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Novel Synthetic Approach to Charge-Compensated Phosphonio-*nido*-Carboranes. Synthesis and Structural Characterization of Neutral Mono and Bis(Phosphonio) *nido-ortho*-Carboranes

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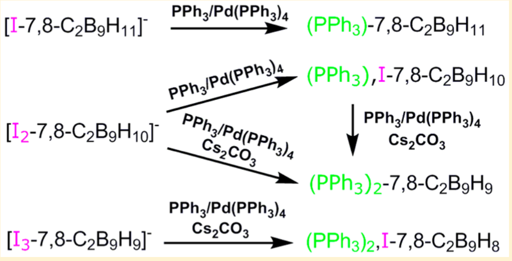
Supporting Information



ABSTRACT: A number of monosubstituted *n*-(triphenylphosphonio)-7,8-dicarba-*nido*-undecaboranes (**2a**, *n* = 1; **2b**, *n* = 3; **2c**, *n* = 5; **2d**, *n* = 9) were prepared via a cross-coupling reaction between the tetrabutylammonium iodo-7,8-dicarba-*nido*-undecaborates (**1a−d**) and PPh_3 in the presence of a $Pd(PPh_3)_4$ catalyst. The substitution rate was found to depend on the iodine position in the carborane cage. Under similar conditions, the reaction of 5,6-diiodo- (**3**) and 9,11-diiodo-7,8-dicarba-*nido*-undecaborate (**5**) anions exclusively yielded the monosubstitution products 5-iodo-6-(triphenylphosphonio)-7,8-dicarba-*nido*-undecaborane (**4**) and 9-iodo-11-(triphenylphosphonio)-7,8-dicarba-*nido*-undecaborane (**6**), respectively. The reaction of tetrabutylammonium 6,9-diiodo-7,8-dicarba-*nido*-undecaborate (**7**) exclusively produced the phosphine substitution product in the open face of the *nido*-carborane, 6-iodo-9-triphenylphosphonio-7,8-dicarba-*nido*-undecaborane (**8**). The addition of a base (Cs_2CO_3, NaH) to the reactions of **3** and **5** with PPh_3 afforded the corresponding bis(triphenylphosphonio)-7,8-dicarba-*nido*-undecaboranes, **9** and **10**. Compound **10** was also prepared from **6** using the general procedure. The reaction of the triiodocarborane tetrabutylammonium 5,6,9-triiodo-7,8-dicarba-*nido*-undecaborate (**11**) with excess PPh_3 in the presence of Cs_2CO_3 and $Pd(PPh_3)_4$ only produced neutral 5-iodo-6,9-bis(triphenylphosphonio)-7,8-dicarba-*nido*-undecaborane (**12**); no positively charged tris(phosphonio) species formed. The compositions of all prepared compounds were determined by multinuclear NMR spectroscopy and high-resolution mass spectrometry. The structures of compounds **2c**, **6**, **8**, **9**, and **12** were established by the X-ray diffraction analysis of single crystals.

INTRODUCTION

The term "charge-compensated" defines a large group of substituted polyhedral boron hydrides containing one or two Lewis base-type ligands directly connected to cage boron atoms. In the case of boron hydrides, "charge compensation" refers to decreasing the overall *negative* charge of the polyhedral anion,[1] that is, each charge-compensating substituent decreases the negative charge of the molecule by one unit. Although one might assume that the substituent itself bears a positive charge, charge-compensated compounds should instead be considered donor−acceptor complexes in which the electron pair of the Lewis base is coordinated with the formal boron cation center formed after hydride abstraction from the parent polyhedral boron cluster.

Because charge-compensated boron hydrides contain Lewis acid and base components, they can easily be classified by these two features. On the basis of the Lewis acid component, all charge-compensated compounds can be classified as charge-compensated boranes, carboranes, and metallacarboranes,[2] with charge-compensated *nido*-carboranes being the most prevalent charge-compensated polyhedral boranes with the most developed synthetic methods. Meanwhile, on the basis of the Lewis base component, all charge-compensated polyhedral boranes can be classified as complexes of amines, ethers, phosphines, and sulfides.[3]

Because of their possibility of ligating transition metal ions, charge-compensated *nido*-carborane compounds played an important role in the development of the metallacarborane chemistry. Unlike dicarbollide ligands, which bear a double negative charge and thus favor the complexation of metal ions in high oxidation states, singly negatively charged charge-compensated dicarbollide ligands were found to preferentially form complexes with transition metals in low oxidation states.[4] It has been previously demonstrated that unsubstituted bis(dicarbollyl) complexes of Fe(II), Co(II), and Ni(II) instantly oxidize in air to form more stable complexes of Fe(III), Co(III), and Ni(III).[5] The use of charge-compensated ligands allowed for the isolation and structural characterization of air-stable bis(dicarbollyl) complexes of Fe(II), Co(II), Ni(II), and Ru(II).[6,7] Later, it was demonstrated that charge-compensated metallacarboranes can catalyze organic reactions.[8]

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Among all the prepared and described charge-compensated *nido*-carboranes, the most underrepresented group is the phosphonio-*nido*-carboranes: only two articles describing their synthesis from *nido*-carboranes have been published.[3g,9] The established synthetic route—the reaction of *nido*-carboranes with phosphines in the presence of an oxidizer—only allows for the synthesis of phosphonio-*nido*-carboranes with the substituent positioned in the open pentagonal face of the *nido*-carborane anion. To stimulate the further development of carborane chemistry, it is very important to search for alternative synthetic routes for B−P bond formation. For example, phosphonio-*nido*-carboranes might be attractive tunable ligands in various metallacarboranes because of the steric and electronic flexibility of phosphines. It has also been demonstrated that similar compounds may serve as agents for mitochondria-targeted boron neutron capture therapy.[10] Herein, a new catalytic approach to mono- and bis(phosphonio)-*nido*-carboranes starting from the corresponding iodo-*nido*-carboranes and phosphines is described.

■ EXPERIMENTAL SECTION

Instrumentation. ^{1}H, ^{11}B{^{1}H}, ^{11}B, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker Avance-400 NMR spectrometer. Boron NMR spectra were referenced to 15% $BF_3 \cdot Et_2O$ in $CDCl_3$ taken as 0 ppm. Phosphorus NMR spectra were referenced to 85% H_3PO_4 taken as 0 ppm. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to the residual peak of the nondeuterated solvent. Chemical shifts were reported in parts per million, and the coupling constants were reported in hertz. Mass spectra were obtained using a Mariner Biospectrometry Workstation by PerSeptive Biosystems and 7-T Bruker Apex-Ultra FTICR. Melting points were measured in sealed capillaries using an SRS OptiMelt apparatus. Chromatography separations were performed in air using SorbTech silica (60 Å, 63−200 μm). Thin-layer chromatography was performed using Merck precoated glass plates (Silica 60 F254) and a palladium stain solution for spot development.

