Inorganic Chemistry
Article
pubs.acs.org/IC

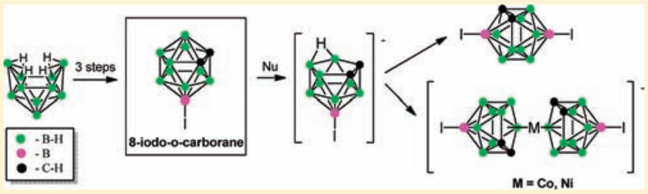
Unfairly Forgotten Member of the Iodocarborane Family: Synthesis and Structural Characterization of 8-Iodo-1,2-dicarba-*closo*-dodecaborane, Its Precursors, and Derivatives.

Alexander V. Safronov,[†] Yulia V. Sevryugina,[†] Satish S. Jalisatgi,[†] Robert D. Kennedy,[‡] Charles L. Barnes,[§] and M. Frederick Hawthorne[†,*]

[†]International Institute of Nano and Molecular Medicine (I^2NM^2), University of Missouri, Columbia, Missouri 65211, United States
[‡]Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States
[§]Department of Chemistry, University of Missouri, Columbia, Missouri 65211, United States

Ⓢ *Supporting Information*

ABSTRACT: 8-Iodo-1,2-dicarba-*closo*-dodecaborane (**7**) was prepared in three steps starting from decaborane-14 with 20% overall yield. In the presence of nucleophiles, compound **7** undergoes selective removal of the boron vertex in the position para to the iodine substituent to form the anionic *nido*-carborane 1-iodo-7,8-dicarba-*nido*-undecaborate. Capping of the corresponding dicarbollide dianion with BI_3 led to formation of the new carborane, 3,10-diiodo-1,2-dicarba-*closo*-dodecaborane (**15**). The same dicarbollide dianion reacts with cobalt and nickel acetylacetonates in anhydrous tetrahydrofuran to form the corresponding bis(dicarbollide) complexes with excellent yields. All compounds were characterized by multinuclear NMR and high-resolution mass spectroscopy. Structures of 2-iododecaborane (**2**), 8-iodo-1,2-dicarba-*closo*-dodecaborane (**7**), 1-ethoxycarbonyl-8-iodo-1,2-dicarba-*closo*-dodecaborane (**10**), cesium 1-iodo-7,8-dicarba-*nido*-undecaborate (**13**), 3,10-diiodo-1,2-dicarba-*closo*-dodecaborane (**15**), and cesium 3,3′-*commo*-(10-iodo-1,2-dicarba-3-cobalta-*closo*-dodecaborane)-(10′-iodo-1′,2′-dicarba-3′-cobalta-*closo*-dodecaborane) (**16**) were established by X-ray analysis of single crystals.



■ INTRODUCTION

Iodinated boron clusters are valuable synthons for the preparation of compounds containing the carborane pharmacophore. These compounds have found applications in different fields of medicine, such as computer tomography contrast agents,[1] transthyretin amyloid disease inhibitors,[2] and boron neutron capture therapy (BNCT) therapeutic agents.[3] Numerous publications have been dedicated to the preparation and further functionalization of diverse iodocarboranes.[4] The number of iodine atoms present in such systems may vary from 1 to 10, and almost all possible isomers have been prepared and structurally characterized.[5] It should be noted that among all halogenated *ortho*-carboranes only iodo derivatives are able to participate in palladium-catalyzed cross-coupling reactions, thus providing synthetically valuable coupling products.

Regardless of such extensive study, one particular iodinated carborane, 8-iodo-1,2-dicarba-*closo*-dodecaborane, has never attracted chemists' attention, even though its spectra were published (without synthetic details) as early as 1974.[6] Unlike other iodocarboranes, which can be conveniently prepared in one or two steps starting from *ortho*-carborane, 8-iodo-1,2-dicarba-*closo*-dodecaborane can only be prepared selectively (as a main product of the reaction, not as one of several possible halogenation or rearrangement isomers[7]) from decaborane.

The title compound attracted our attention because of our previously published work on carborarods, which are unique inorganic molecules of an oligomeric nature constructed from carborane fragments connected through direct carborane C−C bonds[8] or rigid butadiyne linkers.[9] We suggested that after deboronation of 8-iodo-1,2-dicarba-*closo*-dodecaborane both possible *nido* products (1-iodo-7,8-dicarba-*nido*-undecaborate and 10-iodo-7,8-dicarba-*nido*-undecaborate) would be of great interest in creating new inorganic materials containing carborane or metallacarborane fragments. Because we are interested in developing the chemistry and possible applications of new boron-containing materials, we report herein the synthesis and structure of an unfairly forgotten member of the iodocarborane family, 8-iodo-1,2-dicarba-*closo*-dodecaborane, and several of its precursors and derivatives.

■ EXPERIMENTAL SECTION

Materials. Unless otherwise stated, all reactions were carried out in an argon atmosphere using standard Schlenk-line techniques. Decaborane-14 was purchased from Katchem Ltd. (Czech Republic). Thallium acetate, boron triiodide (BI_3), iodine chloride (ICl), cesium fluoride (CsF), cobalt and nickel acetylacetonates (Aldrich), and potassium *tert*-butoxide (Fluka) were used as purchased. Tetrabutylammonium fluoride was purchased from TCI America as a 1 M solution in THF and used as received. Diethyl sulfide (Aldrich) was distilled under argon from calcium hydride (CaH_2) before use. Ethyl

Received: November 30, 2011
Published: February 1, 2012

dx.doi.org/10.1021/ic2025846 | *Inorg. Chem.* 2012, 51, 2629−2637

propiolate (Aldrich) was distilled in an argon atmosphere before use. Tetrahydrofuran (THF) was distilled in an argon atmosphere from sodium benzophenone ketyl before use. Anhydrous toluene, dichloromethane (DCM), acetonitrile (ACN), and hexane were purchased from Taylor Scientific (St. Louis, MO) and used without further purification. Thin-layer chromatography was performed using Merck precoated glass plates (Silica 60 F254). Column chromatography was performed using Merck silica gel (63−200 mesh).

Caution! All operations with decaboranes and thallium compounds must be carried out in a well-ventilated hood using skin protection!

Physical Measurements. ^{1}H, ^{11}B, ^{11}B{^{1}H}, and ^{13}C{^{1}H} NMR spectra were measured on Bruker DRX 500, DRX 300, Avance-400, and Avance-500 NMR spectrometers; 2D spectra were recorded on a Bruker Avance-500 NMR spectrometer. Boron NMR spectra were referenced to 15% $BF_3{\cdot}Et_2O$ in $CDCl_3$. ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were referenced to the residual solvent peak impurity. Chemical shifts are reported in ppm and coupling constants in Hertz. Mass spectra were obtained on an ABI QSTAR and Mariner Biospectrometry Workstation by PerSeptive Biosystems.

X-ray Diffraction Studies. X-ray-quality crystals of **2** were obtained by slow cooling of its hot heptane solution, crystals of **10** and **15** were obtained by slow evaporation of corresponding DCM/hexane solutions, and crystals of **13** were grown by slow evaporation of an acetone solution. Data collection for the crystals **2**, **10**, **13**, and **15** was carried out at −100 °C on a Bruker SMART 1000 CCD area detector system using the ω scan technique with Mo Kα radiation (λ = 0.71073 Å) from a graphite monochromator. X-ray-quality crystals of **16** were grown on slow diffusion of DCM vapor into a solution of the compound dissolved in ACN, and data were collected at 25 °C on a Bruker SMART CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å). Crystals of **7** were obtained by slow cooling of its hot hexane solution, and data were collected on a single flash-cooled crystal (T = −173 °C with Oxford Cryostream LT device) using a Bruker X8 Prospector Ultra X-ray diffractometer system with a three-circle goniometer and APEX II CCD area detector mounted on a D8-platform and equipped with a Cu-IμS (λ = 1.54178 Å) microfocus X-ray source operated at 30 W power. Data reduction and integration were performed with the software package SAINT.[10] Data were corrected for absorption using SADABS.[11] Crystal structures were solved with the direct methods program SHELXS-97 and refined by full matrix least-squares techniques with the SHELXTL[12] suite of programs.

