



Article Nickel(II) and Palladium(II) Complexes with $\eta^5:\kappa^1(N)$ -Coordinated Dicarbollide Ligands Containing Pendant Pyridine Group

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Abstract: A series of *C*- and *B*-substituted *nido*-carborane derivatives with a pendant pyridyl group was prepared. The synthesized compounds were used as ligands in the complexation reactions with bis(triphenylphosphine)nickel(II) and palladium(II) chlorides to give six new metallacomplexes with unusual η^5 : $\kappa^1(N)$ -coordination of the metal center. The single crystal structures of 1-(NC₅H₄-2'-S)-1,2-C₂B₁₀H₁₁, 1-(NC₅H₄-2'-CH₂S)-1,2-C₂B₁₀H₁₁, Cs [7-(NC₅H₄-2'-CH₂S)-7,8-C₂B₉H₁₁] *closo*- and *nido*-carboranes and 3-Ph₃P-3-(4(7)-NC₅H₄-2'-S)-*closo*-3,1,2-NiC₂B₉H₁₀ metallacarboranes were determined using single crystal X-ray diffraction.

Keywords: *nido-*carborane; pyridine; nickel; palladium; half-sandwich metal complexes; synthesis; structure

1. Introduction

nido-Carborane $[nido-7, 8-C_2B_9H_{12}]^-$ is one of the most important members of the family of polyhedral boron hydrides, located at the junction of inorganic and organic chemistry. nido-Carborane (from Latin nidus, meaning "nest") is formed upon the removal of the boron atom adjacent to the carbon atoms from the icosahedral ortho-carborane 1,2- $C_2B_{10}H_{12}$, which has the *closo*-structure (a corruption of *clovo*, from Latin *clovis*, meaning "cage"), under the action of strong nucleophiles and has an open pentagonal face [1,2]. After the removal of endo-hydrogen from nido-carborane, the resulting dicarbollide anion [nido-1/2- $C_2B_9H_{11}$ ²⁻ can act as a ligand similar to a cyclopentadienyl one [3–8]. It is known that transition metal complexes with cyclopentadienyl ligands containing pendant donor groups are good catalysts for various organic reactions [9–16], and some of them are also promising luminescent materials [17,18]. One such pendant substituent is the pyridyl group [19,20]. In addition to the purely scientific interest associated with various types of coordination of such ligands [21–24], it was shown that titanium complexes with the cyclopentadienyl ligand containing the 2-picolyl substituent exhibit high catalytic activity during the ethylene polymerization reaction [25]. Therefore, the synthesis of *nido*-carboranes with a pendant pyridyl group and metallacarboranes based on them is of considerable interest.

To date, the synthesis of many *ortho*-carborane derivatives with a pyridyl group as a substituent has been described [26–38], most of which were obtained by the reaction of lithium derivatives of carboranes with pyridylaldehydes [33–38]. A number of transition



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). metal complexes of various structures with pyridyl *ortho*-carborane ligands were synthesized as well [28,29,31,38–48]. However, only a few examples of *nido*-carborane derivatives with a pyridyl group have been described [39,49–51], and a few transition metal complexes (metallacarboranes) based on them [50]. This is in sharp contrast to *nido*-carborane derivatives with other pendant substituents, such as the Me₂N group, based on which numerous metallacarboranes have been prepared [52–57], and it motivates our interest in research in this area.

In this contribution we describe the synthesis of new *nido*-carborane derivatives with a pendant pyridine group and nickel(II) and palladium(II) complexes thereof (Figure 1).



Figure 1. General view of metal complexes based on *nido*-carboranes with pendant pyridine group.

2. Results and Discussion

2.1. Design of Dicarbollide Ligands with Pendant Pyridine Group: General Principles

There are two main points to consider when designing dicarbollide ligands with a pendant pyridyl group. The first of these is the presence and length of a spacer between the carborane cage and the pyridyl ring. This determines the size and stability of the metallocycle formed during coordination. Clearly, in the absence of such a spacer [49], the formation of only a strained four-membered metallocycle is possible, which is unfavorable for most *d*-metals. Indeed, in structurally characterized iridium complexes with pyridyl substituted *nido*-carborane $[7-(NC_5H_4-2')-7,8-C_2B_9H_{11}]^-$, the latter is coordinated to the metal atom by the κ^2 -type through the nitrogen atom of the pyridyl group and the BH group of *nido*-carborane [58], rather than by the $\eta^5:\kappa^1$ -type. At the same time, in the case of ligands with a monoatomic spacer between the carborane cage and the pyridyl ring, for example, [7-(NC₅H₄-2'-CH₂)-7,8-C₂B₉H₁₁]⁻, metal coordination occurs with the formation of a stable five-membered metallocycle according to the η^5 : κ^1 -type [50]. As for complexes based on *nido*-carborane with a diatomic spacer between the carborane cage and the pyridine heterocycle, to the best of our knowledge, there is only one such complex $[3,3-(\kappa^2(N,O)-NC_5H_4-2''-C(O)O)-3-(\kappa^1(N)-1-NC_5H_4-2'-C(OH)H)-3,1,2-CoC_2B_9H_{10}]$, which was accidentally obtained by leaving the *ortho*-carborane complex *trans*-[Co($\kappa^2(N,O)$ -1- $NC_5H_4-2'-C(O)H-1,2-C_2B_{10}H_{11})_2$ in an acetone solution for several days or weeks under air [40].

The second point is the position of the substitution in the *nido*-carborane basket. Unlike the cyclopentadienide ligand, in which all the carbon atoms in the five-membered ring are identical, the pentagonal face of the dicarbollide ligand is formed by two carbon atoms and three boron atoms. In this case, by introducing a substituent at the carbon atom or boron atom, it is possible to vary both the properties of the ligand itself and the properties of the metal complexes based on it. Firstly, this is due to the different electronic effects of the *nido*-carborane cage substituted at the boron and carbon atoms, which in the case of a short spacer can have a significant effect on the pendant donor group. Another less obvious point

that can affect the stability and reactivity of metal complexes is the mutual orientation of the ligands. Due to the non-equivalence of atoms in the pentagonal face of the dicarbollide ligand, they interact differently with the metal atom, which leads to energetic inequality of different conformations due to the rotation of the dicarbollide ligand around the M–B(10) axis. In particular, for complexes of the d^8 metal ions, such as Ni(II), Pd(II), and Pt(II), the preferred orientation is one in which the angle θ between the L–M–L plane and the B(8)–M–Center(C(1)–C(2)) planes is 90° [59–62]. Another feature is the displacement of the metal atom from the center of the pentagonal face of the ligand towards the boron atoms, the so-called "slippage" of the dicarbollide ligand, which is especially characteristic of nickel(II) bis(dicarbollide) complexes [63,64]. The introduction of substituents at the carbon atoms into the dicarbollide ligand can lead to a significant deviation of the angle θ from the ideal value due to steric repulsion between the ligands [65,66], and in extreme cases, this even results in the isomerization of the dicarbollide ligand [67,68]. It is clear that the position of attachment of the pendant donor group to the dicarbollide ligand will have a significant effect on the structure, and consequently, the properties of the resulting metal complexes [52,69,70].

2.2. Synthesis of nido-Carborane Derivatives with Pendant Pyridine Group

To prepare metallacarboranes with a pendant pyridyl group attached to the boron atom of the dicarbollide ligand, we decided to use the 9-pyridylsulfenyl derivative of *nido*-carborane [9-(HNC₅H₄-2'-S)-7,8-C₂B₉H₁₁] described in the literature [51]. First, via the reaction of the tetramethylammonium salt of *nido*-carborane with 2-pyridylsulfenyl chloride in a mixture of acetonitrile and acetic acid, the *N*-protonated derivative [9-(HNC₅H₄-2'-S)-7,8-C₂B₉H₁₁] (**H**[1]) was obtained, which was then converted to the cesium salt Cs[9-(NC₅H₄-2'-S)-7,8-C₂B₉H₁₁] (**Cs**[1]) via treatment with CsOH in aqueous acetone (Scheme 1).



Scheme 1. Synthesis of Cs[9-(NC₅H₄-2'-S)-7,8-C₂B₉H₁₁] (Cs[1]).

The obtained carboranes were characterized using methods of ¹H, ¹³C, and ¹¹B NMR and IR spectroscopy and mass spectrometry (See Supplementary Materials, Figure S1–S70 and Table S1). The ¹¹B NMR spectrum of **Cs**[1] in acetone- d_6 contains a singlet at -3.1 ppm and seven doublets at -6.8, -15.6, -18.4, -22.5, -24.3, -30.6, and -37.8 ppm with an integral intensity ratio of 1:1:1:2:1:1:1:1, which is significantly different from the spectrum of the *N*-protonated form **H**[1] [51], indicating a rather strong interaction between the carborane cage and the pyridine ring. The ¹H NMR spectrum of **Cs**[1], in addition to the signals of the CH and BH groups of the *nido*-carborane cage, contains a set of signals of the pyridyl group, which appears in the form of two doublets at 8.22 and 7.67 ppm and two triplets at 7.49 and 6.87 ppm.

To obtain a related *nido*-carborane with a pendant pyridyl group attached to the carbon atom, as a development of the known approach to the arylation and heteroarylation of 1-mercapto-*ortho*-carborane [71–74], we used the reaction of the trimethylammonium salt of 1-mercapto-*ortho*-carborane with 2-bromopyridine. The reaction in refluxing ethanol gave a

mixture of the expected pyridyl derivative of *ortho*-carborane $1-(NC_5H_4-2'-S)-1,2-C_2B_{10}H_{11}$ (2) and its deboronation product as the N-protonated intramolecular salt [7-(HNC₅H₄-2'-S)-7,8-C_2B_9H_{11}] (H[3]), which were separated using column chromatography on silica followed by the conversion of the latter to the cesium salt Cs[7-(NC₅H₄-2'-S)-7,8-C_2B_9H_{11}] (Cs[3]) (Scheme 2). The cesium salt Cs[3] was also obtained via the deboronation of the corresponding *ortho*-carborane 2 with CsF in refluxing ethanol (Scheme 2).