Materials. Unless otherwise stated, all reactions were performed under an argon atmosphere using standard Schlenk-line techniques. Tetrabutylammonium salts of 1-iodo-7,8-dicarba-*nido*-undecaborate (**1a**), 3-iodo-7,8-dicarba-*nido*-undecaborate (**1b**), 5-iodo-7,8-dicarba-*nido*-undecaborate (**1c**), and 5,6-diiodo-7,8-dicarba-*nido*-undecaborate (**3**) were prepared from the corresponding *closo*-carboranes according to a previously published procedure.[11] Tetrabutylammonium salts of 9-iodo-7,8-dicarba-*nido*-undecaborate (**1d**) and 9,11-diiodo-7,8-dicarba-*nido*-undecaborate (**5**) were prepared by the iodination of tetrabutylammonium 7,8-dicarba-*nido*-undecaborate according to a previously published procedure.[12] Triphenylphosphine, *N*-iodosuccinimide (NIS), anhydrous dioxane, tetrahydrofuran (THF), and cesium carbonate (Cs_2CO_3) were purchased from Aldrich and used as received. Tetrakis(triphenylphosphine)palladium [$Pd(PPh_3)_4$] was purchased from Strem Chemicals.

*General Preparation Procedure for Triphenylphosphonio-7,8-dicarba-nido-undecaboranes **2a**−**d**.* To a mixture of **1** (25 mg, 0.05 mmol), PPh_3 (26 mg, 0.1 mmol), and $Pd(PPh_3)_4$ taken as solids was added 1 mL of dioxane. The solution was stirred in an argon atmosphere at 90 °C until the starting material was completely consumed. The solvent was removed at reduced pressure, and the product was isolated by column chromatography using a CH_2Cl_2 gradient (0 → 50%) in hexane.

*1-Triphenylphosphonio-7,8-dicarba-nido-undecaborane (**2a**).* Catalyst weight, 8.7 mg (7.5 μmol); time, 40 h; yield, 11 mg (56%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77−7.67 (m, 6H), 7.68−7.64 (m, 3H), 7.58−7.54 (m, 6H), 2.10 (s, 2H, C$_{carb}$−H), 2.5−0.7 (br m, 8H), −2.20 (br m, 1H, B−*H*−B). ^{11}B NMR (128 MHz, $CDCl_3$) δ: −7.9 (d, *J* 140, 2B), −15.5 (d, *J* 139, 2B), −16.6 (d, *J* 151, 1B), −20.9 (d, *J* 151, 2B), −32.1 (dd, J_{B-H} 142, J_{B-H-B} 46, 1B), −34.8 (d, *J* 177, B−P, 1B). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 134.4 (d, *J* 8.8), 132.7 (d, *J* 2.2), 128.9 (d, *J* 11.7), 125.5 (d, *J* 72.6), 43.7 (br s, C$_{carb}$−H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ: 14.0 (q, *J* 172). MS (ESI+): 394.2560 [M − H]$^{+}$ (calcd for $C_{20}H_{26}B_9P$ 395.2646 [M]$^{+}$). mp 191−193 °C.

*3-Triphenylphosphonio-7,8-dicarba-nido-undecaborane (**2b**).* Catalyst weight, 12.0 mg (10 μmol); time −57 h; yield −9.3 mg (47%, white solid). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ: 7.85−7.72 (m, 15H), 2.10 (s, 2H, C$_{carb}$−H), 2.7−0.3 (br m, 8H), −2.63 (br m, 1H, B−*H*−B). ^{11}B NMR (128 MHz, $CDCl_3$) δ: −8.8 (d, *J* 140, 2B), −14.8 (d, *J* 140, 2B), −18.9 (d, *J* 174, 1B, B−P), −21.9 (d, *J* 153, 2B), −28.7 (d, *J* 103, 1B), −36.2 (d, *J* 143, 1B). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 135.1 (d, *J* 8.8), 134.7 (d, *J* 2.9), 130.7 (d, *J* 11.7), 121.8 (d, *J* 73.4), 44.0 (br m, C$_{carb}$−H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ: −1.3 (q, *J* 174). MS (APCI+): 396.3067 [M + H]$^{+}$ (calcd for $C_{20}H_{26}B_9P$ 395.2646 [M]$^{+}$). mp 245−247 °C.

*5-Triphenylphosphonio-7,8-dicarba-nido-undecaborane (**2c**).*[13] Catalyst weight, 6.0 mg (5 μmol); time −17 h; yield −15.0 mg (76%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63−7.47 (m, 15H), 2.36 (s, 1H, C$_{carb}$−H), 2.06 (s, 1H, C$_{carb}$−H), 3.0−0.25 (br m, 8H), −2.36 (br m, 1H, B−*H*−B). ^{11}B NMR (128 MHz, $CDCl_3$) δ: −7.8 (d, *J* 139, 1B), −11.2 (d, *J* 141, 1B), −13.1 (d, *J* 153, 1B), −15.8 (d, *J* 159, 1B), −19.6 (d, *J* 157, 1B), −23.5 (d, *J* 154, 1B), −24.0 (d, *J* 149, 1B, B−P), −32.1 (d, *J* 135, 1B), −37.5 (d, *J* 141, 1B). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 134.4 (d, *J* 9.5), 132.4 (d, *J* 2.9), 128.7 (d, *J* 11.0), 124.4 (d, *J* 71.9), 52.4 (br s, C$_{carb}$−H), 39.0 (br s, C$_{carb}$−H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ: 6.7 (q, *J* 150). MS (APCI+): 396.2596 [M + H]$^{+}$ (calcd for $C_{20}H_{26}B_9P$ 395.2646 [M]$^{+}$). mp 200−202 °C.

*9-Triphenylphosphonio-7,8-dicarba-nido-undecaborane (**2d**).* Catalyst weight, 6.0 mg (5 μmol); time −17 h; yield −14.0 mg (71%, white solid). ^{1}H NMR (400 MHz, acetone-d_6) δ: 7.66−7.77 (m, 15H), 2.44 (s, 1H, C$_{carb}$−H), 2.33 (s, 1H, C$_{carb}$−H), 0.2−1.7 (br m, 8H), −2.94 (br m, 1H, B−*H*−B). ^{11}B NMR (128 MHz, acetone-d_6) δ: −2.3 (d, *J* 139, 1B), −8.7 (d, *J* 149, 1B), −14.2 (d, *J* 153, 1B, B−P), −15.8 (d, *J* 160, 1B), −17.2 (d, *J* 167, 1B), −22.8 (d, *J* 154, 1B), −24.7 (d, *J* 148, 1B), −26.4 (d, *J* 140, 1B), −35.4 (d, *J* 142, 1B). ^{31}P NMR (162 MHz, acetone-d_6) δ: 7.1 (q, *J* 155). mp 207−209 °C. The spectra for the product correspond to the literature data.[3g]

*5-Iodo-6-triphenylphosphonio-7,8-dicarba-nido-undecaborane (**4**).* To a mixture of **3** (100 mg, 0.16 mmol), PPh_3 (84 mg, 0.32 mmol), and $Pd(PPh_3)_4$ (36 mg, 32 μmol) taken as solids was added dioxane (10 mL), and the reaction mixture was stirred at 90 °C for 48 h. The solvent was removed under vacuum, and the crude product was isolated by column chromatography using a CH_2Cl_2 gradient (0 → 100%) in hexane. After evaporation and drying, compound **4** was isolated as a white solid (63 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74−7.52 (m, 15H), 2.49 (s, 1H, C$_{carb}$−H), 2.41 (s, 1H, C$_{carb}$−H), 3.3−1.0 (br m, 7H), −2.14 (br m, 1H, B−*H*−B). ^{11}B NMR (128 MHz, $CDCl_3$): −6.1 (d, *J* 140, 1B), −12.7 (d, *J* 121, 1B), −16.3 (d, *J* 168, 1B), −18.7 (d, *J* 156, 1B), −22.2 − (−22.8) (3B, B−H, B−I, B−P), −29.4 (d, *J* 102, 1B), −35.7 (d, *J* 142, 1B). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 134.9 (d, *J* 8.8), 132.6 (d, *J* 3.5), 128.7 (d, *J* 12.4), 122.5 (d, *J* 71.7), 53.2 (br s, C$_{carb}$−H), 38.9 (br s, C$_{carb}$−H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ: 4.5 (q, *J* 158). MS (ESI^{-}): 519.9386 [M − H]$^{-}$ (calcd for $C_{20}H_{25}B_9PI$ 521.1612 [M]$^{-}$). mp 182−184 °C.

