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Practical Synthesis of 1,12-Difunctionalized *o*-Carborane for the Investigation of Polar Liquid Crystals

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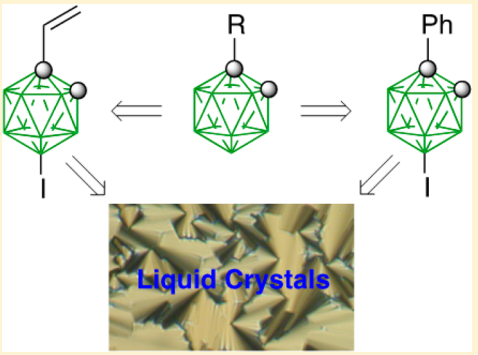
ABSTRACT: Two isomerically pure 1,12-difunctionalized derivatives of *o*-carborane, 12-iodo-1-vinyl (**1b**) and 12-iodo-1-phenyl (**1c**), are conveniently obtained on a practical scale in yields of 22% and 32%, respectively, by monoiodination of the corresponding *o*-carborane derivatives (**4b** and **4c**) followed by separation of the regioisomers by crystallization (**1b**) and chromatography (**1c**). Subsequent functional group transformations gave access to other derivatives, including two liquid-crystalline compounds, in which *o*-carborane is a linear structural element. Regioselectivity of substitution on the carborane cage and on the benzene ring correlates with the inductive effect parameter of the substituent. The preparation of analogous derivatives of *m*-carborane was also investigated.



INTRODUCTION

Among three 12-vertex carboranes, [*closo*-$C_2B_{10}H_{12}$],[1] only the *p*-carborane (**A**; Figure 1) has been broadly used as a linear

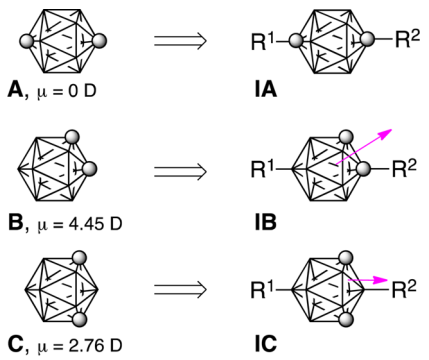


Figure 1. Structures of three isomeric carboranes **A**–**C** and their derivatives **IA**– **IC**. Each vertex represents a BH fragment, and the sphere is a carbon atom. The arrow represents the vector of the cluster's electric dipole.

structural element in the design of molecular-size objects,[2−5] liquid crystals,[6−10] and pharmacological compounds.[11−13] In contrast, there is only one report of *o*-carborane (**B**) as a linear structural element,[14] and no report of such use of *m*-carborane (**C**) substituted in the antipodal positions. In spite of focus on *p*-carborane, it can be argued that the remaining two isomeric and essentially isosteric carboranes have additional properties that are of particular interest for certain molecular and functional designs. Thus, unlike **A**, *o*- and *m*-carboranes have moderate ground-state dipole moments of 4.45 and 2.76 D (benzene), respectively,[15] which are oriented about 30° of the 1,12 axis in **B** and nearly parallel to the 2,9 axis in **C** (Figure 1). In addition, the carbon atoms in the 2,9-disubtituted *m*-carborane (**IC**) are enantiotopic, which raises the possibility of coupling of the electric dipole with molecular chirality, a feature important for some applications including ferroelectric liquid crystals.[16] Wider use of carboranes **B** and **C** in the design of soft materials is hampered, however, by the lack of general access to appropriately functionalized derivatives **IB** and **IC**. Our interest in these compounds is related to liquid crystals and stems from the fundamental question of the role of the molecular electric dipole in liquid-crystalline phase stabilization.[10,17] A comparison of the properties of isosteric mesogenic derivatives **IA**–**IC** would provide an interesting opportunity for such an investigation with possible practical implications.

The synthesis of *p*-carborane derivatives **IA** substituted at antipodal 1,12 positions is accomplished easily by taking advantage of the acidic C–H groups and nucleophilicity of the resulting carbanions.[18] In contrast, the preparation of analogous *o*-carborane derivatives **IB** requires two electrophilic substitution steps: at the boron and carbon atoms, which raises the issue of regioselectivity, regardless of the order of these transformations. As a consequence, a mixture of 1,12 and 1,9 regioisomers (**IB** and **IIB**, respectively; Figure 2) is typically formed, which necessitates isomer separation.

Thus far, five compounds of the general structure **IB** have been reported in the literature. Unfortunately, compounds **1a**–**1c** are lacking any preparative details, and their characterization is incomplete.[14,19−21] Compound **2** was separated from a 1:1 mixture of the two isomers,[22] while **3** was isolated in small amounts by crystallization of the isomeric mixture.[23]

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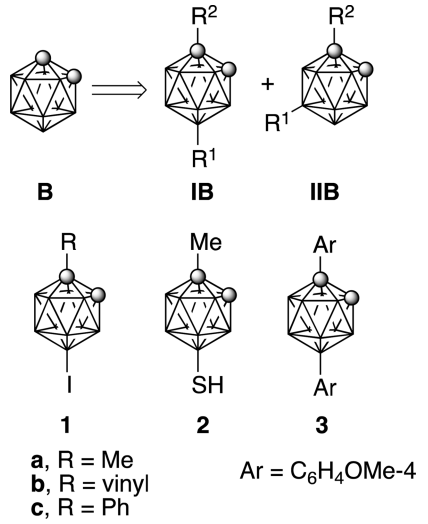


Figure 2. Two isomeric products **IB** and **IIB** obtained from *o*-carborane (**B**) and the structures of the reported isomerically pure 1,12-disubstituted derivatives **IB**.

The preparation of *m*-carborane derivatives **IC** requires yet another synthetic approach and can, in principle, be achieved by deboronation of [*closo*-1,7-$C_2B_{10}H_{12}$] (**C**) followed by reboronation of the [*nido*-$C_2B_9H_{11}$]$^{2-}$ dianion tandem to install a substituent at the B(2) position and the subsequent electrophilic substitution at the antipodal boron atom. Both of these methods are known in the literature[1] but have not been used in the same sequence to obtain disubstituted derivatives. Similar to the case of *o*-carborane, a mixture of regioisomers 2,9 (**IC**) and 2,10 (**IIC**) is expected (Figure 3), and methods for separation need to be developed.

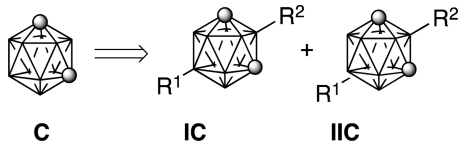


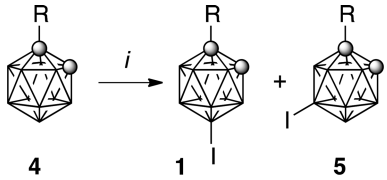
Figure 3. Two isomeric products **IC** and **IIC** formed from *m*-carborane (**C**).

For the purpose of general intermediates, B-iodo derivatives provide the most versatility. Therefore, we initially focused on compounds **1** and expanded our investigation to derivatives **IC**. Here we provide practical synthesis of **1b** and **1c** and demonstrate their further transformations including two examples of liquid-crystalline derivatives. Regioslectivity of the transformations (iodination and nitration) is discussed in terms of the substituent effect. Finally, we describe our attempts at the preparation of 2,9-difunctionalized derivatives of *m*-carborane (**IC**).

