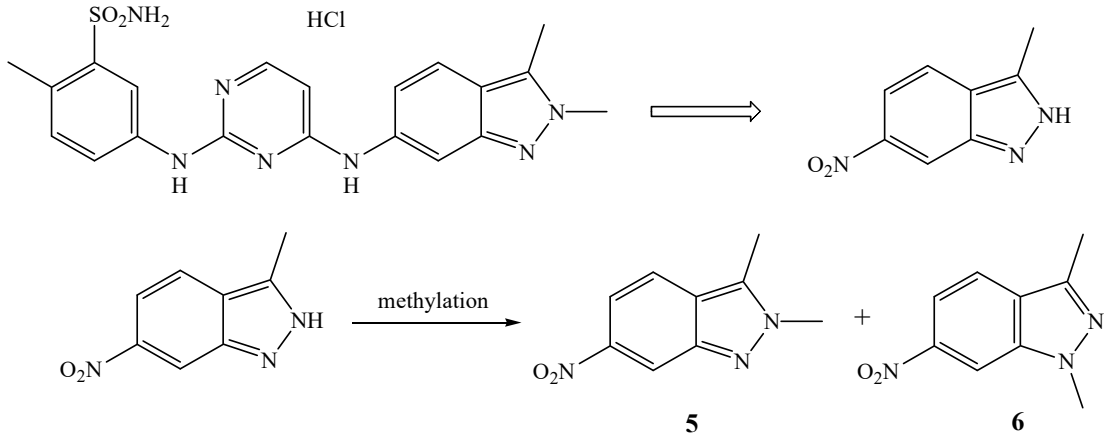
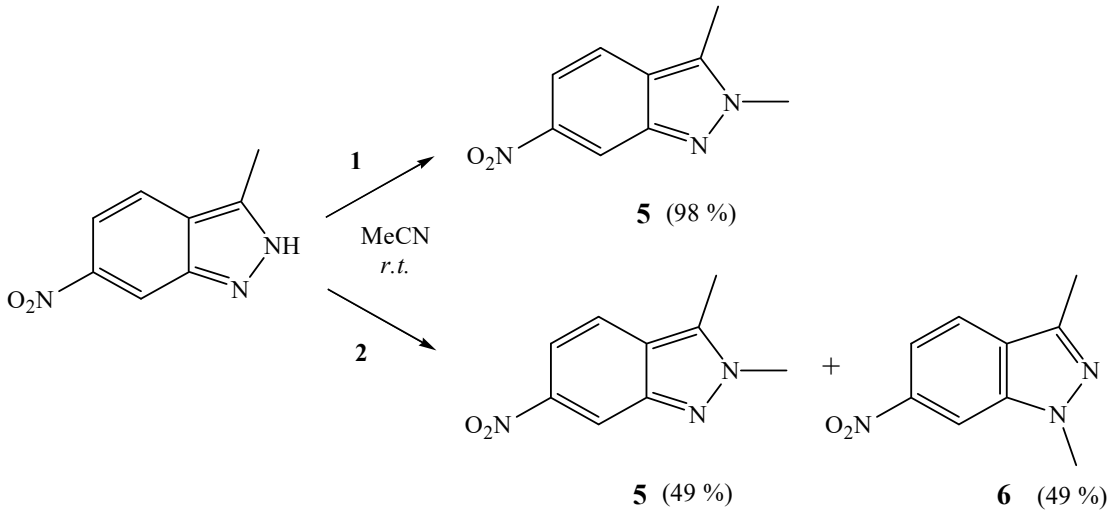


Figure 1. Pazopanib hydrochloride and critical stage of its manufacture.

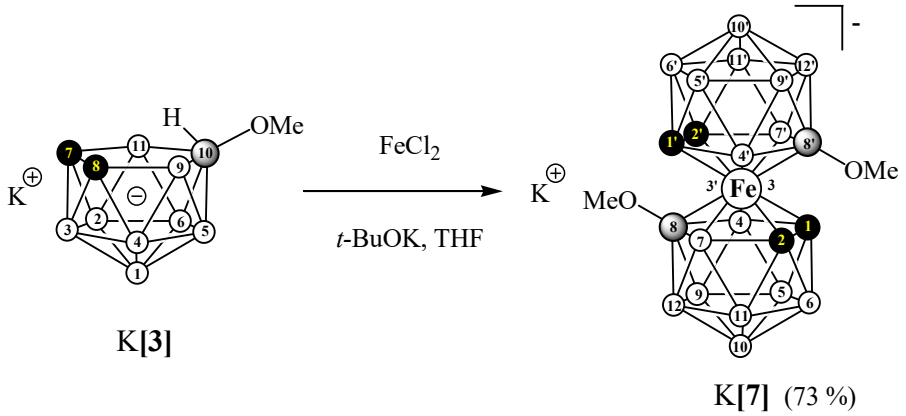
Indeed, the both dimethyloxonium derivatives of *nido*-carborane were found to *N*-methylate 3-methyl-6-nitro-1*H*-indazole, however, the results of these reactions were different (Scheme 3). The reaction of 3-methyl-6-nitro-1*H*-indazole with **2** in acetonitrile at room temperature followed by aqueous alkaline treatment led to a 1:1 mixture of **5** and **6** which were resolved by column chromatography on silica. To our best knowledge, indazole **6** was not described previously. Surprisingly, the reaction of 3-methyl-6-nitro-1*H*-indazole with **1** resulting in the regioselective formation of desired compound **5** with almost a quantitative yield.