Scheme 2. Synthesis of Cs[7-(NC₅H₄-2'-S)-7,8-C₂B₉H₁₁] (Cs[3]).

In the ¹H NMR spectrum of **Cs[3**], the signals of the pyridyl group appear as a doublet at 8.30 ppm, a triplet at 7.70 ppm, a doublet at 7.24 ppm, and a triplet at 7.02 ppm, demonstrating a significant difference in the electronic effects of the *nido*-carborane cage substituted at the boron and carbon atoms.

The solid-state structure of 1-(NC₅H₄-2'-S)-1,2-C₂B₁₀H₁₁·HBr (**2·HBr**) (see Supplementary Materials) was determined using single crystal X-ray diffraction (Figure 2).

The reaction of the trimethylammonium salt of 1-mercapto-*ortho*-carborane with 2bromomethyl pyridine followed by the deboronation of the resulting pyridine-containing *ortho*-carborane 1-(NC₅H₄-2'-CH₂S)-1,2-C₂B₁₀H₁₁ (**4**) was used to prepare the *nido*-carborane derivative with a longer spacer between the carborane cage and the pendant pyridyl group Cs[7-(NC₅H₄-2'-CH₂S)-7,8-C₂B₉H₁₁] (Cs[5]) (Scheme 3). Previously, this approach was used for the synthesis of various alkylsulfenyl derivatives of *ortho*- and *nido*-carboranes including those containing various functional groups [75–79].



Figure 2. General view of 1-(NC₅H₄-2'-S)-1,2-C₂B₁₀H₁₁·HBr showing numbering scheme. Thermal ellipsoids are given at 50% probability level. The closest contacts formed by the Br⁻ anion are shown by dashed lines.



Scheme 3. Synthesis of Cs[7-(NC₅H₄-2'-CH₂S)-7,8-C₂B₉H₁₁] (Cs[5]).

The obtained carboranes were characterized using methods of ¹H, ¹³C, and ¹¹B NMR and IR spectroscopy and mass spectrometry (See Supplementary Materials). In the ¹H NMR spectrum of **4** in acetone- d_6 , the signal of the methylene group appears as a singlet at 4.42 ppm, whereas in the spectrum of **Cs**[**5**], the signals of the methylene group appear as two doublets at 4.13 and 3.89 ppm (²*J*_{HH} = 12.8 Hz) due to chirality of the *C*-monosubstituted *nido*-carborane cage that causes protons to become diastereotopic and magnetically inequivalent.

The solid-state structures of $1-(NC_5H_4-2'-CH_2S)-1,2-C_2B_{10}H_{11}$ (4) and $Cs[7-(NC_5H_4-2'-CH_2S)-7,8-C_2B_9H_{11}]\cdot 0.5Me_2CO$ (Cs[5]·0.5Me₂CO) (see Supplementary Materials) were determined using single crystal X-ray diffraction (Figure 3).



Figure 3. General view of 1-(NC₅H₄-2'-CH₂S)-1,2-C₂B₁₀H₁₁ (4) (left) and Cs[7-(NC₅H₄-2'-CH₂S)-7,8-C₂B₉H₁₁] $\cdot 0.5$ Me₂CO (Cs[5] $\cdot 0.5$ Me₂CO) (right) showing numbering scheme. Thermal ellipsoids are given at 50% probability level. The closest contacts formed by the Cs⁺ cation are shown by dashed lines.

2.3. Synthesis of Nickela- and Platinacarboranes with Pendant Chelating Pyridine Group

The deprotonation of **Cs[1]** with *t*-BuOK in dry THF followed by the addition of triphenylphosphine complexes of nickel(II) or palladium(II) [(Ph₃P)₂MCl₂] (M=Ni, Pd) results in the corresponding metallacarboranes 3-Ph₃P-3-(4(7)-NC₅H₄-2'-S)-*closo*-3,1,2-MC₂B₉H₁₀ (M=Ni (6), Pd (7)), which were isolated in moderate yields after column chromatography on silica (Scheme 4).



Scheme 4. Synthesis of metallacarboranes $3-Ph_3P-3-(4(7)-NC_5H_4-2'-S)-closo-3,1,2-NiC_2B_9H_{10}$ (6) and $3-Ph_3P-3-(4(7)-NC_5H_4-2'-S)-closo-3,1,2-NiC_2B_9H_{10}$ (7).

The obtained metallacarboranes were characterized using methods of ¹H, ¹³C, ¹¹B, and ³¹P NMR spectroscopy, as well as IR and UV spectroscopy and mass spectrometry. The solid-state structure of 3-Ph₃P-3-(4(7)-NC₅H₄-2'-S)-*closo*-3,1,2-NiC₂B₉H₁₀ (6) was determined



using single crystal X-ray diffraction (see Supplementary Materials). A general view of the nickelacarborane molecule is given in Figure 4.

Figure 4. General view of 3-Ph₃P-3-(4(7)-NC₅H₄-2'-S)-*closo*-3,1,2-NiC₂B₉H₁₀ (**6**) showing numbering scheme. Thermal ellipsoids are given at 50% probability level.

The orientation of the σ -donor ligands (the pendant pyridine and triphenylphosphine) with respect to the dicarbollide ligand significantly deviates from the ideal orientation with the θ angle between the N(1)-Ni(1)-P(1) plane and the B(8)-Ni(1)-Center-(C(1)-C(2)) plane being ~ 60°, and the pyridyl group is rotated around the B(9)-S(1) bond toward the carbon atoms of the dicarbollide ligand (Figure 3). No noticeable "slippage" of the dicarbollide ligand was found.

In a similar way, metallacarboranes $3-Ph_3P-3-(1(2)-NC_5H_4-2'-S)-closo-3,1,2-NiC_2B_9H_{10}$ (8) and $3-Ph_3P-3-(1(2)-NC_5H_4-2'-S)-closo-3,1,2-PdC_2B_9H_{10}$ (9) were prepared starting from the *C*-substituted *nido*-carborane **Cs[3]** (Scheme 5). The obtained metallacarboranes were characterized using methods of ¹H, ¹³C, ¹¹B, and ³¹P NMR spectroscopy, as well as IR and UV spectroscopy and mass spectrometry. Unfortunately, we were unable to obtain crystals suitable for X-ray diffraction studies of single crystals.

Metallacarboranes with a more flexible spacer between the dicarbollide ligand and the pyridyl group 3-Ph₃P-3-(1(2)-NC₅H₄-2'-CH₂S)-*closo*-3,1,2-NiC₂B₉H₁₀ (**10**) and 3-Ph₃P-3-(1(2)-NC₅H₄-2'-CH₂S)-*closo*-3,1,2-PdC₂B₉H₁₀ (**11**) were synthesized in a similar way starting from the *C*-substituted *nido*-carborane **Cs**[**5**] (Scheme 6).



Scheme 5. Synthesis of metallacarboranes $3-Ph_3P-3-(1(2)-NC_5H_4-2'-S)-closo-3,1,2-NiC_2B_9H_{10}$ (8) and $3-Ph_3P-3-(1(2)-NC_5H_4-2'-S)-closo-3,1,2-NiC_2B_9H_{10}$ (9).



Scheme 6. Synthesis of metallacarboranes 3-Ph₃P-3-(1(2)-NC₅H₄-2'-CH₂S)-*closo*-3,1,2-NiC₂B₉H₁₀ (**10**) and 3-Ph₃P-3-(1(2)-NC₅H₄-2'-CH₂S)-*closo*-3,1,2-NiC₂B₉H₁₀ (**11**).

The obtained metallacarboranes were characterized using methods of ¹H, ¹³C, ¹¹B, and ³¹P NMR spectroscopy, as well as IR and UV spectroscopy and mass spectrometry. The solid-state structure of 3-Ph₃P-3-(4(7)-NC₅H₄-2'-CH₂S)-*closo*-3,1,2-NiC₂B₉H₁₀ (**10**) was determined using single crystal X-ray diffraction (see Supplementary Materials). A general view of the nickelacarborane molecule is given in Figure 5.

The orientation of the σ -donor ligands (the pendant pyridine and triphenylphosphine) with respect to the dicarbollide ligand strongly deviates from the ideal orientation with the θ angle between the N(1)-Ni(1)-P(1) plane and the B(8)-Ni(1)-Center-(C(1)-C(2)) plane being ~16°. The six-membered ring Ni(1)-C(1)-S(1)-C(3)-C(4)-N(1) adopts a highly distorted boat conformation with a nickel atom and a methylene group located at the bow and stern (Figure 4). No noticeable "slippage" of the dicarbollide ligand was found.



Figure 5. General view of 3-Ph₃P-3-(4(7)-NC₅H₄-2'-CH₂S)-*closo*-3,1,2-NiC₂B₉H₁₀ (**10**) showing numbering scheme. Thermal ellipsoids are given at 50% probability level.