RESULTS

Synthesis. *1,12-Difunctionalized o-Carborane. Isomer Separation.* Initially, we concentrated on three iodo derivatives **1a**−**1c** accessible by iodination of appropriate 1-substituted *o*-carborane derivatives **4a**−**4c** (Scheme 1). Thus, iodination of 1-methyl-*o*-carborane (**4a**)[21,24] with ICl at ambient temperature gave a mixture of isomers **1a** and **5a** in a nearly 1:1 ratio and 60% yield. Attempts at separation of the isomers using

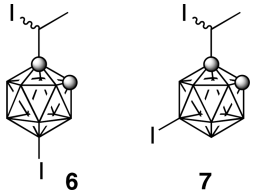
Scheme 1. Iodination of *o*-Carboranes[a]



[a]Reagents and conditions: (i) ICl, CH_2Cl_2, rt for **4a**; I_2, $AlCl_3$ catalyst, CH_2Cl_2, rt, protected from light for **4b**; ICl, $MeSO_3H$, 60 °C for **4c**.

chromatography (SiO_2) or gradient sublimation were unsuccessful.

Iodination of 1-vinyl-*o*-carborane (**4b**)[25,26] was accomplished using the conditions (I_2, catalyst $AlCl_3$, CH_2Cl_2, protected from light) reported for iodination of the parent *o*-carborane (**B**)[27] and resulted in a mixture of isomers **1b** and **5b** in a 3:4 ratio obtained in 80% yield. The two isomers could not be separated by chromatography (SiO_2 untreated or treated[28] with $AgNO_3$). However, the desired isomer **1b** was isolated in 22% yield by recrystallization of the mixture from hexane. Interestingly, when iodination of **4b** was conducted in the presence of ambient light, two byproducts were formed in significant quantities for which structures **6** and **7** were assigned on the basis of ^{1}H NMR spectra.



1-Phenyl-*o*-carborane (**4c**)[25,29,30] was iodinated with ICl in $MeSO_3H$ at 60 °C, giving a mixture of isomers **1c** and **5c** in a 4:5 ratio isolated in 80% yield. Thin-layer chromatography (TLC) analysis demonstrated reasonable separation of the isomers (R_f = 0.39 for **5c** and R_f = 0.32 for **1c** in 4:1 hexane/CH_2Cl_2), and 9-iodo **5c** was isolated in 48% yield while the 12-iodo isomer **1c** was obtained in 32% yield as the more polar fraction by column chromatography.

Thus, isomerically pure compounds **1b** and **1c** were prepared by iodination of the corresponding 1-substituted *o*-carborane and isolated in 22% and 32% yield, respectively.

Functional Group Transformation in 12-Iodo-1-phenyl-o-carborane (1c). The iodine atom in **1c** was used for the Negishi C−C coupling reaction[31−33] to install a pentyl group at the B(12) position, and 12-pentyl-1-phenyl-*o*-carborane (**8**) was obtained in 58% yield (Scheme 2). Subsequent nitration of **8** with HNO_3/H_2SO_4, according to an analogous method for **4c**,[34] resulted in a mixture of isomers 1-(4-nitrophenyl)-12-pentyl-*o*-carborane (**9**) and 1-(3-nitrophenyl)-12-pentyl-*o*-carborane (**10**) in a ratio of 3:1. Chromatographic separation gave the desired **9** isolated in 61% yield as the less polar fraction.

Catalytic reduction of the nitro group in the 4-nitrophenyl derivative **9** gave aniline **11** in 86% yield. Subsequent diazotization of **11** using *t*-BuONO in the presence of $CuBr_2$[35] yielded the 4-bromophenyl derivative **12**, which was contaminated with ∼20% of the 3,4-dibromophenyl derivative **13**. Separation of the pure bromo **12** from the mixture was problematic. To obtain a pure halogen derivative, the amino

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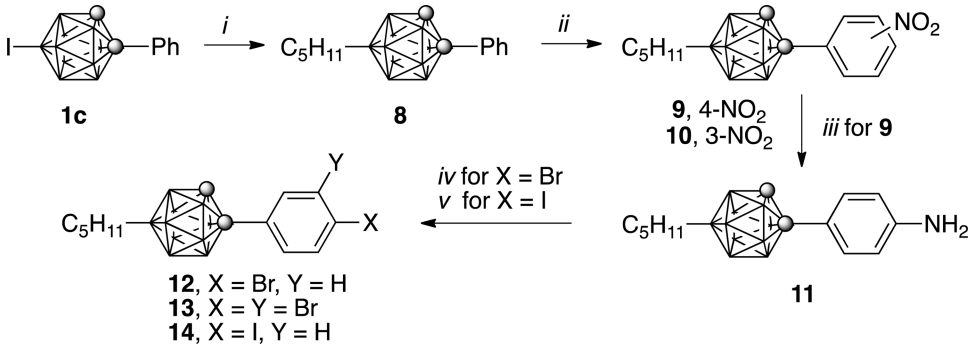
Scheme 2. Synthesis of 1,12-disubstituted *o*-carboranes[a]

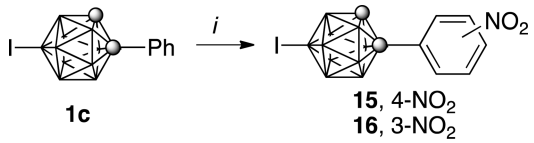


[a]Reagents and conditions: (i) $C_5H_{11}MgBr$, $ZnCl_2$, $Pd(OAc)_2$, $[HPCy_3]^+[BF_4]^-$, THF, reflux, 24 h; (ii) HNO_3/H_2SO_4 (15:85), CH_2Cl_2, 0 °C; (iii) H_2, Pd/C, THF, rt; (iv) *t*-BuONO, $CuBr_2$, MeCN, 0 °C; (v) (1) $[NO]^+[PF_6]^-$ and (2) $[Bu_4N]^+[I]^-$, MeCN, 0 °C.

compound **11** was converted to 1-(4-iodophenyl)-12-pentyl-*o*-carborane (**14**) in 70% yield by diazotization using $[NO]^+[PF_6]^-$ followed by treatment with $[Bu_4N]^+I^-$, according to a general method (Scheme 2).[36]

The 12-iodo-1-phenyl derivative **1c** was nitrated, giving a 1:2 mixture of isomers **15** and **16**, from which the 4-nitro derivative **15** was isolated in 21% yield by chromatography (Scheme 3).

Scheme 3. Nitration of 1c[a]



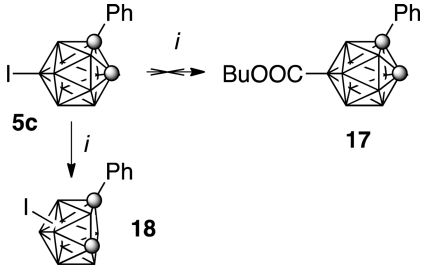
[a]Reagents and conditions: (i) HNO_3/H_2SO_4 (15:85), CH_2Cl_2, 0 °C.

The 3-nitro isomer **16** was obtained in 41% yield as the more polar compound. An alternative method for the preparation of **15** was briefly investigated. Thus, the reaction of 9-iodo-*o*-carborane with (4-nitrophenyl)diazonium salt using general literature conditions[29] gave a complex mixture of products, which contained about 10% of the expected product **15**.

Attempted butoxycarbonylation reaction[37] of **5c** using (*i*-Pr)$_2$NEt (Hunig's base), a non-nucleophilic amine, in *n*-BuOH and the formation of ester **17** resulted in deboronation of **5c** and formation of the nido derivative **18** (Scheme 4). No carbonylation was observed.