*9-Iodo-11-triphenylphosphonio-7,8-dicarba-nido-undecaborane (**6**).* To a mixture of **5** (400 mg, 0.64 mmol), PPh_3 (503 mg, 1.9 mmol), and $Pd(PPh_3)_4$ (75 mg, 64 μmol) taken as solids was added dioxane (30 mL), and the reaction mixture was stirred at 90 °C for 24 h. The solvent was removed under vacuum, and the crude product was isolated by column chromatography using a CH_2Cl_2 gradient (0 → 100%) in hexane. After evaporation and drying, compound **6** was isolated as a pale-orange solid (228 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68−7.56 (m, 15 H), 3.3−0.5 (br m, 7H), 2.65 (s, 1H, C$_{carb}$−H), 2.34 (s, 1H, C$_{carb}$−H), −1.46 (br m, 1H, B−*H*−B). ^{11}B NMR (128 MHz, $CDCl_3$): −2.6 (d, *J* 139, 1B), −5.7 (d, *J* 139, 1B), −12.9 (d, *J* 153, 1B, B−P), −16.0 (d, *J* 168, 1B), −21.9 (d, *J* 146, 1B), −24.4 (d, *J* 176, 1B), −25.9 (s+d, *J* 122, 2B, B−H+B−I), −34.3 (d, *J* 146, 1B). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 133.8 (d, *J* 9.5), 132.9 (d, *J* 2.2), 129.4 (d, *J* 11), 123.9 (d, *J* 71.9), 52.4 (br s, C$_{carb}$−H), 42.8 (br s, C$_{carb}$−H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ: 7.4 (q, *J* 153).

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MS ($\mathrm{ESI^-}$): 519.9292 $[\mathrm{M - H}]^-$ (calcd for $\mathrm{C_{20}H_{25}B_9PI}$ 521.1612 $[\mathrm{M}]^-$). mp 172–174 °C.

*Tetrabutylammonium 6,9-diiodo-7,8-dicarba-nido-undecaborate (**7**).*[14] To a solution of **1c** (100 mg, 0.2 mmol) in 5 mL of THF was added solid NIS (54 mg, 0.24 mmol). The resulting brown solution was stirred at 50 °C for 20 h. The solvent was removed under vacuum, and the product was isolated by column chromatography using a $\mathrm{CH_2Cl_2}$ gradient (0 → 100%) in hexane. After evaporation and drying, compound **7** was isolated as a white solid (78 mg, 62%). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ: 3.14–3.24 (m, 8H, TBA), 3.0–0.7 (br m, 7H), 2.54 (s, 1H, $\mathrm{C_{carb}}$–H), 2.05 (s, 1H, $\mathrm{C_{carb}}$–H), 1.63–1.69 (m, 8H, TBA), 1.46–1.52 (m, 8H, TBA), 1.05 (t, *J* 7.3, 12H, TBA), −2.11 (br m, 1H, B–*H*–B). ^{11}B NMR (128 MHz, $\mathrm{CDCl_3}$): −3.9 (d, *J* 140, 1B), −14.2 (d, *J* 149, 1B), −17.4 (d, *J* 130, 2B), −18.3 (s, 1B, B–I), −21.0 (d, *J* 152, 1B), −26.5 (d, *J* 110, 1B), −32.3 (s, 1B, B–I), −34.9 (d, *J* 145, 1B). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): 59.0 (TBA), 50.6 (br m, $\mathrm{C_{carb}}$–H), 38.5 (br m, $\mathrm{C_{carb}}$–H), 24.0 (TBA), 19.7 (TBA), 13.7 (TBA). MS ($\mathrm{ESI^-}$): 385.9534 $[\mathrm{M}]^-$ (calcd for $\mathrm{C_2B_9H_{10}I_2}$ 385.9746 $[\mathrm{M}]^-$).

*6-Iodo-9-triphenylphosphonio-7,8-dicarba-nido-undecaborane (**8**).* To a mixture of **7** (79 mg, 0.13 mmol), $\mathrm{PPh_3}$ (130 mg, 0.5 mmol), and $\mathrm{Pd(PPh_3)_4}$ (26 mg, 26 μmol) taken as solids was added dioxane (6 mL), and the reaction mixture was stirred at 90 °C for 48 h. The solvent was removed under vacuum, and the crude product was isolated by column chromatography using a $\mathrm{CH_2Cl_2}$ gradient (0 → 100%) in hexane. After evaporation and drying, compound **8** was isolated as a yellow solid (26 mg, 38%). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ: 7.67–7.55 (m, 15 H), 3.7–0.7 (br m, 7H), 2.45 (s, 1H, $\mathrm{C_{carb}}$–H), 2.36 (s, 1H, $\mathrm{C_{carb}}$–H), −2.04 (br s, 1H, B–*H*–B). ^{11}B NMR (128 MHz, $\mathrm{CDCl_3}$): −0.8 (d, 1B, *J* 140), −7.6 (d, 1B, *J* 121), −13.0 – (−14.1) (m, 2B, B–P+B–H), −16.6 (d, 1B, *J* 176), −22.2 (d, 1B, *J* 130), −22.8 (d, 1B, *J* 117), −32.7 (s, 1B, B–I), −33.1 (d, 1B, *J* 130). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): 133.8 (d, *J* 9.5), 132.9 (d, *J* 2.2), 129.4 (d, *J* 11.7), 124.1 (d, *J* 71.9), 51.2 (br s, $\mathrm{C_{carb}}$–H), 40.8 (br s, $\mathrm{C_{carb}}$–H). ^{31}P{^{1}H} NMR (162 MHz, $\mathrm{CDCl_3}$) δ: 7.0 (q, *J* 151). MS ($\mathrm{ESI^-}$): 519.9713 $[\mathrm{M - H}]^-$ (calcd for $\mathrm{C_{20}H_{25}B_9PI}$ 521.1612 $[\mathrm{M}]^-$)

