# Triphenylsilyl as a Protecting Group in the Synthesis of 1,12-Heterodisubstituted *p*-Carboranes

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A triphenylsilyl group is used as an auxiliary in the synthesis of heterodisubstituted *p*-carboranes via triphenylsilyl-*p*-carborane (**1**). The preparation of **1** is statistical, but with recovery of the starting *p*-carborane, the effective conversion to **1** is about 90%. Carborane **1** has been easily converted to its lithium and copper derivatives, which were reacted with a range of electrophiles including alkyl halides: an aryl iodide, an acetylene bromide, and a sulfenyl chloride. The derivatives of **1** are crystalline and UV active, which facilitates their isolation and purification. The $Ph_3Si$ group is efficiently removed with fluoride to give monosubstituted *p*-carboranes **I**, which upon further nucleophilic substitution yield *p*-carboranes **II**. The yields of heterodisubstituted products **II** are higher than for direct, "statistical" syntheses. For example, 12-pentyl-1,12-dicarba-*closo*-dodecaborane-1-carboxylic acid was synthesized from *p*-carborane via **1** in 62% overall yield, a considerable improvement over the 44% yield obtained by direct methods.

## Introduction

Icosahedral *closo*-carboranes are $\sigma$-aromatic, inorganic cage compounds that exhibit reactivities similar to those of some heteroaromatics. They undergo electrophilic substitution reactions and, upon deprotonation of the carbon atoms, form highly nucleophilic carbanions.[1,2] This allows the carboranes to be easily introduced into the framework of organic molecules and make them chemically compatible with the organic structure. Moreover, the unusual shape and stereoelectronic structures of the carboranes coupled with their thermal, chemical, and electrochemical stability makes carboranes, 1,12-dicarba-*closo*-dodecaborane (Figure 1) in particular, attractive structural elements for liquid crystals.[3]

In the course of our studies of boron cluster-containing liquid crystalline materials,[4] we were in need of a simple and efficient method for C-heterodisubstitution of 10- and 12-vertex *p*-carboranes. Such derivatives are rare and can be obtained either by sequential substitution (method A) or by differentiation procedures (method B) shown in Figure 1. The latter method[5] has been demonstrated to be relatively efficient but also very specific and unsuitable for our goals. Another more general approach has been developed for the 10-vertex *p*-carborane;[6] however, the nonstoichiometry of the reaction and the need to monitor product ratios reduces its convenience and reliability.

The overall efficiency of the heterodisubstitution process in Method A and the formation of **II** depends on the efficiency of the preparation of the monosubstituted derivative **I**. Most monosubstitution reactions involving carboranyllithium yield mixtures with statistical or close to statistical distributions of mono- (**I**) and homodisubstituted derivatives (**III**) accompanied by unreacted *p*-carborane.[6−10] This results from a rapid equilibration of the carborane anion species that exists in ethereal solutions.[11] The retardation of the equilibration rates and improved preparation of **I** via Method A has been observed for carboranyllithium in benzene[11] and car-

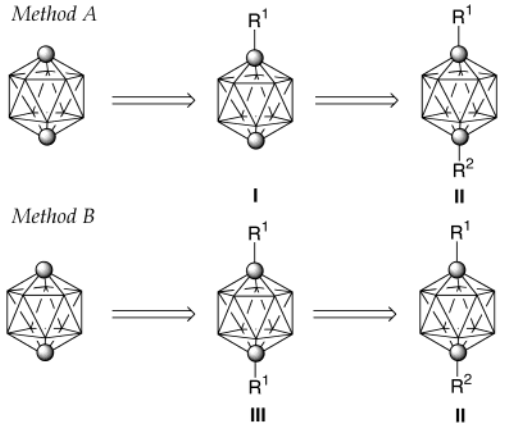


**Figure 1.** Methods available for the heterodisubstitution of *p*-carborane. Circles represent either C−H fragments or carbon atoms, and each vertex represents a B−H fragment.

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(1) Grimes, R. N. *Carboranes*; Academic Press: New York, 1970.
(2) Kaszynski, P. *Collect. Czech. Chem. Commun.* **1999**, *64*, 895.
(3) Kaszynski, P.; Huang, J.; Jenkins, G. S.; Bairamov, K. A.; Lipiak, D. *Mol. Cryst. Liq. Cryst.* **1995**, *260*, 315.
(4) Kaszynski, P.; Douglass, A. G. *J. Organomet. Chem.* **1999**, *581*, 28.
(5) Kahl, S. B.; Kasar, R. A. *J. Am. Chem. Soc.* **1996**, *118*, 1223.
(6) Müller, J.; Baše, K.; Magnera, T. F.; Michl, J. *J. Am. Chem. Soc.* **1992**, *114*, 9721.
(7) Zakharkin, L. I.; Kalinin, V. N.; Zhigareva, G. G. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1970**, 857.
(8) Coult, R.; Fox, M. A.; Gill, W. R.; Herbertson, P. L.; McBride, J. A. H.; Wade, K. *J. Organomet. Chem.* **1993**, *462*, 19.
(9) Yang, X.; Jiang, W.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1992**, *114*, 9719.
(10) Douglass, A. G.; Czuprynski, K.; Mierzwa, M.; Kaszynski, P. *J. Mater. Chem.* **1998**, *8*, 2391.
(11) Zakharkin, L. I.; Grebennikov, A. V.; Kazantsev, A. V. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1967**, 1991.

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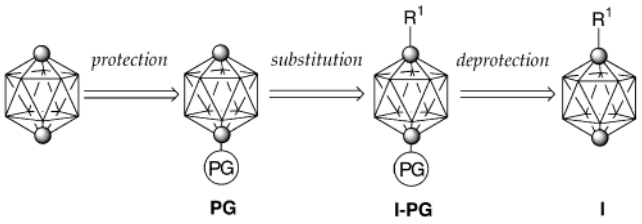
**Scheme 1**




boranylcopper reagents.[12] An elegant application of this approach was recently reported for a nonstatistical synthesis of *p*-carborane-1-carboxaldehyde diethyl acetal obtained in 71% yield via carboranyllithium.[13] This procedure and the subsequent substitution in the 12-position[13] can be extended, in principle, to a variety of 12-alkoxy- and 12-alkyl-*p*-carborane-1-carboxaldehydes, which are potential intermediates for liquid crystals.[14,15] *p*-Carboranylcopper reagents have been effectively used in dimerization,[9,16] ethynylation,[17] vinylation,[17] and nonstatistical arylation reactions.[12,18] In all these cases, the desired monosubstituted products **I** are formed in yields up to 80% and accompanied by various amounts of the starting carborane and the homodisubstituted products **III**.

Occasionally, the statistical distribution of products is acceptable if both mono- and disubstituted derivatives are desired, but usually only the monosubstituted product **I** is needed for further functionalization. It would also be acceptable if **I** and **III** were conveniently separated *and* **III** were easily converted back to the starting carborane. This essentially requires the use of a C-protective group, PG, and the problem of efficient preparation of **II** is reduced to the preparation of **PG** (Scheme 1).

Trialkylsilanes have been used as such protective groups for monosubstitution of *p*-carboranes and also for solubilization purposes.[6,9] They are moderately stable to organolithium bases and are easily cleaved with fluoride anion. The trialkylsilyl derivatives **PG** are UV transparent oils that are inconvenient to purify and handle (particularly in small quantities), and no reliable synthetic procedure for their preparation has appeared in the literature. In searching for a more versatile and convenient to use derivative, we focused on the triphenylsilyl group. Here, we describe the preparation and applications of 1-triphenylsilyl-*p*-carborane (**1**) in syntheses of intermediates for liquid crystalline materials. We report reactions of the lithium salt **1-Li** with alkyl iodides, alkyl bromides, and a sulfenyl chloride and reactions of the copper derivative **1-Cu** with an alkynyl bromide and an aryl iodide.

