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New Approach to the Synthesis of 3-Alkyl-1,2-dicarba-*closo*-dodecaboranes: Reaction of Alkyldichloroboranes with Thallium Dicarbollide

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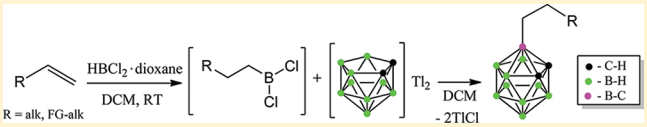
Supporting Information

ABSTRACT: A number of 3-alkyl-substituted 1,2-dicarba-*closo*-dodecaboranes were prepared in good yields via the reaction of alkyldichloroboranes, which were generated *in situ* through hydroboration of the corresponding alkenes with a dichloroborane−dioxane complex, with thallium dicarbollides in anhydrous dichloromethane at room temperature. This reaction also affords insertion products with new thallium dicarbollides prepared from 3-iodo- and 9-iodo-1,2-dicarba-*closo*-dodecaboranes. The synthesized 3-alkyl-1,2-dicarba-*closo*-dodecaboranes can be selectively deboronated at the B(6) atom to form the anionic 3-alkyl-7,8-dicarba-*nido*-undecaborates. All compounds were characterized by NMR and MS techniques.



INTRODUCTION

Carborane chemistry is a special part of polyhedral boron chemistry dedicated to stable boron/carbon clusters. Carborane compounds are numerous and can be divided into multiple classes.[1] The most attention, however, has always been focused on the chemistry of the three isomeric icosahedral dicarba-*closo*-dodecaboranes—*ortho*-, *meta*- and *para*-carboranes—mostly because of their relative inexpensiveness and availability.

The *ortho*-carborane cage consists of two elements, and its reactions can also be divided into two groups: the reactions of boron vertices and the reactions of carbon vertices. The boron-oriented reactions include nucleophile-assisted deboronation of the cage,[2] electrophilic substitution reactions on boron atoms,[3] and palladium-catalyzed cross-coupling of the B−I bonds with a variety of nucleophiles.[4] All of these reactions are regiospecific. Carbon-related reactions are much more diverse and include almost all standard reactions of organic carbanions.[5] The formation of the carborane carbanions is possible because of the pK_a value of the cage C−H bonds (23.3),[6] which is close to the values for terminal acetylenes and indene. The applications of carborane derivatives range from medicinal chemistry[7] to the chemistry of materials[8] and catalysis[9] to rocket fuels.[10] Consequently, the development of new synthetic pathways in carborane chemistry and the synthesis of novel carborane derivatives are very important.

Among the thousands of carborane derivatives prepared and characterized to date, one particular class of substituted carboranes—boron-substituted alkyl carboranes—is poorly represented. The primary reason for this scarcity is that only two synthetic pathways capable of producing the desired compounds are known, and both have serious disadvantages. The first pathway is the palladium-catalyzed cross-coupling reactions of the iodinated carboranes with alkyl metals. However, β-hydride elimination of the intermediate alkyl-palladium species narrows the range of the substrates available for coupling that will provide good yields.[4a] The second route is the insertion of alkyldichloroboranes into the sodium dicarbollide.[11] This route usually gives moderate yields of target compounds. However, the variety of commercially available alkyldichloroboranes is very limited.

Herein, we report a new synthetic approach to 3-alkyl-1,2-dicarba-*closo*-dodecaboranes via the reaction of *in situ* generated alkyldichloroboranes with thallium dicarbollide in dichloromethane solution at room temperature. The method allows for the simple preparation of a variety of title compounds with good yields.

RESULTS AND DISCUSSION

General Considerations. The first chemically isolable and air/moisture-stable derivative of the dicarbollide dianion, i.e., thallium dicarbollide, was prepared by Professor Gordon Stone as early as 1972; it promptly became one of the most useful synthetic tools in metallacarborane chemistry.[12] Multiple derivatives of thallium dicarbollide were prepared and characterized, including structurally, during the last 40 years.[13] Numerous transition and non-transition metal derivatives have been prepared by reactions of the corresponding salts and complexes[14] with thallium dicarbollide. However, until recently, thallium dicarbollide has not been considered as a synthon for the preparation of the substituted *closo*-carboranes.