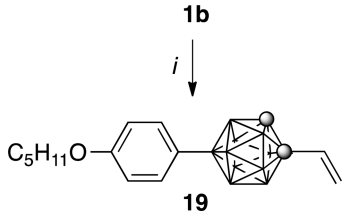
*Functional Group Transformations in **1b***. The iodine atom in **1b** was used to install an aryl group at the B(12) position. Thus, 12-iodo-1-vinyl-*o*-carborane (**1b**) was reacted with 4-(pentyloxy)phenylzinc chloride to give 1-vinyl-12-[4-(pentyloxy)phenyl]-*o*-carborane (**19**) in 65% yield (Scheme 5).

Scheme 4. Attempted Synthesis of Ester 17[a]



[a]Reagents and conditions: (i) CO, $PdCl_2$, Bnap, (*i*-Pr)$_2$NEt, *n*-BuOH, 100 °C, 16 h.

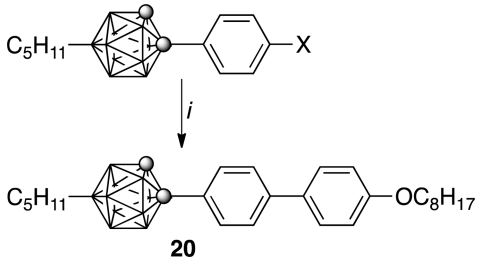
Scheme 5. Negishi Arylation of 1b[a]



[a]Reagents and conditions: (i) (1) 4-$C_5H_{11}OC_6H_4Br$, Mg, (2) $ZnCl_2$, and (3) $Pd(OAc)_2$, $[HPCy_3]^+[BF_4]^-$, THF, reflux, 6 h.

Liquid-Crystalline Compounds. The application of functionalized linear derivatives of *o*-carborane, **1a** and **1b**, was demonstrated by the preparation of two liquid-crystalline compounds. Thus, the impure bromide **12** or iodide **14** was used in Negishi coupling reactions with a 4-(octyloxy)-phenylzinc reagent, resulting in biphenyl **20** isolated in 64% yield (Scheme 6). A similar reaction under Suzuki–Miyaura[38] conditions[39] (aqueous K_2CO_3, toluene, 100 °C) resulted in deboronation of the carborane cage and formation of a highly polar compound, presumably the corresponding nido derivative.

Scheme 6. Synthesis of Biphenyl 20[a]



[a]Reagents and conditions: (i) (1) 4-$C_8H_{17}OC_6H_4Br$, Mg, (2) $ZnCl_2$, and (3) $Pd(dba)_2$, $[HPCy_3]^+[BF_4]^-$, THF, reflux, 15 h.

The vinyl derivative **19** was employed in a Heck C–C coupling reaction,[40] leading to the styrene derivative **21** isolated in 50% yield (Scheme 7). The reaction was conducted in the presence of (*i*-Pr)$_2$NEt (Hunig's base) under anhydrous

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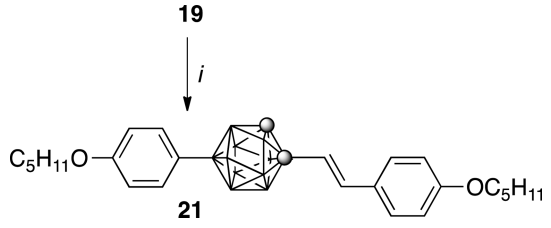
conditions to avoid deboronation and formation of a nido derivative.

Scheme 7. Synthesis of Styrene 21[a]



[a]Reagents and conditions: (i) 4-$C_5H_{11}OC_6H_4I$, $Pd(OAc)_2$, $(o\text{-}MeOPh)_3P$, NMP, $(i\text{-}Pr)_2NEt$, 100 °C, 3 h.

Analysis of these two derivatives, **20** and **21**, by differential scanning calorimetry (DSC) and polarized optical microscopy revealed their mesogenic behavior. The biphenyl derivative **20** exhibits SmA and nematic phases (Figure 4a) identified by their characteristic schlieren and fan textures, as shown in Figure 5. The styrene derivative **21** displays only a nematic phase with the clearing temperature of 101 °C. Interestingly, the crystalline polymorph obtained from solution melts at 121 °C, and the nematic phase is monotropic (Figure 4b). However, the crystalline polymorph formed from the nematic phase has a significantly lower melting temperature, 63 °C, and the nematic phase is enantitropic.

Attempts at 2,9-Difunctionalized m-Carborane. Compound 9-iodo-2-phenyl-*m*-carborane (**22**; Figure 6) was envisioned as a key intermediate to linear molecular materials derived from *m*-carborane (**C**), in analogy to the *o*-carborane derivative **1c**, and two possible routes were briefly explored.

The first route to **22** involved iodination of 2-phenyl-*m*-carborane (**23**),[41] which was prepared by deboronation of *m*-carborane (**C**)[42] and subsequent boronation with $PhBCl_2$.[41] Initially, *m*-carborane (**C**) was deboronated according to a literature procedure[42] using KOH in EtOH at 150 °C, giving the nido salt **24**[Me_3NH] in 56% yield (Scheme 8). The method was modified by using a higher boiling solvent, 2-$EtOC_2H_4OH$ instead of EtOH, which allowed for the reaction to be carried out under normal pressure. The cation in the resulting salt **24**[Me_3NH] was exchanged for Cs^+, more suitable for further transformation, and **24**[**Cs**] was isolated in 76% yield. Lithiation of **24**[**Cs**] with *n*-BuLi and reboronation with $PhBCl_2$, according to a literature procedure,[41] gave **23** in 57% yield.

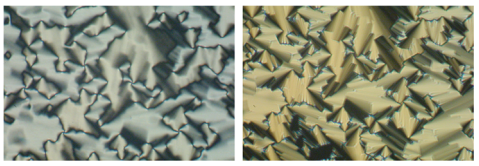


Figure 5. Optical textures of **20** obtained upon cooling from the isotropic phase: (a) nematic phase at 138 °C; (b) SmA phase at 100 °C.

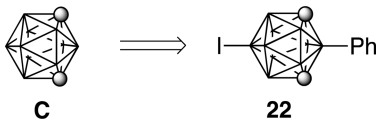
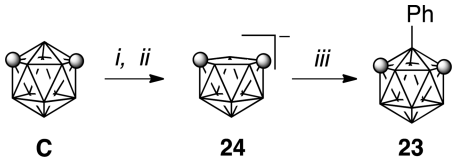


Figure 6. Target compund **22**.

Scheme 8. Synthesis of 23[a]



[a]Reagents and conditions: (i) KOH, 2-$EtOC_2H_4OH$, $[Me_3NH]^+Br^-$, reflux 3 h; (ii) CsOH, MeCN; (iii) *n*-BuLi, $PhBCl_2$, THF, −78 °C.

Attempts at iodination of **23** were unsuccessful, and no desired **22** was isolated or observed. Mild conditions such as I_2 in AcOH at 60 °C and ICl in CH_2Cl_2 or acetic acid at room temperature (rt) or in refluxing CH_2Cl_2 or $MeSO_3H$ at 60 °C gave no reaction. Raising the temperature of the reaction in $MeSO_3H$ to 100 °C resulted in the formation of a complex mixture of starting **23** and several products, presumably resulting from iodination of the phenyl ring, as suggested by ^1H NMR spectra. Manipulation with the temperature did not result in selective iodination, and it appears that the benzene ring is substituted preferentially under these conditions. A complex mixture was also obtained when CF_3SO_3H was used as the solvent.