**Scheme 2**

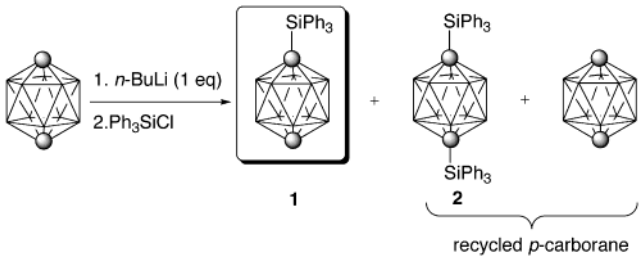
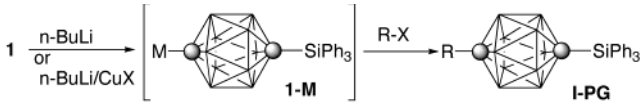



**Table 1. Reactions of 1-Triphenylsilyl-*p*-carborane 1**




| M | reagent R-**X** | **I-PG** | % yield | mp (°C) |
|---|---|---|---|---|
| Li | $C_5H_{11}$-**Br** | **4** | 92 | 114−114.5 |
| | (S)-$C_2H_5CH(CH_3)CH_2$-**Br** | **5** | 95[a] | 98−99 |
| | R−Br[b] (**3**) | **6** | 98[a] | 168−169 |
| | $C_4H_9S$-**Cl** | **7** | (49)[a] | *c* |
| Cu | $C_5H_{11}C{\equiv}C$−**Br** | **8** | 97[a] | 126−126.5 |
| | *p*-$C_7H_{15}O$-$C_6H_4$−**I** | **9** | 31 | 109 |

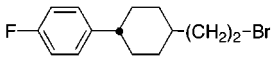
[a] Yield of crude ≥95% pure product. [b] R = 2-(4-(4-fluorophenyl)-cyclohexyl)ethyl. See structure **3** in the text. [c] Not measured.

## Results

**Preparation of 1.** 1-Triphenylsilyl-*p*-carborane (**1**) was obtained from *p*-carborane in the presence of 1.0−1.15 equiv of *n*-BuLi or LDA and conveniently isolated in about 40% yield by hexanes extraction from silica gel (Scheme 2). Treatment of the remaining, less soluble material, presumably the disilylated derivative **2**, with fluoride anion produces a mixture of *p*-carborane and the fluorinated silicon species, which does not interfere with the isolation of the recovered *p*-carborane. This procedure ensures that most of the starting material is recovered, so the yield of **1** corrected for both the recovered and unreacted *p*-carborane is up to 91% in large-scale preparations.

The silylation reactions run in THF appear to proceed faster and give higher yields than those performed in diethyl ether or benzene. In fact, the reaction in benzene takes several hours of stirring for completion.

**Nucleophilic Substitution of 1.** The monoprotected carborane **1** can be easily deprotonated ($pK_a$ = 26.8 for *p*-carborane)[19] with 1 equiv of *n*-BuLi and reacted with electrophiles or converted to other carboranylmetals in analogy to parent *p*-carborane.[1,2,20] Reactions of **1-Li** with alkyl bromides or iodides, including bromide **3**,[21] gave good to excellent yields of the C-alkylated products **4**−**6** (Table 1). To maximize the yield and to prevent alkyl

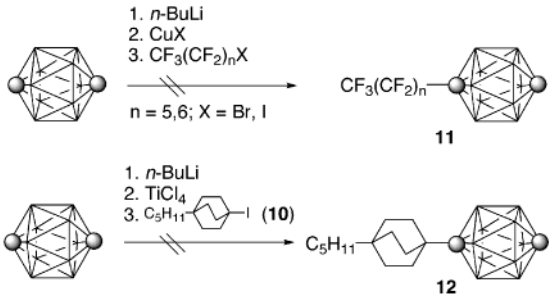



**3**

chain scrambling by lithium−halogen exchange, the reaction had been allowed adequate time (30 min) at ambient temperature to ensure complete consumption of

(12) Fox, M. A.; MacBride, J. A. H.; Peace, R. J.; Wade, K. *J. Chem. Soc., Dalton Trans.* **1998**, 401.
(13) Malan, C.; Morin, C. *Tetrahedron Lett.* **1997**, *38*, 6599.
(14) Thiemann, T.; Vill, V. In *Handbook of Liquid Crystals*; Demus, D., Goodby, J. W., Gray, G. W., Spiess H.-W., Vill, V., Eds.; Wiley-VCH: New York, 1998; Vol. 1; pp 87−113.
(15) Collings, P. J.; Hird, M. *Introduction to Liquid Crystals, Chemistry and Physics*; Taylor & Francis: Bristol, 1997.
(16) Zakharkin, L. I.; Kovredov, A. I. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1973**, 1396.
(17) Zakharkin, L. I.; Kovredov, A. I.; Olshevskaya, V. A. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1986**, 1260.
(18) Schöberl, U.; Magnera, T. F.; Harrison, R. M.; Fleischer, F.; Pflug, J. L.; Schwab, P. F. H.; Meng, X.; Lipiak, D.; Noll, B. C.; Allured, V. S.; Rudalevige, T.; Lee, S.; Michl, J. *J. Am. Chem. Soc.* **1997**, *119*, 3907.
(19) Kruglyak, L. I.; Petrov, E. S.; Kalinin, V. N.; Rys, E. G.; Zakharkin, L. I.; Shatenshtein, A. I. *Russ. J. Gen. Chem.* **1972**, *42*, 2660.
(20) Bregadze, V. I. *Chem. Rev.* **1992**, *92*, 209.
(21) Dąbrowski, R.; Dziaduszek, J.; Szczucinski, T.; Parka, J. *Mol. Cryst. Liq. Cryst.* **1995**, *260*, 201.

**Scheme 3**



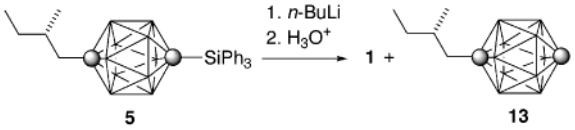

butyllithium, before organic halide was added. The UV-active triphenylsilyl substituent greatly facilitated chromatographic separation, and its crystalline nature simplified handling of small quantities of products in particular. The anion derived from **1** also readily reacted with butane-1-sulfenyl chloride to give the *C*-butylthio derivative **7** (Table 1). Purification and isolation of **7**, however, proved to be problematical. The carbon−sulfur bond exhibits some instability to silica, hindering chromatographic separation and preventing full characterization of this compound. Attempts to synthesize **7** using dibutyl disulfide instead of butane-1-sulfenyl chloride were unsuccessful.

Reaction of a cuprous halide with **1-Li** gave 12-triphenylsilyl-1-carboranylcopper (**1-Cu**), which was reacted with two classes of electrophiles: alkynyl and aryl halides. Reaction of **1-Cu** with 1-bromo-1-heptyne under general alkynylation conditions[17] gave an excellent yield of the acetylene **8**. The crude product was of 95% purity (GC−MS) and was further purified by recrystallization. A similar reaction of **1-Cu** with 1-heptyloxy-4-iodobenzene under general conditions in the presence of pyridine[8] yielded the expected aryl derivative **9**. The reaction run in DME gave 31% yield of **9**, and the remaining unreacted starting **1** was fully recovered despite the long reaction time at elevated temperatures. The same reaction performed in refluxing THF gave **9** in about 15% yield. The addition of a palladium catalyst to the reaction mixture had no effect on the yield.

In an attempt to expand the range of the electrophiles, coupling reactions of perfluoroalkyl halides and 1-iodo-4-pentylbicyclo[2.2.2]octane (**10**) with carboranylmetals were briefly investigated (Scheme 3). Thus, a reaction of carboranylcopper with perfluoroheptyl iodide or perfluorohexyl bromide under standard conditions[22] yielded only the C-halocarborane, presumably formed via metal−halogen exchange, and no expected **11** was observed. Also, a reaction of a carboranyltitanium reagent, prepared from carboranyllithium and $TiCl_4$, with the bridgehead iodide **10**, performed under general literature conditions[23] did not lead to the expected product **12**. These reactions were not investigated further.

The stability of the $Ph_3Si$ group toward butyllithium was examined using **5**, which was treated with 1 equiv of the base at ambient temperature, and the reaction progress was monitored by GC−MS. After 2 h, the reaction mixture showed very little change, but overnight stirring resulted in >85% conversion of the starting carborane **5** into **1** and **13** detected in approximately equal amounts (Scheme 4). The latter is the desilylation

**Scheme 4**




product, while the former arises from cleavage of the 2-methylbutyl group presumably via the E2 elimination of the carboranyl anion and the formation of 2-methylbut-1-ene.