*5,6-Bis(triphenylphosphonio)-7,8-dicarba-nido-undecaborane (**9**).* To a mixture of **3** (200 mg, 0.32 mmol), $\mathrm{PPh_3}$ (250 mg, 0.96 mmol), $\mathrm{Cs_2CO_3}$ (156 mg, 0.5 mmol) and $\mathrm{Pd(PPh_3)_4}$ (37 mg, 32 μmol) taken as solids was added dioxane (17 mL), and the reaction mixture was stirred at 90 °C for 64 h. The white precipitate formed was separated by filtration and dissolved in $\mathrm{CH_2Cl_2}$ (5 mL), and the solution was washed with water (3 × 1 mL) and dried over $\mathrm{MgSO_4}$. The solvent was removed under vacuum, and the residue was recrystallized from a $\mathrm{CH_2Cl_2}$/hexane mixture to give **9** as a white solid (100 mg, 48%) after drying. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ: 7.18–7.51 (m, 30H), 2.5–0.5 (br m, 7H), 1.52 (s, 2H, $\mathrm{C_{carb}}$–H). ^{11}B NMR (128 MHz, $\mathrm{CD_2Cl_2}$): −16.8 (d, *J* 75, 2B), −19 – (−22) (4B), −25.3 (d, *J* 134, 2B), −46.9 (d, *J* 137, 1B). ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{CDCl_3}$) δ: 134.6 (d, *J* 8.8), 131.2 (d, *J* 3.3), 128.03 (d, *J* 11), 126.8 (d, *J* 66.8), 34.2 (br s, $\mathrm{C_{carb}}$–H). ^{31}P{^{1}H} NMR (162 MHz, $\mathrm{CDCl_3}$) δ: 6.1 (m, q-like). MS ($\mathrm{ESI^+}$): 656.2636 $[\mathrm{M + H}]^+$ (calcd for $\mathrm{C_{38}H_{39}B_9P_2}$ 655.3400 $[\mathrm{M}]^+$). mp 333–335 °C (with decomposition).

*9,11-Bis(triphenylphosphonio)-7,8-dicarba-nido-undecaborane (**10**).* The compound was prepared according to the protocol described for the synthesis of **9**. The reaction reached completion after 24 h. Compound **10** was isolated as a white solid (161 mg, 77%). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ: 7.38–7.78 (m, 30 H), 2.3–0.7 (br m, 7H), 1.28 (s, 2H, $\mathrm{C_{carb}}$–H). ^{11}B NMR (128 MHz, $\mathrm{CDCl_3}$): −13.9 (d, *J* 160, 1B), −15.0 (d, *J* 150, 2B), −17 – (−26) (5B), −43.5 (d, *J* 129, 1B). ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{CDCl_3}$): 134.3 (d, *J* 9.5), 131.3 (d, *J* 2.9), 128.5 (d, *J* 11.0), 127.7 (d, *J* 66.8), 125.9 (d, *J* 68), 30.8 (br s, $\mathrm{C_{carb}}$–H). ^{31}P{^{1}H} NMR (162 MHz, $\mathrm{CDCl_3}$) δ: 11.2 (m). MS ($\mathrm{ESI^+}$): 678.5280 $[\mathrm{M + Na}]^+$ (calcd for $\mathrm{C_{38}H_{39}B_9P_2}$ 655.3400 $[\mathrm{M}]^+$; $\mathrm{C_{38}H_{39}B_9P_2Na}$ 678.3298 $[\mathrm{M + Na}]^+$). mp 258–260 °C.

*Synthesis of **10** from **6**.* To a mixture of **6** (12 mg, 23 μmol), $\mathrm{PPh_3}$ (20 mg, 80 μmol), $\mathrm{Cs_2CO_3}$ (24 mg, 70 μmol), and $\mathrm{Pd(PPh_3)_4}$ (3 mg, 2.3 μmol) taken as solids was added dioxane (1 mL), and the reaction mixture was stirred at 90 °C for 60 h. The solvent was removed under vacuum, and the residue was treated by column chromatography using a $\mathrm{CH_2Cl_2}$ gradient (0 → 100%) in hexane. The product **10** was isolated as a white solid after evaporation and drying (9 mg, 60%).

*Tetrabutylammonium 5,6,9-triiodo-7,8-dicarba-nido-undecaborate (**11**).* To a solution of **3** (100 mg, 0.16 mmol) in 2 mL of THF, a solution of NIS (72 mg, 0.32 mmol) in 2 mL of THF was added dropwise, and the reaction mixture was heated to reflux for 48 h. The solvent was removed under vacuum, and the product was isolated by column chromatography using an ethyl acetate gradient (0 → 100%) in hexane to give **11** as a beige solid (69 mg, 58%) after evaporation and drying. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ: 3.19–3.23 (m, 8H, TBA), 2.73 (s, 1H, $\mathrm{C_{carb}}$–H), 2.27 (s, 1H, $\mathrm{C_{carb}}$–H), 1.64–1.71 (m, 8H, TBA), 1.45–1.54 (m, 8H, TBA), 1.05 (t, *J* 7.3, 12H, TBA), 3.3–0.7 (br m, 6H), −2.14 (br m, 1H, B–*H*–B). ^{11}B NMR (128 MHz, $\mathrm{CDCl_3}$): −13.7 [s+d, *J* 138, B–H+B–I], −16.8 (d, *J* 163, 2B), −17.4 (s, B–I), −20.5 (d, *J* 154, 1B), −24.7 (d, *J* 125, 1B), −31.6 (s, 1B, B–I), −33.1 (d, *J* 152, 1B). ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{CDCl_3}$): 59.2 (TBA), 50.6 (br s, $\mathrm{C_{carb}}$–H), 36.9 (br s, $\mathrm{C_{carb}}$–H), 24.2 (TBA), 19.8 (TBA), 13.8 (TBA). MS ($\mathrm{ESI^-}$): 510.8261 $[\mathrm{M - H}]^-$ (calcd for $\mathrm{C_2B_9H_9I_3}$ 511.8712 $[\mathrm{M}]^-$).

*5-Iodo-6,9-bis(triphenylphosphonio)-7,8-dicarba-nido-undecaborane (**12**).* To a mixture of **11** (70 mg, 0.10 mmol), $\mathrm{PPh_3}$ (92 mg, 0.35 mmol), $\mathrm{Cs_2CO_3}$ (326 mg, 0.4 mmol), and $\mathrm{Pd(PPh_3)_4}$ (17 mg, 15 μmol) taken as solids were added dioxane (3 mL) and THF (6 mL), and the reaction mixture was stirred at 70 °C for 120 h. The solvent was removed under vacuum, and the product was isolated by column chromatography using an ethyl acetate gradient (0 → 100%) in hexane to give **12** as a white solid (48.0 mg, 60%) after evaporation and drying. Alternatively, compound **12** was prepared in 59% yield from a mixture of **3** (33 mg, 0.05 mmol), $\mathrm{PPh_3}$ (26 mg, 0.1 mmol), and $\mathrm{Pd(PPh_3)_4}$ (46 mg, 0.04 mmol) after heating in 1 mL of dioxane at 95 °C for 48 h and then isolating the product by column chromatography. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ: 7.43–7.85 (30H), 1.93 (s, 1H, $\mathrm{C_{carb}}$–H), 1.22 (s, 1H, $\mathrm{C_{carb}}$–H), 2.3–0.8 (br m, 6H). ^{11}B NMR (128 MHz, $\mathrm{CDCl_3}$) δ: −18.3 (d, *J* 148, 1B, B–P), −15 to −21 (m, 6B), −27.1 (s, 1B, B–I), −42.3 (d, *J* 135, 1B). ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{CDCl_3}$) δ: 135.2 (d, *J* 8.8), 134.6 (d, *J* 9.5), 132.1 (d, *J* 9.5), 131.6 (d, *J* 14.7), 128.5 (d, *J* 11.7), 128.1 (d, *J* 11), 126.8 (d, *J* 71), 124.9 (d, *J* 68), 34.7 (br s, $\mathrm{C_{carb}}$–H), 31.7 (br s, $\mathrm{C_{carb}}$–H). ^{31}P{^{1}H} NMR (162 MHz, $\mathrm{CDCl_3}$) δ: 9.6 (q-like), 2.5 (q-like). MS ($\mathrm{ESI^+}$): 782.2596 $[\mathrm{M + H}]^+$ (calcd for $\mathrm{C_{38}H_{38}B_9P_2I}$ 781.2367 $[\mathrm{M}]^+$). mp 324–326 °C.