Hawthorne et al. were the first to successfully "build" 3-substituted *closo*-carboranes starting from the dicarbollide

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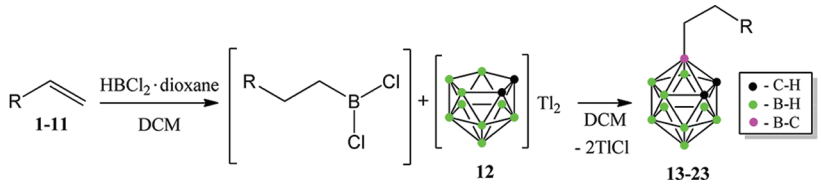
Scheme 1



dianion in 1968.[11a] 3-Phenyl- and 3-ethyl-1,2-dicarba-*closo*-dodecaboranes, among other derivatives, have been prepared by the reaction of sodium dicarbollide with phenyl- and ethyldichloroboranes in tetrahydrofuran (THF). The same strategy was later used for the synthesis of 3-halocarboranes and 3-diphenylamino-1,2-dicarba-*closo*-dodecaborane.[11b] In 1999, the first report of the preparation of 3-alkyl-substituted 1,2-dicarba-*closo*-dodecaboranes was published by our laboratory.[15] The hydroboration of several alkenes by $HBCl_2{\cdot}Me_2S$ in THF in the presence of BCl_3, with subsequent reaction of the formed alkyldichloroboranes with sodium dicarbollide in THF at −78 °C, gave moderate (∼30%) yields of the alkylated products.

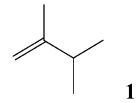
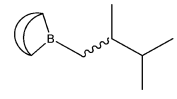
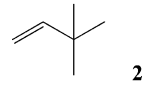
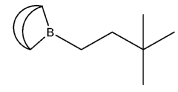
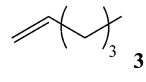
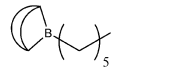
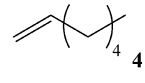
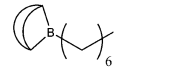
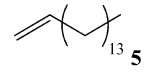
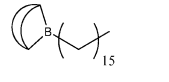
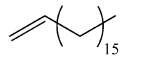
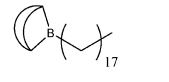
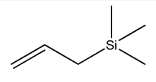
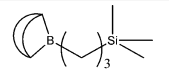
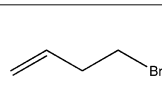
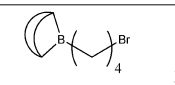
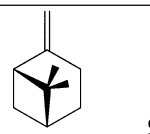
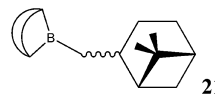
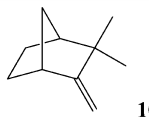
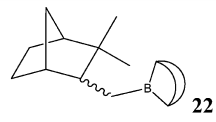
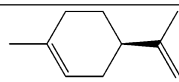
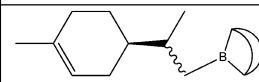
In our recent study,[16] we showed that, like alkali-metal dicarbollide salts, thallium dicarbollide can also be reconstructed to the 3-substituted 1,2-dicarba-*closo*-dodecaborane. According to our synthetic strategy, 3-iodo-1,2-dicarba-*closo*-dodecaborane was prepared in good yield by the reaction of the thallium dicarbollide with boron triiodide in hexane. To further develop synthetic applications of the thallium dicarbollide and make 3-alkyl-1,2-dicarba-*closo*-dodecaboranes more accessible, we combined both of the synthetic strategies developed in our laboratory into one simple and effective procedure.

Synthesis of 3-Alkyl-1,2-dicarba-*closo*-dodecaboranes (13−23). The reaction of the $HBCl_2{\cdot}$dioxane complex with a number of terminal alkenes (**1**−**8**, Scheme 1) in anhydrous DCM for 2 h at room temperature gave a very clean hydroboration reaction.[17] The reaction control was achieved by TLC, which showed an absence of the starting alkene in the reaction mixture after 2 h. Addition of the generated alkyldichloroborane solutions to a suspension of thallium dicarbollide (**12**) in an anhydrous DCM and subsequent reaction at room temperature for 18 h gave good yields of the corresponding 3-alkyl-1,2-dicarba-*closo*-dodecaboranes (**13**−**20**, Scheme 1). The chemical structures of the starting alkenes **1**−**8**, carborane compounds **13**−**20**, and the product are presented in Table 1. The reaction progress was monitored by the color change of the initially yellow (thallium dicarbollide) reaction suspension into the grayish-white (thallium(I) chloride).