3. Methods and Materials

3.1. Materials and Methods

The trimethylammonium salt of 1-mercapto-*ortho*-carborane [78], bis(triphenylphosphine)nickel(II) chloride [(Ph₃P)₂NiCl₂] [80] and bis(triphenylphosphine)palladium(II) chloride [(Ph₃P)₂PdCl₂] [81] were synthesized according to the literature described methods. 2-Bromopyridine and 2-(bromomethyl)-pyridine hydrobromide were purchased from Acros Organics and used without purification. Tetrahydrofuran was dried using standard procedure [82]. The reaction progress was monitored using thin-layer chromatography (Merck F254 silica gel on aluminum plates) and visualized using 0.5% PdCl₂ 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 (¹H), 128.4 MHz (¹¹B), 100.0 MHz (¹³C), and 162 MHz (³¹P) were recorded with a Varian Inova 400 spectrometer. The residual signal of the NMR solvent relative to Me₄Si was taken as an internal reference for ¹H and ¹³C NMR spectra. ¹¹B NMR spectra were referenced using BF₃.Et₂O as an external standard. ³¹P NMR spectra are given relative to 85% H₃PO₄ as an external standard. Infrared spectra were recorded on an FSM-2201 (INFRASPEC, Saint Petersburg, Russia) instrument. UV/Vis spectra were recorded with SF-2000 spectrophotometer (OKB SPECTR LLC, Saint Petersburg, Russia) using 1 cm cuvettes. High resolution mass spectra (HRMS) were measured on a Bruker micrOTOF II instrument using electrospray ionization (ESI).

3.2. Synthesis of $Cs[9-(NC_5H_4-2'-S)-7,8-C_2B_9H_{11}]$ (Cs[1])

Compound **Cs**[1] was prepared from described in the literature *N*-protonated [9-(HNC_5H_4 -2'-S)-7,8-C_2B_9H_{11}] (**H**[1]) (0.30 g, 1.23 mmol) [51] by dissolving it in acetone (7 mL) and reprecipitated with aqueous CsOH (0.28 g, 1.85 mmol in 40 mL of water) to give 0.44 g (95% yield) of cesium salt of 5. ¹H NMR (acetone- d_6 , ppm): δ 8.22 (1H, d, *J* = 4.7 Hz, H_{py}), 7.67 (1H, d, *J* = 8.1 Hz, H_{py}), 7.49 (1H, t, *J* = 7.5 Hz, H_{py}), 6.87 (1H, m, H_{py}), 2.29 (1H, br s, CH_{carb}), 1.86 (1H, br s, CH_{carb}), 2.6 ÷ (-0.1) (8H, br m, BH), -2.38 (1H, br m, BHB).

¹¹B NMR (acetone- d_6 , ppm): δ -3.1 (1B, s), -6.8 (1B, d, J = 138 Hz), -15.6 (1B, J = 138 Hz), -18.4 (2B, d, J = 160 Hz), -22.5 (1B, d, J = 151 Hz), -24.3 (1B, d, J = 139 Hz), -30.6 (1B, d, J = 137 Hz), -37.8 (1B, d, J = 141 Hz).

3.3. Synthesis of 1-(NC₅H₄-2'-S)-1,2-C₂B₁₀H₁₁ (2), [7-(NC₅H₅-2'-S)-7,8-C2B9H11] (H[3]) and Cs[7-(NC5H4-2'-S)-7,8-C2B9H11] (Cs[3])

2-Bromopyridine (0.24 mL, 2.55 mmol) was added to a solution of the trimethylammonium salt of 1-mercapto-*closo*-carborane (0.60 g, 2.55 mmol) in ethanol (30 mL) and the reaction mixture was refluxed for about 5 h, cooled to ambient temperature and evaporated to dryness in vacuum. The obtained product was isolated using column gradient elution chromatography on silica with CH_2Cl_2 :acetone mixture (from 19:1 to 1:1) as an eluent to give 0.17 g (26% yield) of white crystalline product **2** and 0.17 g (27% yield) of white crystalline **H[3]**. Compound **H[3]** was dissolved in acetone (5 mL) and reprecipitated with aqueous CsOH (0.15 g, 1.00 mmol in 30 mL of water) to give 0.26 g (99% yield) of cesium salt of **Cs[3]**.

The cesium salt **Cs**[2] was also obtained by refluxing 2 (0.14 g, 0.55 mmol) in ethanol (10 mL) with cesium fluoride (0.17 g, 1.11 mmol) for 12 h. The precipitate formed was filtered off and the filtrate was evaporated under reduced pressure. The residue was dissolved in acetone (10 mL) and unreacted CsF was filtered off. The filtrate was evaporated *in vacuo* to give a white solid of **Cs**[3] (0.20 g, 97% yield).

Spectral data for **2**. ¹H NMR (acetone-*d*₆, ppm): δ 8.70 (1H, d, *J* = 6.3 Hz, *H*(6)_{py}), 7.95 (1H, t, *J* = 7.4 Hz, *H*(4)_{py}), 7.72 (1H, d, *J* = 7.6 Hz, *H*(3)_{py}), 7.56 (1H, t, *J* = 6.2 Hz, *H*(5)_{py}), 5.12 (1H, br s, CH_{carb}), 3.0 ÷ 1.2 (10H, br m, BH). ¹³C NMR (acetone-*d*₆, ppm): δ 152.1 (*C*(2)_{py}), 151.1 (*C*(6)_{py}), 138.5 (*C*(4)_{py}), 130.9 (*C*(3)_{py}), 125.4 (*C*(5)_{py}), 74.1 (*C*_{carb}S), 65.5 (*C*_{carb}H). ¹¹B NMR (acetone-*d*₆, ppm): δ -1.90 (1B, d, *J* = 143 Hz), -5.15 (1B, d, *J* = 147 Hz), -9.7 (4B, *J* = 160 Hz), -11.6 (2B, d, *J* = 158 Hz), -12.4 (2B, d, *J* = 161 Hz). IR (film, cm⁻¹): 3012 (v_{C-H}), 2976 (v_{C-H}), 2933 (v_{C-H}), 2603 (br, v_{B-H}), 2580 (br, v_{B-H}), 1439, 1423, 1386, 1289. ESI HRMS: *m*/*z* for C₇H₁₅B₁₀SN, calcd. 254.2005 [M + H]⁺, obsd. 254.2008 [M + H]⁺.

Spectral data for H[3]. ¹H NMR (acetone- d_6 , ppm): δ 8.44 (1H, t, J = 4.5 Hz, H_{py}), 8.01 (1H, m, H_{py}), 7.45 (1H, m, H_{py}), 7.27 (1H, m, H_{py}), 2.15 (1H, br s, CH_{carb}), 2.9 ÷ (-0.2) (8H, br m, BH), -2.54 (1H, br m, BHB). ¹¹B NMR (acetone- d_6 , ppm): δ -8.1 (1B, d, J = 144 Hz), -9.7 (1B, d, J = 137 Hz), -13.6 (1B, J = 162 Hz), -15.9 (1B, d, J = 144 Hz), -17.0 (1B, d, J = 133 Hz), -18.0 (1B, d, J = 142 Hz), -21.5 (1B, d, J = 153 Hz), -32.0 (1B, dd, J = 131, J = 31 Hz), -36.1 (1B, d, J = 141 Hz).

Spectral data for **Cs[3**]. ¹H NMR (acetone- d_6 , ppm): δ 8.30 (1H, d, J = 6.2 Hz, $H(6)_{py}$), 7.70 (1H, t, J = 7.7 Hz, $H(4)_{py}$), 7.24 (1H, d, J = 7.8 Hz, $H(3)_{py}$), 7.02 (1H, t, J = 7.3 Hz, $H(5)_{py}$), 2.10 (1H, br s, CH_{carb}), 3.2 \div 0.3 (8H, br m, BH), -2.42 (1H, br m, BHB). ¹³C NMR (acetone- d_6 , ppm): δ 166.0 (C(2)_{py}), 148.6 (C(6)_{py}), 136.5 (C(4)_{py}), 121.4 (C(3)_{py}), 118.9 (C(5)_{py}), 52.6 (C_{carb}S), 50.4 (C_{carb}H). ¹¹B NMR (acetone- d_6 , ppm): δ -8.1 (1B, d, J = 145 Hz, B(11)), -9.7 (1B, d, J = 141 Hz, B(9)), -13.6 (1B, J = 158 Hz, B(3)), -16.0 (1B, d, J = 132 Hz, B(5)), -17.0 (1B, d, J = 138 Hz, B(6)), -17.9 (1B, d, J = 130 Hz, B(4)), -21.5 (1B, d, J = 149 Hz, B(2)), -32.0 (1B, dd, J = 130, J = 40 Hz, B(10)), -36.1 (1B, d, J = 140 Hz, B(1)). IR (film, cm⁻¹): 3010 (v_{C-H}), 2973 (v_{C-H}), 2929 (v_{C-H}), 2350 (br, v_{B-H}), 1441, 1354, 1295. ESI HRMS: m/z for C₇H₁₅B₉SN, calcd. 243.1810 [M]⁻, obsd. 243.1815 [M]⁻.

3.4. Synthesis of 1-(NC_5H_4 -2'- CH_2S)-1,2- $C_2B_{10}H_{11}$ (4)

2-(Bromomethyl)pyridine hydrobromide (0.54 g, 2.12 mmol) was added to a solution of the trimethylammonium salt of 1-mercapto-*closo*-carborane (0.50 g, 2.12 mmol) in ethanol (20 mL) and the reaction mixture was refluxed for about 5 h, cooled to ambient temperature and evaporated to dryness in vacuum. The obtained product was isolated using column gradient elution chromatography on silica with CH₂Cl₂:acetone mixture (from 19:1 to 1:1) as an eluent to give 0.21 g (37% yield) of white crystalline product **3**. ¹H NMR (acetone-*d*₆, ppm): δ 8.52 (1H, d, *J* = 4.8 Hz, *H*(6)_{py}), 7.77 (1H, m, *H*(4)_{py}), 7.47 (1H, d, *J* = 7.9 Hz, *H*(3)_{py}), 7.30 (1H, m, *H*(5)_{py}), 4.93 (1H, br s, CH_{carb}), 4.42 (2H, s, CH₂), 3.3 ÷ 1.4 (10H, br m, BH).