Scheme 3. Methylation of 3-methyl-6-nitro-1*H*-indazole by 9-dimethyloxonium and 10-dimethyloxonium derivatives of *nido*-carborane.

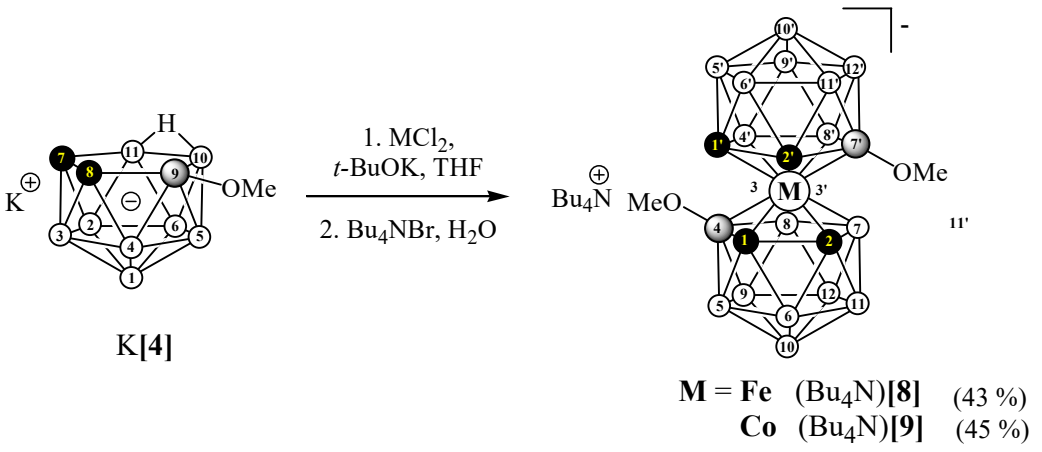
Transition metal complexes with carborane ligands, or metallacarboranes, found application in a wide variety of fields including nuclear fuel reprocessing [40,41], catalysis [42], new material design [43–46], medicine [4,5,47–52], etc. Therefore the obtained methoxy derivatives of *nido*-carborane K[**3**] and K[**4**] were used for synthesis the corresponding iron and cobalt bis(dicarbollide) complexes. Earlier we described the synthesis of symmetric 8,8′-dimethoxy derivative of cobalt bis(dicarbollide) [8,8′-$(MeO)_2$-3,3′-Co(1,2-$C_2B_9H_{10})_2]^-$ by alkylation of the corresponding dihydroxy derivative [53]. In this contribution we report synthesis of analogous paramagnetic 8,8′-dimethoxy derivative of iron bis(dicarbollide) K[8,8′-$(MeO)_2$-3,3′-Fe(1,2-$C_2B_9H_{10})_2$] (K[**7**]) by the reaction of K[**3**] with anhydrous $FeCl_2$ in tetrahydrofuran in the presence of potassium *tert*-butoxide (Scheme 4). The ^{11}B NMR spectrum of $[\mathbf{7}]^-$ contains signals at 114.6, 6.2, −8.0 and −69.1 ppm corresponding to boron atoms, which are

the most distant from the metal atom, and the wide high-field signal at −443.2 ppm due to the boron atoms, which are directly connected to the metal with a general relative integral ratio 2:4:4:2:6.



Scheme 4. Synthesis of 8,8′-dimethoxy derivative of iron bis(dicarbollide).

Unlike the 9-methylsulfide derivative [9-MeS-7,8-$C_2B_9H_{11}$]$^-$, the reaction of asymmetric K[**4**] with anhydrous $FeCl_2$ unexpectedly gave a single isomer [**8**]$^-$ instead of mixture of *rac*- and *meso*-diastereomers (Scheme 5). The ^{11}B NMR spectrum of [**8**]$^-$ contains signals at 109.5, 9.7, 7.5, 1.1, −21.8 and −40.7 ppm corresponding to boron atoms which are the most distant from the metal atom, and the wide high-field signals at −403.4, −431.7, and −461.1 ppm due to the boron atoms, which are directly connected to the metal with general relative integral ratio 2:2:2:2:2:2:2:2:2. Based on the comparison of this spectrum with the ^{11}B NMR spectra of the methylsulfide derivatives *rac*-[4,7′-$(MeS)_2$-3,3′-Fe(1,2-$C_2B_9H_{10})_2$]$^-$ and *meso*-[4,4′-$(MeS)_2$-3,3′-Fe(1,2-$C_2B_9H_{10})_2$]$^-$ [54], we tentatively identified the compound obtained as the 4,7′-isomer *rac*-[4,7′-$(MeO)_2$-3,3′-Fe(1,2-$C_2B_9H_{10})_2$]$^-$. In a similar way, the reaction of K[**4**] with anhydrous $CoCl_2$ in tetrahydrofuran in the presence of potassium *tert*-butoxide gave diamagnetic *rac*-[4,7′-$(MeO)_2$-3,3′-Co(1,2-$C_2B_9H_{10})_2$]$^-$ as the single isomer (Scheme 5). The ^{11}B NMR spectrum of [**9**]$^-$ contains singlets at 13.9 ppm and doublets at 5.2, −0.8, −7.9, −9.0, −19.8, and −24.6 ppm with an integral intensity ratio 2:2:2:4:2:4:2. The ^{1}H NMR spectrum of [**9**]$^-$ contains the 1:1:1:1 quartet of the methoxy group at 3.23 ppm ($^3J_{B,H}$ = 3.9 Hz), signals of the carborane CH groups at 3.81 and 3.70 ppm and broad signal of the BH groups in the range 2.6–0.5 ppm.