The reaction workup is simple and includes filtration of the precipitate with subsequent isolation of the product (in solution) by column chromatography in hexane. After the solvent was evaporated and the products were dried under vacuum, compounds **14** and **17**−**20** were isolated as white solids, and compounds **13**, **15**, and **16** were isolated as viscous, colorless liquids.

The NMR spectra of compounds **13**−**20** showed several characteristic features. The $^{11}B\{^1H\}$ NMR spectra of all compounds consisted of a very specific integral ratio pattern: 2:1:1:3:3. This pattern corresponds well to carborane compounds with a plane of symmetry passing through the middle of the cluster C−C interaction and the substituted boron vertex (C_s point group). The cage boron resonances appeared in the δ range of 0 to −15 ppm, which is characteristic for *closo*-carboranes. In each spectrum, one of the resonances

Table 1. Structures of Terminal Alkenes and 3-Alkyl-1,2-dicarba-*closo*-dodecaboranes and Yields of the Insertion Products

Starting alkene	Product	Yield, %
 **1**	 **13**	66
 **2**	 **14**	62
 **3**	 **15**	65
 **4**	 **16**	64
 **5**	 **17**	60
 **6**	 **18**	66
 **7**	 **19**	76
 **8**	 **20**	44
 **9**	 **21**	76
 **10**	 **22**	57
 **11**	 **23**	56

that appeared at approximately δ −3 ppm (see Supporting Information) was very broad and did not show coupling with the proton in the corresponding ^{11}B NMR spectrum. This signal was assigned as the substituted boron vertex B(3).

In the $^{13}C\{^1H\}$ NMR spectra of all of the compounds, the signal that corresponded to the C−B bond appeared as a very broad multiplet (4−6 ppm wide) in the range δ 15−25 ppm.

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The broadness of the signal can be explained by the spin−spin coupling of the carbon nucleus with the two isotopes of boron ^{11}B and ^{10}B, which have spin numbers of 3/2 and 3, respectively.[18] Theoretically, the signal of such a carbon atom would contain a pair of multiplets: a quartet and a septet. However, poor signal resolution complicated by the low signal-to-noise ratio (for this particular signal) did not allow for the extraction of any individual components.[19] Other signals in the $^{13}C\{^1H\}$ NMR spectra were assigned for compounds on an individual basis (see Supporting Information). The structure of the substituent also affected the $^{13}C\{^1H\}$ NMR spectrum of the product. In particular, compound **13** unexpectedly showed two signals for the cage carbon atoms in the $^{13}C\{^1H\}$ NMR spectrum at δ 57.3 and 57.2 ppm. In the $^{13}C\{^1H\}$ NMR of compound **14**, the signal corresponding to the cage carbon atoms was unique, but it appeared to be broadened ($\Delta_{1/2}$ = 6.5 Hz) compared with the other resonances in the same spectrum ($\Delta_{1/2\ av}$ = 1.6 Hz). This result can be explained by the hindered rotation of the substituents in both compounds **13** and **14** with respect to the cage carbon atoms at room temperature. The corresponding cage carbon resonances in compounds **15**−**20** did not show any broadening and appeared as unique signals.

In the ^1H NMR spectra of all compounds, the cage C−H resonances appeared at δ 3.40 ppm and changed only by hundredths of a ppm for each individual compound. The electron density on the boron atom B(3) was therefore assumed to not significantly change depending on the structure of the substituent, and functional groups separated from the boron atom B(3) by three or more methylene groups did not significantly affect its electron density. In the ^1H NMR spectrum of compound **13**, hindered rotation of the substituent at room temperature was also indicated by the appearance of the CH_2−B(3) methylene group signal as an AB system.