All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms in **2**, **10**, and **13** were located in difference Fourier maps and refined individually. In **16**, all H atoms were included at geometrically idealized positions. In **7** and **15**, only BH hydrogens were included at geometrically idealized positions while H atoms on carbons were located in difference Fourier maps and refined individually; therefore, refinement of H atoms was mixed. Analysis of data statistics for **15** revealed twinning around the [110] direction in space group $P4$, which generated pseudo-422 symmetry. The absolute structure was determined to indicate $P4_1$ as the correct space group. Structure refinement resulted in $R1 = 0.0206$ and $wR2 = 0.0506$ for $I > 2\sigma(I)$, Flack $x = -0.04(4)$, and the twin fraction was estimated to be 0.4. In the crystal structure of **7**, both crystallographically unique molecules exhibited rotational disorder, which made distinguishing between the boron and the carbon atoms at two atom sites difficult. This disorder was modeled using partial occupancies for boron and carbon atoms, which provided the 80:20% ratio for the superimposed rotamers in one of the molecules and the 55:45% ratio in the other. The crystal structure of **7** was solved in space group $Pca2_1$, and the absolute configuration was determined by refinement of the Flack $x = 0.03(1)$ with data collected using Cu Kα radiation. Crystallographic data and details of the data collection and structure refinements of **2**, **7**, **10**, **13**, **15**, and **16** are provided in Table S1 (see Supporting Information).

*2-Iododecaborane (**2**).* Decaborane-14 (**1**, 5.00 g, 40.1 mmol) was dissolved in 35 mL of anhydrous DCM, and anhydrous $AlCl_3$ (0.546 g, 4.03 mmol) was then added to the solution. A solution of ICl (2.08 mL, 41.5 mmol) in 20 mL of anhydrous DCM was added to the reaction mixture in an ice bath over 30 min. The dark brown reaction mixture was heated to reflux for 5 h. An ^{11}B NMR sample was then taken from the reaction mixture, showing >95% conversion of **1**. The reaction mixture was filtered through a paper filter and evaporated to dryness. Recrystallization of the crude reaction mixture from hot heptane gave pure **2** (4.82 g, 48%) as a yellow crystalline solid after drying. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.04−2.61 (br m, 8H, B−H), 0.87 (q, 1H, J 160, B−H), −1.24 (br s, 2H, B−H−B), −1.99 (br s, 2H, B−H−B). ^{11}B NMR (160 MHz, CH_2Cl_2): δ 13.7 [d, 2B, J 151, B(1,3)], 10.6 [d, 1B, J 181, B(6)], 9.4 [d, 1B, J 179, B(9)], 1.4 [d, 2B, J 172, B(5,7)], 0.3 [d, 2B, J 170, B(8,10)], −35.0 [d, 1B, J 159, B(4)], −46.0 [s, 1B, B(2)]. HRMS (APCI): m/z 247.1083 $[M-H]^-$ (calcd for $B_{10}H_{13}I$ 248.1065).

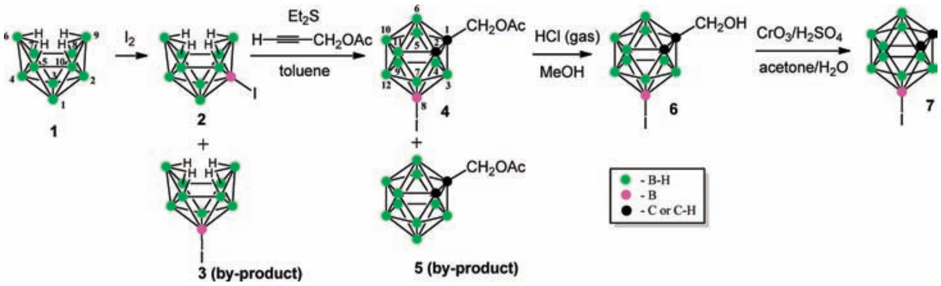
*1-Iododecaborane (**3**).* The pure compound was isolated by recrystallization of evaporated mother liquor after crystallization of **2**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.86−2.36 (br m, 8H, B−H), 1.10 (q, 1H, J 161, B−H), −1.83 (br s, 4H, B−H−B). ^{11}B NMR (128 MHz, $CDCl_3$): δ 13.3 [d, 1B, J 150, B(3)], 9.5 [d, 2B, J 163, B(6,9)], 2.2 [d, 2B, J 164, B(7,8)], 0.4 [s, 1B, B(1)], −0.2 [d, 2B, J 169, B(5,10)], −33.3 [d, 2B, J 160, B(2,4)].

*1-Ethoxycarbonyl-8-iodo-1,2-dicarba-closo-dodecaborane (**10**).* To a solution of 2-iododecaborane (**2**, 10.0 g, 40.3 mmol) in 200 mL of anhydrous toluene Et_2S (8.68 mL, 80.6 mmol) was added, and the resulting solution was heated at 80 °C for 2 h. The reaction mixture was then cooled to room temperature, and ethyl propiolate (4.86 mL, 48.0 mmol) was added via syringe. The resulting solution was heated at 95 °C for 24−36 h. If after that time the ^{11}B NMR of the reaction mixture still showed an unreacted diethylsulfide adduct of **2** (characteristic signal at −43 ppm), more ethyl propiolate (1.22 mL, 12.1 mmol) was added, and the reaction mixture was heated at 95 °C for another 24 h period. After completion, the reaction mixture was diluted with methanol and coevaporated with silica (100 mL). Prepared silica was put on the top of the chromatography column, filled with 400 mL of silica, and washed with hexanes. Evaporation gave **10** (5.68 g, 41%) as a crystallizing colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.31 (q, 2H, ^{3}J 7.1, CH_2), 4.17 (br s, 1H, C_{cb}−H), 3.5−1.6 (m, 10H, B−H), 1.33 (t, 3H, ^{3}J 7.2, CH_3). ^{11}B NMR (160 MHz, $CDCl_3$): δ −0.9 (d, 2B, J 152), −8.88 (d, 1B, J 155), −11.1 (d, 1B, J 150), −12.1 (d, 2B, J 170), −12.7 (d, 1B, J 140), −13.6 (d, 1B, J 161), −14.3 (d, 1B, J 167), −22.6 (s, 1B, B−I). ^{13}C{^{1}H} (125 MHz, $CDCl_3$): δ 160.3 (C═O), 98.2 (C_{cb}−C═O), 65.6 (CH_2), 57.5 (C_{cb}−H), 13.9 (CH_3). HRMS (APCI): m/z 342.1142 $[M]^-$ (calcd for $C_5H_{15}B_{10}IO_2$ 342.1117). The first fraction from the column contained a deiodinated product, 1-ethoxycarbonyl-1,2-dicarba-*closo*-dodecaborane (**11**, 1.74 g, 20%), NMR spectra of which correspond to the literature data.[13]

*8-Iodo-1,2-dicarba-closo-dodecaborane (**7**).* To a cooled (<10 °C) solution of 1-ethoxycarbonyl-8-iodo-1,2-dicarba-*closo*-dodecaborane (**10**, 1.00 g, 2.92 mmol) in 25 mL of THF in air was quickly added 0.1 M LiOH solution (43.8 mL) in one portion. After 10 min, the initially turbid solution became clear and TLC indicated complete reaction. The reaction mixture was quenched by addition of 1 M H_2SO_4 solution (2.19 mL) and extracted with ether (2 × 30 mL). Combined ethereal extracts were washed with brine (5 mL) and dried over Na_2SO_4. Evaporation of ether gave white crystals of **7** (0.77 g, 98%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.66 (s, 2H, C_{cb}−H), 3.2−1.7 (m, 9H, B−H). ^{11}B NMR (160 MHz, $CDCl_3$): δ −0.4 [d, 2B, J 152, B(9,12)], −8.9 [d, 1B, J 154, B(10)], −12.4 [d, 2B, J 164, B(4,7)], −13.4 [d, 2B, J 157, B(5,11)], −14.3 [d, 1B, J 157, B(3)], −16.9 [d, 1B, J 181, B(6)], −22.6 [s, 1B, B(8)]. ^{13}C{^{1}H} (125 MHz, $CDCl_3$): δ 55.1 (C_{cb}−H). HRMS (APCI): m/z 270.1100 $[M]^-$ (calcd for $C_2H_{11}B_{10}I$ 270.0904).

