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Nickel-catalyzed cross-coupling of sterically hindered 1-bromomethyl-*o*-carborane with alkyl and aryl Grignard reagents

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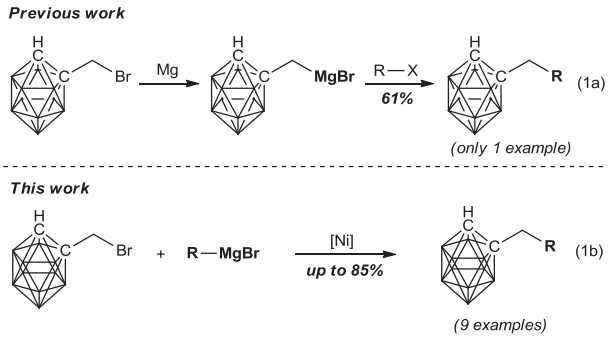
ABSTRACT

A convenient and efficient Ni-catalyzed reaction has been developed for synthesis of mono-substituted *o*-carboranes, involving cross-coupling of readily available and sterically hindered 1-bromomethyl-*o*-carborane with various alkyl and aryl Grignard reagents under mild conditions, and the corresponding *o*-carborane derivatives were obtained in good to excellent yields. This method should provide a new strategy for construction of diverse and useful functionalized boron cluster compounds for medicinal chemistry and material chemistry.

1. Introduction

Icosahedral carboranes (*closo*-$C_2B_{10}H_{12}$) have received increasing interest in medicine science,[1] materials,[2] and catalysis.[3] Recently, some of the very exciting applications of *C*-alkyl-substituted *o*-carboranes include use as hydrophobic pharmacophores for developing new inorganic pharmaceuticals,[4] molecular imaging probes, and radiotherapeutics.[5] Therefore, the development of selective syntheses of alkyl-substituted *o*-carboranes is highly desirable. In general, 1-alkyl-*o*-carboranes are prepared from the condensation reaction of the corresponding alkyl acetylenes with decaborane,[6,7] and the hypertoxicity of decaborane complicates this method. The second method of preparation utilizes the nucleophilic substitution reaction of lithiocarboranes with alkyl halides.[8] However, the preparation of 1-Li-*o*-carborane is complicated by an equilibrium that exists between monolithiocarborane, di-lithiocarborane, and the parent *o*-carborane, which often results in mixtures of mono- and di-substituted derivatives. This problem can be solved by introduction of a *tert*-butyldimethylsilyl protecting group,[8a,b] or by using a chelating solvent (dimethoxyethane).[8c,d] Obviously, a direct C—C bond formation by cross-coupling of an *o*-carboranyl alkyl with alkyl or aryl is an attractive strategy for the synthesis of 1-alkyl-*o*-carboranes. The *o*-carboranyl alkyl–alkyl cross-coupling can be performed by employing the well-known Kumada coupling reaction between *o*-carboranyl alkyl Grignard reagents and alkyl halides.[9]

An attempt was carried out by reacting *o*-carboranyl methyl Grignard reagent with allyl bromide to give 4-(1-carboranyl)-1-butene in moderate yield (Scheme 1, Eq. 1a),[9a] and the reaction has not been extended to other substrates. Unfortunately, 1-carboranylmethylmagnesium bromide can isomerize to 1-methyl-2-carboranylmagnesium bromide. It is caused by the unusual rearrangement that the hydrogen atoms attached to polyhedral carbon are sufficiently labile to permit metalation. In contrast, the coupling of a bulky *o*-carboranyl alkyl halide with an alkyl or aryl metallic reagent has been almost ignored until now.



Scheme 1. Summary of methods used to prepare mono-substituted *o*-carboranes from 1-bromomethyl-*o*-carborane.