**Removal of the Triphenylsilyl Group and Further Substitutions.** Treatment of triphenylsilylcarborane derivatives **I-PG** with a source of fluoride anion cleanly removed the $Ph_3Si$ group forming the corresponding monosubstituted carboranes **I** in high isolated yields (Table 2). The resulting silyl fluorides are nonvolatile and highly polar, and they do not interfere with isolation of pure carboranes. For instance, deprotection of **5**, **4**, and **9** with potassium fluoride/benzyltrimethylammonium hydrogen difluoride or tetrabutylammonium fluoride (TBAF) in THF followed by short-path distillation gave pure **13**−**15**, respectively, while **16**, obtained from **6**, was purified chromatographically. Attempts to obtain 1-butylthio-*p*-carborane (**17**) from **7** using potassium fluoride/benzyltrimethylammonium hydrogen difluoride resulted in preferential reaction at the sulfide, and only *p*-carborane and **1** were detected in the reaction products (GC−MS). It has been previously reported that carborane−sulfur bonds are unstable to strong anions such as butyllithium.[24]

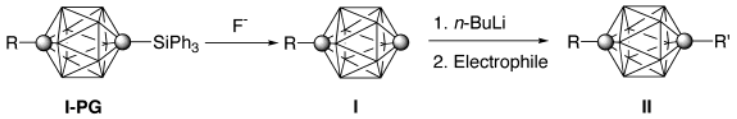
Transformations of the monosubstituted derivatives **I** followed standard procedures involving generation of a carboranylmetal (lithium or copper) and subsequent reaction with an electrophile. Thus, 1-pentyl-*p*-carborane (**14**), a versatile precursor for the synthesis of liquid crystalline materials, was converted to carboxylic acid **18**[10] with $CO_2$ and alkylated with 2-(4-(4-fluorophenyl)-cyclohexyl)ethyl bromide[21] (**3**) to yield the liquid crystal **19** in high isolated yields of about 86% (Table 2). Arylation of carborane **14** with 4-bromo-1-iodobenzene under general conditions[8] led to the two-ring liquid crystal intermediate **20** in 86% yield. In the synthesis of **20**, the reaction occurs preferentially with the iodide, and to ensure high chemoselectivity, a 5-fold excess of 4-bromo-1-iodobenzene was used.

The reactions of the chiral 2-methylbutyl derivative **5** and the preparation of **13** and subsequently carboxylic acid **21** were performed in an analogous way to the *n*-pentyl derivative **4** with similar yields.

In the course of our investigations, we were interested in synthesizing compound **22** in order to compare the effect of substitution of sulfur for the $-CH_2-$ group in **19**. The instability of the carborane carbon−sulfur linkage in the presence of fluoride and to BuLi[24] prevented synthesis via 1-butylthiocarborane (**17**). Therefore, the order of introduction of substituents was reversed, placing the butylthio group last. Thus, the monosubstituted precursor **16**, obtained 88% by desilylation of **6**, was reacted with BuSCl to from **22** (Table 2). The reaction was relatively inefficient, and the product suffered from the same low stability to silica as **7**. Overall separation

(22) McLoughlin, V. C. R.; Thrower, J. *Tetrahedron* **1969**, *25*, 5921.
(23) Reetz, M. T.; Westermann, J.; Steinbach, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 901.
(24) Smith, H. D., Jr.; Obenland, C. O.; Papetti, S. *Inorg. Chem.* **1966**, *5*, 1013.

**Table 2. Desilylation and Formation of Disubstituted *p*-Carboranes**

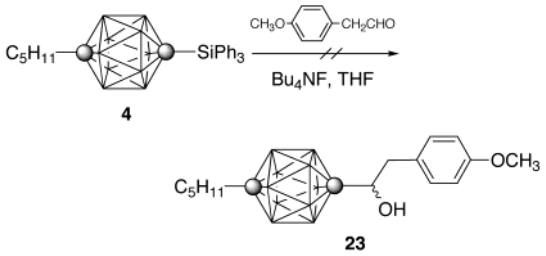



I-PG I II

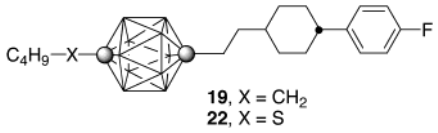
| R | carborane **I-PG** | carborane **I** (yield, %) | electrophile | carborane **II** (yield, %) | R′ | overall yield[b] (%) |
|---|---|---|---|---|---|---|
| *n*-$C_5H_{11}$− | **4** | **14** (96) | $CO_2$ | **18** (77) | −COOH | 68 |
| | | | RBr[a] (**3**) | **19** (86) | −R[a] | 76 |
| | | | *p*-$BrC_6H_4I$ | **20** (86) | *p*-$C_6H_4Br$ | 76 |
| (*S*)-$C_2H_5CH(CH_3)CH_2$− | **5** | **13** (82) | $CO_2$ | **21** (68) | −COOH | 58 |
| R-[a] | **6** | **16** (88) | *n*-$C_4H_9SCl$ | **22** (40)[c] | −$SC_4H_9$-*n* | 35 |
| *n*-$C_4H_9S$− | **7** | **17** (0)[d] | *e* | *e* | *e* | |
| *p*-$C_7H_{15}O$-$C_6H_4$− | **9** | **15** (96) | *e* | *e* | *e* | 27 |

[a] R = 2-(4-*trans*-(4-fluorophenyl)cyclohexyl)ethyl. See structure **3** in the text. [b] Yield based on starting *p*-carborane. [c] Unstable to chromatographic separation on silica. [d] See text. [e] Not attempted.

**Scheme 5**




of **22** from starting material **16** by chromatography produced material in 40% yield and >95% purity (by GC−MS).




Finally, we investigated the generation of carboranyl anions directly from the triphenylsilyl derivatives **I-PG**. The study was inspired by the report of successful in situ generation of *o*-carboranyl anions from trimethylsilyl-*o*-carboranes in the presence of fluoride and its efficient reactions with carbonyl compounds.[25] It was hoped to extend this methodology to *p*-carboranes and to synthesize alcohol **23** by a tetrabutylammonium fluoride-promoted reaction of **4** (Scheme 5). A complex mixture of products was formed and although there was evidence for the formation of **23** (GC−MS), this could not be isolated from the mixture by chromatography. The presumably very low yield of **23** in comparison to yields for the reactions of *o*-carboranes can be rationalized on the basis of the lower acidity of the *p*-carborane compared to its ortho isomer ($\Delta pK_a = 4.8$)[19] and to the 1−2% of water in TBAF,[26] which upsets kinetics and equilibria.

## Discussion and Conclusions

In choosing a protecting group (PG, Scheme 1) for blocking one carbon site in *p*-carborane, we sought to satisfy the following criteria:

(1) The protected intermediate **PG** must be synthesized efficiently and in high yield, either directly or with effective recovery of the starting *p*-carborane.

(2) The intermediate should be easy to handle and stable to long-term storage.

(3) The PG group should be stable to reaction conditions such as BuLi, which is typically used in the substitution process.

(4) The PG group should be easily and cleanly removed and not interfere with product isolation.

The triphenylsilyl group satisfies all these criteria. The preparation of **1** is straightforward and suitable for large-scale synthesis. The isolated yield for the preparation of **1** is less than statistical (40% based on used *p*-carborane), but most of the *p*-carborane can be easily recovered and the overall yield of **1** is about 90%. Triphenylsilyl-*p*-carborane **1** and its derivatives are crystalline compounds, and even alkyl derivatives such as **4** and **5** are solids melting at about 100 °C. In addition, UV activity of the $Ph_3Si$ group facilitates monitoring reactions by TLC and chromatographic separation of products. Overall, the crystallinity and the presence of the chromophore greatly simplifies manipulation, storage, and use of these intermediates, especially on small scales.

The benefits of the $Ph_3Si$ group are apparent in the preparation of monoaryl derivative **15**. Direct arylation of *p*-carborane with 1-heptyloxy-4-iodobenzene results in a mixture of products and starting materials, which is difficult to separate. The same product **15** is easily obtained via the triphenylsilyl derivative **9**, which exhibits significantly different chromatographic behavior and solubility from the starting compounds. Although the overall yield of **15** obtained via **1** is only 26% compared to the typical ≥50% in the direct arylation method,[12] the simplicity of separation and the full recovery of unreacted **1** provides a clear synthetic advantage. The $Ph_3Si$ chromophore also facilitated the isolation of acetylene derivative **8**, which otherwise would be completely transparent above 210 nm.[27]

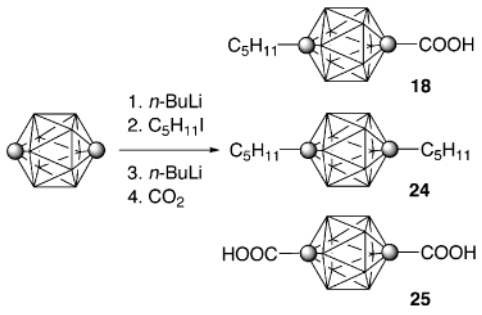
The triphenylsilyl group appears to be relatively stable toward BuLi and also under typical C-substitution conditions, including the use of organocopper reagents. The high stability of the $Ph_3Si$ group is reflected in high yields and purity (>95%) of alkyl and acetylene derivatives **4**−**6** and **8**. The silyl group is cleanly removed from the carborane, and the monosubstituted carboranes such as

(25) Cai, J.; Nemoto, H.; Nakamura, H.; Singaram, B.; Yamamoto, Y. *Chem. Lett.* **1996**, 791.