*Tetrabutylammonium 1-Iodo-7,8-dicarba-nido-undecaborate (**12**).* To the solid 8-iodo-1,2-dicarba-*closo*-dodecaborane (**7**, 300 mg, 1.11 mmol), 5.6 mL (5.60 mmol) of 1 M TBAF in THF was added, and the reaction mixture was heated at reflux for 4 h (TLC control). The reaction mixture was evaporated to dryness and diluted with 10 mL of distilled water. The white precipitate formed was filtered on a glass frit and washed with water (10 mL) and ether (5 mL) to give **12** (539 mg, 97%) as a white solid. ^{1}H NMR (500 MHz, acetone-d_6):

Scheme 1



δ 3.46 (m, 8H, TBA−CH$_2$), 2.45 to −0.09 (m, 10H, B−*H*), 1.84 (m, 10H, C$_{cb}$−*H* + TBA−CH$_2$), 1.45 (m, 8H, TBA−CH$_2$), 0.98 (t, 12H, ^3J 7.5, TBA−CH$_3$), −2.29 (br m, 1H, B−*H*−B). ^{11}B NMR (160 MHz, acetone-d$_6$): δ −9.9 [d, 2B, *J* 136, B(9,11)], −13.8 [d, 2B, *J* 140, B(5,6)], −15.6 [d, 1B, *J* 164, B(3)], −20.0 [d, 2B, *J* 152, B(2,4)], −32.1 [d, 1B, *J* 136, B(10)], −38.7 [s, 1B, B(1)]. ^{13}C{^{1}H} (100 MHz, acetone-*d*$_6$): δ 59.4 (TBA), 45.2 (br, C$_{cb}$−H), 24.4, 20.4, 13.9 (TBA). HRMS (TIS): *m*/*z* 260.0790 [M]$^-$ (calcd for $C_2H_{11}B_9I$ 260.0775).

*Cesium 1-Iodo-7,8-dicarba-nido-undecaborate (**13**).* A solution of 8-iodo-1,2-dicarba-*closo*-dodecaborane (**7**, 300 mg, 1.11 mmol) and CsF (506 mg, 3.33 mmol) in anhydrous ethanol was heated to reflux for 18 h (TLC control). The reaction mixture was evaporated to dryness, redissolved in acetone, and filtered. Acetone was evaporated, and the residue was recrystallized from hot water to give **13** as a white crystalline solid (391 mg, 90%) after drying. ^{1}H NMR (500 MHz, acetone-*d*$_6$): δ 3.00 to −0.03 (m, 10H, B−*H*), 1.85 (s, 2H, C$_{cb}$−*H*), −2.35 (br m, 1H, B−*H*−B). ^{11}B NMR (160 MHz, acetone-*d*$_6$): δ −6.9 [d, 2B, *J* 141, B(9,11)], −10.9 [d, 2B, *J* 134, B(5,6)], −12.6 [d, 1B, *J* 165, B(3)], −17.0 [d, 2B, *J* 150, B(2,4)], −29.1 [d, 1B, *J* 115, B(10)], −35.8 [s, 1B, B(1)]. ^{13}C{^{1}H} (125 MHz, acetone-*d*$_6$): δ 44.8 (br, C$_{cb}$−H). HRMS (TIS) *m*/*z* for $C_2H_{11}B_9I$ [M]$^-$ calcd 260.0775, found 260.0387.

*3,10-Diiodo-1,2-dicarba-closo-dodecaborane (**15**).* Thallium dicarbollide was prepared from **7** by a standard procedure.[14] To a suspension of dry thallium dicarbollide (150 mg, 0.225 mmol) in 1 mL of anhydrous hexane, a solution of BI$_3$ (97.0 mg, 0.248 mmol) in 1 mL of anhydrous hexane was added dropwise at 0 °C. The reaction mixture was allowed to warm to room temperature and was then stirred for 18 h. The precipitate of thallium iodide was filtered on a glass frit and washed with ether (3 mL). The product was isolated by column chromatography on silica using a DCM gradient (0 → 40%) in hexane. Compound **15** was obtained as a white crystalline solid (54.0 mg, 61%) after evaporation and drying. ^{1}H NMR (400 MHz, CDCl$_3$): δ 3.94 (br s, 2H, C$_{cb}$−*H*), 3.7−1.7 (m, 8H, B−*H*). ^{11}B NMR (128 MHz, CDCl$_3$): δ −0.1 [d, 2B, *J* 154, B(9,12)], −7.7 [d, 1B, *J* 155, B(8)], −11.6 [br d, 2B, *J* 170, B(4,7)], −11.9 [br d, 2B, *J* 177, B(5,11)], −13.4 [d, 1B, *J* 194, B(6)], −23.7 [s, 1B, B(10)], −30.7 [s, 1B, B(3)]. ^{13}C{^{1}H} (125 MHz, CDCl$_3$): δ 60.8 (*C*$_{cb}$−H). HRMS (APCI): *m*/*z* 394.9803 [M−H]$^-$ (calcd for $C_2H_{10}B_{10}I_2$ 395.9875).

*Tetrabutylammonium 3,3′-commo-(10-Iodo-1,2-dicarba-3-cobalta-closo-dodecaborane)-(10′-iodo-1′,2′-dicarba-3′-cobalta-closo-dodecaborane) (**16**).* To a solution of tetrabutylammonium 1-iodo-7,8-dicarba-*nido*-undecaborate (**12**, 150 mg, 0.299 mmol) in 3 mL of anhydrous THF, a solution of *t*BuOK (52.0 mg, 0.449 mmol) in 1 mL of anhydrous THF was added dropwise, and the reaction mixture was stirred at room temperature for 2 h. A solution of Co(acac)$_2$ (46.0 mg, 0.179 mmol) in 1 mL of anhydrous THF was then added to the reaction mixture and stirred at room temperature for 12 h. After quenching with methanol (4 mL), the reaction mixture was coevaporated with 2 mL of silica and placed on top of a chromatography column filled with 8 mL of silica in hexanes. Elution of a single orange band with CHCl$_3$ gradient (0 → 100%) in hexanes gave **16** (116 mg, 95%) as an orange solid after evaporation and drying. ^{1}H NMR (400 MHz, CDCl$_3$): δ 3.87 (br s, 4H, C$_{cb}$−*H*), 3.14 (m, 8H, TBA−CH$_2$), 1.64 (m, 8H, TBA−CH$_2$), 1.47 (m, 8H, TBA−CH$_2$), 1.04 (t, 12H, ^3J 7.5, TBA−CH$_3$). ^{11}B NMR (128 MHz, CDCl$_3$): δ 5.6 (d, 2B, *J* 114), −5.2 (d, 8B, *J* 125), −12.7 (s, 2B, B−I), −16.3 (d, 4B, *J* 94), −22.2 (br m, 2B). ^{13}C{^{1}H} (100 MHz, CDCl$_3$): δ 59.3 (TBA), 51.9 (*C*$_{cb}$−H), 24.2, 19.9, 13.9 (TBA). HRMS (TIS): *m*/*z* 575.1299 [M−H]$^-$ (calcd for $C_4H_{20}B_{18}CoI_2$ 576.0771).

*Tetrabutylammonium 3,3′-commo-(10-Iodo-1,2-dicarba-3-nickela-closo-dodecaborane)-(10′-iodo-1′,2′-dicarba-3′-nickela-closo-dodecaborane) (**17**).* Following the procedure described above for **16**, paramagnetic nickel(III) complex **17** was prepared as a dark red solid (97%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.00−12.00 (br s, ∼4H, C$_{cb}$−*H*), 3.18 (br s, 8H, TBA−CH$_2$), 1.71 (br s, 8H, TBA−CH$_2$), 1.53 (br s, 8H, TBA−CH$_2$), 1.09 (br s, 12H, TBA−CH$_3$). ^{11}B NMR (128 MHz, CDCl$_3$): δ 9.9 (br s), −38.0 (br s), −57.2 (br s). ^{13}C{^{1}H} (100 MHz, CDCl$_3$): δ 60.2, 24.6, 20.3, 14.1 (TBA). HRMS (TIS): *m*/*z* 575.0603 [M]$^-$ (calcd for $C_4H_{20}B_{18}NiI_2$ 575.0795).