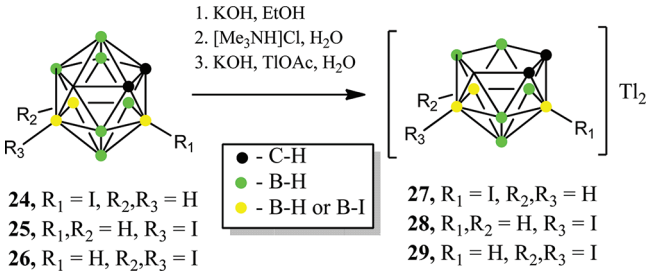
To test the reaction on more complex reagents, we decided to use several terpenes as starting materials. We chose (1*S*)-(−)-*β*-pinene (**9**), camphene (**10**), and D-limonene (**11**) because these compounds contain a terminal double bond as a structural element. The hydroboration of all three compounds with the subsequent thallium dicarbollide reaction gave, after isolation and purification, expected products **21**−**23** as white solids in good yields (Table 1).

Compounds **21**−**23** were also characterized by the NMR and MS techniques. The ^{11}B NMR spectra of compounds **21**−**23** were indistinguishable from those of compounds **13**−**20** and exhibited the same signal ratio pattern and range of chemical shifts. The ^1H and $^{13}C\{^1H\}$ NMR spectra of products **21**−**23** were complex because compounds **9**−**11** produced mixtures of diastereomers during the hydroboration step. The compositions of all mixtures were determined using GC/MS. Product **21** showed a 1:5 ratio of diastereomers, product **22** formed a 1:8 mixture, where the larger number most likely corresponds to the more stable *endo*-isomer.[20] Compound **23** showed a product ratio of approximately 1:1, which could be explained by the weaker asymmetric induction (by the ring) in the hydroboration of the auxiliary vinyl group compared to that of exocyclic double bond. In accordance with the previously published data,[21] the hydroboration of D-limonene produced only the hydroboration product of the exocyclic double bond; the hydroboration thus left the double bond in the six-membered ring intact and provided an opportunity for further functionalization. The presence of this double bond was clearly observed by the appearance of the resonance at δ 5.39 ppm in the ^1H NMR spectrum of **23**. The presence of the double bond was also supported by the occurrence of two closely positioned signals in the $^{13}C\{^1H\}$ NMR spectrum of **23**, at δ 121.10 and 121.05 ppm. These signals share a cross-peak in the $^1H-^{13}C\{^1H\}$ HMQC NMR of **23**.

Synthesis of 3-(3′-Trimethylsilyl-1′-propyl)-6-iodo-1,2-dicarba-*closo*-dodecaborane (31) and 3-(3′-Trimethylsilyl-1′-propyl)-9-iodo-1,2-dicarba-*closo*-dodecaborane (32). One of the most interesting yet very challenging tasks in polyhedral borane and carborane chemistry is vertex differentiation.[22] Differentiation helps make drug delivery vehicles more specific for a given biological target, e.g., a specific type of a tumor. Also, the vertex-differentiated carboranes may be exploited in the design and synthesis of new types of metal−organic frameworks (MOFs).[23] In the current study, we attempted to model possible templates for vertex differentiation in *ortho*-carboranes.

Using the well-established procedure for the synthesis of thallium dicarbollide,[12,16] we prepared three new members of this family starting from 3-iodo-1,2-dicarba-*closo*-dodecaborane (**24**, Scheme 2), 9-iodo-1,2-dicarba-*closo*-dodecabrane (**25**),

Scheme 2



and 9,12-diiodo-1,2-dicarba-*closo*-dodecaborane (**26**). The iodinated thallium dicarbollides **27**−**29** were prepared in excellent yields and used in subsequent reactions after being thoroughly dried.

For the insertion reactions into compounds **27**−**29**, we chose 3-trimethylsilylpropyldichloroborane (**30**, Scheme 3) for several reasons. First, it produced a very high yield of insertion product **19** in the reaction with unsubstituted thallium dicarbollide. Second, the NMR spectra of **19** were relatively simple, which allowed for unambiguous characterization of the product. Third, it can easily be transformed into a number of functionalized derivatives using common organic synthesis methods. The reaction of 3-trimethylsilylpropyldichloroborane (**30**) with compounds **27** and **28** gave products **31** and **32**, respectively, in moderate yields. Compound **29** showed no insertion products, even after reaction for 48 h at room temperature or overnight at reflux.