¹³C NMR (acetone-d₆, ppm): δ 155.1 (*C*(2)_{py}), 149.7 (*C*(6)_{py}), 137.5 (*C*(4)_{py}), 123.8 (*C*(3)_{py}), 123.2 (*C*(5)_{py}), 75.4 (*C*_{carb}S), 68.7 (*C*_{carb}H), 43.3 (CH₂). ¹¹B NMR (acetone-*d*₆, ppm): δ – 2.1 (1B, d, *J* = 148 Hz), -5.4 (1B, d, *J* 148 = Hz), -9.4 (4B, *J* = 154 Hz), -11.9 (2B, d, *J* = 181 Hz), -12.4 (2B, d, *J* = 159 Hz). IR (film, cm⁻¹): 3071 (ν_{C-H}), 3019 (ν_{C-H}), 2933 (ν_{C-H}), 2600 (br, ν_{B-H}), 1594, 1574, 1475, 1439. ESI HRMS: *m*/*z* for C₈H₁₇B₁₀SN, calcd. 268.2162 [M + H]⁺, obsd. 268.2155 [M + H]⁺.

3.5. Synthesis of Cs[7-(NC₅H₄-2'-CH₂S)-7,8-C₂B₉H₁₁] (Cs[5])

Compound 4 (0.19 g, 0.71 mmol) was dissolved in ethanol (20 mL) and cesium fluoride (0.22 g, 1.42 mmol) was added. The solution was refluxed for about 20 h. The precipitate formed was filtered off and the filtrate was evaporated under reduced pressure. The residue was dissolved in acetone (15 mL) and unreacted CsF was filtered off. The filtrate was evaporated *in vacuo* to give a white solid of 4 (0.27 g, 98% yield). ¹H NMR (acetone-*d*₆, ppm): δ 8.46 (1H, d, *J* = 4.2 Hz, *H*(6)_{py}), 7.68 (1H, t, *J* = 7.6 Hz, *H*(4)_{py}), 7.40 (1H, d, *J* = 7.8 Hz, *H*(3)_{py}), 7.17 (1H, m, *H*(5)_{py}), 4.13 (1H, d, *J* = 12.8 Hz, *CH*₂), 3.89 (1H, d, *J* = 12.8 Hz, *CH*₂), 1.63 (1H, br s, *CH*_{carb}), 3.2 ÷ 0.2 (8H, br m, BH), -2.57 (1H, br m, BHB). ¹³C NMR (acetone-*d*₆, ppm): δ 159.9 (*C*(2)_{py}), 149.0 (*C*(6)_{py}), 136.2 (*C*(4)_{py}), 123.4 (*C*(3)_{py}), 121.6 (*C*(5)_{py}), 52.3 (*C*_{carb}H), 43.2 (CH₂). ¹¹B NMR (acetone-*d*₆, ppm): δ -9.3 (1B, d, *J* = 137 Hz), -10.4 (1B, d, *J* = 135 Hz), -14.9 (1B, *J* = 159 Hz), -17.2 (3B, d, *J* = 139 Hz), -22.1 (1B, d, *J* = 148 Hz), -32.9 (1B, dd, *J* = 124, *J* = 32 Hz), -36.8 (1B, d, *J* = 138 Hz). IR (film, cm⁻¹): 3059 (v_{C-H}), 3011 (v_{C-H}), 2972 (v_{C-H}), 2928 (v_{C-H}), 2528 (br, v_{B-H}), 1597, 1570, 1479, 1439, 1253. ESI HRMS: *m/z* for C₇H₁₅B₉SN, calcd. 257.1962 [M]⁻, obsd. 257.1967 [M]⁻.

3.6. General Procedure for Synthesis of Metallacarboranes 6-11

To solution of *nido*-carborane derivative **2**, **4** or **5** in anhydrous THF under argon atmosphere, the 3-fold excess of potassium *tert*-butoxide was added. The reaction mixture was stirred at ambient temperature for about 10 min and the 1.1-fold excess of phosphine complexes [(Ph₃P)₂MCl₂] (M=Ni, Pd) was added to one portion. Immediately, a dark brown solution was observed. The resulting mixture was stirred at ambient temperature for about 30 min and the solvent was evaporated to dryness under vacuum conditions. The target complex was isolated using column chromatography on silica using CH₂Cl₂ as eluent. If necessary, an additional column chromatography on silica using hexane as eluent was performed to purify the complex from uncoordinated triphenylphosphine.

3-*Ph*₃*P*-3-(4(7)-*N*C₅*H*₄-2'-*S*)-*closo*-3,1,2-*Ni*C₂*B*₉*H*₁₀ (**6**). The synthesis was carried out using **Cs**[1] (0.15 g, 0.40 mmol), *t*-BuOK (0.13 g, 1.20 mmol), and [(PPh₃)₂NiCl₂] (0.29 g, 0.44 mmol) in THF (15 mL) to give brown solid of **6** (0.08 g, 31% yield). ¹H NMR (CD₂Cl₂, ppm): δ 7.79 (7H, m, PPh₃ + *H*_{py}), 7.50 ÷ 7.36 (9H, br m, PPh₃), 7.21 (1H, d, *J* = 8.5 Hz, *H*_{py}), 7.03 (1H, t, *J* = 7.7 Hz, *H*_{py}), 6.03 (1H, t, *J* = 6.7 Hz, *H*_{py}), 2.77 (1H, br s, *CH*_{carb}), 2.44 (1H, br s, *CH*_{carb}), 2.6 ÷ 0.1 (8H, br m, BH). ¹³C NMR (CD₂Cl₂, ppm): δ 152.6 (C_{py}), 135.0 (C_{py}), 134.23 (d, *J* = 9.7 Hz, Ph), 130.8 (Ph), 128.62 (d, *J* = 9.2 Hz, Ph), 125.0 (*C*_{py}), 117.2 (*C*_{py}), 33.0 (*C*_{carb}H), 31.3 (*C*_{carb}H). ¹¹B NMR (CD₂Cl₂, ppm): δ -1.0 (1B, d, *J* = 119 Hz), -8.0 (2B, s + d, *J* = 127 Hz), -10.8 (2B, d, *J* = 124 Hz), -16.4 (1B, d, *J* = 144 Hz), -19.8 (1B, d, *J* = 150 Hz), -23.4 (2B, d, *J* = 138 Hz). ³¹P NMR (CD₂Cl₂, ppm): δ 31.2 (PPh₃). IR (film, cm⁻¹): 3039 (v_{C-H}), 2992 (v_{C-H}), 2940 (v_{C-H}), 2877 (v_{C-H}), 2556 (br, v_{B-H}), 1471, 1455, 1438, 1392, 1364, 1226, 1194. ESI HRMS: *m*/*z* for C₂₅H₂₉B₉NiNPS, calcd. *m*/*z* 563.2079 [M + H]⁺, obsd. *m*/*z* 563.2071 [M + H]⁺. UV (acetone, nm): λ 207, 247, 275, 323.

3-*Ph*₃*P*-3-(4(7)-*NC*₅*H*₄-2'-*S*)-*closo*-3,1,2-*PdC*₂*B*₉*H*₁₀ (7). The synthesis was carried out using **Cs**[1] (0.15 g, 0.40 mmol), *t*-BuOK (0.13 g, 1.20 mmol), and [(PPh₃)₂PdCl₂] (0.31 g, 0.44 mmol) in THF (15 mL) to give dark brown solid of 7 (0.06 g, 25% yield). ¹H NMR (acetone-*d*₆, ppm): δ 7.80 (6H, m, *PPh*₃), 7.60 ÷ 7.47 (10H, br m, *PPh*₃ + *H*_{py}), 7.38 (2H, *H*_{py}), 6.40 (1H, m, *H*_{py}), 4.48 (1H, br s, *CH*_{carb}), 3.75 (1H, br s, *CH*_{carb}), 3.4 ÷ (-0.5) (8H, br m, BH). ¹³C NMR (acetone-*d*₆, ppm): δ 152.5 (*C*_{py}), 136.3 (*C*_{py}), 134.30 (d, *J* = 12.6 Hz, Ph), 131.1 (Ph), 128.73 (d, *J* = 10.3 Hz, Ph), 124.6 (*C*_{py}), 117.1 (*C*_{py}), 55.0 (*C*_{carb}H). ¹¹B NMR (acetone-*d*₆, ppm): δ 18.5 (1B, d, *J* = 136 Hz), -5.9 (2B, d, *J* = 146 Hz), -9.0 (2B, s + d, *J* = 142 Hz), -10.8

(2B, d, *J* = 144 Hz), -22.0 (1B, d, *J* = 140 Hz), -25.1 (1B, d, *J* = 131 Hz). ³¹P NMR (acetone- d_6 , ppm): δ 32.1 (PPh₃). IR (film, cm⁻¹): 2964 (ν_{C-H}), 2933 (ν_{C-H}), 2857 (ν_{C-H}), 2560 (br, ν_{B-H}), 1594, 1483, 1459, 1435, 1415, 1249. ESI HRMS: *m*/*z* for C₂₅H₂₉B₉PdNPS, calcd. *m*/*z* 610.1782 [M + H]⁺, obsd. *m*/*z* 610.1771 [M + H]⁺. UV (acetone, nm): λ 206, 247, 269, 327.