(26) Cox, D. P.; Terpinski, J.; Lawrynowicz, W. *J. Org. Chem.* **1984**, *49*, 3216.

(27) Kaszynski, P.; Tesh, K. F.; Young, V. G., Jr., submitted.

**Scheme 6**




**13**−**16** are readily separated from the silyl fluoride cleavage products, either by distillation or chromatography. The auxiliary $Ph_3Si$ group allows for clean high-yield sequence of substitution, and the products require very little purification.

The overall yields of heterodisubstituted carboranes are high, about 70−80%, based on **1** or about 60−70% based on starting *p*-carborane. This is significantly higher than might be expected from "statistical" synthesis of these derivatives through either method A or method B in Figure 1. The advantage of using a protective group in synthesis of heterodisubstituted carboranes is clearly demonstrated by the example of 12-pentyl-*p*-carborane-1-carboxylic acid **18**. When *p*-carborane was sequentially treated with 1 equiv of BuLi, alkylated with 1 equiv of pentyl iodide, treated with another 1 equiv of BuLi, and carboxylated with $CO_2$, the acid **18** was isolated in 44% yield[10] along with 20% of dipentylcarborane **24** and 29% of the diacid **25** (Scheme 6). This compares to the overall yield of 62% of **18** obtained from *p*-carborane via **1**. In the case of acid **18**, however, separation of the products in the statistical synthesis of 12-pentyl-*p*-carborane-1-carboxylic acid (**18**, Scheme 6) is facilitated by the very different properties (acidity and solubility) of the products, and in addition, both acids and **24**[28] are useful compounds. This is not necessarily the case for other syntheses, e.g., that of **19**, where byproducts are not useful, mixtures may not be so easily separated and where it is vital that precious intermediates such as the precursor bromide **3**[21] to **16** are used efficiently.

Thus, the synthetic utility of **1** has been demonstrated with alkyl, aryl, alkynyl, and alkylthio electrophiles producing important intermediates and liquid crystalline materials such as **19** and **22**.[29] This method should be suitable for use with other types of electrophiles,[1,20] and since the chemistry of the 10- and 12-vertex carboranes is similar, its application to 10-vertex carborane chemistry should be straightforward and complementary to the other recently reported method.[30] Alternatively, the triphenylsilyl group may be used as derivatizating reagent for aiding separation of carborane derivatives.

## Experimental Section

Melting points are uncorrected. $^1$H, $^{13}$C, and $^{11}$B NMR spectra were recorded in $CDCl_3$ at 300, 75.4, and 64.2 MHz, respectively, and referenced to the solvent ($^1$H and $^{13}$C) or to $B(OMe)_3$, unless specified otherwise. IR spectra were recorded by deposition of a thin film from solution onto sodium chloride disks. Mass spectrometry was performed using a Hewlett-Packard 5890 instrument (GC−MS). The specific rotations of chiral compounds were measured in chloroform using 1 g/100 mL concentrations at 22 °C for 589 nm radiation. Elemental analysis was provided by Atlantic Microlab, Norcross, GA. Toluene, tetrahydrofuran, ether, and dimethoxyethane (DME) were each dried by distillation from Na. Carbon dioxide was obtained from dry ice and dried by bubbling through concentrated sulfuric acid. *p*-Carborane was purchased from Katchem (Czech Republic) and (S)-(+)-1-bromo-2-methylbutane from Aldrich. Chromatographic separations were performed on silica plates using Chromatotron.

**1-Triphenylsilyl-1,12-dicarba-*closo*-dodecaborane (1).** *p*-Carborane (7.92 g, 55 mmol) dissolved in dry ether (100 mL) was treated with 2.5 M BuLi (22.3 mL, 55 mmol) at −78 °C. The mixture was stirred for 10 min, warmed to 0 °C, and stirred for 15 min. Triphenylsilyl chloride (16.43 g, 55 mmol) in dry ether (100 mL) was added dropwise at 0 °C, and the mixture was stirred at rt for 2 h. The resulting solution was filtered through a silica gel plug that was well washed with $CH_2Cl_2$, and the filtrate was carefully evaporated leaving white solid (19.5 g). The unreacted carborane (2.66 g, 34% yield) was sublimed into a dry ice−acetone trap. The residue was dissolved in warm hexanes (400 mL), filtered through a silica gel plug (5 cm), and washed well with hexanes (600 mL). Evaporation of the hexane wash gave pure **1** (8.84 g, 40% yield): mp 177−178 °C; $^1$H NMR $\delta$ 1.2−3.6 (br m, 10 H), 2.86 (br s, 1H), 7.32−7.46 (m, 9H), 7.54 (dd, $J_1$ = 7.1 Hz, $J_2$ = 1.4 Hz, 6H); $^{13}$C NMR $\delta$ 68.74, 72.73, 127.46, 130.09, 131.07, 137.25; $^{11}$B NMR $\delta$ −14.1 (od, $J_{BH}$ = 162 Hz), −13.6 (od, $J_{BH}$ = 151 Hz); IR 2605, 1103, 738, 699 cm$^{-1}$; MS *m*/*e* 405−399 (max at 403, 7, M), 259 (100). Anal. Calcd for $C_{20}H_{26}B_{10}Si$: C, 59.67; H, 6.51. Found: C, 59.78; H, 6.50.

Further washing of the silica plug with $CH_2Cl_2$ gave 9.50 g of white, poorly soluble material, presumably **2**, that was treated with $Bu_4NF$ (1 g) and NaF (3 g) in $CH_2Cl_2$ (30 mL). After stirring overnight, the mixture was diluted with hexanes filtered through a silica gel plug and washed with hexanes. After careful evaporation of the solvent, *p*-carborane (1.74 g) was sublimed into a dry ice−acetone trap. This brings total of the recovered carborane to 4.40 g (56% yield) and the yield of **1** to 91%, based on the consumed carborane.

**1-Pentyl-12-triphenylsilyl-1,12-dicarba-*closo*-dodecaborane (4).** A solution of 1-triphenylsilyl-*p*-carborane (**1**, 14.07 g, 35 mmol) in dry THF (100 mL) was cooled to −78 °C and *n*-BuLi (1.6 M in hexanes, 35 mmol, 22 mL) added dropwise to form a suspension. The mixture was warmed to room temperature (redissolution occurred) and stirred for 30 min. The reaction mixture was recooled to −78 °C and 1-iodopentane (6.93 g, 35 mmol) added. The mixture was warmed to room temperature and stirred for 90 min. The solvent was removed and the crude product passed through a silica plug eluted with $CH_2Cl_2$. Removal of the solvent yielded a light-yellow oil solidifying on standing (16.2 g, 98% yield, 96% pure by GC), which was recrystallized from pentane at −20 °C to give 15.20 g (92% yield) of white crystalline product: mp 114−114.5 °C; $^1$H NMR $\delta$ 0.78 (t, $J$ = 7.3 Hz, 3H), 0.95−1.23 (m, 6H), 1.49−1.53 (m, 3H), 1.2−3.6 (br m, 10H), 7.30−7.44 (m, 9H), 7.52 (dd, $J_1$ = 7.6 Hz, $J_2$ = 1.4 Hz, 6H); $^{13}$C NMR $\delta$ 13.88, 22.17, 28.67, 31.18, 39.10, 65.48, 90.15, 127.44, 130.04, 131.32, 137.24; $^{11}$B NMR $\delta$ −13.4 (d, $J_{BH}$= 164 Hz), −12.4 (d, $J_{BH}$= 151 Hz); IR 2600, 1428, 1104, 740, 698 cm$^{-1}$; MS *m*/*e* 474−470 (max at 472, 4, M), 259 (100). Anal. Calcd for $C_{25}H_{36}B_{10}Si$: C, 63.52; H, 7.68. Found: C, 63.43; H, 7.66.