Scheme 5. Synthesis of 4,7′-dimethoxy derivatives of iron and cobalt bis(dicarbollides).

The reason for the formation of solely the 4,7′-isomers of the dimethoxy derivatives of iron and cobalt bis(dicarbollides) is not very clear, but it probably caused by a lower stability of the corresponding 4,4′-isomers.

3. Materials and Methods

3.1. General Procedures and Instrumentation

The potassium salt of 7,8-dicarba-*nido*-caborane was prepared according to the literature procedure [55]. Dimethoxymethane, tetrahydrofuran and iron(II) chloride were purchased from Sigma-Aldrich and used without further purification. Triethylamine, pyridine, 3-Methyl-6-nitro-1*H*-indazole, ethyl acetate and benzene were commercially analytical grade reagents and used without further treatment. Acetonitrile was dried by distillation over CaH_2 using the standard procedure [56]. Anhydrous $CoCl_2$ was prepared by dehydration of $CoCl_2 \cdot 6H_2O$ using the standard procedure [57]. The reaction progress was monitored by a TLC (Merck F254 silica gel on aluminum plates) and visualized using 0.5% $PdCl_2$ in 1% HCl in aq. MeOH (1:10). Acros Organics silica gel (0.060–0.200 mm) was used for column chromatography. The NMR spectra at 400.1 MHz (^{1}H), 128.4 MHz (^{11}B) and 100.0 MHz (^{13}C) were recorded with a Bruker Avance-400 spectrometer (Bruker, Zurich, Switzerland) (See Supplementary Materials). The residual signal of the NMR solvent relative to tetramethylsilane was taken as the internal reference standard for ^{1}H and ^{13}C NMR spectra. ^{11}B NMR spectra were referenced using $BF_3 \cdot Et_2O$ as the external standard. Infrared spectra were recorded on an IR Prestige-21 (SHIMADZU) instrument (Shimadzu Corporation, Duisburg, Germany). High resolution mass spectra (HRMS) were measured on a Bruker micrOTOF II instrument (Bruker, Bremen, Germany) using electrospray ionization (ESI). The measurements were done in a negative ion mode (3200 V); mass range from *m*/*z* 50 to *m*/*z* 3000; external or internal calibration was done with ESI Tuning Mix, Agilent (Santa Clara, CA, USA). A syringe injection was used for solutions in acetonitrile (flow rate 3 mL/min). Nitrogen was applied as a dry gas; interface temperature was set at 180 °C. The electron ionization mass spectra were obtained with a Kratos MS 890 instrument (Kratos Analytical Ltd, Manchester, UK) operating in a mass range of *m*/*z* 50–800.

3.2. Synthesis

3.2.1. Preparation of 10-Me_2O-7,8-$C_2B_9H_{11}$ (**1**), 9-Me_2O-7,8-$C_2B_9H_{11}$ (**2**), K[10-MeO-7,8-$C_2B_9H_{11}$] (K[**3**]), and K[9-MeO-7,8-$C_2B_9H_{11}$] (K[**4**])

The potassium salt of 7,8-dicarba-*nido*-undecaborate (1.00 g, 5.80 mmol) and mercury(II) chloride (1.60 g, 5.80 mmol) in a mixture of benzene (20 mL) and dimethoxymethane (20 mL) was heated under reflux for about 4 h. After cooling to room temperature, the solution was decanted, and the residue was washed with benzene. The washings were combined with the solution and evaporated under reduced pressure. The column chromatography on silica gel was used for the separation of the substances with ethyl acetate as an eluent to give white crystalline products **1**–**4**. The first fraction (TLC R_F = 0.88) contained **2**, the second (TLC R_F = 0.81) contained **1**, the third (TLC R_F = 0.62) was identified as **4**, and the fourth (TLC R_F = 0.17) contained **3**.