RESULTS AND DISCUSSION

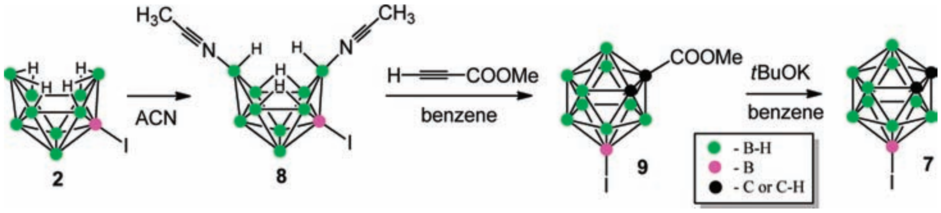
General Considerations. There is a well-known synthetic strategy for the synthesis of *ortho*-carboranes from decaborane.[15] The same reaction sequence was initiated here with introduction of iododecaborane into the scheme. Iodination of decaborane **1** (Scheme 1) by molecular iodine[16] gave two isomers (**2** and **3**), which could be separated by fractional crystallization. Reaction of the 2-iododecaborane (**2**) with propargyl acetate in the presence of a nucleophile (acetonitrile or diethylsulfide) afforded 1-acetoxymethyl-1,2-dicarba-*closo*-dodecaborane (**4**). Subsequent acid hydrolysis of **4** and Jones oxidation/decarboxylation of hydroxymethyl intermediate **6** provided target 8-iodo-1,2-dicarba-*closo*-dodecaborane (**7**).

Synthesis appeared to be complicated by a number of details.

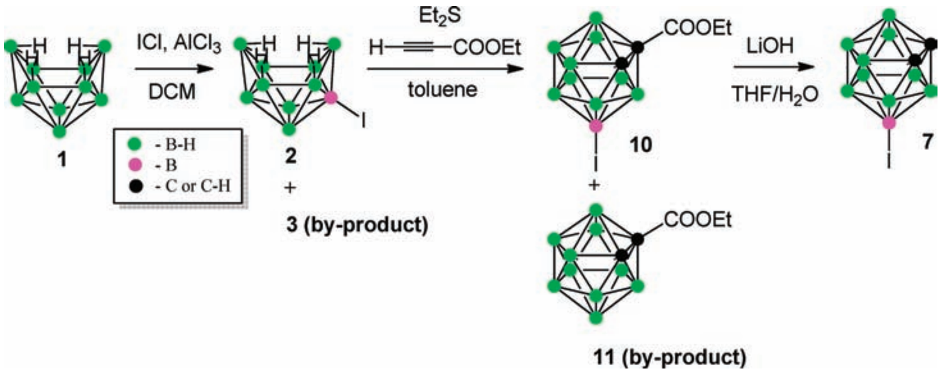
1) During the synthesis of **4**, substantial deiodination of 2-iododecaborane (**2**) occurred, which not only decreased the yield of the target compound but also led to the necessity of separating two carboranes, **4** and **5**;
2) Jones oxidation of **6** was irreproducible; addition of the Jones reagent to the acetone solution of **6** resulted in an incomplete reaction with a substantial amount of starting material remaining. The best results were achieved by addition of the acetone solution of **6** to at least a 10-fold excess of Jones reagent, and even in this case, the yield of **7** did not exceed 60%;
3) The overall yield of this scheme was approximately 8% (in the best case).

A different synthetic strategy was developed in a paper dedicated to the NMR study of 8-iodo-1,2-dicarba-*closo*-dodecaborane.[6] The authors prepared 1-methoxycarbonyl-8-iodo-1,2-dicarba-*closo*-dodecaborane (**9**, Scheme 2) starting from the acetonitrile adduct of 2-iododecaborane (**8**) and methyl propiolate. Subsequent reaction of **9** with excess *t*BuOK in benzene accompanied by spontaneous decarboxylation gave **7** with an unreported yield.[17]

Scheme 2



Scheme 3



The best parts of both synthetic strategies were combined in this report to make preparation of **7** as simple as possible.

*Synthesis of 2-Iododecaborane (**2**).* Iodination of decaborane with 1.05 equiv of ICl in the presence of a catalytic amount of $AlCl_3$ in DCM gives a mixture of two isomeric products, **2** and **3**, in an approximate ratio 2:1 (by NMR) nearly quantitatively (Scheme 3). Compound **2** was separated by fractional crystallization of the product mixture from heptane in which it appeared to be less soluble than isomer **3**. The typical isolated yield of pure product **2** was 45−55%, calculated on the basis of starting decaborane. Both compounds **2** and **3** are toxic and have very unpleasant odors.

The $B\{^1H\}$ NMR of **2** showed a characteristic 2:1:1:2:2:1:1 pattern, which corresponded very well to the expected symmetry of the compound. The extreme upfield resonance at δ −45.6 ppm did not show splitting in its ^{11}B NMR and therefore corresponded to the iodinated boron vertex. Other signals in the boron NMR were assigned based on correlation NMR spectroscopy data (see Supporting Information).

In several cases, it was possible to separate pure isomer **3** by recrystallization of the evaporated mother liquor after separation of **2**. However, having pure compound **3** was not important to this study because after carborane formation it would yield 9-iodo-1,2-dicarba-*closo*-dodecaborane, the product which could be easily prepared by electrophilic iodination of *ortho*-carborane.[18] Comparisons of ^{11}B NMR spectra of the reaction mixture after iodination with the spectra of pure isomers **2** and **3** (with peak assignments) are shown in Figure 1.

The crystal structure of **2** determined by X-ray structure analysis is shown in Figure 2. The structure unambiguously shows the position of the iodine substituent on the decaborane cage. The B−I distance was determined to be 2.181(4) Å, which lies within the range of distances known for iodinated borane clusters.[5]

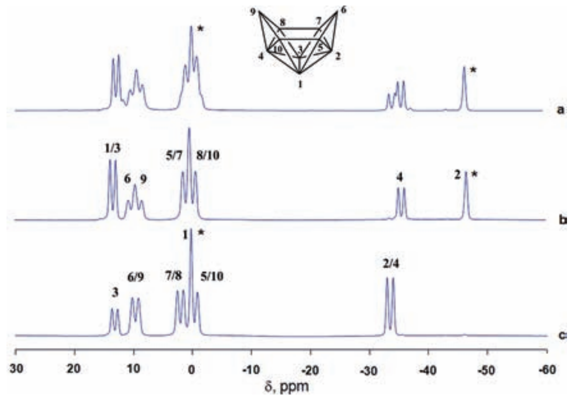


Figure 1. Comparison of the ^{11}B NMR spectra of the reaction mixture (a) after iodination of decaborane-14 by ICl, pure **2** (b), and pure **3** (c) in CH_2Cl_2. Signals corresponding to B−I vertices are marked by asterisks.

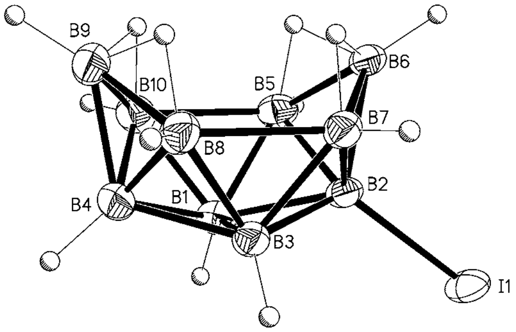


Figure 2. ORTEP representation of compound **2**, showing the crystallographic numbering scheme. In all figures atoms are represented by thermal ellipsoids at the 40% probability level.

*Synthesis of 1-Ethoxycarbonyl-8-iodo-1,2-dicarba-closo-dodecaborane (**10**).* Reaction of **2** with diethylsulfide in dry toluene at 80 °C over 2 h gave the corresponding adduct that slowly reacted with ethyl propiolate to give a mixture of **10** and **11** (Scheme 3). The reaction was monitored by ^{11}B NMR for the disappearance of the signal at $\delta \approx -43$ ppm, characteristic of the diethylsulfide adduct of **2**. An additional amount of ethyl propiolate was added if the integral ratio of product to starting material was unchanged by NMR. The reaction was typically complete in 2−3 days with up to an extra 0.5 equiv of ethyl propiolate added to the reaction mixture.