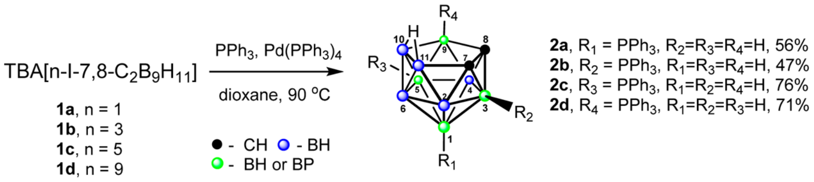
RESULTS AND DISCUSSION

As mentioned in the Introduction, all charge-compensated phosphonio-*nido*-carboranes described to date contained the substituent in the open pentagonal face of the carborane ligand. The two possible positional isomers, namely, 9-phosphonio-7,8-dicarba-*nido*-undecaborane and 10-phosphonio-7,8-dicarba-*nido*-undecaborane, were prepared using two synthetic approaches: (1) indirectly, via the thermal ligand rearrangement of semisandwich nickelacarboranes containing phosphine ligands[3f] with subsequent decomposition of the complex or (2) directly, by the reaction of *nido*-carboranes or dicarbollide dianions with phosphines in the presence of an oxidizing agent, such as $\mathrm{FeCl_3}$ or AgBr.[3g,9] The question of whether the reaction of an iodocarborane with a phosphine under the conditions of B–I bond activation characteristic of the Pd-catalyzed cross-coupling protocol[15] would afford phosphonio-*nido*-carboranes was of interest.

Pd-Catalyzed Reaction of Monoiodo-7,8-dicarba-*nido*-undecaborate Anions with $\mathrm{PPh_3}$. For the current study, triphenylphosphine was chosen as the phosphine component of the reaction because (1) it allowed the comparison of some of the products with previously described compounds and (2) it was inexpensive and commercially available, with well-known spectroscopic behavior.

The study began with an attempt to prepare a previously described and previously characterized 9-phosphonio-*nido*-

Scheme 1



carborane (**2d**). For this purpose, the reaction of *nido*-carborane **1d** with PPh_3 was conducted in the presence of 10 mol % $Pd(PPh_3)_4$ in dioxane[16] at 90 °C. After 17 h, the ^{11}B NMR spectrum of the reaction mixture showed no resonances corresponding to the starting material **1d**. The reaction cleanly proceeded toward the product, which contained no B—I signal in the ^{11}B NMR spectrum but instead showed a new doublet at δ −14.2 ppm (J_{B-P} 155 Hz), which persisted in the $^{11}B\{^1H\}$ NMR. A comparison of the NMR spectra of the reaction mixture with the previously published data[3g] confirmed the identity of the product **2d** (Scheme 1). Reaction workup afforded the product **2d** in 71% isolated yield (see the Experimental Section).

This reaction was successfully applied to the syntheses of other mono(phosphonio)-*nido*-carboranes (**2a**—**c**) from the corresponding monoiodinated *nido*-carboranes (**1a**—**c**). It should be mentioned that the reaction times and the catalyst amounts reported in the Experimental Section were optimized for each iodo-*nido*-carborane (see below). The general synthetic scheme for the preparation of the mono(phosphonio)-7,8-dicarba-*nido*-undecaboranes **2a**—**d** is presented in Scheme 1.

A search for the optimal reaction conditions revealed a strong dependence of the reaction rate on the position of the iodine in the carborane cage. Under the same conditions, the reaction rates decreased in the order **2d** > **2c** > **2a** > **2b**. In Table 1, the yields of products **2a**—**d** as determined by $^{11}B\{^1H\}$ NMR in 24 h time intervals are presented. Although the electron density distribution in *closo*-carboranes has been studied in multiple theoretical investigations, which better explained the reactivity and substituent effects in *closo*-carboranes and made them more predictable, such studies have not been performed on *nido*-carboranes to the best of the authors' knowledge. Thus, an explanation for this reactivity pattern in iodo-*nido*-carboranes should be sought in a separate study.

Table 1. Yields of Products 2a—d Determined by $^{11}B\{^1H\}$ NMR

product[a]	24 h	48 h	120 h	144 h
2a	30	55	90	100
2b	40	50	85	95
2c	60	100		
2d	100			

[a] Reaction conditions: 1 mmol of iodo-*nido*-carborane, 1.5 mmol of PPh_3, 0.1 mmol of $Pd(PPh_3)_4$, 2 mL of dioxane, 90 °C.

The structures of compounds **2a**—**d** were initially established based on their NMR spectra. The ^1H NMR spectra of **2a**—**d** contained several groups of characteristic signals. For example, the phenyl ring protons of the triphenylphosphine substituent appeared as a group of multiplet signals at low field, between δ 7 and 8 ppm. The carborane C—H resonances appeared as one (**2a** and **2b**) or two (**2c** and **2d**) signals (depending on the symmetry of the compounds) in the normal range (2—3 ppm). The ^1H NMR spectra of all the products also revealed a characteristic broad resonance in the range from −2 to −3 ppm corresponding to the bridging hydrogen in the open pentagonal face of the carborane cage. The number of signals in the ^{11}B NMR spectra of **2a**—**d** was determined by the symmetry of the substitution. The signals corresponding to the B—P vertices were readily identified in the $^{11}B\{^1H\}$ NMR spectra due to their doublet shape. In the $^{31}P\{^1H\}$ NMR spectra of all the compounds, the phosphine substituent signals were observed as quartets because of spin-coupling with the ^{11}B nuclei ($I = 3/2$); the coupling constants J_{P-B} ranged from 150 to 174 Hz. The corresponding chemical shifts in the $^{31}P\{^1H\}$ NMR spectra also depended on the position of the phosphine in the cage, ranging from 14.0 ppm for compound **2a**, through 7.1 ppm for **2d** and 6.7 ppm for **2c**, to −1.3 ppm for compound **2b** (see the Experimental Section). The high-resolution mass spectrometry (HRMS) data for compounds **2a**—**d** confirmed the suggested molecular compositions.

Single crystals of compound **2c** were obtained, and X-ray diffraction analysis of them was performed. The compound was found to contain a *nido*-carborane unit in which boron atom B(5) is bonded to the triphenylphosphine molecule (Figure 1).