The second attempt at the synthesis of **22** was envisioned with a reversed sequence of reactions: iodination of *m*-carborane (**C**) followed by deboronation and finally reboronation with $PhBCl_2$. Thus, **C** was iodinated to form **25** in 80% yield using a mixture of iodine and periodic acid in acetic acid in the presence of sulfuric acid.[43] The resulting 9-iodo-*m*-

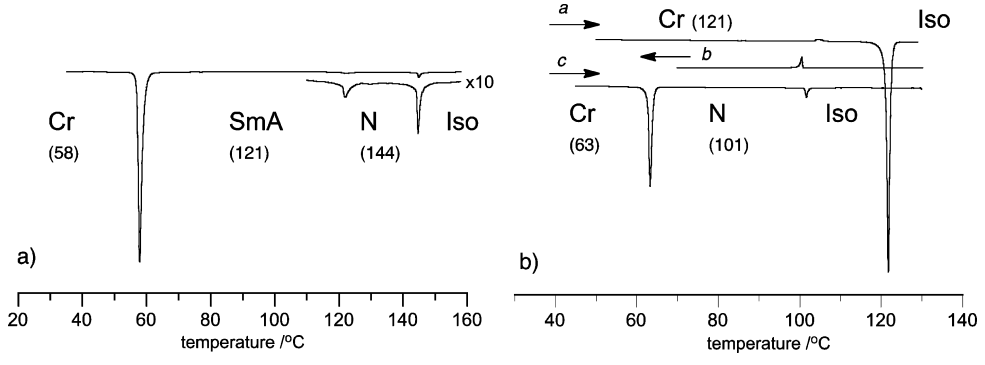


Figure 4. DSC trace for (a) biphenyl **20** and (b) styrene **21**. The high-temperature portion of trace a is enlarged 10 times. The numbers in parentheses indicate transition temperatures. Graph b is a superimposition of three traces: first heating (a), cooling (b), and second heating (c).

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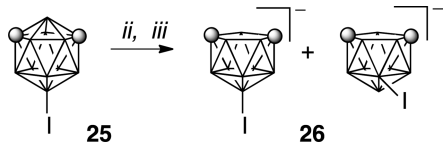
carborane (**25**)[44] was deboronated using the 2-EtOC$_2$H$_4$OH method to give Cs$^+$ salt **26**[**Cs**] as a mixture of isomers B(6)-I and B(1)-I in a ratio of ~2:1 and 57% yield (Scheme 9), which

Scheme 9. Preparation of the Nido Anion 26[a]



[a]Reagents and conditions: (i) I_2, HIO_3, AcOH, CCl_4, H_2SO_4; (ii) KOH, 2-EtOC$_2$H$_4$OH, [Me$_3$NH]$^+$Br$^-$, reflux 3 h; (iii) CsOH, MeCN.

is similar to previously reported results.[45] Unfortunately, attempts at reboronation of **26**[**Cs**] using $PhBCl_2$ under the same conditions as those for **24**[**Cs**] with or without tetramethylethylenediamine did not give the desired **22**, and only unreacted **26** was observed by NMR. In some experiments, however, analysis of the nonpolar fraction revealed possible traces of the expected product **22**, while the polar fraction (MeOH eluent) contained the B(6)-I isomer of **26**.

DISCUSSION

The preparation of isomerically pure derivatives of *o*-carborane **1b** and **1c** relies on simple separation methods: crystallization and chromatographic separation. The former method often appears moderately effective, as demonstrated for **1b** and 1,12-diaryl-*o*-carborane **3**,[23] while the latter permits the quantitative separation of isomers. Among the three isomeric mixtures investigated here, only that obtained from **4c** showed the separation of products on TLC, permitting separation by classical chromatographic methods (R_f values in a 4:1 hexane/CH_2Cl_2 system: **1a** and **5a**, R_f = 0.37; **1b** and **5b**, R_f = 0.43; **1c**, R_f = 0.32; **5c**, R_f = 0.39). Overall, two important building blocks for linear molecules, compounds **1b** and **1c**, containing functionalizable phenyl, vinyl, and iodine groups, are available in three steps from $B_{10}H_{14}$ and estimated yields of about 16% and 26%, respectively, taking advantage of the recently discovered high-yield procedure[30] for alkyne insertion to $B_{10}H_{12}\cdot(MeCN)_2$.

Functional group transformations in *o*-carborane derivatives revealed that nitration of the benzene ring in derivatives of 1-phenyl-*o*-carborane is sensitive to the nature of the antipodal substituent[46] at the B(12) position, as is evident from variation of the ratio *K* of the two isomers 4-nitro and 3-nitro (Figure 7). Analysis of the results for **1c**, **8**, and the parent **4c**[47] shows that the observed trend in ln *K* follows that of the Hammett

R	*K*	$\sigma_{p(R)}$	$I_{(R)}$
C_5H_{11}	3	-0.16	-0.01
H	3	0	0
I	0.5	0.18	0.42

Figure 7. Ratio *K* of two regioisomers obtained by nitration of 1-phenyl-*o*-carborane derivatives and selected substituent parameters.

substituent parameter.[48] Quantitative analysis of the data suggests a better fit of ln *K* values with the inductive parameter $I_{(R)}$ rather than with $\sigma_{p(R)}$, which is in agreement with our recent results in the transmission of electronic effects through the [*closo*-1-CB$_{11}$H$_{12}$]$^-$ cluster.[49] Although a trend is observed, more data points are necessary for a meaningful analysis and a better understanding of the effect of the antipodal substituent in *o*-carborane on the benzene ring reactivity. Such compounds are now, in principle, available from the iodo derivative **1c**.

A much weaker substituent effect was observed in iodination of 1-substituted *o*-carborane derivatives. For all three derivatives **4a**–**4c**, the ratio of the 12-iodo and 9-iodo isomers (**1** and **5**, respectively) was diminishing in the order **4a** (1.12), **4c** (0.78), and **4b** (0.76), which follows a trend in the substituent's inductive parameter $I_{(R)}$ value:[48] −0.01 (methyl), 0.12 (phenyl), and 0.13 (vinyl).[50] These results suggest that electron-withdrawing substituents on the benzene ring would disfavor antipodal substitution and should be avoided to maximize the yield of the desired 1,12-disubstituted derivatives and make the process practical. For instance, substituents at the C(1) positions such as 4-I-C$_6$H$_4$ ($I_{(R)}$ = 0.18)[48] or 4-NO$_2$-C$_6$H$_4$ ($I_{(R)}$ = 0.26)[48] are expected to give more than 60% of the 1,9 isomer. On the other hand, electron-donating substituents on the benzene ring will favor the antipodal substitution but also activate the aromatic ring toward electrophilic substitution.