Such a decrease in the reactivity of iodinated thallium dicalbollides toward alkyldichloroboranes requires special explanations. It is well known that iodination of *ortho*-carborane cage decreases its solubility in organic solvents. For example, 9-iodo-1,2-dicarba-*closo*-dodecarborane can be easily recrystallized from hexanes,[3a] while for crystallization of 8,9,10,12-tetraiodo-1,2-dicarba-*closo*-dodecaborane an EtOH−H_2O mixture was used[24a] and for 4,5,7,8,9,10,11,12-octaiodo-1,2-dicarba-*closo*-decaborane an acetone−MeOH mixture.[24b] Salts of iodinated *nido*-carboranes are soluble only in polar organic solvents and water,[24c,d] and thallium dicarbollides are insoluble in most organic solvents.[13] We suggest that reactions between thallium dicarbollides and alkyldichloroboranes most likely take

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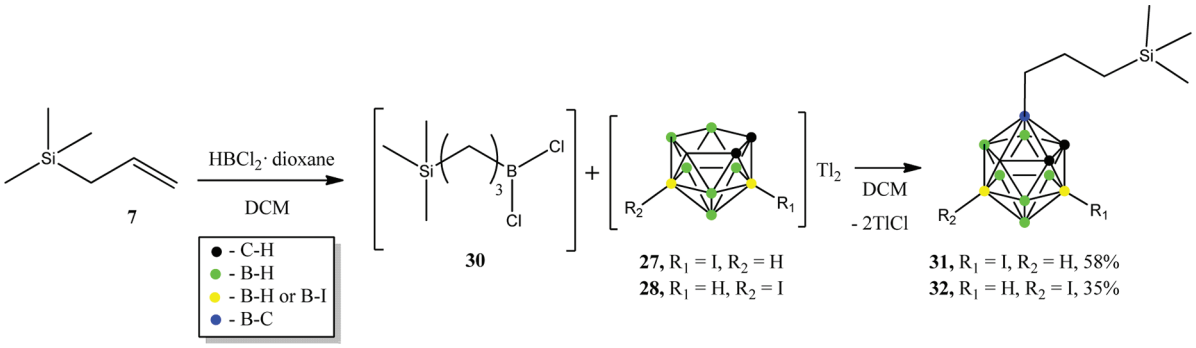
Scheme 3



place on the surface of solid thallium dicarbollide, from which separate molecules pass into solution and react to form *closo*-products. It seems very probable that even compared with monoiodinated compounds, **27** and **28**, solubility of the diiodinated thallium dicarbollide **29** in DCM is so insignificant that no visible reaction occurs in the case of this compound.

The isolation of the compounds **31** and **32** was analogous to that of compounds **13**–**23**, except for the column chromatography required for compound **32**, which was performed in 1% ethyl acetate–hexane. Compound **31** was a white solid, and compound **32** was a viscous, yellowish oil. The ^{1}H NMR spectra of both compounds showed signals characteristic of the trimethylsilylpropyl group, the carborane B–H vertices, and the carborane C–H resonances. As expected, the ^{1}H NMR spectrum of **32** showed two C–H resonances (δ 3.53 and 3.70 ppm), which result from the lack of a symmetry plane in the compound.

The ^{11}B{^{1}H} NMR spectrum of **31** contained a rather unusual 3:6:1 pattern that ranged from δ 0 to −30 ppm. In the ^{11}B NMR spectrum of **31**, the signal at δ −29.1 ppm did not split into a doublet; this lack of splitting allowed its unambiguous assignment as the B(6)–I resonance. The chemical shift of this signal was close to that exhibited by the parent *closo*-carborane **24** (δ −29.4 ppm).[16] The resonance at δ −1.9 ppm, which integrated as 3B, showed obvious asymmetry in the ^{11}B{^{1}H} NMR spectrum. In the ^{11}B NMR spectrum, it was split into a doublet with unequal intensities of the two components. This observation allowed us to assume that this signal contained the unique resonance of the alkyl-substituted B(3) atom overlapping with the other cage signal. The ^{11}B{^{1}H} NMR spectrum of **32** contained six resonances in an intensity ratio 1:1:1:1:5:1 because of the lack of symmetry in the molecule. The resonances at δ −4.0 and −17.1 ppm did not show proton couplings in the ^{11}B NMR spectrum, which allowed for their assignment as the B(3)–CH_2 and B(9)–I resonances, respectively. The ^{13}C{^{1}H} NMR spectra of compounds **31** and **32** were similar, with only the carborane C–H resonances exhibiting different chemical shifts and quantities: one cage C–H resonance appeared for compound **31** (δ 61.9 ppm), and two resonances (δ 53.1 and 57.0 ppm) appeared for compound **32**. Resonances that corresponded to the CH_2–B(3) bonds appeared in the spectra of both compounds at δ 19.7 ppm.