1. Yield 0.23 g (22%). ^{1}H NMR ($CDCl_3$, ppm): δ 4.17 (s, 6H, OC*H*$_3$), 2.03 (s, 2H, C*H*$_{carb}$), 2.9–0.1 (br s, 8H, B*H*), −2.6 (br s, 1H, B*H*B). ^{13}C NMR ($CDCl_3$, ppm): δ 73.4 (OCH_3), 43.1 (CH_{carb}). ^{11}B NMR ($CDCl_3$, ppm): δ −8.8 (s, 1B), −12.4 (d, *J* = 144 Hz, 2B), −16.9 (d, *J* = 137 Hz, 2B), −21.8 (d, *J* = 150 Hz, 2B), −22.3 (d, *J* = 126 Hz, 1B), −39.5 (d, *J* = 145 Hz, 1B). IR (film, cm^{-1}): 3035 (br, $\nu_{C–H}$), 2963 (br, $\nu_{C–H}$), 2918 (br, $\nu_{C–H}$), 2849 (br, $\nu_{C–H}$), 2545 (br, $\nu_{B–H}$), 1464, 1447, 1425, 1260. MS (EI) for $C_4H_{17}B_9O$: calcd. *m/z* 178 [M]$^+$, obsd. *m/z* 178 [M]$^+$.

2. Yield 0.21 g (20%). ^{1}H NMR ($CDCl_3$, ppm): δ 4.12 (s, 6H, OC*H*$_3$), 2.02 (s, 1H, C*H*$_{carb}$), 1.94 (s, 1H, C*H*$_{carb}$), 2.6–0.1 (br s, 8H, B*H*), −2.5 (br s, 1H, B*H*B). ^{13}C NMR ($CDCl_3$, ppm): δ 72.0 (OCH_3), 41.5 (CH_{carb}), 34.4 (CH_{carb}). ^{11}B NMR ($CDCl_3$, ppm): δ 8.3 (s, 1B), −12.9 (d, *J* = 128 Hz, 1B), −13.8 (d, *J* = 131 Hz, 1B), −19.1 (d, *J* = 166 Hz, 1B), −21.9 (d, *J* = 135 Hz, 1B), −22.8 (d, *J* = 126 Hz, 1B), −25.3 (d, *J* = 151 Hz, 1B), −34.0 (dd, *J* = 137 Hz, *J* = 54 Hz, 1B), −39.9 (d, *J* = 144 Hz, 1B). IR (film, cm^{-1}): 3031 (br,

$\nu_{C–H}$), 2963 (br, $\nu_{C–H}$), 2925 (br, $\nu_{C–H}$), 2863 (br, $\nu_{C–H}$), 2524 (br, $\nu_{B–H}$), 1464, 1448, 1423, 1260. MS (EI) for $C_4H_{17}B_9O$: calcd. *m/z* 178 $[M]^+$, obsd. *m/z* 178 $[M]^+$.

K[**3**]. Yield 0.33 g (28%). ^{1}H NMR (acetone-d_6, ppm): δ 3.22 (q (1:1:1:1), $^3J_{B,H}$ = 3.7 Hz, 3H, OCH_3), 1.47 (s, 2H, CH_{carb}), 2.7–0.0 (br s, 8H, B*H*), −0.6 (br s, 1H, B*H*B). ^{13}C NMR (acetone-d_6, ppm): δ 56.8 (OCH_3), 38.3 (CH_{carb}). ^{11}B NMR (acetone-d_6, ppm): δ −8.7 (s, 1B), −12.4 (d, *J* = 137 Hz, 2B), −17.5 (d, *J* = 136 Hz, 2B), −24.1 (d, *J* = 156 Hz, 2B), −25.4 (d, *J* = 167 Hz, 1B), −40.6 (d, *J* = 143 Hz, 1B). IR (film, cm^{-1}): 3031 (br, $\nu_{C–H}$), 2983 (br, $\nu_{C–H}$), 2931 (br, $\nu_{C–H}$), 2885 (br, $\nu_{C–H}$), 2526 (br, $\nu_{B–H}$), 1458, 1394, 1206. ESI HRMS for $C_3H_{14}B_9O^-$: calcd. *m/z* 164.1926, obsd. *m/z* 164.1926.

K[**4**]. Yield 0.18 g (15%). ^{1}H NMR (acetone-d_6, ppm): δ 3.17 (q (1:1:1:1), $^3J_{B,H}$ = 3.8 Hz, 3H, OCH_3), 1.53 (s, 1H, CH_{carb}), 1.34 (s, 1H, CH_{carb}), 2.5–0.0) (br s, 8H, B*H*), −3.0 (br s, 1H, B*H*B). ^{13}C NMR (acetone-d_6, ppm): δ 55.1 (OCH_3), 39.6 (CH_{carb}), 25.8 (CH_{carb}). ^{11}B NMR (acetone-d_6, ppm): δ 11.2 (s, 1B), −12.3 (d, *J* = 132 Hz, 1B), −16.2 (d, *J* = 136 Hz, 1B), −19.7 (d, *J* = 157 Hz, 1B), −21.7 (d, *J* = 151 Hz, 1B), −25.5 (d, *J* = 135 Hz, 2B), −31.3 (dd, *J* = 138 Hz, *J* = 55 Hz, 1B), −38.7 (d, *J* = 136 Hz, 1B). IR (film, cm^{-1}): 3035 (br, $\nu_{C–H}$), 2986 (br, $\nu_{C–H}$), 2948 (br, $\nu_{C–H}$), 2930 (br, $\nu_{C–H}$), 2525 (br, $\nu_{B–H}$), 1483, 1451, 1209. ESI HRMS for $C_3H_{14}B_9O^-$: calcd. *m/z* 164.1926, obsd. *m/z* 164.1927.