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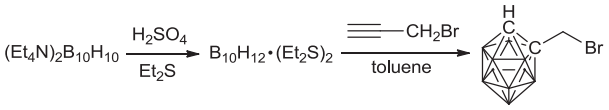
The C–halogen bonds in 1-halomethyl-*o*-carboranes have been thought to be inert toward many reagents,[9a] probably a result of strong electron-withdrawing inductive effect and steric hindrance reasons, thus, developing reactions that replace halogen atoms in the side chain of an *o*-carborane cage fragment with other functional groups is a challenging theme in organic chemistry. Inspired by the transition metal catalyzed cross-coupling reaction of alkyl halides,[10] we initiated a study to develop a transition metal catalyzed alkylation and arylation of *o*-carboranylmethyl halides. Herein, we disclose the first example of a catalytic C–C bond construction reaction using sterically hindered 1-bromomethyl-*o*-carborane and alkyl or aryl Grignard reagents, and the corresponding mono-substituted *o*-carboranes were obtained in good to excellent yields. This investigation will open up the possibility of control synthesis of functionally substituted *o*-carborane derivatives.

2. Results and discussion

The 1-bromomethyl-*o*-carborane (1-$BrCH_2$-1,2-$C_2B_{10}H_{11}$) was prepared by following procedures (Scheme 2). First, the cage-opening reaction of *closo*-$(Et_4N)_2B_{10}H_{10}$ with 2 equiv of concentrated sulfuric acid (H_2SO_4) and 2 equiv of diethyl sulfide (Et_2S) produced *arachno*-$B_{10}H_{12}(Et_2S)_2$ intermediate. 1-Bromomethyl-*o*-carborane was synthesized from *arachno*-$B_{10}H_{12}(Et_2S)_2$ by treatment with propargyl bromide in toluene.

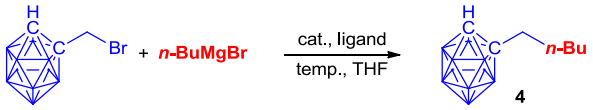


Scheme 2. Synthesis of 1-bromomethyl-*o*-carborane.

With the aim of getting a high yield and reliable route to mono-substituted *o*-carborane clusters, the following research was started. A preliminary screening study using sterically hindered 1-$BrCH_2$-1,2-$C_2B_{10}H_{11}$ and *n*-butylmagnesium bromide (*n*-BuMgBr) was undertaken. For the initial studies, reactions were performed under nitrogen atmosphere in dry THF and the reaction temperature was held constant at 40 °C. We hypothesized that an appropriate transition metal catalyst would increase the yield of the desired products. To test this hypothesis, a variety of transition metal salts, such as Pd, Ni, and Cu salts, were introduced into the catalytic system. The effects of different catalysts on this coupling reaction were summarized in Table 1. No coupling product was observed in the absence of any catalyst (entry 1). When Cu(I) salts were added to the reaction system, the cross-coupling reaction proceeded poorly, and the 1-(*n*-Pentyl)-1,2-dicarba-*closo*-dodecaborane (**4**) was yielded in a yield ranging from 15% to 25% (entries 2–4). When $CuCl_2$ was utilized as catalyst, the yield of **4** increased to 43% (entry 5). Furthermore, when $NiCl_2$ was utilized as catalyst in reaction system, compound **4** was produced with the highest yield of 46% (entries 6). However, palladium complexes were much less effective than nickel catalyst (entries 7 and 8). The results revealed that Ni(II) catalyst gave the highest catalytic activity.