3-*Ph*₃*P*-3-(1(2)-*N*C₅*H*₄-2'-*S*)-*closo*-3,1,2-*Ni*C₂*B*₉*H*₁₀ (**8**). The synthesis was carried out using **Cs**[**3**] (0.20 g, 0.58 mmol), *t*-BuOK (0.19 g, 1.74 mmol), and [(PPh₃)₂NiCl₂] (0.42 g, 0.64 mmol) in THF (15 mL) to give brown solid of **8** (0.07 g, 22% yield). ¹H NMR (acetone-*d*₆, ppm): δ 8.04 (6H, m, *PPh*₃), 7.73 ÷ 7.43 (10H, br m, *PPh*₃ + *H*_{py}), 7.39 (1H, m, *H*_{py}), 7.29 (1H, m, *H*_{py}), 6.45 (1H, m, *H*_{py}), 3.44 (1H, br s, *CH*_{carb}), 2.7 ÷ 0.5 (9H, br m, BH). ¹³C NMR (acetone-*d*₆, ppm): δ 151.7 (*C*_{py}), 136.4 (*C*_{py}), 135.05 (d, *J* = 10.0 Hz, Ph), 134.2, 131.8 (Ph), 131.1 (Ph), 130.3, 128.48 (d, *J* = 10.0 Hz, Ph), 120.3 (*C*_{py}), 119.0 (*C*_{py}). ¹¹B NMR (acetone-*d*₆, ppm): δ -2.5 (1B, d, *J* = 120 Hz), -7.0 (1B, d, *J* = 138 Hz), -10.8 (1B, d, *J* = 143 Hz), -11.8 (1B, d, *J* = 120 Hz), -14.6 (2B, d, *J* = 126 Hz), -18.1 (2B, d, *J* = 135 Hz), -20.7 (1B, d, *J* = 153 Hz). ³¹P NMR (acetone-*d*₆, ppm): δ 43.7 (PPh₃). IR (film, cm⁻¹): 3084 (v_{C-H}), 3062 (v_{C-H}), 2968 (v_{C-H}), 2931 (v_{C-H}), 2860 (v_{C-H}), 2559 (br, v_{B-H}), 1598, 1440, 1421, 1364. ESI HRMS: *m*/*z* for C₂₅H₂₉B₉NiNPS, calcd. *m*/*z* 563.2079 [M + H]⁺, obsd. *m*/*z* 563.2064 [M + H]⁺. UV (acetone, nm): λ 213, 325, 397.

3-*Ph*₃*P*-3-(1(2)-*NC*₅*H*₄-2'-*S*)-*closo*-3,1,2-*PdC*₂*B*₉*H*₁₀ (**9**). The synthesis was carried out using **Cs**[**3**] (0.19 g, 0.51 mmol), *t*-BuOK (0.17 g, 1.53 mmol), and [(PPh₃)₂PdCl₂] (0.39 g, 0.56 mmol) in THF (15 mL) to give dark brown solid of **9** (0.10 g, 33% yield). ¹H NMR (acetone-*d*₆, ppm): δ 7.88 (6H, m, *PPh*₃), 7.61 ÷ 7.47 (10H, br m, *PPh*₃ + *H*_{py}), 7.40 (1H, m, *H*_{py}), 7.36 (1H, m, *H*_{py}), 6.67 (1H, t, *J* = 6.4 Hz, *H*_{py}), 3.85 (1H, br s, *CH*_{carb}), 3.6 ÷ (-0.1) (9H, br m, BH). ¹³C NMR (acetone-*d*₆, ppm): δ 150.2 (*C*_{py}), 137.1 (*C*_{py}), 134.87 (d, *J* = 11.7 Hz, Ph), 134.0, 131.5 (Ph), 129.8, 128.89 (d, *J* = 10.9 Hz, Ph), 120.4 (*C*_{py}), 119.6 (*C*_{py}), 39.4 (*C*_{carb}H). ¹¹B NMR (acetone-*d*₆, ppm): δ 1.9 (1B, d, *J* = 138 Hz), -3.4 (1B, d, *J* = 121 Hz), -6.3 (1B, d, *J* = 124 Hz), -12.7 (1B, d, *J* = 132 Hz), -13.7 (3B, d, *J* = 157 Hz), -22.4 (1B, d, *J* = 147 Hz), -25.3 (1B, d, *J* = 133 Hz). ³¹P NMR (acetone-*d*₆, ppm): δ 45.4 (PPh₃). IR (film, cm⁻¹): 3091 (v_{C-H}), 2965 (v_{C-H}), 2932 (v_{C-H}), 2861 (v_{C-H}), 2554 (br, v_{B-H}), 1595, 1442, 1250. ESI HRMS: *m/z* for C₂₅H₂₉B₉PdNPS, calcd. *m/z* 632.1636 [M + NH₄]⁺, obsd. *m/z* 628.1990 [M + NH₄]⁺; calcd. *m/z* 632.1601 [M + Na]⁺, obsd. *m/z* 632.1636 [M + NH₄]⁺. UV (acetone, nm): λ 207, 215, 323.

3-*Ph*₃*P*-3-(1(2)-*N*C₅*H*₄-2'-*CH*₂*S*)-*closo*-3,1,2-*Ni*C₂*B*₉*H*₁₀ (**10**). The synthesis was carried out using **Cs**[**5**] (0.12 g, 0.31 mmol), *t*-BuOK (0.10 g, 0.93 mmol), and [(PPh₃)₂NiCl₂] (0.22 g, 0.34 mmol) in THF (15 mL) to give brown solid of **10** (0.06 g, 34% yield). ¹H NMR (DMSO-*d*₆, ppm): δ 8.76 (1H, d, *J* = 5.3 Hz, *H*_{py}), 7.73 (1H, t, *J* = 7.7 Hz, *H*_{py}), 7.59 (1H, m, *H*_{py}), 7.54 ÷ 7.40 (8H, br m, *PPh*₃), 7.40 ÷ 7.29 (7H, br m, *PPh*₃), 7.10 (1H, t, *J* = 6.6 Hz, *H*_{py}), 4.63 (1H, d, *J* = 13.6 Hz, *CH*₂), 4.23 (1H, d, *J* = 13.6 Hz, *CH*₂), 2.3 ÷ 0.9 (9H, br m, BH). ¹³C NMR (CDCl₃, ppm): δ 152.7 (*C*_{py}), 139.3 (*C*_{py}), 133.8 (d, *J* = 8.9 Hz, Ph), 130.5 (Ph), 128.4 (d, *J* = 11.6 Hz, Ph + *C*_{py}), 123.4 (*C*_{py}). ¹¹B NMR (CDCl₃, ppm): δ -7.7 (1B, d, *J* = 158 Hz), -9.8 (3B), -13.3 (2B, d, *J* = 130 Hz), -17.6 (2B), -22.5 (1B). ³¹P NMR (CDCl₃, ppm): δ 37.4 (PPh₃). IR (film, cm⁻¹): 2965 (v_{C-H}), 2928 (v_{C-H}), 2857 (v_{C-H}), 2544 (br, v_{B-H}), 1609, 1483, 1439, 1356, 1186, 1158, 1122. ESI HRMS: *m/z* for C₂₆H₃₁B₉NiNPS, calcd. *m/z* 594.2501 [M + NH₄]⁺, obsd. *m/z* 594.2543 [M + NH₄]⁺. UV (acetone, nm): λ 206, 243, 291, 323.

3-*Ph*₃*P*-3-(1(2)-*N*C₅*H*₄-2'-*CH*₂*S*)-*closo*-3,1,2-*Pd*C₂*B*₉*H*₁₀ (**11**). The synthesis was carried out using **Cs**[**5**] (0.23 g, 0.59 mmol), *t*-BuOK (0.20 g, 1.77 mmol), and [(PPh₃)₂PdCl₂] (0.46 g, 0.65 mmol) in THF (15 mL) to give dark brown solid of **9** (0.10 g, 27% yield). ¹H NMR (CD₂Cl₂, ppm): δ 8.12 (1H, m, *H*_{py}), 7.64 (1H, t, *J* = 7.9 Hz, *H*_{py}), 7.55 ÷ 7.37 (9H, br m, *PPh*₃ + *H*_{py}), 7.36 ÷ 7.27 (7H, br m, *PPh*₃), 6.82 (1H, t, *J* = 6.6 Hz, *H*_{py}), 4.59 (1H, m, *CH*₂), 4.03 (1H, m, *CH*₂), 2.5 ÷ 0.5 (9H, br m, BH). ¹³C NMR (CD₂Cl₂, ppm): δ 152.1 (*C*_{py}), 139.2 (*C*_{py}), 134.0 (d, *J* = 8.6 Hz, Ph), 130.8 (Ph), 128.4 (d, *J* = 11.6 Hz, Ph), 123.6 (*C*_{py}). ¹¹B NMR (CD₂Cl₂, ppm): δ -4.5 (1B, d, *J* = 149 Hz), -6.6 (1B, d, *J* = 119 Hz), -9.5 (1B, d, *J* = 143 Hz), -10.7 (1B, d, *J* = 140 Hz), -14.2 (2B), -15.0 (2B), -24.6 (1B). ³¹P NMR (CD₂Cl₂, ppm): δ 47.6 (PPh₃). IR (film, cm⁻¹): 2968 (v_{C-H}), 2928 (v_{C-H}), 2861 (v_{C-H}), 2552 (br, v_{B-H}), 1602, 1487, 1435, 1399,

1312, 1190. ESI HRMS: m/z for C₂₆H₃₁B₉PdNPS, calcd. m/z 642.2194 [M + NH₄]⁺, obsd. m/z 642.2190 [M + NH₄]⁺. UV (acetone, nm): λ 207, 251, 325.