3.2.2. Reactions of 10-Me_2O-7,8-$C_2B_9H_{11}$ and 9-Me_2O-7,8-$C_2B_9H_{11}$ with Triethylamine

To a solution of **1** (0.10 g, 0.49 mmol) or **2** (0.10 g, 0.49 mmol) in acetonitrile (1 mL), trimethylamine (0.68 mL, 4.90 mmol) was added. The mixture was stirred at room temperature for about 1 h and the solution was evaporated under reduced pressure to give yellow crystalline products (Et_3NMe)[**3**] or (Et_3NMe)[**4**], respectively.

(Et_3NMe)[**3**]. Yield 0.13 g (97%). ^{1}H NMR (acetone-d_6, ppm): δ 3.57 (q, *J* = 7.2 Hz, 6H, *Et$_3$NMe*$^+$), 3.22 (q (1:1:1:1), $^3J_{B,H}$ = 3.7 Hz, 3H, OCH_3), 3.19 (s, 3H, Et_3NMe^+), 1.45 (tt, *J* = 7.2 Hz, *J* = 1.9 Hz, 11H, Et_3NMe^+ + CH_{carb}), 2.7–0.0 (br s, 8H, B*H*), −0.6 (br s, 1H, B*H*B). ^{13}C NMR (acetone-d_6, ppm): δ 56.2 (OCH_3), 55.9 (t, Et_3NMe^+), 46.4 (t, Et_3NMe^+), 38.3 (CH_{carb}), 7.2 (Et_3NMe^+). ^{11}B NMR (acetone-d_6, ppm): δ −8.7 (s, 1B), −12.4 (d, *J* = 132 Hz, 2B), −17.5 (d, *J* = 135 Hz, 2B), −24.2 (d, *J* = 155 Hz, 2B), −25.5 (d, *J* = 171 Hz, 1B), −40.5 (d, *J* = 140 Hz, 1B). IR (film, cm^{-1}): 3030 (br, $\nu_{C–H}$), 2982 (br, $\nu_{C–H}$), 2929 (br, $\nu_{C–H}$), 2886 (br, $\nu_{C–H}$), 2819, 2524 (br, $\nu_{B–H}$), 1456, 1391, 1376, 1303, 1260, 1205. ESI HRMS for $C_3H_{14}B_9O^-$: calcd. *m/z* 164.1926, obsd. *m/z* 164.1925.

(Et_3NMe)[**4**]. Yield 0.14 g (98%). ^{1}H NMR (acetone-d_6, ppm): δ 3.55 (q, *J* = 7.2 Hz, 6H, Et_3NMe^+), 3.17 (s, 6H, OCH_3 + Et_3NMe^+), 1.53 (s, 1H, CH_{carb}), 1.44 (tt, *J* = 7.2 Hz, *J* = 1.9 Hz, 9H, Et_3NMe^+), 1.34 (s, 1H, CH_{carb}), 2.5–0.0 (br s, 8H, B*H*), −2.9 (br s, 1H, B*H*B). ^{13}C NMR (acetone-d_6, ppm): δ 55.9 (t, Et_3NMe^+), 55.2 (OCH_3), 46.4 (t, Et_3NMe^+), 39.3 (CH_{carb}), 25.9 (CH_{carb}), 7.2 (Et_3NMe^+). ^{11}B NMR (acetone-d_6, ppm): δ 11.0 (s, 1B), −12.4 (d, *J* = 131 Hz, 1B), −16.2 (d, *J* = 137 Hz, 1B), −19.7 (d, *J* = 156 Hz, 1B), −21.6 (d, *J* = 151 Hz, 1B), −25.5 (d, *J* = 139 Hz, 2B), −31.2 (dd, *J* = 139 Hz, *J* = 55 Hz, 1B), −38.7 (d, *J* = 135 Hz, 1B). IR (film, cm^{-1}): 3395, 3214, 3034 (br, $\nu_{C–H}$), 2987 (br, $\nu_{C–H}$), 2949 (br, $\nu_{C–H}$), 2931 (br, $\nu_{C–H}$), 2821, 2520 (br, $\nu_{B–H}$), 1486, 1456, 1396 1208. ESI HRMS for $C_3H_{14}B_9O^-$: calcd. *m/z* 164.1926, obsd. *m/z* 164.1944.