In addition, the activities of cross-coupling reaction of 1-$BrCH_2$-1,2-$C_2B_{10}H_{11}$ with *n*-BuMgBr in the presence of some ligands were also examined. When the reaction was carried out in the presence of $NiCl_2$ salt as catalyst, the use of Π-carbon and phosphine ligands resulted in the decrease of yields of **4** (Table 1, entries 9–12). It is noteworthy that the addition of *N*-methyl-2-pyrrolidone (NMP) leaded to significant improvement of the product yield (entry 13). However, the similar ligands, such as L-Proline and 1,10-Phen, did not have apparent effects on this reaction (entries 14 and 15). Of the factors investigated, the ligand had the largest impact on yield

Table 1
Optimization of conditions for cross-coupling[a]

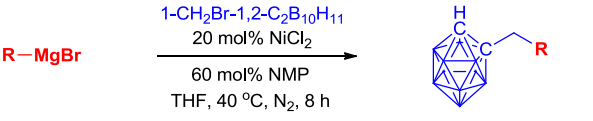


Entry	Cat.	Ligand (mol %)	Temp (°C)	Yield (%)[b]
1	—	—	40	0
2	CuCl	—	40	25
3	CuBr	—	40	18
4	CuI	—	40	15
5	$CuCl_2$	—	40	43
6	$NiCl_2$	—	40	46
7	$PdCl_2$	—	40	16
8	$Pd(PPh_3)_2Cl_2$	—	40	14
9	$NiCl_2$	Isoprene (40)	40	18
10	$NiCl_2$	1-Phenyl-1-propyne (40)	40	22
11	$NiCl_2$	PPh_3 (40)	40	9
12	$NiCl_2$	PCy_3 (40)	40	12
13	$NiCl_2$	NMP (40)	40	80
14	$NiCl_2$	L-Proline (40)	40	29
15	$NiCl_2$	1,10-Phen (40)	40	37
16	$NiCl_2$	NMP (10)	40	56
17	$NiCl_2$	NMP (20)	40	78
18	**$NiCl_2$**	**NMP (60)**	**40**	**85**
19	$NiCl_2$	NMP (80)	40	73
20	$NiCl_2$	NMP (100)	40	63
21	$NiCl_2$	NMP (60)	25	60
22	$NiCl_2$	NMP (60)	60	71
23	$NiCl_2$	NMP (60)	80	68

[a] Reaction conditions: 1-bromomethyl-*o*-carborane (0.5 mmol), *n*-BuMgBr (1.0 mmol), catalyst (0.1 mmol), ligand, THF (2 mL), at 40 °C under N_2 for 8 h; PCy_3=tricyclohexyl phosphine.
[b] Determined by GC analysis.

where the optimal condition was NMP. With respect to the amount of ligand, it was noted that when the amount of NMP was increased from 40 mol % to 60 mol %, the yield of **4** increased to 85% (entry 18), whereas the yield decreased to 56% when 10 mol % NMP was employed (entry 16). On increasing the reaction temperature from 25 °C to 80 °C, the yield of **4** was ranged from 60% to 85% (entries 21–23). Therefore, the optimal conditions for the Ni-catalyzed synthesis of mono-substituted *o*-carboranes are as follows: 20 mol % $NiCl_2$ as the catalyst, 60 mol % NMP as the ligand, 2.0 equiv of Grignard reagents as the coupling partners of 1-$BrCH_2$-1,2-$C_2B_{10}H_{11}$, and the reactions were performed at 40 °C under N_2.

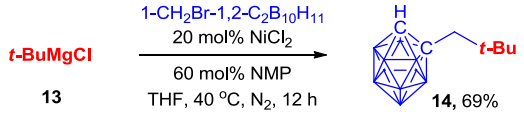
With the optimized conditions in hand, we subsequently carried out the Ni-catalyzed cross-coupling reaction of 1-$BrCH_2$-1,2-$C_2B_{10}H_{11}$ with a variety of alkyl and aryl Grignard reagents to afford mono-substituted *o*-carboranes, which can be used to build up an array of carborane-derived materials. These experimental results are summarized in Schemes 3–5. The cross-coupling of 1-$BrCH_2$-1,2-$C_2B_{10}H_{11}$ with unbranched and branched primary alkyl Grignard reagents afforded the desired products in 73–83% isolated yields (Scheme 3). Interestingly, satisfactory result was ob-