During the course of the reaction, substantial deiodination of the cage occurred (20−30% yield of **11**). It is well known that the B−I bond in carboranes is extremely stable and undergoes activation only by Pd(0) compounds at elevated temperatures.[19] A special study of the mechanism of deiodination in this reaction was not performed. However, it seems more feasible for iodine to leave from 2-iododecaborane or its diethylsulfide adduct rather than from carborane **10**.

Because the only related synthetic work described in the literature[6] does not mention any deiodination using the acetonitrile adduct, we decided to check if the reaction proceeds differently in this case. The reaction sequence described by Aufderheide and Sprecher[6] was repeated, and the nature of the Lewis base was found to have no influence on the reaction result. Boron NMR of the reaction mixture after refluxing **2** in anhydrous acetonitrile for 2 h shows a mixture of iodinated and deiodinated adducts. Pure compound **8** (Scheme 2) was separated by crystallization[20] with 40% yield and introduced into the reaction with ethyl propiolate in benzene. NMR analysis of the reaction mixture showed that further deiodination occurred during this step, and a mixture of **10** and **11** was formed. It was thus suggested as highly probable that iodine loss did not proceed through isomerization of the iodine substituents towards the cage open face followed by elimination because formation of isomeric iodocarborane species was never observed. Interestingly, isomeric 1-iododecaborane (**3**, Scheme 3) showed no trace of deiodinated product by NMR even after stirring overnight at reflux temperature in acetonitrile. This phenomenon would best be the subject of a separate study.

A number of different conditions for carborane synthesis were attempted while trying to avoid iodine elimination, including different nucleophiles (diethylsulfide, acetonitrile, *N*,*N*-dimethylaniline), different solvents (benzene, toluene, acetonitrile, [BMIM]BF_4 ionic liquid[21]), and different temperature modes, but deiodination occurred under all given conditions. The highest overall yield and best ratio of **10**:**11** were achieved when carrying out reaction of **2** with diethylsulfide and ethyl propiolate at 95 °C in toluene until the starting material was completely consumed. Separation of products could easily be achieved by column chromatography on silica. Standard yields of products were 35−45% for target compound **10** and 20−30% for deiodinated product **11**.

The ^1H NMR spectrum of **10** contains resonances for the ethyl group and carborane C−H protons. The presence of the electron-withdrawing ethoxycarbonyl group on the neighboring carbon atom in combination with the iodine substituent on the cage decreases the electron density on the carborane C−H bond, shifting its signal to a lower field (δ 4.17 ppm). The $^{11}B\{^1H\}$ NMR spectrum of **10** consists of eight resonances with integral ratios of 2:1:1:2:1:1:1:1, arising from the lack of a symmetry plane in the molecule. Signals are situated within the range from 0 to −25 ppm, which is characteristic for *closo*-carboranes. The only resonance that does not split into a doublet in the ^{11}B NMR is positioned at δ −22.6 ppm and unambiguously assigned as a B−I resonance.

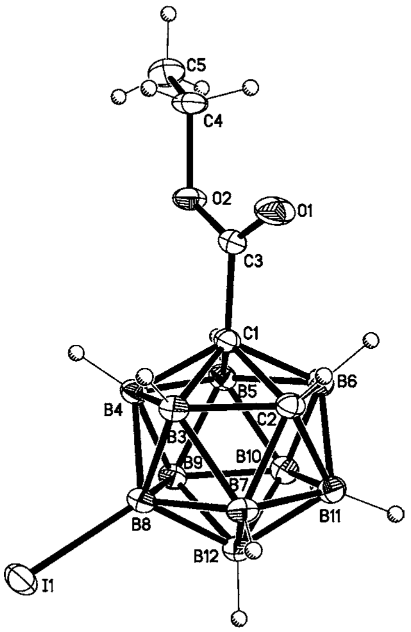


Figure 3. ORTEP representation of compound **10**, showing the crystallographic numbering scheme.

The structure of compound **10** was determined by a single-crystal X-ray diffraction study (Figure 3). The compound shows icosahedral geometry typical for *closo*-carboranes. The position of the iodine substituent on the cage with respect to the C−C interaction corresponds to that expected for the 8-iodocarborane derivative. The B−I distance of 2.169(2) Å is in good agreement with the literature data.[5]

Synthesis of 8-Iodo-1,2-dicarba-closo-dodecaborane (7). Saponification of ester **10** by LiOH in a water−THF mixture with subsequent quenching by H_2SO_4 gave compound **7** in quantitative yield. Saponification was accompanied by a spontaneous decarboxylation reaction, which could only be explained by the presence of iodine because carborane carboxylic acids have successfully been prepared from noniodinated carborane esters in quantitative yields.[13] Attempts to find the best reaction conditions were performed using a number of methods, including different bases (LiOH, NaOH, KOH, $Ca(OH)_2$, $Ba(OH)_2$, *t*BuOK), different solvents (acetone, methanol, THF), and different temperatures. The best results for saponification of **10** were achieved with 1.5 mol equiv of 0.1 M LiOH in a water−THF mixture at room temperature. This reaction is usually complete in 10−15 min. Quenching the reaction mixture with 1 M H_2SO_4 avoided undesirable formation of the *nido* product. After workup, compound **7** was isolated as a white solid.

The ^1H NMR spectrum of **7** is rather simple and consists of only two sets of resonances for C−H and B−H protons. The resonance of the former appeared as a broad singlet at δ 3.66 ppm, which is very close to the corresponding chemical shifts of its isomers (3.87 ppm for 3-iodo-1,2-dicarba-*closo*-dodecaborane[22] and 3.66 and 3.86 ppm for 9-iodo-1,2-dicarba-*closo*-dodecaborane[18]). Carbon NMR shows only one signal at δ 55.1 ppm, corresponding to symmetrically situated carbon vertices. The $^{11}B\{^1H\}$ NMR of **7** shows seven resonances in the relative ratio 2:1:2:2:1:1:1 which corresponds very well to a cluster with a plane of symmetry going through the middle of the carborane C−C bond and including the B(8)−I bond. The unique signal that does not split into a doublet in the ^{11}B NMR spectrum was assigned as B(8). The chemical shift of this resonance is the same as for compound **10** (δ −22.6 ppm). All other boron resonances were assigned based on the results of $^{11}B\{^1H\}$−$^{11}B\{^1H\}$

COSY spectroscopy (see Experimental Section and Supporting Information).

The crystal structure of 8-iodo-1,2-dicarba-*closo*-dodecaborane (**7**) was determined by single-crystal X-ray diffraction (Figure 4).

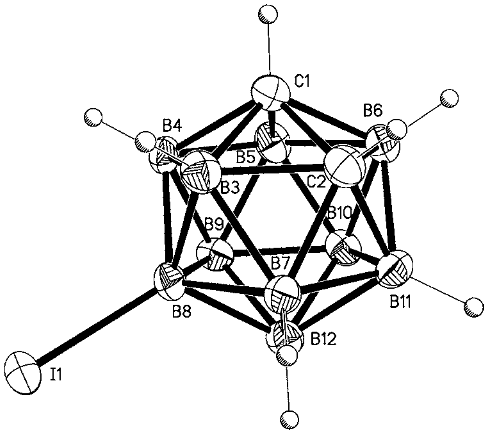


Figure 4. ORTEP representation of compound **7**, showing the crystallographic numbering scheme.