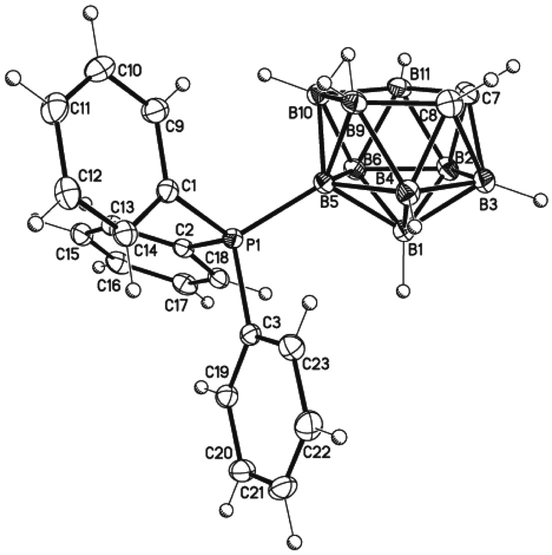


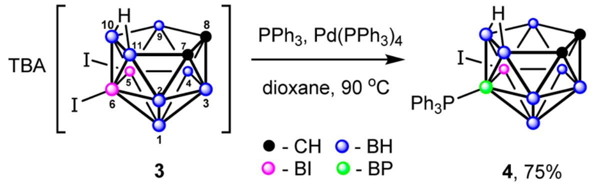
Figure 1. Thermal ellipsoid representation of compound **2c**.

The determined B(5)—P distance was 1.9355(15)Å. This value is comparable to the range of 1.905—1.931 Å reported for B—P distances in several structurally characterized phosphonio-*nido*-carboranes.[3g,9]

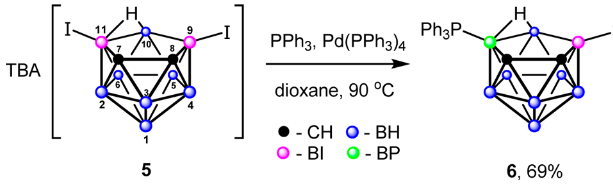
Pd-Catalyzed Reaction of Diiodo-7,8-dicarba-*nido*-undecaborate Anions with PPh_3. After the successful synthesis of mono(phosphonio)-*nido*-carboranes **2a**—**d** and optimization of the reaction conditions, this approach was applied to the synthesis of bis(phosphonio)-*nido*-carborane compounds. When used in the formation of transition metal complexes, these neutral compounds may be considered arene analogues from a theoretical perspective.[17]

Two previously characterized[18] diiodo-*nido*-carboranes—5,6-diiodo- (**3**) and 9,11-diiodo-7,8-dicarba-*nido*-undecaborate (**5**) anions—were chosen as starting materials. Surprisingly, the reactions of diiodo-*nido*-carboranes **3** and **5** under conditions optimizing the phosphine cross-coupling led exclusively to the formation of the monosubstituted products **4** and **6** (Schemes 2 and 3). Attempts to achieve disubstitution by the addition of extra phosphine and/or prolongation of the reaction were unsuccessful.

Scheme 2



Scheme 3



Both products **4** and **6** were isolated and characterized by NMR spectroscopy. The ^{1}H NMR spectra of both compounds revealed signals characteristic of triphenylphosphine and *nido*-carborane. Both compounds contained bridging hydrogen, which appeared in the NMR spectra at −2.14 and −1.46 ppm for **4** and **6**, respectively. The uncharacteristic downfield shift of the bridging hydrogen signal in **6** was explained by the presence of both the electron-withdrawing iodine substituent and a phosphine molecule in the open pentagonal face of the *nido*-carborane. The ^{11}B NMR spectra of both products **4** and **6** showed an increased number of signals characteristic of the C_1 symmetry of the molecules. In the ^{31}P{^{1}H} NMR spectra, the signals corresponding to the triphenylphosphine substituents in **4** and **6** appeared as sharp quartets at 4.5 (J_{P-B} 158 Hz) and 7.4 (J_{P-B} 153 Hz) ppm, respectively. The compositions of both molecules were supported by the HRMS data (see the Experimental Section).

Single crystals of **6** were obtained and studied by X-ray diffraction. According to the study, the iodine and triphenylphosphine substituents in the structure of **6** are attached to boron atoms on both sides of the cage C–C connectivity in the open pentagonal face of the *nido*-carborane (Figure 2). The distances between the cage boron atoms and substituents B(9)–I(1) and B(11)–P(1) are 2.185(4) Å and 1.923(4) Å, respectively, which are in the normal range for B–I and B–P bonds in carboranes.

In both starting compounds **3** and **5**, the iodine substituents are chemically equivalent. Thus, it was interesting to study, by analogy with the monoiodinated *nido*-carboranes **1a–d**, whether the reactivity of iodinated boron vertices is different in the case of nonsymmetrically disubstituted *nido*-carboranes. For this purpose, a new diiodinated carborane, tetrabutylammonium 6,9-diiodo-7,8-dicarba-*nido*-undecaborate (**7**), was prepared via the iodination of **1c** with *N*-iodosuccinimide in THF (Scheme 4). The reaction of **7** with PPh$_3$ in the presence of Pd(PPh$_3$)$_4$ led to the formation of compound **8**, in which only the iodine substituent in the open pentagonal face of the *nido*-carborane was exchanged with triphenylphosphine.

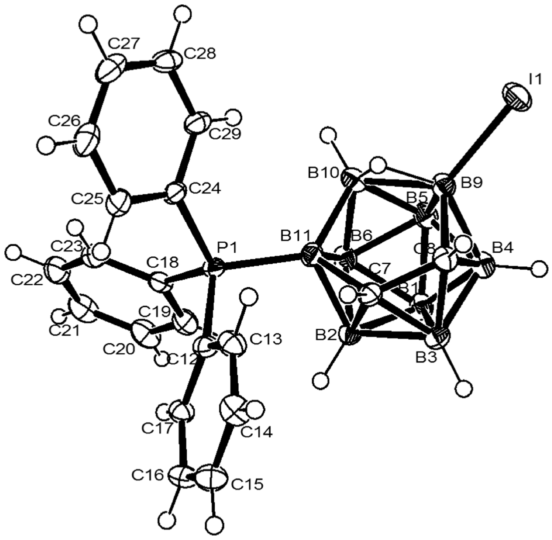


Figure 2. Thermal ellipsoid representation of compound **6**.

Unlike starting material **7**, which revealed two singlet resonances in the ^{11}B NMR spectrum at −18.3 and −32.3 ppm belonging to iodinated atoms B(9) and B(6), respectively, **8** only produced one signal for the iodinated boron vertex in its ^{11}B NMR spectrum, which was located at −32.7 ppm. A new doublet resonance, partially overlapped with a B–H resonance, appeared at ca. −13 ppm. The ^{31}P{^{1}H} NMR spectrum of **8** contained a unique quartet signal at 7.0 ppm (J_{P-B} 151 Hz), which was very close to the chemical shift of substituted atom B(9) in phosphonio-*nido*-carborane **1d** (7.1 ppm).