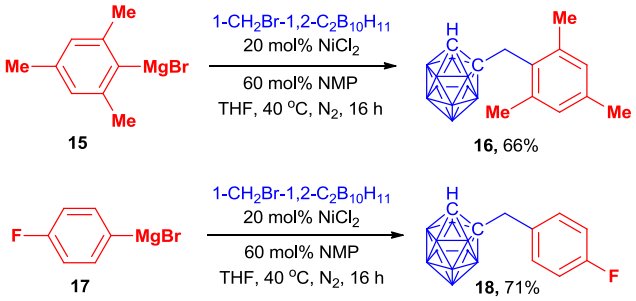
R = *n*-Pr (**1**)
R = *n*-Bu (**3**)
R = *n*-Pentyl (**5**)
R = *n*-Octyl (**7**)
R = $CH_2CH_2CH(CH_3)_2$ (**9**)
R = $CH_2CH_2CH{=}CH_2$ (**11**)

R = *n*-Pr (**2**), 78%
R = *n*-Bu (**4**), 83%
R = *n*-Pentyl (**6**), 80%
R = *n*-Octyl (**8**), 73%
R = $CH_2CH_2CH(CH_3)_2$ (**10**), 75%
R = $CH_2CH_2CH{=}CH_2$ (**12**), 63%

Scheme 3. Cross-coupling of alkyl Grignard reagents.



Scheme 4. Cross-coupling of *t*-butylmagnesium bromide.



Scheme 5. Cross-coupling of aryl Grignard reagents.

tained with functionalized Grignard reagent, for instance, alkenyl group was readily tolerated. The ^{1}H NMR spectrum showed four peaks at 2.18 ppm (t, 2H, J=8.5 Hz), 1.46–1.43 ppm (m, 2H), 1.27–1.25 ppm (m, 6H), 0.88 ppm (t, 3H, J=6.8 Hz), and ^{13}C NMR spectrum showed several peaks at 38.1, 31.3, 29.2, 28.6, 22.4, 13.9 ppm, which corresponded to the chemical shift for the *n*-hexyl group observed in the spectrum of an authentic standard of **6**. The $NiCl_2$ method also worked effectively with bulky tertiary alkyl Grignard reagent (Scheme 4). The preparation of the compound **14** from *t*-butylmagnesium bromide in the presence of $NiCl_2$ produced the target product in 69% yield, and the NMR, and MS data of the isolated product were consistent with the desired molecule.

o-Carborane clusters with phenyl substituents are particularly useful backbone structure for a variety of applications including medicinal drug design and macromolecular construction, but can be difficult to synthesize under mild conditions.[11] The 4-fluorophenylmethyl *o*-carborane (**18**) was successfully prepared from 4-fluorophenyl Grignard reagent in greater than 70% yield, which was a similar reaction condition employed for the sterically hindered 2,4,6-trimethylphenylmethyl derivative compound **16** (Scheme 5). The ^{1}H NMR spectrum showed a typical pattern for di-substituted phenyl ring, which had two peaks at 7.15–7.09 (m, 2H), 7.06 (dd, J=11.8, 5.4 Hz, 2H), and the melting point, MS spectra were consistent with the desired product **18**.

All products were fully characterized by ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy as well as Infrared spectra, Mass spectra, and Elemental analyses. The molecular structure of **16** was further confirmed by single-crystal X-ray analyses. Fig. 1 shows the representative structure of **16**. The C(1)–C(9) distance of 1.539(2) Å is significantly shorter than the C(1)–C(2A) distance of 1.694(2) Å. X-ray analyses confirmed that **16** is molecular compound without any significant intermolecular interactions.