3.7. Single Crystal X-ray Diffraction Study

Single crystal X-ray diffraction experiments for 2·HBr, 4, Cs[5]·0.5Me₂CO, 8, and 10 were carried out using SMART APEX2 CCD diffractometer (λ (Mo-K α) = 0.71073 Å, graphite monochromator, ω -scans) at 140 K (See Supplementary Materials). Collected data were processed using the SAINT and SADABS programs incorporated into the APEX2 program package [83]. The structure was solved using the direct methods and refined using the full-matrix least-squares procedure against F² in anisotropic approximation. The refinement was carried out with the SHELXTL program [84]. The CCDC numbers (2294563 for 2·HBr, 2294561 for 4, 2294562 for Cs[5]·0.5Me₂CO, 2294564 for 8, and 2294565 for 10) contain the Supplementary Materials for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (accessed on 9 October 2023).

4. Conclusions

A series of *C*- and *B*-substituted *nido*-carborane derivatives with a pyridyl pendant group was prepared. The obtained compounds were used as ligands in the complexation with $[(Ph_3P)_2NiCl_2]$ and $[(Ph_3P)_2PdCl_2]$ to give the corresponding $\eta^5:\kappa^1(N)$ coordinated complexes of nickel(II) and palladium(II), 3-Ph_3P-3-(4(7)-NC_5H_4-2'-S)-*closo*-3,1,2-MC_2B_9H_{10}, 3-Ph_3P-3-(1(2)-NC_5H_4-2'-S)-*closo*-3,1,2-MC_2B_9H_{10}, and 3-Ph_3P-3-(1(2)-NC_5H_4-2'-CH_2S)-*closo*-3,1,2-MC_2B_9H_{10} (M=Ni, Pd). The study of the catalytic activity of the obtained complexes is in progress.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/ijms242015069/s1, The NMR spectra of compounds 1–11 and crystallographic data on compounds 2, 4, 5, 8, and 10.

Author Contributions: Experiment design, synthesis, IR and UV spectroscopy studies, and manuscript writing, M.Y.S.; synthesis, D.K.S.; NMR spectroscopy studies, S.A.A.; synthesis, S.V.T.; single crystal X-ray diffraction experiments, K.Y.S.; supervision and manuscript concept, I.B.S. All authors have read and agreed to the published version of the manuscript.

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References

- 1. Hawthorne, M.F.; Young, D.C.; Garrett, P.M.; Owen, D.A.; Schwerin, S.G.; Tebbe, F.N.; Wegner, P.A. Preparation and characterization of the (3)-1,2- and (3)-1,7-dicarbadodecahydroundecaborate(-1) ions. J. Am. Chem. Soc. **1968**, *90*, 862–868. [CrossRef]
- Grimes, R.N. Chapter 7—Eleven-Vertex Carboranes. In *Carboranes*, 3rd ed.; Academic Press: London, UK, 2016; pp. 179–247. [CrossRef]
- Hawthorne, M.F.; Young, D.C.; Wegner, P.A. Carbametallic boron hydride derivatives. I. Apparent analogs of ferrocene and ferricinium ion. J. Am. Chem. Soc. 1965, 87, 1818–1819. [CrossRef]
- Hawthorne, M.F.; Pilling, R.L. Carbametallic boron hydride derivatives. III. The π-C₅H₅Fe(π-B₉C₂H₁₁) system. *J. Am. Chem. Soc.* 1965, 87, 3987–3988. [CrossRef]
- Zalkin, A.; Templeton, D.H.; Hopkins, T.E. The crystal and molecular structure of C₅H₅FeB₉C₂H₁₁. *J. Am. Chem. Soc.* 1965, *87*, 3988–3990. [CrossRef]
- Hawthorne, M.F.; Young, D.C.; Andrews, T.D.; Howe, D.W.; Pilling, R.L.; Pitts, A.D.; Reintjes, M.; Warren, L.F.; Wegner, P.A. π-Dicarbollyl derivatives of the transition metals. Metallocene analogs. *J. Am. Chem. Soc.* 1968, 90, 879–896. [CrossRef]

- Grimes, R.N. Chapter 13—Metallacarboranes of the Transition and Lanthanide Elements. In *Carboranes*, 3rd ed.; Academic Press: London, UK, 2016; pp. 711–903. [CrossRef]
- 8. Kar, S.; Pradhan, A.N.; Ghosh, S. Polyhedral metallaboranes and metallacarboranes. In *Comprehensive Organometallic Chemistry IV*; Elsevier: Amsterdam, The Netherlands, 2022; Volume 9, pp. 263–369. [CrossRef]
- Jutzi, P.; Siemeling, U. Cyclopentadienyl compounds with nitrogen donors in the side-chain. J. Organomet. Chem. 1995, 500, 175–185. [CrossRef]
- 10. Siemeling, U. Chelate complexes of cyclopentadienyl ligands bearing pendant O-donors. Chem. Rev. 2000, 100, 1495–1526. [CrossRef]
- 11. Butenschön, H. Cyclopentadienylmetal complexes bearing pendant phosphorus, arsenic, and sulfur ligands. *Chem. Rev.* 2000, 100, 1527–1564. [CrossRef]
- 12. Müller, C.; Vos, D.; Jutzi, P. Results and perspectives in the chemistry of side-chain-functionalized cyclopentadienyl compounds. *J. Organomet. Chem.* **2000**, *600*, 127–143. [CrossRef]
- 13. Krut'ko, D.P. Zirconium and titanium complexes with side-chain functionalized cyclopentadienyl ligands. *Russ. Chem. Bull.* 2009, 58, 1745–1771. [CrossRef]
- 14. Son, K.; Waymouth, R.M. Stereospecific styrene polymerization and ethylene–styrene copolymerization with titanocenes containing a pendant amine donor. *J. Polym. Sci. A* 2010, *48*, 1579–1585. [CrossRef]
- Batuecas, M.; Esteruelas, M.A.; García-Yebra, C.; Oñate, E. Redox isomerization of allylic alcohols catalyzed by osmium and ruthenium complexes containing a cyclopentadienyl ligand with a pendant amine or phosphoramidite group: X-ray structure of an η³-1-hydroxyallyl-metal-hydride intermediate. *Organometallics* 2010, 29, 2166–2175. [CrossRef]
- 16. Varga, V.; Večeřa, M.; Gyepes, R.; Pinkas, J.; Horáček, M.; Merna, J.; Lamač, M. Effects of the linking of cyclopentadienyl and ketimide ligands in titanium half-sandwich olefin polymerization catalysts. *ChemCatChem* **2017**, *9*, 3160–3172. [CrossRef]
- 17. Dunlop, D.; Večeřa, M.; Gyepes, R.; Kubát, P.; Lang, K.; Horáček, M.; Pinkas, J.; Šimková, L.; Liška, A.; Lamač, M. Luminescent cationic Group 4 metallocene complexes stabilized by pendant *N*-donor groups. *Inorg. Chem.* **2021**, *60*, 7315–7328. [CrossRef]
- Urbán, B.; Dunlop, D.; Gyepes, R.; Kubát, P.; Lang, K.; Horáček, M.; Pinkas, J.; Šimková, L.; Lamač, M. Luminescent zirconocene complexes with pendant phosphine chalcogenide donor groups. *Organometallics* 2023, 42, 1373–1385. [CrossRef]
- Krut'ko, D.P.; Kirsanov, R.S.; Belov, S.A.; Borzov, M.V.; Churakov, A.V. Complexes of titanium and zirconium based on [C₅Me₄CH₂-(2-C₅H₄N)] ligand. *J. Organomet. Chem.* 2007, 692, 1465–1471. [CrossRef]
- Ackroyd, N.C.; Katzenellenbogen, J.A. Pyridyl-cyclopentadiene Re(CO)₂⁺ complexes as a compact core system for SPECT ligand development. *Organometallics* 2010, 29, 3669–3671. [CrossRef]
- 21. Chen, D.; Li, Y.; Wang, B.; Xu, S.; Song, H. Reactions of pyridyl side-chain-functionalized cyclopentadienes with metal carbonyl: Intramolecular C-H activation of pyridine. *Organometallics* **2006**, *25*, 307–310. [CrossRef]
- Lin, J.; Ma, Z.-H.; Li, F.; Zhao, M.-X.; Liu, X.-H.; Zheng, X.-Z. Reactions of pyridyl side chain functionalized cyclopentadiene with ruthenium carbonyl. *Trans. Met. Chem.* 2009, 34, 855–859. [CrossRef]
- Ma, Z.-H.; Han, Y.-X.; Wang, H.; Han, Z.-G.; Zheng, X.-Z.; Lin, J. Synthesis and crystal structures of three metal carbonyl complexes based on pyridyl side chain functionalized tetramethylcyclopentadienyl ligand. *Chin. J. Struct. Chem.* 2015, 34, 931–937.
- Zhang, S.; Liu, K.; Zhu, B. Reactions of pyridine-2-ethyl/methyl cyclopentadienes with metal carbonyls. J. Coord. Chem. 2018, 71, 16–18. [CrossRef]
- Blais, M.S.; Chien, J.C.W.; Rausch, M.D. Pendent aminoalkyl-substituted monocyclopentadienyltitanium compounds and their polymerization behavior. Organometallics 1998, 17, 3775–3783. [CrossRef]
- 26. Coult, R.; Fox, M.A.; Gill, W.R.; Herbertson, P.L.; MacBride, J.A.H.; Wade, K. C-arylation and C-heteroarylation of icosahedral carboranes via their copper(I) derivatives. *J. Organomet. Chem.* **1993**, *462*, 19–29. [CrossRef]
- Alekseyeva, E.S.; Batsanov, A.S.; Boyd, L.A.; Fox, M.A.; Hibbert, T.G.; Howard, J.A.K.; MacBride, J.A.H.; Mackinnon, A.; Wade, K. Intra- and inter-molecular carboranyl C−H···N hydrogen bonds in pyridyl-containing *ortho*-carboranes. *Dalton Trans.* 2003, 475–482. [CrossRef]
- Wang, X.; Jin, G.-X. Preparation, structure, and olefin polymerization behavior of a picolyl-functionalized carborane nickel(II) complex. Organometallics 2004, 23, 6319–6322. [CrossRef]
- 29. Wang, X.; Jin, G.-X. Preparation, structure, and ethylene polymerization behavior of half-sandwich picolyl-functionalized carborane iridium, ruthenium, and rhodium complexes. *Chem. Eur. J.* **2005**, *11*, 5758–5764. [CrossRef] [PubMed]
- Lu, J.-Y.; Wan, H.; Zhang, J.; Wang, Z.; Li, Y.; Du, Y.; Li, C.; Liu, Z.-T.; Liu, Z.-W.; Lu, J. Palladium-catalyzed direct cross-coupling of carboranyllithium with (hetero)aryl halides. *Chem. Eur. J.* 2016, 22, 17542–17546. [CrossRef]
- 31. Islam, M.J.; Smith, M.D.; Peryshkov, D.V. Sterically encumbered dianionic dicarboranyl pincer ligand (C₅H₃N)(C₂B₁₀H₁₁)₂ and its CNC nickel(II) complex. *J. Organomet. Chem.* **2018**, *867*, 208–213. [CrossRef]
- Anderson, K.P.; Mills, H.A.; Mao, C.; Kirlikovali, K.O.; Axtell, J.C.; Rheingold, A.L.; Spokoyny, A.M. Improved synthesis of icosahedral carboranes containing exopolyhedral B-C and C-C bonds. *Tetrahedron* 2019, 75, 187–191. [CrossRef]
- Terrasson, V.; Planas, J.G.; Prim, D.; Viñas, C.; Teixidor, F.; Light, M.E.; Hursthouse, M.B. Cooperative effect of carborane and pyridine in the reaction of carboranyl alcohols with thionyl chloride: Halogenation versus oxidation. *J. Org. Chem.* 2008, 73, 9140–9143. [CrossRef]
- 34. Terrasson, V.; Planas, J.G.; Viñas, C.; Teixidor, F.; Prim, D.; Light, M.E.; Hursthouse, M.B. *closo-o*-Carboranylmethylamine-pyridine associations: Synthesis, characterization, and first complexation studies. *Organometallics* **2010**, *29*, 4130–4134. [CrossRef]