X-ray diffraction analysis of the crystal structure of compound **8** revealed that it contained an *ortho*-carborane fragment in which the triphenylphosphine substituent was situated in the open pentagonal face of the carborane cage, next to the carbon atom (Figure 3). Iodine was connected to the boron atom in the lower pentagonal belt of the *nido*-carborane. Because of the presence of two independent molecules in the elementary unit of **8**, the B(9)–P(1) distances were determined to be 1.911(3) and 1.906(3) Å, and the B–I(1) distances were 2.196(3) and 2.195(3) Å.

On the basis of the NMR and X-ray data for **8**, it was concluded that the reactivity of diiodinated *nido*-carboranes toward catalytic phosphine substitution follows the same trend as the reactivity of the corresponding monoiodo-*nido*-carboranes.

Pd-Catalyzed Reaction of Diiodo-7,8-dicarba-*nido*-undecaborate Anions with PPh$_3$ in the Presence of Cs$_2$CO$_3$. In the search for an efficient means of synthesizing bis(phosphonio)-*nido*-carboranes, the use of a base in the reaction of diiodocarboranes **3** and **5** with PPh$_3$ was tested. This decision was based on the observation that all products prepared so far were electroneutral (zwitterionic). In the case of double substitution, the product would be positively charged unless the bridging hydrogen was removed.

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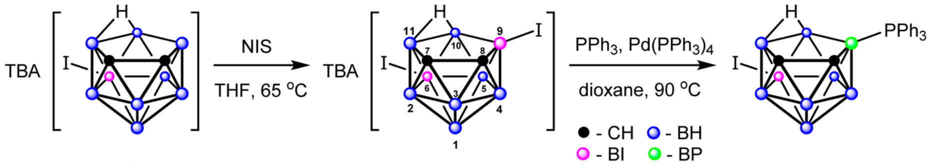
Inorg. Chem. 2015, 54, 4143–4150

Scheme 4



1c **7**, 62% **8**, 38%

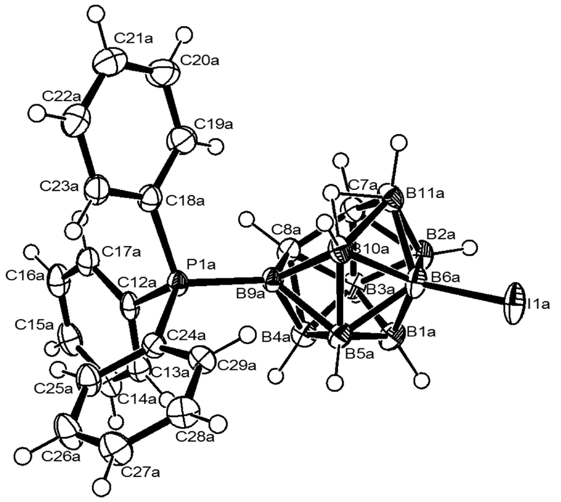
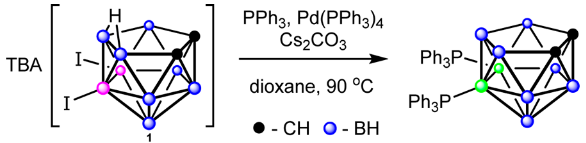


Figure 3. Thermal ellipsoid representation of compound **8** (one enantiomer shown).

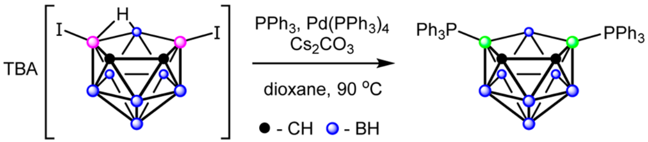
In the presence of a base such as Cs_2CO_3 or NaH, the reaction of diiodo-*nido*-carboranes **3** and **5** with PPh_3 and a catalytic amount of $Pd(PPh_3)_4$ in dioxane produced the desired compounds **9** and **10** in good yields (Schemes 5 and 6). The isolation of products **9** and **10** was facilitated by their insolubility in dioxane at room temperature (see the Experimental Section). Cesium carbonate became the preferred base due to its solubility in polar organic solvents.

Scheme 5



3 **9**, 48%

Scheme 6



5 **10**, 77%

As expected, in the ^1H NMR spectra of both **9** and **10**, the broad high-field resonance of the bridging hydrogen was not observed. The symmetry of both the ^1H and ^{11}B NMR spectra corresponded to the C_s symmetry of the products. For example, in contrast to the ^1H NMR spectra of **4** and **6**, resonances corresponding to the cage C–H bonds appeared as unique signals in the spectra of **9** and **10**. The total integration of the phenyl C–H resonances with respect to the cage C–H resonances was 15:1, which also suggested double substitution. In the $^{11}B\{^1H\}$ NMR spectra of both compounds, the signals appeared in a very compact manner, preventing the doublets corresponding to the substituted boron atoms B(5/6) in **9** and B(9/11) in **10** from being distinguished from the remaining boron resonances. The $^{31}P\{^1H\}$ NMR spectra of both compounds revealed broad unique resonances at 6.1 and 11.2 ppm for **9** and **10**, respectively. The HRMS data for **9** and **10** corresponded to the double substitution products.

Single crystals of compound **9** were obtained and studied by X-ray diffraction. The molecule was found to contain a *nido*-carborane fragment with two triphenylphosphine molecules positioned at atoms B(5) and B(6) in the lower pentagonal belt of the cage (Figure 4). The bond lengths B(5)–P(1) and B(6)–P(2) were found to be 1.953(2) Å and 1.939(2) Å, respectively. This slight elongation of the B–P distances could be explained by the bulkiness of the triphenylphosphine substituents. Because of their proximity, the phenyl rings of the two phosphine molecules adopt a gear set conformation.

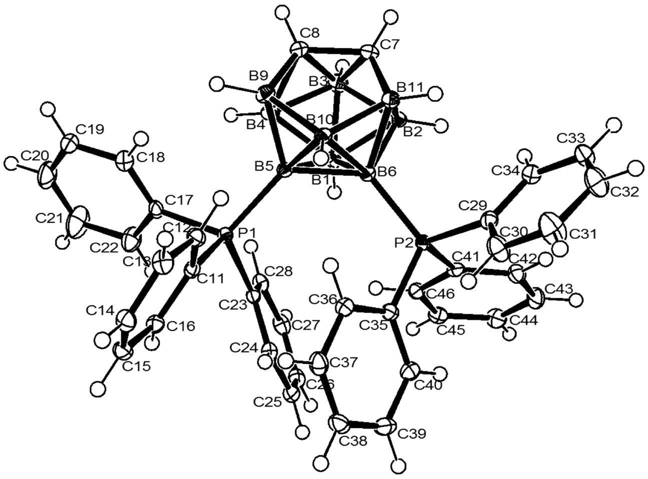
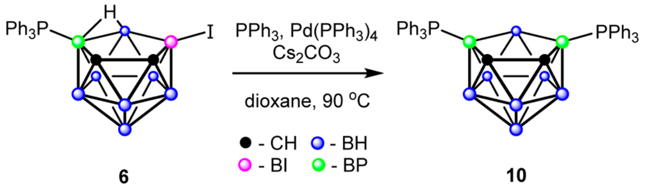


Figure 4. Thermal ellipsoid representation of compound **9**.