A plausible reaction pathway is depicted in Scheme 6. After formation of nickel(I) halide complex **A**, fast transmetalation with the Grignard reagent leads to the key intermediate [L_nNi(I)–R] (**B**). This kind of complex has been demonstrated to promote homolytic cleavage of carbon–halogen bonds to give Ni(II)–X complex **C** and a carbon radical. Subsequent coordination of this radical with **C** affords intermediate diorgano-Ni(III) **D**. Reductive elimination from **D** gives the cross-coupling product and regenerates the nickel(I) species [L_nNi(I)–X] (**A**), which can re-enter the catalytic cycle.[10b,12]

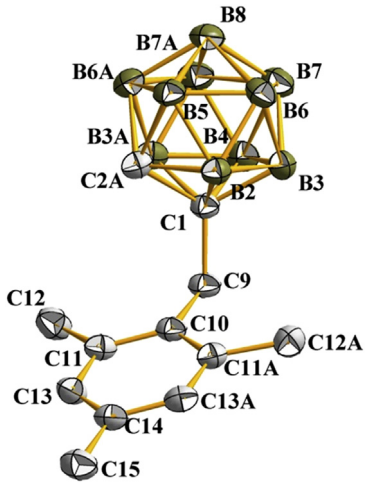
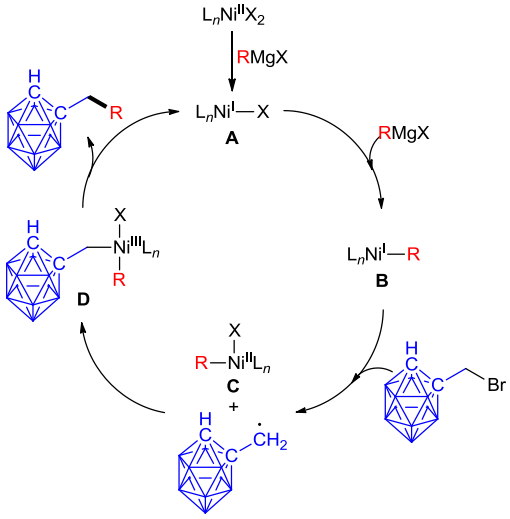


Fig. 1. Molecular structure of **16**. Selected bond lengths (Å) and angles (deg): C1–C9, 1.539(2); C1–C2A, 1.694(2); C1–B3, 1.7136(17); C1–B4, 1.716(3); C9–C10, 1.517(2); C10–C11, 1.4062(16); C11–C12, 1.5133(19); C11– C13, 1.4001(19); C13–C14, 1.3894(17); C14–C15, 1.509(3); C9–C1–C2, 120.96(11); C9–C1–B3, 119.03(8); C9–C1–B4, 117.47(14); C2–C1–B3A, 61.34(8); C2–C1–B3, 111.34(11); C2–C1–B4, 112.04(11); B3–C1–B3A, 112.00(13); B3–C1–B4, 61.95(7); C10–C9–C1, 117.32(14); C11–C10–C9, 120.11(8); C11–C10–C11A, 119.65(16); C13–C11–C10, 119.13(12); C13–C11–C12, 117.87(12); C10–C11–C12, 122.97(12); C14–C13–C11, 122.09(13); C13–C14–C13A, 117.89(17); C13–C14–C15, 121.05(8).



Scheme 6. A plausible reaction pathway.

3. Conclusion

In conclusion, we have synthesized the mono-substituted *o*-carborane clusters bearing alkyl or phenyl substituents by transition metal catalyzed cross-coupling reaction of 1-bromomethyl-*o*-carborane with Grignard reagents under mild conditions. A series of transition metals (Cu, Ni, and Pd salts) and different ligands were evaluated for their ability to enhance the yields of desired *o*-carboranes. Among these catalytic systems, the nickel salt $NiCl_2$ showed the highest catalytic activity. Furthermore, the addition of NMP was found to be efficient to improve the yield of this Ni-catalyzed reaction. Using a variety of Grignard reagents including alkyl and aryl organomagnesium reagents, the corresponding mono-substituted *o*-carboranes were observed in good to excellent yields. Products were isolated using simple chromatographic methods and structures confirmed spectroscopically and through

comparison to authentic standards. This methodology enables the efficient synthesis of a variety of functionalized *o*-carborane clusters derived from 1-haloalkyl-*o*-carboranes.