- Di Salvo, F.; Camargo, B.; García, Y.; Teixidor, F.; Viñas, C.; Planas, J.G.; Light, M.E.; Hursthouse, M.B. Supramolecular architectures in *o*-carboranylalcohols bearing *N*-aromatic rings: Syntheses, crystal structures and melting points correlation. *CrystEngComm* 2011, 13, 5788–5806. [CrossRef]
- Peng, B.; Nie, Y.; Miao, J.; Zhang, Z.; Xu, M.; Sun, G. Synthesis, structures and photophysical properties of (*o*-carboranyl)-(pyridyl)methanols. *J. Mol. Struct.* 2012, 1007, 214–219. [CrossRef]
- Di Salvo, F.; Paterakis, C.; Tsang, M.Y.; García, Y.; Viñas, C.; Teixidor, F.; Planas, J.G.; Light, M.E.; Hursthouse, M.B.; Choquesillo-Lazarte, D. Synthesis and crystallographic studies of disubstituted carboranyl alcohol derivatives: Prevailing chiral recognition? *Cryst. Growth Des.* 2013, 13, 1473–1484. [CrossRef]
- Tsang, M.Y.; Viñas, C.; Teixidor, F.; Planas, J.G.; Conde, N.; SanMartin, R.; Herrero, M.T.; Domínguez, E.; Lledós, A.; Vidossich, P.; et al. Synthesis, structure, and catalytic applications for *ortho-* and *meta-*carboranyl based NBN pincer-Pd complexes. *Inorg. Chem.* 2014, 53, 9284–9295. [CrossRef]
- Teixidor, F.; Laromaine, A.; Kivekäs, R.; Sillanpää, R.; Viñas, C.; Vespalec, R.; Horakova, H. Synthesis, reactivity and complexation studies of *N*,*S exo*-heterodisubstituted *o*-carborane ligands. Carborane as a platform to produce the uncommon bidentate chelating (pyridine)N-C-C-C-S(H) motif. *Dalton Trans.* 2008, 345–354. [CrossRef]
- Di Salvo, F.; Teixidor, F.; Viñas, C.; Planas, J.G.; Light, M.E.; Hursthouse, M.B.; Aliaga-Alcalde, N. Metallosupramolecular chemistry of novel chiral *closo-o*-carboranylalcohol pyridine and quinoline ligands: Syntheses, characterization, and properties of cobalt complexes. *Cryst. Growth Des.* 2012, *12*, 5720–5736. [CrossRef]
- Di Salvo, F.; Teixidor, F.; Viñas, C.; Planas, J.G. A distinct tetradentate N₂O₂-type ligand: (*o*-Carboranyl)bis(2-hydroxymethyl)pyridine. Z. Anorg. Allg. Chem. 2013, 639, 1194–1198. [CrossRef]
- 42. Bae, H.J.; Kim, H.; Lee, K.M.; Kim, T.; Eo, M.; Lee, Y.S.; Do, Y.; Lee, M.H. Heteroleptic tris-cyclometalated iridium(III) complexes supported by an *o*-carboranyl-pyridine ligand. *Dalton Trans.* **2013**, *42*, 8549–8552. [CrossRef]
- 43. Di Salvo, F.; Tsang, M.Y.; Teixidor, F.; Viñas, C.; Planas, J.G.; Crassous, J.; Vanthuyne, N.; Aliaga-Alcalde, N.; Ruiz, E.; Coquerel, G.; et al. A racemic and enantiopure unsymmetric diiron(III) complex with a chiral *o*-carborane-based pyridylalcohol ligand: Combined chiroptical, magnetic, and nonlinear optical properties. *Chem. Eur. J.* 2014, 20, 1081–1090. [CrossRef]
- Tsang, M.Y.; Teixidor, F.; Viñas, C.; Choquesillo-Lazarte, D.; Aliaga-Alcalde, N.; Planas, J.G. Synthesis, structures and properties of ironIII complexes with (*o*-carboranyl)bis-(2-hydroxymethyl)pyridine: Racemic versus meso. *Inorg. Chim. Acta* 2016, 448, 97–103. [CrossRef]
- 45. Tsang, M.Y.; Rodríguez-Hermida, S.; Stylianou, K.C.; Tan, F.; Negi, D.; Teixidor, F.; Viñas, C.; Choquesillo-Lazarte, D.; Verdugo-Escamilla, C.; Guerrero, M.; et al. Carborane bis-pyridylalcohols as linkers for coordination polymers: Synthesis, crystal structures, and guest-framework dependent mechanical properties. *Cryst. Growth Des.* **2017**, *17*, 846–857. [CrossRef]
- 46. Tsang, M.Y.; Viñas, C.; Teixidor, F.; Choquesillo-Lazarte, D.; Planas, J.G. Crystalline inclusion compounds of a palladacyclic tetraol host featuring *o*-carborane units. *Eur. J. Inorg. Chem.* **2017**, 2017, 4589–4598. [CrossRef]
- 47. Guo, S.-T.; Cui, P.-F.; Gao, Y.; Jin, G.-X. Regioselective B-H/C-H activation and metal-metal bond formation induced by half-sandwich metals complexes at hydroxy-substituted *o*-carboranes. *Dalton Trans.* **2018**, *47*, 13641–13646. [CrossRef]
- 48. Islam, M.J.; Park, K.C.; Manley, O.M.; Smith, M.D.; Makris, T.M.; Peryshkov, D.V. Room-temperature aerobic C-CN bond activation in nickel(II) cyanomethyl dicarboranyl complex. *Organometallics* **2023**, *42*, 1997–2004. [CrossRef]
- Viñas, C.; Laromaine, A.; Teixidor, F.; Horakova, H.; Langauf, A.; Vespalec, R.; Mata, I.; Molins, E. Synthesis and investigation of the boron cluster anion [7-(2'-pyridyl)-7,8-nido-dicarbaundecaborate] and its protonated form. *Dalton Trans.* 2007, 3369–3377. [CrossRef]
- Lee, J.-D.; Lee, Y.-J.; Son, K.-C.; Han, W.-S.; Cheong, M.; Ko, J.; Kang, S.O. Synthesis, characterization, and reactivity of new types of constrained geometry group 4 metal complexes derived from picolyl-substituted dicarbollide ligand systems. *J. Organomet. Chem.* 2007, 692, 5403–5413. [CrossRef]
- 51. Frank, R.; Grell, T.; Hiller, M.; Hey-Hawkins, E. Electrophilic substitution of the *nido*-dicarbaborate anion 7,8-*nido*-C₂B₉H₁₂⁻ with sulfenyl chlorides. *Dalton Trans.* **2012**, *41*, 6155–6161. [CrossRef]
- 52. Park, J.-S.; Kim, D.-H.; Kim, S.-J.; Ko, J.; Kim, S.H.; Cho, S.; Lee, C.-H.; Kang, S.O. Preparation and reactions of a half-sandwich dicarbollyl nickel(II) complex containing a dimethylamino pendent group. *Organometallics* **2001**, *20*, 4483–4491. [CrossRef]
- Lee, J.-D.; Lee, Y.-J.; Son, K.-C.; Cheong, M.; Ko, J.; Kang, S.O. New types of constrained geometry group 4 metal complexes derived from the aminomethyldicarbollyl ligand system: Synthesis and structural characterization of mono-dicarbollylamino and bis-dicarbollylamino group 4 metal complexes. *Organometallics* 2007, 26, 3374–3384. [CrossRef]
- 54. Lee, J.-D.; Kim, S.-K.; Kim, T.J.; Han, W.-S.; Lee, Y.-J.; Yoo, D.-H.; Cheong, M.; Ko, J.; Kang, S.O. Dicarbollylamine ligand as a tunable template for σ,σ- and π,σ-bonding modes: Syntheses, structures, and theoretical studies of η⁵:η¹-coordinated constrained-geometry group 13 metal complexes. *J. Am. Chem. Soc.* **2008**, *130*, 9904–9917. [CrossRef] [PubMed]
- 55. Kang, S.O.; Lee, J.-D. New types of charge-compensated metallacarboranes: Synthesis, characterization, and structural studies of [(η⁵-RC₂B₉H₉CH₂NMe₂)Cr(μ-Cl)Cl]₂ (R = H, Me). J. Organomet. Chem. 2015, 798, 121–124. [CrossRef]
- Liu, D.; Qiu, Z.; Xie, Z. Synthesis, structure, and alkyne insertion of a mixed-sandwich zirconacarborane alkyl. *Inorg. Chem. Front.* 2015, 2, 467–472. [CrossRef]