The structure was solved and refined in the orthorhombic space group $Pca2_1$ with lattice parameters a = 13.0692(3) Å, b = 7.0568(2) Å, and c = 22.1755(6) Å. Interestingly, by surveying the crystallographic entries in the Cambridge Structural Database (CSD) we encountered a report on an "iodo-1,2-dicarba-*closo*-dodecaborane"[23] which, by a diagram displayed in CSD, corresponded to the 8-iodo-1,2-dicarba-*closo*-dodecaborane. In this 1967 publication, the authors only reported unit cell parameters (a = 12.160(50) Å, b = 7.210(50) Å, and c = 13.280(50) Å, R factor of 0.24) and stated that "refinement of the structure is being continued" in space group $P2_1/c$. Although the 1967 structure was collected at room temperature while our structure was collected at 100 K, we strongly believe that the difference in unit cell parameters is the result of an incorrect placement of this report in CSD. Our conclusions are supported by the sentence "one of the carbon atoms lies diametrically opposite to the B-atom linked with the halogen" in the 1967 report. This conformation points to 9-iodo-1,2-dicarba-*closo*-dodecaborane. In addition, the aforementioned unit cell parameters and space group of the "iodo-1,2-dicarba-*closo*-dodecaborane" match those reported for the recently determined structure of 9-iodo-1,2-dicarba-*closo*-dodecaborane.[5] The single-crystal X-ray diffraction analysis reported herein is thus the first crystal structure report of 8-iodo-1,2-dicarba-*closo*-dodecaborane.

The work presented here revealed the B(8)−I distance to be 2.189(7) Å, which is in excellent agreement with other such distances in the literature.[5] Compared to the B−I distance in **10** (2.169(2) Å), the distance in **7** is longer, likely due to the electron-withdrawing properties of ethoxycarbonyl group. This discrepancy in distance implies a lower electron density at B(8) in **10**. A similar but less obvious tendency is observed when we compare the B−I bond length in 8-iodo-1,2-dicarba-*closo*-dodecaborane (**7**) to those in 3-iodo-[25a] and 9-iodo-1,2-dicarba-*closo*-dodecaboranes.[5] The B−I bond shortens as boron becomes more electropositive:[24] 9-I-1,2-$C_2B_{10}H_{11}$ (2.181(5) Å) ≈ 8-I-1,2-$C_2B_{10}H_{11}$ (2.189(7) Å) ≫ 3-I-1,2-$C_2B_{10}H_{11}$ (2.167(6) Å).

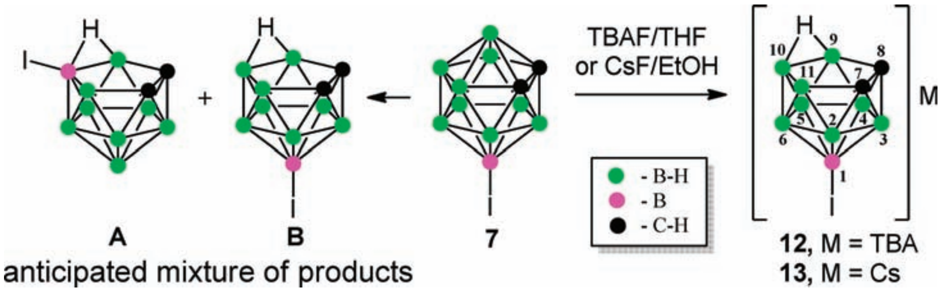
In the solid state, 8-iodo-1,2-dicarba-*closo*-dodecaborane cages display intermolecular C−H···I−B contacts of 3.11, 3.28, and 3.29 Å, which are all within the range reported for such interactions.[5,25] There are two crystallographically unique carborane cages in the crystal structure of **7**, and both display a disorder due to superimposed rotamers of 8-iodo-1,2-dicarba-*closo*-dodecaborane. As a result, weak (3.28 and 3.29 Å) H···I−B contacts could be regarded as either B−H···I−B or C−H···I−B intermolecular interactions depending on a particular orientation of a cluster.

*Synthesis of Tetrabutylammonium (**12**) and Cesium (**13**) 1-Iodo-7,8-dicarba-nido-undecaborates.* Reaction of **7** with TBAF in THF[26a,b] or CsF in EtOH[26c] at reflux led to deboronation of **7** and formation (monitored by NMR) of a single product (Scheme 4). The ^{11}B NMR spectrum of the compound shows six resonances with integral ratios of 2:2:1:2:1:1. Because both possible nido isomers **A** and **B** (Scheme 4) would theoretically give the same NMR pattern, $^{11}B\{^1H\}-^{11}B\{^1H\}$ correlation NMR spectroscopy was employed to assign the structure of the compound. Analysis of cross-peaks allowed the unambiguous assignment of the compound as isomer **B** with the B−I bond perpendicular to the open pentagonal face of the *nido* cage. Such selectivity cannot be explained based solely on the inductive effect of the iodine atom because one would expect to have less electron density and thus more reactivity toward nucleophiles from boron atom B(3) rather than B(6) since the former is situated closer to the iodinated boron vertex. However, the effective atom charge distribution in substituted carboranes often does not obey simple rules and must be analyzed with computational methods.

X-ray crystal structure determination established **13** as the structure inferred from NMR studies (Figure 5). The compound shows the ubiquitous *nido*-carborane geometry with the substituted B(8)−I bond perpendicular to the open pentagonal face. Polyhedral bond distances lie within the normal range, and the B(8)−I distance is 2.198(4) Å, which is in good agreement with that in other iodinated boron clusters.[5]

*Synthesis of 3,10-Diiodo-1,2-dicarba-closo-dodecaborane (**15**).* Recently, we discovered a new synthetic route to 3-iodo-1,2-dicarba-*closo*-dodecaborane via reaction of thallium dicarbollide with BI_3 in anhydrous hexane.[14a] The same strategy was applied to preparation of the first *ortho*-carborane that had

Scheme 4



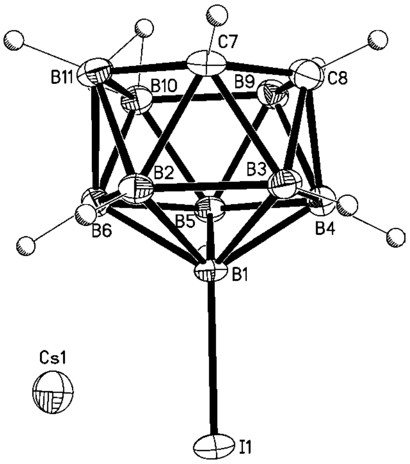


Figure 5. ORTEP representation of compound **13**, showing the crystallographic numbering scheme.

iodine substituents in para positions with respect to each other (Scheme 5).

Thallium dicarbollide **14** was prepared according to the standard procedure with nearly quantitative yield.[14] After thorough drying of **14** in an Abderhalden apparatus using methanol as a jacket heater, compound **14** was introduced into reaction with a solution of boron triiodide in anhydrous hexane. Compound **15** was isolated from the reaction mixture in 61% yield by column chromatography.

^{1}H NMR of **15** shows the signal for carborane C–H vertices at δ 3.94 ppm and a broad multiplet (δ range 1.7–3.7 ppm) characteristic for carborane B–H bonds. The carborane C–H resonance is shifted downfield compared to **7**, which could be explained by the presence of the second iodine substituent in the cage. Such a shift is typical for polyiodinated carboranes, such as 3,6-diiodo-1,2-dicarba-*closo*-dodecaborane (C–H resonance at δ 4.12 ppm) and 3,6,9,12-tetraiodo-1,2-dicarba-*closo*-dodecaborane (δ 4.50 ppm).[27] ^{11}B NMR of **15** exhibited the integral ratio pattern 2:1:4:1:1:1, which can be predicted based on the symmetry plane dissecting the cage C–C interaction and including both B–I bonds. There are two resonances at δ −23.7 and −30.7 ppm that do not show coupling in ^{11}B NMR, allowing for their assignment to iodinated boron vertices. It is very important to note that the chemical shifts of these boron atoms allowed for their easy assignment. The resonance at δ −23.7 ppm was assigned as B(10) because a similar boron atom in compound **7** appeared at δ −22.6 ppm, and the resonance at δ −30.7 was assigned to boron atom B(3) because it was very close to the value for the same boron atom in 3-iodo-1,2-dicarba-*closo*-dodecaborane (δ −29.4 ppm).[22] Correlation ^{11}B{^{1}H}–^{11}B{^{1}H} NMR spectra confirmed this assignment and allowed the assignment of the remaining signals (see Experimental Section). The ^{13}C{^{1}H} spectrum of **15** contains the signal for the cage C–H resonances at δ 60.8 ppm. Such a strong (~5 ppm) downfield shift of the carborane C–H resonance could also be explained by a negative inductive effect of the two iodine substituents.