While iodination of **4c** is selective for the cluster, iodination of **23** suffers from a more balanced nucleophilicity of the benzene ring and carborane cage compared to the *o*-carborane analogue **4c**. The *m*-carboran-2-yl group is less electron-withdrawing (σ_p = 0.15) than the *o*-carboran-1-yl group (σ_p = 0.43),[48] and the benzene ring is not as deactivated toward electrophilic substitution. At the same time, the *m*-carborane cage has diminished reactivity in **23**. Conceivably, 2-iodo-*m*-carborane could be successfully monoiodinated, although on the basis of the results for iodination of *o*-carborane derivatives (vide supra), poor selectivity for the desired 2,9-diiodo derivative can be expected ($I_{(R)}$ = 0.42 for iodine).[48]

CONCLUSIONS

We have demonstrated that two 1,12-difunctionalized derivatives of *o*-carborane, **1b** and **1c**, can conveniently be obtained on a practical scale in the pure form. Through standard chemical transformations, this opens up access to a number of derivatives in which *o*-carborane plays the role of a linear structural element with a moderate dipole moment. Application of these building blocks, **1b** and **1c**, has been demonstrated with two examples of liquid-crystalline materials **20** and **21**. Results suggest that regioselectivity of substitution on the carborane cage and benzene ring correlates with the inductive effect parameter $I_{(R)}$ of the substituent.

Attempts at the preparation of *m*-carborane with two substituents in the antipodal positions (the 2,9 pattern) have been unsuccessful thus far, largely because of the more balanced nucleophilicity of the molecular fragments and hence poor regioslectivity.

EXPERIMENTAL SECTION

Reactions were carried out under argon, and subsequent manipulations were conducted in air. NMR spectra were obtained at 128.4 MHz (^{11}B) and 400.1 MHz (^{1}H) in $CDCl_3$ unless otherwise specified. ^{1}H NMR spectra were referenced to the solvent and ^{11}B NMR chemical shifts to an external boric acid sample in CH_3OH that was set to 18.1 ppm.

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12-Iodo-1-methyl-*o*-carborane (1a) and 9-Iodo-1-methyl-*o*-carborane (5a).[19] A mixture of **4a** (50 mg, 0.3 mmol)[21,24] and ICl (73 mg, 0.45 mmol) in CH_2Cl_2 (2 mL) was stirred at rt for 3 days. The solvent was evaporated, and the resulting solid residue was passed through a silica gel plug (4:1 hexane/CH_2Cl_2; R_f = 0.37), giving 52 mg (60% yield) of a mixture of isomers **1a** and **5a** in a ratio of 10:11 established by ^{1}H NMR (400 MHz, $CDCl_3$, characteristic signals): major isomer, δ 2.06 (s, CH_3), 3.85 (br s, 1H); minor isomer, δ 1.92 (s, CH_3), 3.67 (br s, 1H).

12-Iodo-1-vinyl-*o*-carborane (1b) and 9-Iodo-1-vinyl-*o*-carborane (5b).[20] A mixture of **4b** (288 mg, 1.16 mmol),[25,26] iodine (310 mg, 1.20 mmol), and catalytic amounts of $AlCl_3$ (16 mg, 0.12 mmol) in dry CH_2Cl_2 (5 mL) was stirred at rt, overnight, under an argon atmosphere, and protected from light (aluminum foil). The solvent was evaporated, and the residue was passed through a silica gel plug (4:1 hexane/CH_2Cl_2; R_f = 0.43), giving 280 mg (80% yield) of a mixture of **1b** and **5b** in a 3:4 ratio. Crystallization (hexane, 3 mL, rt) gave 60 mg of **1b**, while subsequent crystallization of the mother liquor (hexane, 1 mL, 0 °C) gave an additional 15 mg (22% combined yield) of pure **1b** as colorless crystals. Mp: 148−149 °C (lit.[20] mp 148−148.5 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.5−3.3 (m, 9H), 3.73 (br s, 1H), 5.43 (d, J = 10.5 Hz, 1H), 5.60 (d, J = 16.7 Hz, 1H), 5.87 (dd, J_1 = 16.9 Hz, J_2 = 10.4 Hz, 1H). ^{11}B NMR (128 MHz, $CDCl_3$): δ −17.3 (s, 1B), −11.6 (d, J = 146 Hz, 4B), −10.6 (d, J = 152 Hz, 2B), −7.0 (d, J = 155 Hz, 2B), −0.1 (d, J = 151 Hz, 1B).

The mother liquor contained both isomers **5b** and **1b** in a 4:1 ratio. ^{1}H NMR (400 MHz, $CDCl_3$, major characteristic signals): δ 3.93 (br s, 1H), 5.44 (d, J = 10.5 Hz, 1H), 5.65 (d, J = 16.3 Hz, 1H), 5.97 (dd, J_1 = 16.8 Hz, J_2 = 10.5 Hz, 1H). {^{1}H}^{11}B NMR (128 MHz, $CDCl_3$, major characteristic signals): δ −15.9 (1B), −12.0 (2B), −11.7 (4B), −7.0 (2B), −3.2 (1B).

Iodination run in the presence of ambient light resulted in a mixture containing ∼25% of two byproducts identified as **6** and **7**. ^{1}H NMR (400 MHz, $CDCl_3$, major characteristic signals): δ 1.70 (d, J = 6.8 Hz, 3H), 4.22 (br s, 1H), 4.48 (q, J = 6.7 Hz, 1H). ^{1}H NMR (400 MHz, $CDCl_3$, minor characteristic signals): δ 1.76 (d, J = 6.7 Hz, 3H), 4.42 (br s, 1H), 4.56 (q, J = 6.8 Hz, 1H).

12-Iodo-1-phenyl-*o*-carborane (1c) and 9-Iodo-1-phenyl-*o*-carborane (5c).[19] A mixture of **4c** (1.50 g, 6.8 mmol) and ICl (1.10 g, 6.8 mmol) in $MeSO_3H$ (8 mL) was stirred at 60 °C overnight. The resulting mixture was cooled and poured into ice water. The products were extracted (CH_2Cl_2), the extracts were dried (Na_2SO_4), and the solvents were evaporated. The solid residue (2.11 g) was separated on a silica gel column (10:1 hexane/CH_2Cl_2) to give (1.11 g, 48% of yield) of **5c** as the first fraction (4:1 hexane/CH_2Cl_2; R_f = 0.39). Recrystallization from hexane gave pure **5c** as white crystals. Mp: 102−103 °C (lit.[19] mp 93−94 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.5−3.3 (m, 9H), 4.25 (br s, 1H), 7.33−7.38 (m, 2H), 7.40−7.45 (m, 1H), 7.46−7.50 (m, 2H). ^{11}B NMR (128 MHz, $CDCl_3$): δ −15.9 (s, 1B), −12.4 (d, J = 162 Hz, 2B), −11.1 (d, J = 172 Hz, 2B), −9.7 (d, J = 169 Hz, 2B), −7.1 (d, J = 158 Hz, 2B), −2.8 (d, J = 150 Hz, 1B). Anal. Calcd for $C_8H_{15}B_{10}I$: C, 27.75; H, 4.37. Found: C, 27.94; H, 4.18.

Isomer **1c** was isolated as the second fraction (750 mg, 32% yield; 4:1 hexane/CH_2Cl_2; R_f = 0.32) and purified by recrystallization from hexane, giving **1c** as white crystals. Mp: 149−150 °C (lit.[19] 145−146 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.5−3.3 (m, 9H), 4.05 (br s, 1H), 7.31−7.37 (m, 2H), 7.39−7.46 (m, 3H). ^{11}B NMR (128 MHz, $CDCl_3$): δ −16.7 (s, 1B), −11.5 (d, 2B), −10.8 (d, 2B), −10.2 (d, 2B), −6.9 (d, J = 157 Hz, 2B), −0.2 (d, J = 159 Hz, 1B). Anal. Calcd for $C_8H_{15}B_{10}I$: C, 27.75; H, 4.37. Found: C, 27.92; H, 4.29.