3.2.3. Reaction of 9-Me_2O-7,8-$C_2B_9H_{11}$ with Pyridine

Compound **2** (0.10 g, 0.49 mmol) and pyridine (4.90 mmol, 0.4 mL) were stirred at room temperature for about 1 h and the solution was evaporated under reduced pressure to give yellow crystalline product (*N*-MePy)[**4**]. Yield 0.12 g (98%). ^{1}H NMR (acetone-d_6, ppm): δ 9.16 (d, *J* = 5.9 Hz, 2H, *o*-H_{Ar}), 8.75 (t, *J* = 7.8 Hz, 1H, *p*-H_{Ar}), 8.29 (m, 2H, *m*-H_{Ar}), 4.66 (s, 3H, NCH_3), 3.16 (q (1:1:1:1), $^3J_{B,H}$ = 3.8 Hz, 3H, OCH_3), 1.53 (s, 1H, CH_{carb}), 1.34 (s, 1H, CH_{carb}), 2.5–0.0 (br s, 8H, B*H*), −3.0 (br s, 1H, B*H*B). ^{13}C NMR (acetone-d_6, ppm): δ 145.8 (t, *o*-C_{Ar}), 145.5 (*p*-C_{Ar}), 128.2 (*m*-C_{Ar}), 55.0 (OCH_3), 48.3 (t, NCH_3), 39.6 (CH_{carb}), 25.9 (CH_{carb}). ^{11}B NMR (acetone-d_6, ppm): δ 11.2 (s, 1B), −12.3 (d, *J* = 131 Hz, 1B), −16.2 (d, *J* = 137 Hz, 1B), −19.7 (d, *J* = 158 Hz, 1B), −21.7 (d, *J* = 147 Hz, 1B), −25.5 (d, *J* = 136 Hz,

2B), −31.1 (dd, *J* = 139 Hz, *J* = 55 Hz, 1B), −38.7 (d, *J* = 135 Hz, 1B). IR (film, cm^{-1}): 3139, 3133, 3074, 2955 (br, $\nu_{C–H}$), 2930 (br, $\nu_{C–H}$), 2917 (br, $\nu_{C–H}$), 2890 (br, $\nu_{C–H}$), 2848, 2823, 2516 (br, $\nu_{B–H}$), 1636, 1498, 1490, 1287, 1259, 1207. ESI HRMS for $C_3H_{14}B_9O^-$: calcd. *m/z* 164.1926, obsd. *m/z* 164.1943.

3.2.4. Reactions of 10-Me_2O-7,8-$C_2B_9H_{11}$ and 9-Me_2O-7,8-$C_2B_9H_{11}$ with 3-Methyl-6-nitro-1*H*-indazole

a. To a solution of **1** (30 mg, 0.17 mmol) in dried acetonitrile (1 mL) under an Ar atmosphere 3-methyl-6-nitro-1*H*-indazole (20 mg, 0.11 mmol) was added. The mixture was stirred at room temperature for about 5 days and the solution was evaporated under reduced pressure. An aqueous solution of 30% KOH (5 mL) was added. The solution was dropped off and the formed yellow residue was washed with water and extracted with AcOEt. The residue was purified form the remained *nido*-carborane by column chromatography with 1:3 *n*-hexane/AcOEt to give the only product 5 as a yellow solid (20 mg, 98%). This product has been described previously and our obtained NMR data perfectly matched with data represented in the literature [36–38].

b. The procedure was analogous to that described for **3.2.4(a)** using **2** (30 mg, 0.17 mmol) and 3-methyl-6-nitro-1*H*-indazole (20 mg, 0.11 mmol) to give the mixture 1:1 of **5** and **6**. Products were separated by column chromatography with 1:3 *n*-hexane/AcOEt. The first band (TLC R_F = 0.35) contained **5** (10 mg, 49%), the second (TLC R_F = 0.20) was identified as **6** (10 mg, 49%).

NMR data for **5**. ^{1}H NMR (DMSO-d_6, ppm): δ 8.52 (d, *J* = 1.6 Hz, 1H, *H*-7), 7.94 (d, *J* = 9.1 Hz, 1H, *H*-5), 7.74 (dd, *J* = 9.1 Hz, *J* = 1.9 Hz, 1H, *H*-6), 4.16 (s, 3H, 2-CH_3), 2.68 (s, 3H, 3-CH_3).

NMR data for **6**. ^{1}H NMR (DMSO-d_6, ppm): δ 8.63 (d, *J* = 1.4 Hz, 1H, *H*-7), 7.95 (d, *J* = 8.8 Hz, 1H, *H*-5), 7.90 (dd, *J* = 8.8 Hz, *J* = 1.7 Hz, 1H, *H*-6), 4.10 (s, 3H, 2-CH_3), 2.54 (s, 3H, 3-CH_3). ^{13}C NMR (DMSO-d_6, ppm): δ 146.2, 141.5, 139.4, 126.0, 121.8, 114.2, 107.0, 36.0, 11.8.