The structure of **15** was determined by single-crystal X-ray studies (Figure 6). The molecular geometry of **15** is unprecedented among the known diiodo-1,2-dicarba-*closo*-dodecaboranes because the icosahedral carborane fragment has two exopolyhedral B–I bonds situated in a para position with respect to each other. The bond lengths for B(3)–I and B(10)–I are 2.151(9) and 2.135(8) Å, respectively. Analysis of the solid-state packing of **15** reveals intermolecular I···I contacts of 3.9076(8) Å formed along the crystallographic [110] direction. Similar to other iodinated 1,2-dicarba-*closo*-dodecaboranes,[5] the crystal structure of **15** also displays weak intermolecular C–H···I–B contacts of 3.26(3) Å (C–H···I angle of 120.9(19)°).

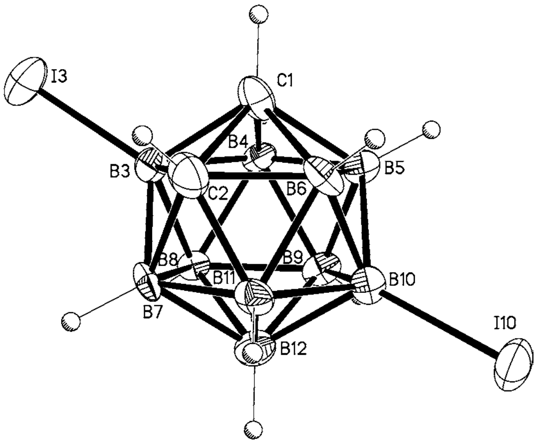
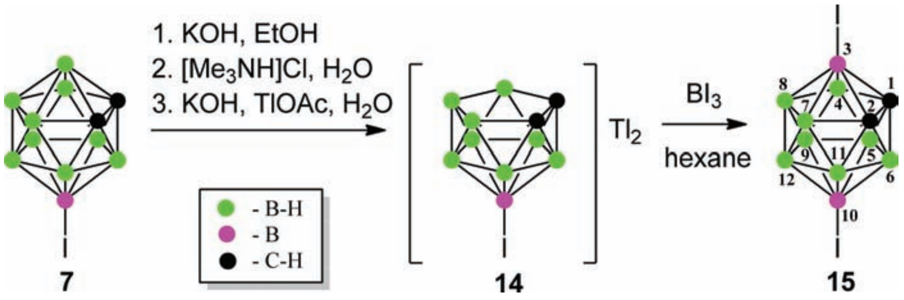


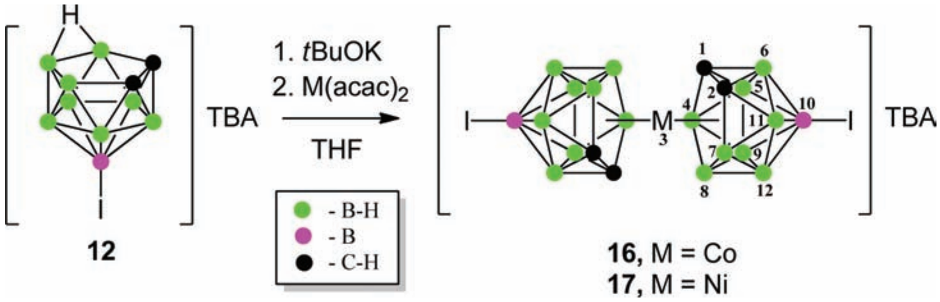
Figure 6. ORTEP representation of compound **15**, showing the crystallographic numbering scheme.

*Synthesis of Tetrabutylammonium 3,3′-commo-(10-Iodo-1,2-dicarba-3-cobalta-closo-dodecaborane)-(10′-iodo-1′,2′-dicarba-3′-cobalta-closo-dodecaborane) (**16**) and Tetrabutylammonium 3,3′-commo-(10-Iodo-1,2-dicarba-3-nickela-closo-dodecaborane)-(10′-iodo-1′,2′-dicarba-3′-nickela-closo-dodecaborane) (**17**).* One of the most important properties of *nido*-carboranes is their ability to form stable π complexes with transition metal ions.[28] Compound **12** readily reacted with *t*BuOK in anhydrous THF to produce the dicarbollide dianion in solution. Reaction of the latter with anhydrous

Scheme 5



Scheme 6



$Co(acac)_2$ or $Ni(acac)_2$ led to formation of the corresponding anionic cobalt(III) and nickel(III) dicarbollide complexes **16** and **17** in excellent yields as orange and deep red solids, respectively (Scheme 6).

Diamagnetic complex **16** was characterized by multinuclear NMR spectroscopy and mass spectroscopy. The ^{1}H NMR spectrum of **16** contains, in addition to signals for the TBA counterion, signals for carborane C−H bonds with the characteristic chemical shift of δ 3.87 ppm and a broad multiplet signal corresponding to cage B−H fragments. $^{11}B\{^{1}H\}$ NMR contains a set of five resonances with integral intensities of 1:4:1:2:1. The resonance at δ −12.7 ppm exhibits no splitting in the proton-coupled boron NMR spectrum and was assigned as the resonance of two B−I vertices. Paramagnetic complex **17** was characterized by NMR and mass spectroscopy.

It was possible to exchange the cation in **16** for cesium by growing single crystals of the product from ACN saturated with CsCl. The X-ray crystal structure of cesium salt of **16** is shown in Figure 7.

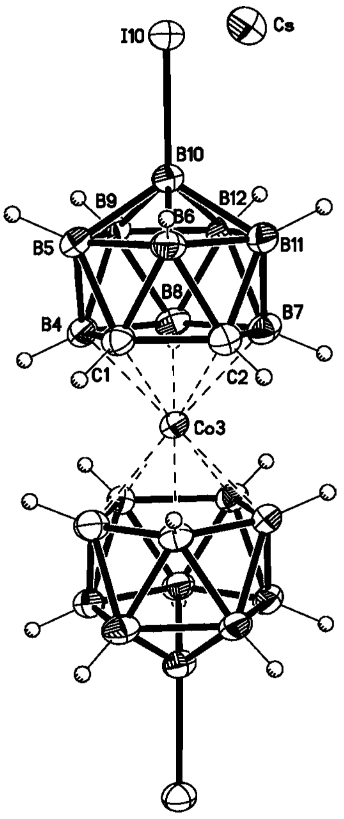


Figure 7. ORTEP representation of compound **16**, showing the crystallographic numbering scheme.

The structure of **16** consists of two η^5-coordinated dicarbollide ligands ($C_2B_9H_{10}I^{2-}$) sandwiching a cobalt center in a cisoid conformation. Two dicarbollide ligands are related by a 2-fold axis passing through the cobalt atom along the *b* axis. The distance from the cobalt atom to the pentagonal bonding face of the dicarbollide ligand is 1.46 Å, which is typical for bis(dicarbollide)-cobalt(III) anions. The averaged Co−C and Co−B distances are 2.044(4) and 2.088(5) Å, respectively. The η^5-coordinated C_2B_3 faces are nearly parallel (the dihedral angle is 3.25°). The B−I bond is 2.191(5) Å, which correlates well with other published data.[5] The intramolecular I···I distance is 12.112 Å. The solid-state structure of **16** displays a complex network of interchanging bis(dicarbollide)cobalt and Cs···I layers along the crystallographic *c* axis. Between the layers, iodinated bis(dicarbollide)cobalt molecules display intermolecular I···I contacts of 3.980(7) and 4.035(7) Å with B−I···I angles of 93.8° and 91.8°, respectively.

■ CONCLUSIONS

An effective synthetic pathway to a new member of the iodocarborane family, 8-iodo-1,2-dicarba-*closo*-dodecaborane, has been developed. The compound undergoes transformations that are characteristic for the carborane cage. The selective character of deboronation of the title compound allows the synthesis of linear inorganic and organometallic derivatives. We anticipate that these species will serve as valuable starting materials for the synthesis of low-dimensional nanomaterials and functionalized carborarods currently under investigation in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic files in CIF format for compounds **2**, **7**, **10**, **13**, **15**, and **16**, details of structures refinement, and spectral information for all prepared compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: 573-882-7016. Fax: 573-884-6900. E-mail: hawthornem@missouri.edu.