**1-((*S*)-2-Methylbutyl)-12-triphenylsilyl-1,12-dicarba-*closo*-dodecaborane (5).** Compound **5** was obtained from carborane **1** (1.75 g, 4.35 mmol) and (S)−(+)-1-bromo-2-methylbutane (0.69 g, 4.57 mmol, 0.56 mL) as described for **4**. The resulting light-yellow oil of crude product solidified on standing (1.95 g, 95% yield, 98% pure by GC). Analytical samples were purified by chromatography (hexanes/$CH_2Cl_2$, 9:1 ratio): mp 98−99 °C; $[\alpha]^{22}_D$ +0.08° ($CHCl_3$); $^1$H NMR $\delta$ 0.70 (t, $J$ = 7.1 Hz, 3H), 0.71 (d, $J$ = 6.3 Hz, 3H), 0.82−0.95 (m, 1H), 1.0−3.1 (br m, 10H), 1.08−1.21 (m, 2H), 1.37 (dd, $J_1$=14.8 Hz, $J_2$=6.2 Hz, 1H), 1.53 (dd, $J_1$=14.8 Hz, $J_2$=3.7 Hz, 1H), 2.61 (br s, 1H), 7.30−7.33 (m, 6H), 7.38−7.45 (m, 3H),

(28) Douglass, A. G.; Both, B.; Kaszynski, P. *J. Mater. Chem.* **1999**, *9*, 683.
(29) Properties of new liquid crystals will be reported elsewhere.
(30) Janoušek, Z.; Kaszynski, P. *Polyhedron* **1999**, *18*, 3517.

7.51−7.54 (m, 6H); $^{13}$C NMR $\delta$ 11.01, 19.98, 29.69, 34.30, 46.01, 65.97, 89.84, 127.42 130.02, 131.32, 137.23; $^{11}$B NMR $\delta$ −12.1 (d, $J_{BH}$ = 172 Hz), −13.5 (d, $J_{BH}$ = 160 Hz); IR 2601, 1428, 1105 cm$^{-1}$; MS *m/e* 475−469 (max at 473, 7, M), 259 (100). Anal. Calcd for $C_{25}H_{36}B_{10}Si$: C, 63.52; H, 7.68. Found: C, 64.08; H, 7.92.

**1-[2-[4-*trans*-(4-Fluorophenyl)cyclohexyl]ethyl]-12-triphenylsilyl-1,12-dicarba-*closo*-dodecaborane (6).** Compound **6** was obtained from carborane **1** (0.511 g, 1.27 mmol) and 2-[4-*trans*-(4-fluorophenyl)cyclohexyl]ethyl bromide[21] (**3**, 0.362 g, 1.27 mmol) as described for **4**. Crude product was obtained in 98% yield (0.752 g). Recrystallization from toluene/isooctane gave pure white crystals (0.553 g, 72% yield): mp 168−169 °C; $^1$H NMR $\delta$ 0.89−1.06 (m, 5H), 1.20−1.40 (m, 2H), 1.55−1.85 (m, 6H), 2.38 (m, 1H), 1.0−3.3 (br m, 10H), 6.92 (m, $J_{HH}$ = 8.7 Hz, $J_{HF}$ = 8.7 Hz, 2H), 7.09 (m, $J_{HH}$ = 8.7 Hz, $J_{HF}$ = 5.6 Hz, 2H), 7.38−7.51 (m, 9H), 7.64 (d, $J$ = 6.8 Hz, 6H); $^{13}$C NMR $\delta$ 33.06, 34.16, 36.25, 36.74, 36.81, 43.56, 65.56, 90.09, 114.87 (d, $J_{CF}$ = 21 Hz), 127.68 (d, $J_{CF}$ = 7 Hz), 130.04, 131.30, 137.23, 143.07 (d, $J_{CF}$ = 3 Hz), 161.10 (d, $J_{CF}$ = 243 Hz); $^{11}$B NMR $\delta$ −13.3 (m); IR 2923, 2602, 1510, 1428, 1104, 736, 699 cm$^{-1}$. Anal. Calcd for $C_{34}H_{43}B_{10}FSi$: C, 67.29; H, 7.14. Found: C, 67.32; H, 7.17.

**Butane-1-sulfenyl Chloride.**[31] Dibutyl disulfide (25 mmol, 4.75 mL) was dissolved in dry toluene (10 mL) and cooled to −30 °C (dry ice/acetonitrile bath). At this temperature, a solution of sulfuryl chloride (25 mmol, 2.0 mL) in dry toluene (5 mL) was added dropwise. Stirring the mixture for 30 min at room temperature gave a red/orange solution of butane-1-sulfenyl chloride that was used immediately in subsequent transformations.

**1-Butylthio-12-triphenylsilyl-1,12-dicarba-*closo*-dodecaborane (7).** A solution of the lithium salt **1-Li** obtained from **1** (2.0 g, 5 mmol) as described for **4** was reacted with butane-1-sulfenyl chloride in toluene (10 mmol, 4.4 mL) at −78 °C. The reaction was warmed to room temperature and stirred for 90 min. The crude product was flushed through a 1 in. silica plug washed with ether (75 mL), and the solvents were removed. The product was then washed through a second silica plug eluted with ether (100 mL) to yield 2.5 g of orange product that was purified by column chromatography (hexanes) producing an off-white powder (1.21 g, 49% yield): $^1$H NMR $\delta$ 1.5−3.5 (br m, 10H) 0.91 (t, $J$ = 7.3 Hz, 3H), 1.31−1.44 (m, 2H), 1.57−1.69 (m, 2H), 3.06 (t, $J$ = 7.4 Hz, 2H), 7.35−7.55 (m, 15H); $^{13}$C NMR $\delta$ 13.45, 21.68, 30.87, 38.33, 71.52, 102.89, 127.74, 130.34, 130.51, 137.21; $^{11}$B NMR $\delta$ −13.6 (d, $J_{BH}$ = 178 Hz); IR 2628, 1428, 1347, 1144, 1105, 1088 cm$^{-1}$.

**1-(1-Heptynyl)-12-triphenylsilyl-1,12-dicarba-*closo*-dodecaborane (8).** 1-Triphenylsilyl-*p*-carborane (**1**, 0.20 g, 0.50 mmol) was dissolved in dry THF (5 mL) and cooled to −70 °C, and a 2.5 M solution of BuLi in hexane (0.23 mL, 0.58 mmol) was added. The resultant solution was brought to room temperature and after 15 min of stirring was cooled to −70 °C, after which time dried CuBr (0.100 g, 0.69 mmol) was added to a vigorously stirred solution. The mixture was warmed and left to stir for 1 h. A solution of 1-bromo-1-heptyne[32] (0.120 g, 0.67 mmol) in dry THF (3 mL) was added, and the mixture was gently refluxed under stirring for 48 h. The crude mixture was diluted with hexanes and passed through a silica gel plug, which was washed with hexanes. Solvents were removed, leaving 0.240 g of crystalline 95% pure (by GCMS) crude product in 97% yield. Analytical sample (0.091 g, 37% yield) was obtained by repeated recrystallization from isopropanol (recrystallization from pentane was less effective): mp 126.0−126.5 °C; $^1$H NMR $\delta$ 1.15−3.6 (br m, 16H), 0.84 (t, $J$ = 6.9 Hz, 3H), 1.99 (t, $J$ = 7 Hz, 2H), 7.30−7.47 (m, 9H), 7.47−7.56 (m, 6H); $^{13}$C NMR $\delta$ 13.88, 18.35, 21.99, 27.65, 30.80, 67.41, 75.11, 77.12, 81.62, 127.51, 130.16, 131.00, 137.21; $^{11}$B NMR $\delta$ −10.2 (d, $J_{BH}$ = 151 Hz), −12.6 (d, $J_{BH}$ = 155 Hz); IR 2612, 1428, 1106, 1083, 740, 698 cm$^{-1}$; MS *m/e* 499−493 (max at 496, 8, M), 259 (100). Anal. Calcd for $C_{27}H_{36}B_{10}Si$: C, 65.28; H, 7.30. Found: C, 65.07; H, 7.18.