3.2.5. Synthesis of K[8,8′-$(MeO)_2$-3,3′-Fe(1,2-$C_2B_9H_{10})_2$] (K[**7**])

To a solution of K[**3**] (0.20 g, 0.98 mmol) in dried tetrahydrofuran under argon atmosphere potassium *tert*-butoxide (0.55 g, 4.92 mmol) and anhydrous $FeCl_2$ (0.62 g, 4.92 mmol) were added. The reaction mixture was refluxed for 12 h and left overnight in the air. The solid was filtered off and the filtrate was evaporated under reduced pressure. The residue was dissolved in acidified water (1 mL of HCl in 30 mL of H_2O) and extracted by diethyl ether (2 × 30 mL). Organic fractions were collected and evaporated under reduced pressure to give 0.15 g (73%) of dark red solid. ^{1}H NMR (acetone-d_6, ppm): δ 79.7 (br s, 4H, CH_{carb}/B*H*), 53.5 (br s, 4H, CH_{carb}/B*H*), 29.5 (br q, *J* = 129 Hz, 2H, B*H*), 2.7 (br m, 4H, B*H*), −6.0 (s, 6H, OCH_3), −10.1 (br q, *J* = 166 Hz, 4H, B*H*), −24.1 (br q, 2H, B*H*). ^{13}C NMR (acetone-d_6, ppm): δ 70.2 (OCH_3), −398.0 (CH_{carb}), −408.0 (CH_{carb}). ^{11}B NMR (acetone-d_6, ppm): δ 114.6 (d, 2B), −6.2 (d, 4B), −8.0 (d, 4B), −69.1 (d, 2B), −443.2 (br s, 6B). IR (film, cm^{-1}): 3034 (br, $\nu_{C–H}$), 2952 (br, $\nu_{C–H}$), 2926 (br, $\nu_{C–H}$), 2856 (br, $\nu_{C–H}$), 2564 (br, $\nu_{B–H}$), 1696, 1488, 1458, 1377. ESI HRMS for $C_6H_{26}B_{18}FeO_2^-$: calcd. *m/z* 381.3077, obsd. *m/z* 381.3069.

3.2.6. Synthesis of (Bu_4N)[4,7′-$(MeO)_2$-3,3′-Fe(1,2-$C_2B_9H_{10})_2$] ((Bu_4N)[**8**])

To a solution of K[**4**] (0.20 g, 0.98 mmol) in dried tetrahydrofuran under argon atmosphere potassium *tert*-butoxide (0.55 g, 4.92 mmol) and anhydrous $FeCl_2$ (0.62 g, 4.92 mmol) were added. The reaction mixture was refluxed for 12 h. and left overnight in the air. The solid was filtered off and the filtrate was evaporated under reduced pressure. The residue was dissolved in acidified water (1 mL of HCl in 30 mL of H_2O) and extracted by diethyl ether (2 × 30 mL). Organic fractions were collected and evaporated under reduced pressure. The resedue was dissolved in water (10 mL) and reprecipitated by tetrabutylammonium bromide (0.16 g, 0.5 mmol) in water (5 mL) to give 0.13 g (43%) of dark red solid. ^{1}H NMR (acetone-d_6, ppm): δ 69.4 (br s, 2H, CH_{carb}/B*H*), 66.3 (br s, 2H, CH_{carb}/B*H*), 60.8 (br s, 2H, CH_{carb}/B*H*), 53.9 (br s, 2H, CH_{carb}/B*H*), 41.6 (br q, *J* = 135 Hz, 4H, B*H*), 28.6 (br m, 2H, B*H*), 3.0 (m, 8H, Bu_4N^+), 2.9 (s, 6H, OCH_3), 1.4 (m, 8H, Bu_4N^+), 0.9 (m, 8H, Bu_4N^+), 0.7 (m, 12H, Bu_4N^+), −2.8 (br q, *J* = 170 Hz, 2H, B*H*), −7.6 (br q, 4H, B*H*). ^{13}C NMR (acetone-d_6, ppm): δ 77.7 (OCH_3), 58.1 (t, Bu_4N^+), 23.1 (Bu_4N^+), 19.1 (Bu_4N^+), 12.7 (Bu_4N^+), −475.2 (CH_{carb}), −500.1 (CH_{carb}).

^{11}B NMR (acetone-d_6, ppm): δ 109.5 (d, 2B), 9.7 (d, 2B), 7.5 (d, 2B), 1.1 (d, 2B), −21.8 (d, 2B), −40.7 (d, 2B), −403.4 (br s, 2B), −431.7 (br s, 2B), −461.1 (br s, 2B). IR (film, cm^{-1}): 2963 (br, $\nu_{C–H}$), 2933 (br, $\nu_{C–H}$), 2876 (br, $\nu_{C–H}$), 2824 (br, $\nu_{C–H}$), 2559 (br, $\nu_{B–H}$), 1482, 1462, 1381. ESI HRMS for $C_6H_{26}B_{18}FeO_2^-$: calcd. *m/z* 381.3077, obsd. *m/z* 381.3068.