1-Phenyl-*o*-carborane (4c).[29,30] **4c** was prepared in 67% yield by arylation of *o*-carborane (**B**) according to a literature procedure.[29] ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.5−3.6 (m, 10H), 4.05 (br s, 1H), 7.31−7.36 (m, 2H), 7.39−7.46 (m, 3H). ^{11}B NMR (128 MHz, $CDCl_3$): δ −12.5 (d, J = 172 Hz, 2B), −11.0 (d, 2B), −10.5 (d, J = 168 Hz, 2B), −8.7 (d, J = 156 Hz, 2B), −4.1 (d, J = 152 Hz, 1B), −1.8 (d, J = 147 Hz, 1B).

12-Pentyl-1-phenyl-*o*-carborane (8). A solution of $C_5H_{11}MgBr$ (22 mmol) was added to a solution of dry $ZnCl_2$ (3.60 g, 26.4 mmol) in dry tetrahydrofuran (THF; 30 mL) under an argon atmosphere at rt; the resulting mixture was stirred at rt for 15 min, and then $Pd(OAc)_2$ (200 mg, 0.3 mmol) and tricyclohexylphosphonium tetrafluoroborate (220 mg, 0.6 mmol) were added, followed by **1c** (1.98 g, 5.72 mmol). The mixture was refluxed for 24 h, 5% HCl was added, the products were extracted into Et_2O, the extracts were dried (Na_2SO_4), and the solvents were evaporated. The oily residue was passed through a silica gel plug (hexane), giving 0.95 g (58% yield) of **8** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.70−0.78 (m, 2H), 0.87 (t, J = 6.8 Hz, 3H), 1.20−1.32 (m, 6H), 1.5−3.5 (m, 9H), 3.91 (br s, 1H), 7.29−7.35 (m, 2H), 7.36−7.40 (m, 1H), 7.48−7.52 (m, 2H). ^{11}B NMR (128 MHz, $CDCl_3$): δ −12.4 (d, J = 156 Hz, 2B), −11.2 (d, J = 154 Hz, 4B), −8.2 (d, J = 150 Hz, 2B), −1.3 (d, J = 149 Hz, 1B), 7.7 (s, 1B). HRMS. Calcd for $C_{13}H_{26}B_{10}$: m/z 292.2973. Found: m/z 292.2995.

1-(4-Nitrophenyl)-12-pentyl-*o*-carborane (9) and 1-(3-Nitrophenyl)-12-pentyl-*o*-carborane (10). A mixture of fuming HNO_3 and concentrated H_2SO_4 (10 mL, 15:85) was added to a solution of **8** (600 mg, 2.1 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 4 h, kept at −15 °C overnight, and poured into water. The products were extracted (CH_2Cl_2), the extracts were dried (Na_2SO_4), and the solvent was evaporated. The solid residue was separated on a silica gel column (12:1 hexane/AcOEt), giving 423 mg (61% yield) of **9**, which was further recrystallized from hexane, giving white crystals. Mp: 91−92 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.72−0.79 (m, 2H), 0.87 (t, J = 6.8 Hz, 3H), 1.21−1.32 (m, 6H), 1.50−3.3 (m, 9H), 3.97 (br s, 1H), 7.68 (d, J = 9.1 Hz, 2H), 8.19 (d, J = 9.1 Hz, 2H). ^{11}B NMR (128 MHz, $CDCl_3$): δ −11.3 (m, 6B), −7.7 (d, J = 148 Hz, 2B), −1.0 (d, J = 151 Hz, 1B), 8.8 (s, 1B). Anal. Calcd for $C_{13}H_{25}B_{10}NO_2$: C, 46.55; H, 7.51; N, 4.25. Found: C, 46.79; H, 7.74; N, 4.25.

Further elution of the column (12:1 hexane/AcOEt) gave 148 mg (21% yield) of the meta isomer **10**, which was recrystallized from hexane, giving white crystals. Mp: 95−96 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.72−0.79 (m, 2H), 0.87 (t, J = 6.8 Hz, 3H), 1.21−1.33 (m, 6H), 1.50−3.3 (m, 9H), 3.97 (br s, 1H), 7.56 (t, J = 8.1 Hz, 1H), 7.87 (dd, J_1 = 8.0 Hz, J_2 = 1.1 Hz, 1H), 8.27 (dd, J_1 = 9.0 Hz, J_2 = 2.0 Hz, 1H), 8.35 (t, J = 2.0 Hz, 1H). ^{11}B NMR (128 MHz, $CDCl_3$): δ −11.3 (m, 6B), −7.8 (d, J = 154 Hz, 2B), −0.9 (d, J = 152 Hz, 1B), 8.5 (s, 1B). Anal. Calcd for $C_{13}H_{25}B_{10}NO_2$: C, 46.55; H, 7.51; N, 4.25. Found: C, 46.79; H, 7.51; N, 4.13.

1-(4-Aminophenyl)-12-pentyl-*o*-carborane (11). A mixture of **9** (318 mg, 0.95 mmol) and 10% Pd/C (25 mg) in THF (5 mL) was stirred overnight under positive pressure of H_2. The solvent was evaporated, and the residue was passed through a silica gel plug (CH_2Cl_2), giving 250 mg (86% yield) of amine **11**. An analytically pure sample was obtained by recrystallization from hexane, giving white crystals. Mp: 91−92 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.65−0.78 (m, 2H), 0.85 (t, J = 6.8 Hz, 3H), 1.20−1.35 (m, 6H), 1.5−3.3 (m, 9H), 3.77 (br s, 1H), 4.4 (br s, 2H), 6.60 (d, J = 8.7 Hz, 2H), 7.30 (d, J = 8.7 Hz, 2H). ^{11}B NMR (128 MHz, $CDCl_3$): δ −11.7 (m, 6B), −8.5 (d, J = 147 Hz, 2B), −1.2 (d, J = 152 Hz, 1B), 7.1 (s, 1B). Anal. Calcd for $C_{13}H_{27}B_{10}N$: C, 51.11; H, 8.91; N, 4.59. Found: C, 51.30; H, 8.93; N, 4.66.

1-(4-Bromophenyl)-12-pentyl-*o*-carborane (12). According to a general literature procedure,[35] a solution of **11** (100 mg, 0.33 mmol) in MeCN (0.5 mL) was slowly added to a solution of *t*-BuONO (0.50 mmol) in dry MeCN (1.5 mL) containing $CuBr_2$ (90 mg, 0.40 mmol) at 0 °C. The resulting mixture was stirred for 10 min, then warmed to rt, and stirred for 1 h. 10% HCl was added, the products were extracted (CH_2Cl_2), the organic layer was dried (Na_2SO_4), and the solvents were evaporated. The residue was passed through a silica gel plug (hexane), giving 102 mg (84% yield) of bromide **12** as a white solid, contaminated with dibromo derivative **13** (∼20% based on ^{1}H NMR). The mixture was inseparable either by chromatography or by distillation, and crude **12** was used for further transformations. ^{1}H NMR (400 MHz, $CDCl_3$, major signals): δ 0.68−0.77 (m, 2H), 0.87 (t, J = 6.8 Hz, 3H), 1.20−1.32 (m, 8H), 1.5−3.3 (m, 9H), 3.86 (br s, 2H), 7.36 (d, J = 8.8 Hz, 2H), 7.45 (d, J = 8.8 Hz, 2H). ^{1}H NMR (400 MHz, $CDCl_3$, minor signals): δ 7.29 (dd, J_1 = 8.6 Hz, J_2 = 2.4 Hz, 1H), 7.56 (d, J = 8.6 Hz, 1H), 7.73 (d, J = 2.3 Hz, 1H). {^{1}H}^{11}B NMR (128

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MHz, $CDCl_3$): δ −11.3 (m, 6B), −8.1 (2B), −1.1 (1B), 8.1 (1B). HRMS. Calcd for $C_{13}H_{24}B_{10}Br$: *m*/*z* 369.2048. Found: *m*/*z* 369.2025.