**1-Heptyloxy-4-iodobenzene.**[33] A mixture of 4-iodophenol (5.0 g, 23 mmol), potassium carbonate (7.0 g, 276 mmol), 1-bromoheptane (4 mL, 25 mmol), and Aliquat 336 (1 mL) in dry acetone (50 mL) was vigorously stirred under reflux. After 3 h, the mixture was filtered, the filtrate was concentrated, and the residue dissolved in $CH_2Cl_2$ (25 mL) passed through a silica gel plug. The solvents were removed, and the residue was distilled on Kugelrohr (90−120 °C/1.0 Torr) to give 6.83 g (93% yield) of a colorless oil: $^1$H NMR $\delta$ 0.87 (t, $J$ = 6.5 Hz, 3H), 1.20−1.44 (m, 8H), 1.70−1.75 (m, 2H), 3.88 (t, $J$ = 6.6 Hz, 2H), 6.65 (d, $J$ = 4.75 Hz, 2H), 7.51 (d, $J$ = 4.75 Hz, 2 H); $^{13}$C NMR $\delta$ 14.0, 22.5, 25.9, 29.0, 29.1, 31.7, 68.1, 116.7, 138.1, 159.0; MS *m/e* 318 (15, M), 220 (100).

**1-(4-Heptyloxyphenyl)-12-triphenylsilyl-1,12-dicarba-*closo*-dodecaborane (9).** 1-Triphenylsilyl-*p*-carborane (**1**, 0.400 g, 1.00 mmol) dissolved in dry DME (5 mL) was treated with 2.5 M BuLi in hexanes (0.4 mL, 1.00 mmol) at −70 °C. The resulting white precipitation disappeared upon warming up to ambient temperature, and cuprous bromide (0.25 g, 1.74 mmol) dried in vacuo, was added at once producing a dark red solution. After 20 min, dry pyridine (0.65 mL) was added followed by 1-heptyloxy-4-iodobenzene (0.36 g, 1.13 mmol). The mixture was stirred at 100 °C for 16 h, cooled, diluted with hexanes, and passed through a silica gel plug that was washed with $CH_2Cl_2$. Solvents were removed, and the residue was separated on silica gel ($CH_2Cl_2$/hexanes, 1:6 ratio) and recrystallized from hexanes giving 0.182 g (31% yield, 92% based on recovered starting material) of white crystals: mp 109 °C; $^1$H NMR $\delta$ 1.0−3.8 (br m, 10H), 0.87 (t, $J$ = 6.8 Hz, 3H), 1.20−1.50 (m, 8H), 1.69−1.72 (m, 2H), 3.84 (t, $J$ = 6.5 Hz, 2H), 6.63 (d, $J$ = 8.9 Hz, 2H), 7.04 (d, $J$ = 8.9 Hz, 2H), 7.30−7.50 (m, 9H), 7.57 (dd, $J_1$=8.1 Hz, $J_2$=1.3 Hz, 6H); $^{13}$C NMR $\delta$ 14.06, 22.57, 25.91, 28.98, 29.10, 31.72, 66.5, 67.91, 91.0, 113.66, 127.49, 127.92, 129.33, 130.11, 131.18, 137.25, 159.10; $^{11}$B NMR (128 MHz) $\delta$ −12.0 ($J_{BH}$ = 175 Hz), −13.4 ($J_{BH}$ = 175 Hz); IR 2952, 2610, 1511, 1254, 1183, 1105, 1092, 698 cm$^{-1}$. Anal. Calcd for $C_{33}H_{44}B_{10}OSi$: C, 66.74; H, 7.64. Found: C, 66.54; H, 7.47.

**1-Iodo-4-pentylbicyclo[2.2.2]octane (10).** The iodide was prepared according to a general procedure.[34] 4-Pentylbicyclo-[2.2.2]octan-1-ol (0.50 g, 1.64 mmol) and 55% HI (15 mL) were stirred at 100 °C overnight. The resulting dark mixture was poured into water and extracted with hexanes. The organic layer was washed with aqueous sodium bisulfite, dried, and concentrated, leaving 0.79 g of crude oily product, which was short-path distilled (130 °C/0.08 Torr) to give 0.76 g (97% yield) of the product: $^1$H NMR $\delta$ 0.86 (t, $J$ = 7.0 Hz, 3H), 0.95−1.38 (m, 8H), 1.52 (m, 6H), 2.44 (m, 6H); $^{13}$C NMR $\delta$ 14.04, 22.62, 23.07, 27.48, 32.63, 34.70, 40.97, 41.71, 47.88; MS *m/e* 180 (15), 179 (100), 109 (54), 95 (76).

**1-((*S*)-2-Methylbutyl)-1,12-dicarba-*closo*-dodecaborane (13).** Compound **13** was obtained from 1-(2-methylbutyl)-12-triphenylsilyl-*p*-carborane (**5**, 1.06 g, 2.24 mmol) as described for **14** (method B). The crude product was distilled (105−109 °C/1.5 Torr) to give a colorless oil (0.397 g, 82% yield): $^1$H NMR $\delta$ 0.75 (t, $J$ = 7.1 Hz, 3H), 0.75 (d, $J$ = 6.2 Hz, 3H), 0.9−1.0 (m, 1H), 1.0−3.1 (br m, 10H), 1.11−1.19 (m, 2H), 1.37 (dd, $J_1$ = 14.8 Hz, $J_2$ = 6.2 Hz, 1H), 1.53 (dd, $J_1$ = 14.8 Hz, $J_2$ = 3.7 Hz, 1H), 2.61 (br s, 1H); $^{13}$C NMR $\delta$ 11.08, 20.05, 29.74, 34.60, 45.76, 58.34, 84.89; $^{11}$B NMR $\delta$ −13.4 (d, $J_{BH}$ = 164 Hz), −16.2 (d, $J_{BH}$ = 162 Hz); IR 2961, 2607, 1462, 1069, 732 cm$^{-1}$; MS *m/e* 185−177 (max at 182, 7, M − Et), 57 (100), 56 (57). Anal. Calcd for $C_7H_{22}B_{10}$: C, 39.22; H, 10.34. Found: C, 39.33; H, 10.28.

**1-Pentyl-1,12-dicarba-*closo*-dodecaborane (14). Method A.** 1-Triphenylsilyl-12-pentyl-*p*-carborane (**4**, 5.0 g, 10.6 mmol) was dissolved in THF (15 mL). Potassium fluoride (0.62 g, 10.6

(31) Thea, S.; Cevasco, G. *Tetrahedron Lett.* **1988**, *29*, 2865.

(32) 1-Bromo-1-heptyne (bp 56−57 °C/10 Torr, Straus, F.; Kollek, L.; Heyn, W. *Chem. Ber.* **1930**, *63*, 1937) was prepared from 1-heptyne according to a general procedure: Brandsma, L. *Preparative Acetylenic Chemistry, Studies in Organic Chemistry 34*, 2nd ed.; Elsevier: 1988; p 150.

(33) Bruce, D. W.; Dunmur, D. A.; Lalinde, E.; Maitlis, P. M.; Styring, P. *Liq. Cryst.* **1988**, *3*, 385.

(34) Adcock, W.; Kok, G. B. *J. Org. Chem.* **1985**, *50*, 1079.

mmol) and benzyltrimethylammonium hydrogen difluoride (0.40 g, 2.12 mmol) were added, and the mixture was stirred overnight at room temperature. The solvent was removed by rotary evaporation, hexanes (50 mL) were added, and the mixture was filtered through a 1 in. layer of silica gel and eluted with hexanes. Removal of the solvent and distillation gave the product as a colorless oil (1.33 g, 89% yield): $^1$H NMR $\delta$ 0.83 (t, $J$ = 7.2 Hz, 3H), 1.06−1.22 (m, 6H), 1.59 (br t, $J$ = 8.3 Hz, 2H), 2.62 (br s, 1H), 1.0−3.2 (br m); $^{13}$C NMR $\delta$ 13.85, 22.23, 28.99, 31.22, 38.93, 57.94, 85.00; $^{11}$B NMR $\delta$ −13.7 (d, $J_{BH}$ = 168 Hz), −16.2 (d, $J_{BH}$ = 162 Hz); IR (neat) 2956, 2931, 2607, 1465, 1071, 730 cm$^{-1}$; MS *m/e* 188−175 (max at 185, 100, M − Et), 57 (89). Anal. Calcd for $C_7H_{22}B_{10}$: C, 39.22; H, 10.34. Found: C, 39.37; H, 10.28.

**Method B.** A mixture of silane **4** (0.300 g, 0.64 mmol) and $Bu_4NF$ (0.40 g, 1.5 mmol) in THF (15 mL) was stirred at room temperature overnight. Hexanes were added, and the mixture was filtered through a silica gel plug and washed with hexanes. Solvents were evaporated, and the semicrystalline residue (0.260 g) was distilled twice (Kugelrohr; 155 °C/13 Torr) to give 1-pentyl-1,12-dicarba-*closo*-dodecaborane (0.153 mg, 96% yield) as a colorless oil.