■ ACKNOWLEDGMENTS

We gratefully acknowledge the National Science Foundation (CHE-0702774) for financial support of this work. We thank Dr. Mark Lee and Brett Meers for measuring mass spectra of the compounds and Dr. Charles F. Campana for valuable discussions.

■ REFERENCES

(1) (a) Wilbur, D. S. US Patent WO 9505202, 1995. (b) Srivastava, R. R.; Hamlin, D. K.; Wilbur, D. S. *J. Org. Chem.* **1996**, *61*, 9041. (c) Martin Jimenez, J.; Speck, U.; Carretero Colon, J. M.; Martinez Sans, A.; Bohle, F.; Krause, W. Patent EP 0700918A1, 1995.

(2) Julius, R. L.; Farha, O. K.; Chiang, J.; Perry, L. J.; Hawthorne, M. F. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 4808.

(3) (a) Hawthorne, M. F.; Lee, M. W. *J. Neurooncol.* **2003**, *62*, 33. (b) Hawthorne, M. F.; Shelly, K.; Li, F. *Chem. Commun.* **2002**, 547. (c) Hawthorne, M. F.; Maderna, A. *Chem. Rev.* **1999**, *99*, 3421.

(4) For recent examples, see: (a) Sevryugina, Y.; Julius, R. L.; Hawthorne, M. F. *Inorg. Chem.* **2010**, *49*, 10627. (b) Aizawa, K.; Ohta, K.; Endo, Y. *Heterocycles* **2010**, *80*, 369. (c) Himmelspach, A.; Finze, M. *Eur. J. Inorg. Chem.* **2010**, 2012. (d) Kabytaev, K. Z.; Mukhin, S. N.; Glukhov, I. V.; Starikova, Z. A.; Bregadze, V. I.; Beletskaya, I. P. *Organometallics* **2009**, *28*, 4758. (e) Mukhin, S. N.; Kabytaev, K. Z.; Zhigareva, G. G.; Glukhov, I. V.; Starikova, Z. A.; Bregadze, V. I.; Beletskaya, I. P. *Organometallics* **2008**, *27*, 5937. (f) Beletskaya, I. P.; Bregadze, V. I.; Ivushkin, V. A.; Petrovskii, P. V.; Sivaev, I. B.; Sjöberg, S.; Zhigareva, G. G. *J. Organomet. Chem.* **2004**, *689*, 2920. For general information, see: Grimes, R. N. *Carboranes*, 2nd ed.; Academic Press: New York, 2011.

(5) Puga, A. V.; Teixidor, F.; Sillanpää, R.; Kivekäs, R.; Viñas, C. *Chem.—Eur. J.* **2009**, *15*, 9764 and references therein.

(6) Aufderheide, B. E.; Sprecher, R. F. *Inorg. Chem.* **1974**, *13*, 2286.

(7) (a) Gregor, V.; Stuchlík, J. *Collect. Czech. Chem. Commun.* **1973**, *38*, 3623. (b) Zakharkin, L. I.; Kalinin, V. N.; Lozovskaya, V. S. *Russ. Chem. Bull., Chem. Ser.* **1968**, 1780.

(8) Yang, X.; Jiang, W.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1992**, *114*, 9719.

(9) Herzog, A.; Jalisatgi, S. S.; Knobler, C. B.; Wedge, T. J.; Hawthorne, M. F. *Chem.—Eur. J.* **2005**, *11*, 7155.

(10) *SAINT*, v 7.68A; Bruker AXS Inc.: Madison, WI, 2009.

(11) Sheldrick, G. M. *SADABS 2008/1*; Gottingen, Germany, 2008.

(12) Sheldrick, G. M. *SHELXTL*, version 6.14; Bruker AXS, Inc.: Madison, WI, 2001.

(13) Scobie, M.; Threadgill, M. D. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2059.

(14) (a) Safronov, A. V.; Hawthorne, M. F. *Inorg. Chim. Acta* **2011**, *375*, 308. (b) Manning, M. J.; Knobler, C. B.; Hawthorne, M. F.; Do, Y. *Inorg. Chem.* **1991**, *30*, 3591.

(15) (a) Heying, T. L.; Ager, J. W. Jr.; Clark, S. L.; Mangold, D. J.; Oldstein, H. L.; Hillman, M.; Polak, R. J.; Szymanski, J. W. *Inorg. Chem.* **1963**, *2*, 1089. (b) Fein, M. M.; Grafstein, D.; Paustian, J. E.; Bobinski, J.; Lichstein, B. M.; Mayes, N.; Schwartz, N. N.; Cohen, A. S. *Inorg. Chem.* **1963**, *2*, 1115.

(16) Hillman, M. *J. Am. Chem. Soc.* **1960**, *82*, 1096.

(17) In the Ph.D. thesis by B. E. Aufderheide (Synthesis, boron-11 NMR shift assignments and correlations for halogenated decaboranes, carboranes and derivatives, and thermal rearrangements of 1-phenyl-3-fluoro-*o*-carborane, Carnegie-Mellon University, 1975) the yield of product **9** (Scheme 2) was not specified. The reported yield of the **9** → **7** step was 60%.

(18) Andrews, J. S.; Zayas, J.; Jones, M. Jr. *Inorg. Chem.* **1985**, *24*, 3715.

(19) Marshall, W. J.; Young, R. J. Jr.; Grushin, V. V. *Organometallics* **2001**, *20*, 523.

(20) NMR data for **8**. ^{1}H NMR (CD_3CN, 400 MHz): 2.53 (d, 3H, *J* 2, ACN), 2.41 (d, 3H, *J* 1.88, ACN), 2.12 to −1.21 (br m, 9H, B−H), −4.73 (br s, 2H, B−H−B). $^{13}C\{^1H\}$ NMR (CD_3CN, 100 MHz): 111.1, 110.4 ($C\equiv N$), 4.19, 4.17 (CH_3). ^{11}B NMR (CD_3CN, 128 MHz): −4.6 [d, 1B, *J* 133, B(4)], −14.2 [s, 1B, B(2)], −18.4 [d, 2B, B(5,7)], −19.2 [d, 2B, B(8,10)], −29.3 [d, 1B, *J* 155, B(9)], −30.7 [d, 1B, *J* 144, B(6)], −39.1 [d, 2B, *J* 146, B(1,3)].

(21) Li, Y.; Carroll, P. J.; Sneddon, L. G. *Inorg. Chem.* **2008**, *47*, 9193.

(22) Li, J.; Logan, C. F.; Jones, M. Jr. *Inorg. Chem.* **1991**, *30*, 4866.

(23) Andrianov, V. G.; Stanko, V. I.; Struchkov, Yu. T.; Klimova, A. I. *Zh. Strukt. Khim.* **1967**, *8*, 707.

(24) (a) Bregadze, V. I. *Chem. Rev.* **1992**, *92*, 209. (b) Kalinin, V. N.; Ol'shevskaya, V. A. *Russ. Chem. Bull., Int. Ed.* **2008**, *57*, 815.

(25) (a) Barberá, G.; Viñas, C.; Teixidor, F.; Rosair, G. M.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **2002**, 3647. (b) Fox, M. A.; Hughes, A. K. *Coord. Chem. Rev.* **2004**, *248*, 457.

(26) (a) Tomita, H.; Luu, H.; Onak, T. *Inorg. Chem.* **1991**, *30*, 812. (b) Fox, M. A.; Gill, W. R.; Herbertson, P. L.; MacBride, J. A. H.; Wade, K. *Polyhedron* **1996**, *15*, 565. (c) Yoo, J.; Hwang, J.-W.; Do, Y. *Inorg. Chem.* **2001**, *40*, 568.

(27) Yamazaki, H.; Ohta, K.; Endo, Y. *Tetrahedron Lett.* **2005**, *46*, 3119.

(28) For recent reviews on chemistry of metallacarboranes of transition metals, see: (a) Corsini, M.; Fabrizi de Biani, F.; Zanello, P. *Coord. Chem. Rev.* **2006**, *250*, 1351. (b) Chizhevsky, I. T. *Coord. Chem. Rev.* **2007**, *251*, 1590. (c) Deng, L.; Xie, Z. *Coord. Chem. Rev.* **2007**, *251*, 2452. (d) Xie, Z. *Coord. Chem. Rev.* **2002**, *231*, 23.