Compound **10** was also successfully prepared from compound **6** by additional reaction with PPh_3 and a catalytic amount of $Ph(PPh_3)_4$ in the presence of Cs_2CO_3 (Scheme 7). This reaction could be used to introduce a different phosphine (or another substituent) into the carborane cage in compound **6** or **4**.

Pd-Catalyzed Reaction of Triiodo-7,8-dicarba-*nido*-undecaborate Anion with PPh_3 in the Presence of Cs_2CO_3. After neutral bis(phosphonio)-*nido*-carboranes were synthesized from diiodocarboranes, it was interesting to determine whether the discovered reaction would afford positively charged tris(phosphonio)-*nido*-carboranes when triiodo-*nido*-carboranes were used as starting materials.

Scheme 7



Although several isomers of triiodo-*closo*- and triiodo-*nido*-carboranes are known,[17a,19] these compounds are not commonly used in carborane chemistry because of the difficulties associated with their synthesis. For the goals of the current study, a new triiodo-*nido*-carborane—tetrabutylammonium 5,6,9-triiodo-7,8-dicarba-*nido*-undecaborate (**11**)—was prepared in good yield via the iodination of **3** by NIS in THF at reflux temperature (Scheme 8).

The reaction of **11** with PPh_3 in the presence of Cs_2CO_3 and a catalytic amount of $Pd(PPh_3)_4$ afforded a single product according to the ^{11}B NMR spectrum of the reaction mixture. The ^{11}B and $^{11}B\{^1H\}$ NMR spectra of product **12** were not informative, consisting of a group of overlapping resonances in the range from −15 to −30 ppm and a unique signal at −42 ppm with an integral ratio of 8:1. The ^1H NMR spectrum of **12** contained phosphine phenyl ring signals in the range 7.4−7.8 ppm, two distinctive cage C−H resonances at 1.93 and 1.22 ppm, and a very broad resonance in the range of 0.8−2.3 ppm corresponding to the cage B−H bonds. The integral intensity of the aromatic signals with respect to each of the cage C−H resonances was 30:1, which indicated the presence of two phosphine substituents in the molecule. The same conclusion was drawn from the $^{31}P\{^1H\}$ NMR spectrum of **12**, in which two quartet-like signals of equal intensity were observed at 9.6 and 2.5 ppm.

The initial assignment of the structure of **12** (Scheme 8) as 5-iodo-6,9-bis(triphenylphosphonio)-7,8-dicarba-*nido*-undecaborane was based on two assumptions. First, on the basis of previous observations of the iodine substitution rate, it was suggested that one of the two triphenylphosphine substituents is positioned in the open pentagonal face of the *nido*-carborane. Second, although the structure of compound **9** demonstrated that two bulky triphenylphosphine substituents can share the same triangular face of the *nido*-carborane, in the case of the 5,6,9-triiodinated compound, it would be reasonable to suggest that the second triphenylphosphine substituent is located at B(6) to minimize steric repulsion between the first phosphine substituent and the bis(triphenylphosphine)palladium fragment during the second substitution reaction.

X-ray-quality crystals of **12** were obtained, and the structure of this molecule was studied by X-ray diffraction (Figure 5). The structure supported the suggested arrangement of substituents in the molecule. Two triphenylphosphine substituents are positioned in different pentagonal belts of the *nido*-carborane. The boron atom B(5) bearing the iodine substituent is situated in the lower pentagonal belt and is connected to both triphenylphosphine-substituted boron atoms B(6) and B(9). The distances B(9)−P(1) and B(6)−P(2) were found to be 1.901(6) and 1.941(6) Å, respectively. The B(5)−I(1) distance was determined to be 2.183(7) Å.

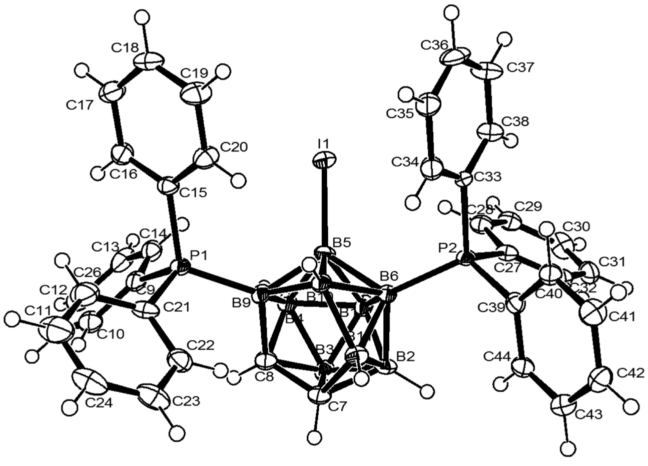
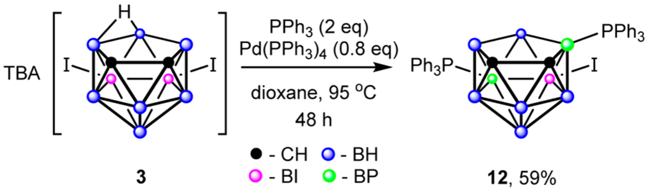


Figure 5. Thermal ellipsoid representation of compound **12**.

It is important to mention that compound **12** was also prepared by the reaction of diiodo-*nido*-carborane **3** with 2 mol equiv of PPh_3 in the presence of 0.8 mol equiv of the catalyst (Scheme 9). It was assumed that, in this case, the reaction proceeds through the formation of an intermediate *closo*-palladacarborane analogous to the process described for the phosphine ligand migration during the thermolysis of 3,3-$(PPh_3)_2$-3,1,2-$NiC_2B_9H_{11}$ to produce 3-H-3,4-$(PPh_3)_2$-3,1,2-$NiC_2B_9H_{10}$.[20]

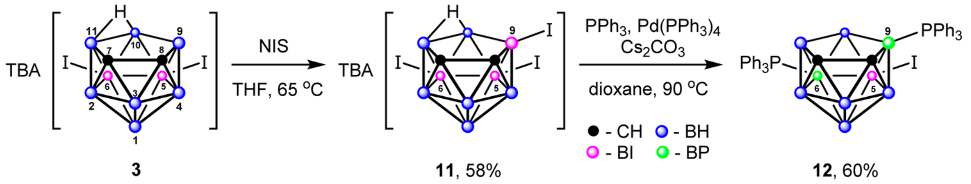
Scheme 9



■ CONCLUSIONS

A new synthetic approach was established for the synthesis of charge-compensated phosphonio-*nido*-carboranes via the reaction of the corresponding iodo-*nido*-carboranes with triphenylphosphine in the presence of a Pd(0) catalyst. It was demonstrated that (1) in the case of monoiodinated *nido*-carboranes, the reaction rate depends on the position of the iodine substituent in the carborane cage; (2) in the absence or presence of a base in the reaction system, diiodinated

Scheme 8



carboranes are able to form mono- or disubstitution products, respectively; (3) the residual iodine atoms in phosphonio-*nido*-carboranes can be further substituted using a Pd-catalyzed cross-coupling protocol; and (4) in the case of triiodinated *nido*-carboranes, the reaction stops at the disubstitution stage.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Boron NMR spectra of compounds **2a−d**, **4**, **6**, **8**, **9**, **10**, and **12**; X-ray experimental and crystallographic files in CIF format for compounds **2c**, **6**, **8**, **9**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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