**1-(4-Heptyloxyphenyl)-1,12-dicarba-*closo*-dodecaborane (15).** Compound **15** was obtained from 1-(4-heptyloxyphenyl)-12-triphenylsilyl-*p*-carborane (**9**, 0.100 g, 0.169 mmol) as described for **14** (method B). The crude product was distilled (130 °C/0.1 Torr) to give 0.054 g (96% yield) of a colorless oil that solidified upon standing: mp 42.5−43 °C; $^1$H NMR $\delta$ 1.0−3.8 (br m, 10H), 0.91 (t, $J$ = 6.8 Hz, 3H), 1.24−1.30 (m, 9H), 1.55−1.60 (m, 2H), 3.56 (t, $J$ = 6.4 Hz, 2H), 6.57 (d, $J$ = 8.9 Hz, 2H), 7.21 (d, $J$ = 8.9 Hz, 2H); $^{13}$C NMR $\delta$ 14.26, 22.95, 26.28, 29.35, 29.45, 32.09, 67.93, 82.96, 114.27, 128.64, 128.87, 159.79; $^{11}$B NMR (128 MHz) $\delta$ −13.2 ($J_{BH}$ = 164 Hz), −16.0 ($J_{BH}$ = 165 Hz); IR 2929, 2610, 1512, 1255, 1183 cm$^{-1}$; MS *m/e* 337−331 (max at 335, 13, M), 239−231 (max at 236, 100). Anal. Calcd for $C_{15}H_{30}B_{10}O$: C, 53.86; H, 9.04. Found: C, 53.63; H, 8.90.

**1-[2-[4-*trans*-(4-Fluorophenyl)cyclohexyl]ethyl]-1,12-dicarba-*closo*-dodecaborane (16).** Compound **16** was obtained from 1-[2-[4-*trans*-(4-fluorophenyl)cyclohexyl]ethyl]-12-triphenylsilyl-*p*-carborane (**6**, 0.520 g, 0.85 mmol) as described for **14** (method A). The silica gel plug was washed with $CH_2Cl_2$, and the resulting crude material was purified by Chromatotron chromatography (hexanes) giving the product (0.260 g, 88% yield). An analytical sample was obtained by recrystallization twice from pentane: mp 106−107 °C; $^1$H NMR $\delta$ 0.92−1.15 (m, 5H), 1.21−1.45 (m, 2H), 1.60−1.90 (m, 6H), 2.37 (m, 1H), 2.61 (br s, 1H), 1.0−3.1 (br m, 10H), 6.93 (m, $J_{HH}$ = 8.7 Hz, $J_{HF}$ = 8.7 Hz, 2H), 7.10 (m, $J_{HH}$ = 8.7 Hz, $J_{HF}$ = 5.6 Hz, 2H); $^{13}$C NMR $\delta$ 33.09, 34.17, 36.50, 36.59, 36.80, 57.97, 84.95, 114.89 (d, $J_{CF}$ = 21 Hz), 127.98 (d, $J_{CF}$ = 7 Hz), 143.03 (d, $J_{CF}$ = 3 Hz), 161.10 (d, $J_{CF}$ = 243 Hz); $^{11}$B NMR $\delta$ −16.1 (d, $J_{BH}$ = 169 Hz), −13.6 (d, $J_{BH}$ = 162 Hz); IR 2920, 2607, 1510, 1221 cm$^{-1}$; MS *m/e* 350−346 (max at 348, 26, M − Et), 135 (87), 122 (100). Anal. Calcd for $C_{16}H_{29}B_{10}F$: C, 55.14; H, 8.39. Found: C, 55.22; H, 8.32.

**Attempted Synthesis of 1-Butylthio-1,12-dicarba-*closo*-dodecaborane (17).** 1-Butylthio-12-triphenylsilyl-*p*-carborane (**7**, 670 mg, 1.42 mmol) was dissolved in THF (5 mL), and potassium fluoride (82 mg, 1.42 mmol) and benzyltrimethylammonium hydrogen difluoride (76 mg, 0.4 mmol) were added. The reaction was stirred at room temperature and monitored by TLC. After 54 h, no starting material remained, and the THF was evaporated off. Hexanes (20 mL) were added, and the product was filtered through a silica plug eluted with hexanes (100 mL) and separated by chromatography (hexanes). All materials isolated were analyzed by GC/MS and NMR. GC/MS and $^1$H NMR analysis showed *p*-carborane and 1-triphenylsilyl-*p*-carborane (**1**) but no desired product.

**12-Pentyl-1,12-dicarba-*closo*-dodecaborane-1-carboxylic acid (18).** A solution of 1-pentyl-*p*-carborane (**14**, 0.385 g, 1.8 mmol) in dry THF (10 mL) was cooled to −78 °C and *n*-BuLi (1.6 M in hexanes, 1.9 mmol, 1.2 mL) added. The resulting solution was warmed to room temperature and stirred for 20 min, and dry carbon dioxide was bubbled through the reaction for 1.5 h. The solvent was removed to yield an off-white solid that was treated with 1 M HCl (15 mL). The product was extracted with ether (3 × 15 mL), the combined organic phases were dried ($Na_2SO_4$), and the solvent was evaporated to give 0.391 g (84% yield) of the white crude product, which was sublimed (130 °C/0.5 Torr) to give 0.359 g (77% yield) of white crystals identical with the original sample.[10]

**1-[2-[4-*trans*-(4-Fluorophenyl)cyclohexyl]ethyl]-12-pentyl-1,12-dicarba-*closo*-dodecaborane (19).** 1-Pentyl-*p*-carborane (**14**, 161 mg, 0.75 mmol) in dry THF (7.5 mL) under nitrogen was cooled to −78 °C and BuLi (1.92 M in hexanes, 0.40 mL, 0.787 mmol) added dropwise. The mixture was stirred for 30 min at room temperature and then recooled to −78 °C. The 2-[4-*trans*-(4-fluorophenyl)cyclohexyl]ethyl bromide[21] (**3**, 221 mg, 0.787 mmol) in dry THF (7.5 mL) was added dropwise, the reaction was allowed to warm to room temperature and stirred for 90 min, and then the solvent was removed by rotary evaporation. The product was dissolved in $CH_2Cl_2$ and filtered through a 1 in. layer of silica eluted with $CH_2Cl_2$. Purification was effected by chromatography (hexanes) giving 268 mg (86% yield) followed by repeated recrystallization from pentane (200 mg, 64% yield): mp 96.3 °C (DSC); $^1$H NMR $\delta$ 0.80 (t, $J$ = 7.3 Hz, 3H), 0.90−1.40 (m, 13H), 1.53−1.70 (m, 6H), 1.78−1.82 (m, 2H), 2.37 (m, 1H), 1.0−3.2 (br m), 6.89−6.93 (m, $J$ = 8.7 Hz, 6H), 7.06−7.11 (m, 2H); $^{13}$C NMR $\delta$ 13.85, 22.22, 29.15, 31.24, 33.12, 34.19, 35.34, 36.80, 36.86, 43.60, 79.37, 104.74, 114.90 (d, $J_{CF}$ = 21 Hz), 128.00 (d, $J_{CF}$ = 8 Hz), 143.08 (d, $J_{CF}$ = 3 Hz), 161.13 (d, $J_{CF}$ = 243 Hz); $^{11}$B NMR $\delta$ −13.8 (d, $J_{BH}$ = 161 Hz); IR 2603, 1508, 1221, 830 cm$^{-1}$. Anal. Calcd for $C_{21}H_{39}B_{10}F$: C, 60.25; H, 9.39. Found: C, 60.36; H, 9.35.