3.2.7. Synthesis of (Bu_4N)[4,7′-$(MeO)_2$-3,3′-Co(1,2-$C_2B_9H_{10})_2$] ((Bu_4N)[**9**])

To a solution of K[**4**] (0.20 g, 0.98 mmol) in dried tetrahydrofuran under argon atmosphere potassium *tert*-butoxide (1.10 g, 9.83 mmol) was added. The mixture was stirred at *r.t.* for 30 min and the anhydrous $CoCl_2$ (1.27 g, 9.83 mmol) was added. The reaction mixture was refluxed for 18 h. The solid was filtered off and the filtrate was evaporated under reduced pressure. The residue was dissolved in water (30 mL) and extracted by diethyl ether (2 × 30 mL). Organic fractions were collected and evaporated under reduced pressure. The residue was dissolved in water (10 mL) and reprecipitated by tetrabutylammonium bromide (0.16 g, 0.5 mmol) in water (5 mL) to give 0.14 g (45%) of orange solid. ^{1}H NMR (acetone-d_6): δ 3.81 (s, 2H, CH_{carb}), 3.70 (s, 2H, CH_{carb}), 3.45 (m, 8H, Bu_4N^+), 3.23 (q (1:1:1:1), $^3J_{B,H}$ = 3.9 Hz, 6H, OCH_3), 1.84 (m, 8H, Bu_4N^+), 1.45 (m, 8H, Bu_4N^+), 1.00 (t, 12H, Bu_4N^+), 2.6–0.5 (br s, 16H, B*H*). ^{13}C NMR (acetone-d_6): δ 58.5 (t, Bu_4N^+), 55.6 (OCH_3), 44.9 (CH_{carb}), 23.5 (Bu_4N^+), 19.5 (Bu_4N^+), 13.0 (Bu_4N^+). ^{11}B NMR (acetone-d_6): δ 13.9 (s, 2B), 5.2 (d, J = 139 Hz, 2B), −0.8 (d, J = 137 Hz, 2B), −7.9 (d, J = 142 Hz, 4B), −9.0 (d, J = 142 Hz, 2B), −19.8 (d, J = 152 Hz, 4B), −24.6 (d, J = 170 Hz, 2B). IR (film, cm^{-1}): 3035 (br, $\nu_{C–H}$), 2961 (br, $\nu_{C–H}$), 2926 (br, $\nu_{C–H}$), 2874 (br, $\nu_{C–H}$), 2853 (br, $\nu_{C–H}$), 2559 (br, $\nu_{B–H}$), 1712, 1478, 1459, 1379. ESI HRMS for $C_6H_{26}B_{18}CoO_2^-$: calcd. *m/z* 384.3059, obsd. *m/z* 384.3052.

4. Conclusions

The reaction of *nido*-carborane $[7,8\text{-}C_2B_9H_{12}]^-$ with dimethoxymethane in the presence of mercury(II) chloride lead to a mixture of four products that can be separated by column chromatography. The first two products represent symmetrical and asymmetrical charge compensated dimethyloxonium derivatives of *nido*-carborane 10-Me_2O-7,8-$C_2B_9H_{11}$ and 9-Me_2O-7,8-$C_2B_9H_{11}$, whereas two other products are the corresponding methoxy derivatives of *nido*-carborane $[10\text{-MeO-}7,8\text{-}C_2B_9H_{11}]^-$ and $[9\text{-MeO-}7,8\text{-}C_2B_9H_{11}]^-$. It was demonstrated, that dimethyloxonium derivatives of *nido*-carborane can act as active methylating agents. The reaction of the symmetrical methoxy derivative $[10\text{-MeO-}7,8\text{-}C_2B_9H_{11}]^-$ with anhydrous $FeCl_2$ in tetrahydrofuran in the presence of *t*-BuOK results in the corresponding iron bis(dicarbollide) complex [8,8′-$(MeO)_2$-3,3′-Fe(1,2-$C_2B_9H_{10})_2]^-$, whereas the similar reactions of the asymmetrical methoxy derivative $[9\text{-MeO-}7,8\text{-}C_2B_9H_{11}]^-$ with $FeCl_2$ and $CoCl_2$ give solely the 4,7′-isomers [4,7′-$(MeO)_2$-3,3′-M(1,2-$C_2B_9H_{10})_2]^-$ (M = Fe, Co) rather than a mixture of *rac*-4,7′- and *meso*-4,4′-isomers.

Supplementary Materials: The following are available online at http://www.mdpi.com/2304-6740/7/4/46/s1, NMR spectra of compounds **1**–**9**.

Author Contributions: M.Y.S. designed the studies, performed synthesis of the *nido*-carborane and metallacarborane derivatives, analyzed data and wrote the paper, S.A.E. performed synthesis of *nido*-carborane derivatives and study of their stability; I.D.K. performed the NMR studies; A.A.S. performed experiments on alkylation of 3-methyl-6-nitro-1*H*-indazole and wrote the paper; I.B.S. designed the studies, analyzed data and wrote the paper.

Funding: This work was supported by the Russian Science Foundation (Grant No. 17-73-10321).

Acknowledgments: The NMR spectral data were obtained using equipment of Center for Molecular Structure Studies at A. N. Nesmeyanov Institute of Organoelement Compounds. The basic physical and organizational structures, facilities and power supplies needed for the operation of the institute are partially supported by Ministry of Science and Higher Education of the Russian Federation.

Conflicts of Interest: The authors declare no conflict of interest.

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