Synthesis of Tetrabutylammonium 3-Hexadecyl-7,8-dicarba-*nido*-undecaborate (33) and 3-Octadecyl-7,8-dicarba-*nido*-undecaborate (34). One of the most important applications of boron materials is boron neutron capture therapy (BNCT).[7d,f] The delivery of boron atoms into the tumor can be achieved via liposomes that contain boron compounds both inside the vesicle and in the lipid bilayer.[25] We decided to prepare analogues of the 7-hexadecyl-7,8-dicarba-*nido*-undecaborate anion, which is being used for liposome membrane preparation, through the deboronation of compounds **17** and **18**. The reaction of **17** and **18** with TBAF in THF solution at reflux gave clear deboronation of both substrates with the formation of the target tetrabutylammonium 3-hexadecyl-7,8-dicarba-*nido*-undecaborate (**33**) and 3-octadecyl-7,8-dicarba-*nido*-undecaborate (**34**) as white solids in 95% yields. Both compounds were characterized using multinuclear NMR and MS. In both cases, the reaction was regiospecific and led only to removal of the unsubstituted boron vertex.[26]

Boron-substituted *nido*-compounds are also interesting with respect to the synthesis of organometallic complexes. For example, *nido*-compounds that can be prepared from the diastereomeric *closo*-carboranes **21**–**23** can theoretically be used as chiral ligands in the well-known rhodacarborane hydrogenation catalyst[27] developed by Hawthorne and co-workers.

CONCLUSIONS

An effective synthetic pathway to a new class of 3-alkyl-substituted 1,2-dicarba-*closo*-dodecaboranes was developed. Alkyldichloroboranes generated from alkenes and dichloroborane underwent very clean insertion reactions with thallium dicarbollides. The reaction also proceeds in the case of substituted dicarbollides and, thus, provides an opportunity to achieve vertex differentiation in *ortho*-carboranes. These species may become a valuable starting point for the synthesis of the new carborane-based materials.

EXPERIMENTAL SECTION

Materials. All reactions were carried out in an argon atmosphere using standard Schlenk line techniques. Thallium dicarbollide was prepared according to the published procedure[16] and dried in an Abderhalden apparatus using methanol as a jacket heater. The dichloroborane–dioxane complex (3 M solution in DCM) was purchased from Aldrich. 2,3-Dimethyl-1-butene, 3,3-dimethyl-1-butene, 1-hexene, 1-heptene, 4-bromo-1-butene, and allyltrimethylsilane (Aldrich) were distilled under an argon atmosphere prior to reactions; 1-hexadecene, 1-octadecene, (1*S*)-(−)-β-pinene, D-limonene (Aldrich), and camphene (Fisher) were used as provided. Dichloromethane (DCM) was freshly distilled in an argon atmosphere over CaH_2 prior to use. Column chromatography was performed in air using Merck silica gel (63–200 mesh). Thin-layer chromatography was run on Merck precoated glass plates (silica 60 F254) using a palladium stain solution for spot developing.

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

Physical Measurements. ^{1}H, ^{11}B, $^{11}B\{^{1}H\}$, $^{13}C\{^{1}H\}$, and 2D NMR spectra were measured on a Bruker Avance-400 NMR spectrometer. Boron NMR spectra were referenced to 15% $BF_3{\cdot}Et_2O$ in $CDCl_3$. The ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra were referenced to the residual solvent peak impurity. Chemical shifts are in ppm; coupling constants are reported in Hz. GC/MS analyses were performed on a ThermoScientific ISQ GC/MS machine. Mass spectra were obtained on a Mariner Biospectrometry Workstation by PerSeptive Biosystems.