- Liu, D.; Qiu, Z.; Xie, Z. Synthesis, structure, and reactivity of mixed-sandwich zirconacarborane methyl complex (η⁵-C₅Me₅)[η¹:η⁵-(Me₂NCH₂CH₂)C₂B₉H₁₀]ZrMe. J. Organomet. Chem. **2016**, 822, 144–153. [CrossRef]
- Axtell, J.C.; Kirlikovali, K.O.; Djurovich, P.I.; Jung, D.; Nguyen, V.T.; Munekiyo, B.; Royappa, A.T.; Rheingold, A.L.; Spokoyny, A.M. Blue phosphorescent zwitterionic iridium(III) complexes featuring weakly coordinating *nido*-carborane-based ligands. *J. Am. Chem. Soc.* 2016, 138, 15758–15765. [CrossRef]
- Mingos, D.M.P.; Forsyth, M.I.; Welch, A.J. X-Ray crystallographic and theoretical studies on 'slipped' metallacarboranes. J. Chem. Soc., Chem. Commun. 1977, 605–607. [CrossRef]
- 60. Mingos, D.M.P. Molecular-orbital studies on carbametallaboranes. Part 1. Icosahedral carbaplatinaborane polyhedral. *J. Chem. Soc. Dalton Trans.* **1977**, 602–610. [CrossRef]
- Mingos, D.M.P.; Forsyth, M.I.; Welch, A.J. Molecular and crystal structure of 3,3-bis(triethylphosphine)-1,2-dicarba- 3-platinadodecaborane(11), and molecular-orbital analysis of the 'slip' distortion in carbametallaboranes. *J. Chem. Soc. Dalton Trans.* 1978, 1363–1374. [CrossRef]
- 62. Kennedy, R.D.; Kennedy, J.D. The contrarotational fluxionality of [3,3-(PMe₂Ph)₂-*closo*-3,1,2-PtC₂B₉H₁₁] and related species. *Dalton Trans.* **2015**, 44, 9620–9629. [CrossRef]
- 63. Sivaev, I.B.; Bregadze, V.I. Chemistry of nickel and iron bis(dicarbollides). A review. J. Organomet. Chem. 2000, 614–615, 27–36. [CrossRef]
- 64. Nan, R.; Li, Y.; Zhu, Z.; Qi, F.; Xiao, X.-Q. Nickelacarborane-supported bis-*N*-heterocyclic carbenes. *J. Am. Chem. Soc.* 2023, 145, 15538–15546. [CrossRef] [PubMed]
- Semyonov, D.K.; Slushko, G.K.; Stogniy, M.Y.; Anufriev, S.A.; Godovikov, I.A.; Suponitsky, K.Y.; Bregadze, V.I.; Sivaev, I.B. Interligand interactions in half-sandwich nickelacarboranes with phosphine ligands: Away from skeletal rearrangements. Organometallics 2023, 42, 2522–2530. [CrossRef]
- 66. Semyonov, D.K.; Stogniy, M.Y.; Suponitsky, K.Y.; Sivaev, I.B. Half-sandwich nickelacarboranes derived from [7-(MeO(CH₂)₂S)-7,8-C₂B₉H₁₁]⁻. *Inorganics* **2023**, *11*, 127. [CrossRef]
- Mandal, D.; Man, W.Y.; Rosair, G.M.; Welch, A.J. Steric versus electronic factors in metallacarborane isomerisation: Nickelacarboranes with 3,1,2-, 4,1,2- and 2,1,8-NiC₂B₉ architectures and pendant carborane groups, derived from 1,1'-bis(*o*-carborane). *Dalton Trans.* 2016, 45, 15013–15025. [CrossRef] [PubMed]
- 68. Mandal, D.; Rosair, G.M. Exploration of bis(nickelation) of 1,1'-bis(o-carborane). *Crystals* **2021**, *11*, 16. [CrossRef]
- 69. Stogniy, M.Y.; Erokhina, S.A.; Suponitsky, K.Y.; Markov, V.Y.; Sivaev, I.B. Synthesis and crystal structures of nickel(II) and palladium(II) complexes with *o*-carboranyl amidine ligands. *Dalton Trans.* **2021**, *50*, 4967–4975. [CrossRef]
- 70. Stogniy, M.Y.; Erokhina, S.A.; Suponitsky, K.Y.; Sivaev, I.B.; Bregadze, V.I. Coordination ability of 10-EtC(NHPr)=HN-7,8-C₂B₉H₁₁ in the reactions with nickel(II) phosphine complexes. *Crystals* **2021**, *11*, 306. [CrossRef]
- 71. Hao, E.; Friso, E.; Miotto, G.; Jori, G.; Soncin, M.; Fabris, C.; Sibrian-Vazquez, M.; Vicente, M.G.H. Synthesis and biological investigations of tetrakis(*p*-carboranylthio-tetrafluorophenyl)chlorin (TPFC). *Org. Biomol. Chem.* **2008**, *6*, 3732–3740. [CrossRef]
- Gibbs, J.H.; Wang, H.; Bhupathiraju, N.V.S.D.K.; Fronczek, F.R.; Smith, K.M.; Vicente, M.G.H. Synthesis and properties of a series of carboranyl-BODIPYs. J. Organomet. Chem. 2015, 798, 209–213. [CrossRef]
- 73. Kellert, M.; Lönnecke, P.; Riedl, B.; Koebberling, J.; Hey-Hawkins, E. Enlargement of a modular system—Synthesis and characterization of an *s*-triazine-based carboxylic acid ester bearing a galactopyranosyl moiety and an enormous boron load. *Molecules* **2019**, *24*, 3288. [CrossRef]
- Alpatova, V.A.; Rys, E.G.; Kononova, E.G.; Khakina, E.A.; Markova, A.A.; Shibaeva, A.V.; Kuzmin, V.A.; Ol'shevskaya, V.A. Multicomponent molecular systems based on porphyrins, 1,3,5-triazine and carboranes: Synthesis and characterization. *Molecules* 2022, 27, 6200. [CrossRef] [PubMed]
- Stogniy, M.Y.; Sivaev, I.B.; Petrovskii, P.V.; Bregadze, V.I. Synthesis of monosubstituted functional derivatives of carboranes from 1-mercapto-*ortho*-carborane: 1-HOOC(CH₂)_nS-1,2-C₂B₁₀H₁₁ and [7-HOOC(CH₂)_nS-7,8-C₂B₉H₁₁]⁻ (*n* = 1-4). *Dalton Trans.* 2010, 39, 1817–1822. [CrossRef] [PubMed]
- Stogniy, M.Y.; Zakharova, M.V.; Sivaev, I.B.; Godovikov, I.A.; Chizov, A.O.; Bregadze, V.I. Synthesis of new carborane-based amino acids. *Polyhedron* 2013, 55, 117–120. [CrossRef]
- 77. Stogniy, M.Y.; Sivaev, I.B.; Godovikov, I.A.; Starikova, Z.A.; Bregadze, V.I.; Qi, S. Synthesis of new ω-amino- and ω-azidoalkyl carboranes. *New J. Chem.* **2013**, *37*, 3865–3868. [CrossRef]
- Stogniy, M.Y.; Erokhina, S.A.; Druzina, A.A.; Sivaev, I.B.; Bregadze, V.I. Synthesis of novel carboranyl azides and "click" reactions thereof. J. Organomet. Chem. 2019, 904, 121007. [CrossRef]
- 79. Druzina, A.A.; Stogniy, M.Y. Synthesis of cholesterol derivatives based on *closo-* and *nido-*carboranes. *Russ. Chem. Bull.* **2021**, 70, 527–532. [CrossRef]
- Standley, E.A.; Smith, S.J.; Müller, P.; Jamison, T.F. A broadly applicable strategy for entry into homogeneous nickel(0) catalysts from air-stable nickel(II) complexes. *Organometallics* 2014, 33, 2012–2018. [CrossRef]
- Itatani, H.; Bailar, J.C. Homogenous catalysis in the reactions of olefinic substances. V. Hydrogenation of soybean oil methyl ester with triphenylphosphine and triphenylarsine palladium catalysts. J. Am. Oil Chem. Soc. 1967, 44, 147–151. [CrossRef]
- 82. Armarego, W.L.F.; Chai, C.L.L. Purification of Laboratory Chemicals, 6th ed.; Butterworth-Heinemann: Burlington, UK, 2009.

- 83. APEX2 and SAINT; Bruker AXS Inc.: Madison, WI, USA, 2014.
- 84. Sheldrick, G.M. Crystal structure refinement with SHELXL. Acta Cryst. C 2015, 71, 3–8. [CrossRef]

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