1-(4-Iodophenyl)-12-pentyl-*o*-carborane (14). According to a modified general literature procedure,[36] a solution of **11** (130 mg, 0.43 mmol) in MeCN (1 mL) was added dropwise to a solution of $[NO]^+[PF_6]^-$ (82 mg, 0.47 mmol) in dry MeCN (3 mL) at −15 °C. The mixture was stirred for 1 h at −15 °C, then $[Bu_4N]^+I^-$ (173 mg, 0.47 mmol) was added in one portion, and stirring was continued for 1 h at 0 °C. The mixture was warmed to rt and stirred for 15 min, and the solvent was evaporated. The resulting residue was passed through a silica gel plug (hexane), and the crude product was purified further on a silica gel column (hexane), giving 130 mg (70% yield) of iodide **14**. An analytically pure sample was obtained by recrystallization from hexane as white crystals. Mp: 54−55 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.68−0.77 (m, 2H), 0.87 (t, *J* = 6.9 Hz, 3H), 1.22−1.32 (m, 6H), 1.5−3.3 (m, 9H), 3.86 (br s, 1H), 7.22 (d, *J* = 8.8 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 2H). ^{11}B NMR (128 MHz, $CDCl_3$): δ −11.9 (m, 6B), −8.1 (d, *J* = 151 Hz, 2B), −1.2 (d, *J* = 150 Hz, 1B), 8.1 (s, 1B). Anal. Calcd for $C_{13}H_{25}B_{10}I$: C, 37.50; H, 6.05. Found: C, 38.07; H, 6.07.

12-Iodo-1-(4-nitrophenyl)-*o*-carborane (15) and 12-Iodo-1-(3-nitrophenyl)-*o*-carborane (16). To a solution of **1c** (100 mg, 0.3 mmol) in CH_2Cl_2 (2 mL) was added at 0 °C a mixture of HNO_3 (fuming) and concentrated H_2SO_4 (1.5 mL, 15:85). The reaction mixture was stirred at 0 °C and poured into water. The products were extracted (CH_2Cl_2), the extracts were dried (Na_2SO_4), and the solvent was evaporated. The 100 mg of residue, containing isomers **15** and **16** in a 1:2 ratio, was separated by column chromatography (SiO_2; 8:1 hexane/AcOEt).

15 (4-nitro isomer): 25 mg (21% yield). R_f = 0.27. Mp: 199−201 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.5−3.3 (m, 9H), 4.12 (br s, 1H), 8.21 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 2H). ^{11}B NMR (128 MHz, $CDCl_3$): δ −16.1 (s, 1B), −11.2 (d, *J* = 115 Hz, 4B), −10.2 (d, *J* = 154 Hz, 2B), −6.4 (d, *J* = 158 Hz, 2B), 0.1 (d, *J* = 155 Hz, 1B). HRMS. Calcd for $C_8H_{14}B_9INO_2$ (M-BH): *m*/*z* 382.0914. Found: *m*/*z* 382.0917.

16 (3-nitro isomer): 48 mg (41% yield). R_f = 0.23. Mp: 174−176 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.5−3.3 (m, 9H), 4.13 (br s, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.81 (d, *J* = 7.5 Hz, 1H), 8.26−8.34 (m, 2H). ^{11}B NMR (128 MHz, $CDCl_3$): δ −16.3 (s, 1B), −11.2 (d, *J* = 135 Hz, 4B), −10.2 (d, *J* = 145 Hz, 2B), −6.4 (d, *J* = 158 Hz, 2B), 0.3 (d, *J* = 155 Hz, 1B). HRMS. Calcd for $C_8H_{14}B_9INO_2$ (M-BH): *m*/*z* 382.0914. Found: *m*/*z* 382.0916.

Attempted Preparation of 17 by Butoxycarbonylation of 5c. A solution of **5c** (100 mg, 0.29 mmol), Hunig's base (0.45 mmol), $PdCl_2$ (1.0 mg, 2 mol %), and Bnap (7 mg) in *n*-butanol (1 mL) was saturated with CO, and the mixture was kept at 100 °C under positive pressure for 16 h. The mixture was cooled, the solvent was evaporated, and the residue was passed through a silica gel plug (CH_2Cl_2), giving 90 mg of the nido salt **18**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.5−3.3 (m, 10H), 1.50 (d, *J* = 6.6 Hz, 6H), 1.55 (d, *J* = 6.7 Hz, 6H), 1.57 (t, *J* = 7.3 Hz, 3H), 2.53 (br s, 1H), 3.23−3.32 (m, 1H), 3.80−3.90 (m, 1H), 7.05−7.10 (m, 2H), 7.16 (t, *J* = 7.5 Hz, 2H), 7.25−8.29 (m, 2H). $\{^1H\}^{11}$B NMR (128 MHz, CD_3CN): δ −33.6 (1B), −29.7 (1B), −24.8 (1B), −21.1 (1B), −18.4 (1B), −15.8 (1B), −13.2 (1B), −10.2 (1B), −7.8 (1B).

1-Vinyl-12-[4-(pentyloxy)phenyl]-*o*-carborane (19). A solution of 4-$C_5H_{11}OC_6H_4MgBr$ (3.35 mmol, freshly prepared from 4-$C_5H_{11}OC_6H_4Br$ and Mg in 5 mL of THF) was added under an argon atmosphere to a solution of dry $ZnCl_2$ (545 mg, 4.0 mmol) in dry THF (5 mL). The resulting mixture was stirred at rt for 15 min, and then $Pd(OAc)_2$ (23 mg, 0.034 mmol) and $[HPCy_3]^+[BF_4]^-$ (25 mg, 0.068 mmol) were added followed by **1b** (200 mg, 0.67 mmol). The reaction mixture was refluxed for 6 h, 5% HCl was added, the products were extracted (Et_2O), the extracts were dried (Na_2SO_4), and the solvents were evaporated. The residue was passed through a silica gel column (6:1 hexane/CH_2Cl_2), giving 150 mg (65% yield) of **19** as a white solid. An analytically pure sample was obtained by recrystallization from hexane. Mp: 65 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (t, *J* = 7.1 Hz, 3H), 1.30−1.42 (m, 4H), 1.5−3.3 (m, 9H), 1.76 (quint, *J* = 7.1 Hz, 2H), 3.70 (br s, 1H), 3.91 (t, *J* = 6.6 Hz, 2H), 5.40 (d, *J* = 10.5 Hz, 1H), 5.63 (d, *J* = 16.9 Hz, 1H), 6.05 (dd, J_1 = 16.9 Hz, J_2 = 10.5 Hz, 1H), 6.77 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H). ^{11}B NMR (128 MHz, $CDCl_3$): δ −12.1 (m, 6B), −8.2 (d, *J* = 153 Hz, 2B), −1.3 (d, *J* = 155 Hz, 1B), 6.1 (s, 1B). Anal. Calcd for $C_{15}H_{28}B_{10}O$: C, 54.18; H, 8.49. Found: C, 54.45; H, 8.48.