Common Procedure for the Synthesis of 3-Alkyl-1,2-dicarba-*closo*-dodecaboranes (13−23). A 3 M solution of $HBCl_2$−dioxane complex in DCM (0.340 mL, 1.02 mmol) was added dropwise, over a period of 10 min, to a stirred solution of alkene (1.02 mmol) in 1 mL of DCM. The reaction mixture was stirred at room temperature for 2 h. After that time, the solution of the formed alkyldichloroborane was added via syringe to a suspension of thallium dicarbollide (500 mg, 0.924 mmol) in 2 mL of DCM over a period of 5 min, and the reaction mixture was vigorously stirred at room temperature for 18 h. The reaction mixture was filtered through a paper filter, and the white precipitate of thallium(I) chloride was washed on a filter with 5 mL of DCM. The solution was co-evaporated with silica and placed on top of a silica column in hexane. The products were eluted with pure hexane, evaporated, and dried under vacuum to give compounds **14** and **17**−**23** as white solids and compounds **13**, **15**, and **16** as clear, colorless liquids. The yields of the compounds are presented in Table 1. NMR and MS data for the prepared compounds can be found in the Supporting Information.

Synthesis of Thallium 3-Iodo-7,8-dicarba-*nido*-undecaborate (27), 5-Iodo-7,8-dicarba-*nido*-undecaborate (28), and 5,6-Diiodo-7,8-dicarba-*nido*-undecaborate (29). All compounds were prepared according to the published procedure[11] starting from 3-iodo-1,2-dicarba-*closo*-dodecaborane (**24**), 9-iodo-1,2-dicarba-*closo*-dodecaborane (**25**), and 9,12-diiodo-1,2-dicarba-*closo*-dodecaborane (**26**). The products were isolated as bright yellow solids (**27** and **28**) and a beige solid (**29**). The yields of the compounds were 95%, 94%, and 92%, respectively.

Synthesis of 3-(3′-Trimethylsilyl-1′-propyl)-6-iodo-1,2-dicarba-*closo*-dodecaborane (31) and 3-(3′-Trimethylsilyl-1′-propyl)-9-iodo-1,2-dicarba-*closo*-dodecaborane (32). The compounds were prepared according to the common procedure (described above) starting from thallium 3-iodo-7,8-dicarba-*nido*-undecaborate (**27**) and thallium 5-iodo-7,8-dicarba-*nido*-undecaborate (**28**). Isolation of the products was achieved by column chromatography in hexane (**31**) and 1% EtOAc−hexane (**32**). After drying under vacuum, the compounds were isolated as a white solid (**31**) or a yellowish clear liquid (**32**) in 58% and 35% yields, respectively. Similar reaction of the thallium 5,6-diiodo-1,2-dicarba-*closo*-dodecaborane (**29**) with 3-trimethylsilyldichloroborane (**30**) gave no products; all of the thallium dicarbollide was isolated, unchanged, from the reaction mixture. NMR and MS data for the prepared compounds can be found in the Supporting Information.

Synthesis of Tetrabutylammonium 3-Hexadecyl-7,8-dicarba-*nido*-undecaborate (33) and 3-Octadecyl-7,8-dicarba-*nido*-undecaborate (34). To a solution of compound **17** (0.100 g, 0.272 mmol) in 2 mL of THF was added 1.36 mL of a 1 M TBAF in THF (1.36 mmol), and the reaction mixture was heated at reflux for 18 h. The solvent was removed under reduced pressure, and 5 mL of water was added to the residue to induce precipitation. The precipitate was filtered on a fine-porosity glass filter and washed with water (3 portions of 5 mL). After drying under vacuum over P_2O_5, compound **33** was isolated as a white solid (0.155 g, 95%). Compound **34** was prepared according to the same procedure and isolated as a white powder (yield 95%). NMR and MS data for the prepared compounds can be found in the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Spectral characterization: NMR data and spectra for compounds **13**−**23** and **31**−**34**, GC/MS spectra for compounds **13**−**16** and **19**−**23**, MS data for compounds **13**−**23**, **27**−**29**, and **31**−**34**, and mass spectra for compounds **27**−**29**. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ DEDICATION

Dedicated to the memory of Prof. F. Gordon A. Stone.

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