**1-(4-Bromophenyl)-12-pentyl-1,12-dicarba-*closo*-dodecaborane (20).** 1-Pentyl-*p*-carborane (**14**, 1.58 g, 7.37 mmol) was dissolved in dry DME (25 mL), and BuLi (2.4 M in DME, 3.2 mL, 7.7 mmol) was added at −78 °C. The mixture was warmed to 0 °C, and after 15 min, dry CuI (2.0 g) was added. The resulting yellowish solution was stirred for 20 min at room temperature, and freshly distilled pyridine (4.5 mL) was added, which caused the formation of a yellow precipitate. *p*-Bromoiodobenzene (10.5 g, 37 mmol) was added in one portion, and the resulting dark brown solution was stirred at 95 °C for 50 h. The mixture was cooled, hexanes (20 mL) were added, and the resulting dark brown suspension was filtered through a silica plug washed with hexanes. The filtrate was evaporated, leaving 11.0 g of white, crystalline solid that was placed in a sublimator. Starting *p*-bromoiodobenzene (7.74 g, 27 mmol) was recovered as the first fraction (110−115 °C/16 Torr) followed by **20** (2.35 g, 86% yield) at 120 °C/0.1 Torr. An analytical sample was obtained by resublimation (105−125 °C/0.1 Torr) and recrystallization from pentane at −78 °C twice: mp 81−82 °C; $^1$H NMR $\delta$ 0.81 (t, $J$ = 7.2 Hz, 3H), 1.05−1.40 (m, 6H), 1.62 (br t, $J$ = 7.0 Hz, 2H), 1.2−3.6 (br m, 10H), 7.03 (d, $J$ = 8.7 Hz, 2H), 7.25 (d, $J$ = 8.7 Hz, 2H); $^{13}$C NMR $\delta$ 13.86, 22.21, 29.13, 31.19, 37.88, 50.55, 79.79, 81.60, 122.68, 128.88, 131.08, 135.47, 137.08; $^{11}$B NMR $\delta$ −13.6 (d, $J$ = 165 Hz); IR 2607, 1492, 1062, 1012, 734 cm$^{-1}$; MS *m/e* 373−365 (max at 369, 100, M). Anal. Calcd for $C_{13}H_{25}B_{10}Br$: C, 42.28; H, 6.82; Br, 21.63. Found: C, 42.15; H, 6.86; Br, 21.56.

**12-((*S*)-2-Methylbutyl)-1,12-dicarba-*closo*-dodecaborane-1-carboxylic Acid (21).** It was obtained from 1-(2-methylbutyl)-*p*-carborane (**13**, 0.292 g, 1.36 mmol) as described for **18**. Crude product (0.310 g, 88% yield) was purified by sublimation (135 °C/0.6 Torr) giving 0.240 g (68% yield) white crystals: mp 117−119 °C; $[\alpha]^{22}_D$ +0.15° ($CHCl_3$); $^1$H NMR (acetone-$d_6$) $\delta$ 0.77 (t, 3H), 0.78 (d, 3H), 0.95−1.07 (m, 1H), 1.1−3.4 (br m, 10 H), 1.13−1.26 (m, 2H), 1.44−1.52 (m, 1H), 1.67−1.73 (m, 1H); $^{13}$C NMR $\delta$ 11.30, 20.25, 35.52, 45.67, 76.62, 84.35, 163.35; $^{11}$B NMR $\delta$ −13.1 (d, $J_{BH}$ = 162 Hz); IR 2959 (br), 2614, 1717, 1283 cm$^{-1}$. Anal. Calcd for $C_8H_{22}B_{10}O_2$: C, 37.19; H, 8.39. Found: C, 37.43; H, 8.39.

**1-Butylthio-12-[2-[4-*trans*-(4-fluorophenyl)cyclohexyl]-ethyl]-1,12-dicarba-*closo*-dodecaborane (22).** The 1-[2-[4-*trans*-(4-fluorophenyl)cyclohexyl]ethyl]-*p*-carborane (**16**, 211 mg, 0.605 mmol) was dissolved in dry THF (2 mL) and the solution cooled to −78 °C using a dry ice/acetone bath. *n*-BuLi

(1.92 M in THF, 0.65 mmol, 0.35 mL) was added dropwise, and then the reaction was warmed to room temperature and stirred for 30 min. The reaction was again cooled to −78 °C, and butyl sulfenyl chloride solution (1.21 mmol) was added dropwise. The reaction was warmed to room temperature and stirred for 90 min. After removal of the solvents, ether was added and the crude product was flushed through a 1 in. silica plug eluted with ether (75 mL). The more volatile sulfur-containing impurities were removed by short-path distillation yielding 195 mg of crude product. The product was then purified by column chromatography (hexanes) producing a white powder (106 mg, 40% yield, >95% pure by GC−MS). The analytical sample produced by repeated recrystallization from pentane did not give satisfactory elemental analysis results: mp 89.4 °C (DSC); $^1$H NMR $\delta$ 0.80−1.10 (m, 7H), 1.21−1.45 (m, 7H), 1.50−1.75 (m, 4H), 1.75−1.82 (m, 2H), 2.37 (m, 1H), 2.52 (t, $J$ = 7.1 Hz, 2H), 1.0−3.1 (br m, 10H), 6.92 (m, $J_{HH}$ = 8.7 Hz, $J_{HF}$ = 8.7 Hz, 2H), 7.09 (m, $J_{HH}$ = 8.7 Hz, $J_{HF}$ = 5.6 Hz, 2H); $^{13}$C NMR $\delta$ 13.52, 21.85, 29.69, 30.27, 33.08, 34.15, 35.23, 35.77, 36.79, 43.56, 76.07, 79.56, 114.89 (d, $J_{CF}$ = 21 Hz), 127.98 (d, $J_{CF}$ = 7 Hz), 142.99 (d, $J_{CF}$ = 3 Hz), 161.10 (d, $J_{CF}$ = 243 Hz); $^{11}$B NMR $\delta$ −13.4 (d, $J_{BH}$ = 164 Hz); IR 2926, 2605, 1510, 1220 cm$^{-1}$; MS *m/e* 439−433 (max at 437, 31, M), 135 (100), 122 (68), 109 (70). Anal. Calcd for $C_{20}H_{37}B_{10}FS$: C, 55.01; H, 8.54. Found: C, 56.38; H, 8.68.

**Attempted Synthesis of 1-(12-Pentyl-1,12-dicarba-*closo*-dodecaborane)-1-hydroxy-2-(4-methoxyphenyl)ethane (23).** A solution of anhydrous tetrabutylammonium fluoride[26] (138 mg, 0.529 mmol) in dry THF (1 mL) was added dropwise to a stirred solution of 4-methoxyphenylethanal (79 mg, 0.529 mmol), itself synthesized by oxidation[35] of 4-methoxyphenethanol and 1-triphenylsilyl-12-pentyl-*p*-carborane (**4**, 250 mg, 0.529 mmol) in dry THF (3 mL). An immediate yellow coloration was noted that became red as stirring continued for 1 h. Ether (15 mL) was added, and the organic phase was washed with water (2 × 5 mL). The organic phase was dried over magnesium sulfate and the solvent removed to yield 288 mg of yellow solid. TLC analysis revealed a minimum of seven products that were partially separated by chromatography (hexanes/ether). 1-Pentyl-1,12-dicarbadodecaborane, triphenylsilyl fluoride, triphenylsilyl hydroxide, 4-methoxyphenylethanal, and its aldol condensation product were all identified by GC−MS. Additionally, traces of product **23** were identified by GC−MS (*m/e* 366−362 max at 364), but it could not be isolated by further chromatography.

**1,12-Dipentyl-1,12-dicarba-*closo*-dodecaborane (24).** Isolated in 20% yield as the hexane extract from the basic solution of acids in synthesis of **18**:[10] bp 129−132 °C/ 0.8 Torr; $^1$H NMR $\delta$ 0.80 (t, $J$ = 7.2 Hz, 6H), 1.04−1.19 (m, 12H), 1.2−3.4 (br m, 10H); 1.56 (t, $J$ = 8.1 Hz, 4H), $^{13}$C NMR $\delta$ 13.87, 22.24, 29.17, 31.26, 37.74, 79.27; $^{11}$B NMR $\delta$ −13.9 (d, $J_{BH}$= 163 Hz); IR 2955, 2601, 1465 cm$^{-1}$; MS *m/e* 258−249 (max at 255, 100%, M − Et). Anal. Calcd for $C_{12}H_{32}B_{10}$: C, 50.66; H, 11.34. Found: C, 50.68; H, 11.26.

**1,12-Dicarba-*closo*-dodecaborane-1,12-dicarboxylic Acid (25).** Isolated in 29% yield as the hexane-insoluble fraction of acids in synthesis of **18**:[10] mp 327 °C (dec, DSC) (lit.[5] mp 356−357 °C); $^1$H NMR (acetone-$d_6$) $\delta$ 1.2−3.4 (br m, 10H), 9.5 (br s, 2H); $^{13}$C NMR $\delta$ 79.87, 162.98; $^{11}$B NMR $\delta$ −13.9 (d, $J_{BH}$ = 170 Hz); IR 2617, 1715, 1280 cm$^{-1}$. Anal. Calcd for $C_4H_{12}B_{10}O_4$: C, 20.69; H, 5.21. Found: C, 20.73; H, 5.24.

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