1-[4-(Octyloxy)-4-biphenylyl]-12-pentyl-*o*-carborane (20). A solution of 4-$C_8H_{17}OC_6H_4MgBr$ (2.0 mmol, freshly prepared from $C_8H_{17}OC_6H_4Br$ and Mg in 5 mL of THF) was added to a solution of $ZnCl_2$ (0.36 mmol) in THF (5 mL) under an argon atmosphere. The mixture was stirred at rt for 15 min, and $Pd_2(dba)_3$ (0.005 mmol) was added, followed by either impure bromide **12** or iodide **14** (0.1 mmol). The mixture was stirred at 50 °C overnight, 5% HCl was added, the products were extracted (Et_2O), the organic layers were dried (Na_2SO_4), the solvents were evaporated, and the crude product was purified using a silica gel column (10:1 hexane/CH_2Cl_2), giving 25 mg (64% yield) of biphenyl **20** as white crystals, which was recrystallized from hexane. Mp: 58 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.70−0.79 (m, 2H), 0.87 (t, *J* = 6.8 Hz, 3H), 0.89 (t, *J* = 6.7 Hz, 3H), 1.21−1.41 (m, 14H), 1.42−1.51 (m, 2H), 1.5−3.3 (m, 9H), 1.80 (quint, *J* = 7.0 Hz, 2H), 3.92 (br s, 1H), 3.99 (t, *J* = 6.6 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 8.9 Hz, 2H), 7.52 (d, *J* = 8.7 Hz, 2H). ^{11}B NMR (128 MHz, $CDCl_3$): δ −11.1 (m, 6B), −8.2 (d, *J* = 149 Hz, 2B), −1.2 (d, *J* = 145 Hz, 1B), 8.2 (s, 1B). Anal. Calcd for $C_{27}H_{46}B_{10}O_2$: C, 65.28; H, 9.74. Found: C, 65.47; H, 9.56.

1-[2-[4-(Pentyloxy)phenyl]ethenyl]-12-[4-(pentyloxy)-phenyl]-*o*-carborane (21). A mixture of **19** (94 mg, 0.28 mmol), 1-iodo-4-(pentyloxy)benzene (81 mg, 0.28 mmol), and Hunig's base (0.07 mL, 0.42 mmol) in dry NMP (3 mL) was stirred for 3 h at 100 °C and cooled, 5% HCl was added, the organic products were extracted (hexane), the organic layer was dried (Na_2SO_4), and the solvents were evaporated. The product was separated by chromatography (10:1 hexane/EtOAc), giving 70 mg (50% yield) of **21** as white crystals, which were recrystallized (hexane and then MeCN). Mp: 121 °C. ^{1}H NMR: δ 0.77−0.87 (m, 2H), 0.92 (t, *J* = 6.8 Hz, 3H), 0.93 (t, *J* = 6.8 Hz, 3H), 1.20−1.49 (m, 6H), 1.5−3.3 (m, 9H), 1.71−1.83 (m, 4H), 3.76 (br s, 1H), 3.92 (t, *J* = 6.6 Hz, 2H), 3.96 (t, *J* = 6.6 Hz, 2H), 6.19 (d, *J* = 15.7 Hz, 1H), 6.77 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 15.6 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 2H), 7.23−7.32 (m, 4H). ^{11}B NMR (128 MHz, $CDCl_3$): δ −11.2 (m, 6B), −8.3 (d, *J* = 150 Hz, 2B), −1.2 (d, *J* = 151 Hz, 1B), 6.0 (s, 1B). Anal. Calcd for $C_{26}H_{42}B_{10}O_2$: C, 63.12; H, 8.65. Found: C, 63.21; H, 8.54.

Cesium 1,7-Dicarbadodecahydroundecaborate (24[Cs]). A mixture of *m*-carborane (**C**; 2.0 g, 13.7 mmol) and KOH (1.54 g, 27.5 mmol) in freshly distilled 2-ethoxyethanol (15 mL) was refluxed for 3 h under an argon atmosphere. The solvent was evaporated and water was added, followed by $[Me_3NH]^+Br^-$ (14 mmol). The resulting precipitation of the nido salt **24**[**Me$_3$NH**] was filtered, washed with water, and dried. The crude salt (2.0 g, 76% yield) was dissolved in MeCN, CsOH (10.5 mmol) was added, and the solvent was evaporated to dryness, giving salt **24**[**Cs**]. $\{^1H\}^{11}$B NMR (128 MHz, CD_3CN): δ −35.3 (1B), −34.2 (1B), −22.6 (2B), −21.4 (2B), −5.7 (1B), −4.5 (2B).

2-Phenyl-*m*-carborane (23).[41] A solution of 1.6 M *n*-BuLi in hexane (0.48 mmol) was added to a solution of **24**[**Cs**] (100 mg, 0.37 mmol) in THF under an argon atmosphere at −40 °C. After 1 h, the mixture was warmed to rt, stirred for 1 h, and cooled to −40 °C, and neat $PhBCl_2$ (158 mg, 0.50 mmol) was added. Stirring was continued for 1 h, and the mixture was warmed to rt and stirred for 1 h. 5% HCl was added, the products were extracted (Et_2O), the extracts were dried (Na_2SO_4), and the solvents were evaporated. The crude product was purified on a silica gel plug (hexane), giving 50 mg (60% yield) of **23** as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.5−3.3 (m, 9H), 3.21 (s, 2H), 7.28−7.42 (m, 3H), 7.63 (d, *J* = 6.8 Hz, 2H). $\{^1H\}^{11}$B NMR (128 MHz, $CDCl_3$): δ −15.8 (1B), −12.8 (3B), −11.9 (2B), −10.5 (1B), −7.1 (1B), −5.6 (2B).

9-Iodo-*m*-carborane (25).[44] A mixture of *m*-carborane (**C**; 100 mg, 0.68 mmol), HIO_3 (66 mg, 0.38 mmol), I_2 (132 mg, 0.52 mmol), acetic acid (0.9 mL), CCl_4 (0.1 mL), and H_2SO_4 (0.05 mL) was stirred at 80 °C for 36 h. Water was added, the products were extracted into

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hexane, the organic layers were dried (Na_2SO_4), and the solvents were evaporated. The crude product was passed through a silica gel plug (hexane and then 6:1 hexane/CH_2Cl_2), giving 140 mg (76% yield) of **25** as a white crystalline solid. ^{11}B NMR (128 MHz, CD_3CN): δ −23.6 (s, 1B), −18.4 (d, J = 183 Hz, 1B), −16.3 (d, J = 184 Hz, 1B), −12.8 (d, J = 159 Hz, 2B), −11.6 (d, J = 158 Hz, 2B), −8.5 (d, J = 153 Hz, 1B), −5.4 (d, J = 166 Hz, 2B).

Cesium 6-Iodo-7,9-carborate and 1-Iodo-7,9-carborate (26[Cs]). **26**[Cs] was prepared in 57% yield by deboronation of **25** according to the procedure described for **24**.

1-Iodo derivative (minor isomer). $\{^1H\}^{11}$B NMR (128 MHz, CD_3CN): δ −35.6 (1B), −32.2 (1B), −22.0 (2B), −19.4 (2B), −4.0 (1B), −2.7 (2B).

6-Iodo derivative (major isomer). $\{^1H\}^{11}$B NMR (128 MHz, CD_3CN): δ −40.0 (1B), −31.1 (1B), −20.5 (2B), −19.5 (2B), −5.8 (1B), −2.7 (2B).

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Notes

The authors declare no competing financial interest.

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