4. Experimental section

4.1. General information

Unless otherwise stated, all chemical reagents were purchased and used as received from Aladdin Industrial Inc. without further purification. Solvents were purchased from Guangdong Guanghua Sci-Tech Co., Ltd. Magnesium, 1-bromopropane, 1-bromobutane, 1-bromopentane, 1-bromooctane, *tert*-butylmagnesium chloride, and *N*-methyl-2-pyrrolidone were purchased and used as received from Meryer (Shanghai) Chemical Technology Co., Ltd. 1-$BrCH_2$-1,2-$C_2B_{10}H_{11}$ were synthesized according to literature procedures. Reactions were monitored using thin layer chromatography (TLC) plates. *o*-Carborane-containing species were visualized with 0.2% $PdCl_2$ in hydrochloric acid (3.0 M) which, upon heating, gave dark brown spots. Column chromatography was accomplished with ultrapure silica gel (Yucheng Chemical Co., Ltd.).

The ^1H, ^{13}C, and ^{11}B NMR spectra were recorded on a Bruker AV500 spectrometer. ^1H chemical shifts are reported in ppm relative to the residual proton signal of the NMR solvents. Coupling constants (J) are reported in Hertz (Hz). The ^1H NMR spectra of *o*-carboranes typically exhibit a broad signal between 3.00 and −0.75 ppm arising from the protons attached to the boron atoms of the cage, which were not reported separately in the ensuing assignments. ^{13}C chemical shifts are reported in ppm relative to the carbon signal of the NMR solvents. ^{11}B chemical shifts are reported in ppm relative to an external standard of $BF_3\cdot Et_2O$. Low resolution mass spectra were obtained on a Thermo ITQ700 instrument using electron impact ionization. Infrared spectra were obtained on a Bruker Tensor 27 spectrometer using KBr pellets. Melting points were obtained on a standard melting point apparatus and are uncorrected. Gas chromatograph were obtained on a Shimadzu GC-2014C.

4.2. General synthetic procedure

1-Bromomethyl-*o*-carborane (119 mg, 0.5 mmol), $NiCl_2$ (13 mg, 0.1 mmol) and NMP (30 mg, 0.3 mmol) were added to a 25-mL Schlenk flask charged with a magnetic stirrer. The flask was evacuated and backfilled with nitrogen, and then dry THF (4 mL) and freshly prepared Grignard reagents (1.0 mmol) were added to the flask under a stream of nitrogen. After completion of the reaction, the resulting solution was cooled to room temperature, and the reaction was quenched with a saturated aqueous solution of NH_4Cl (4 mL), and the product was extracted with diethyl ether (10 mL×3). The organic layer was dried over $MgSO_4$. The solvent was removed with the aid of a rotary evaporator, and the residue was purified by column chromatography on silica gel using *n*-hexane as eluent to provide the desired product.

*4.2.1. 1-(n-Butyl)-1,2-dicarba-closo-dodecaborane (**2**).*[8a] Eluent: hexane. Yield 78% (79 mg). Colorless liquid. ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 3.55 (s, 1H), 2.21–2.17 (m, 2H), 1.46–1.40 (m, 2H), 1.31–1.28 (m, 2H), 0.89 (t, 3H, J=7.3 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 75.4, 60.9, 37.8, 31.2, 22.1, 13.6. ^{11}B NMR ($CDCl_3$, 160 MHz, ppm): δ −2.4 (d, J=148.8 Hz, 1B), −5.9 (d, J=147.9 Hz, 1B), −8.8–(−13.6) (m, 8B). FTIR (KBr, cm^{-1}): ν 3066, 2961, 2934, 2874, 2593, 1467, 1442, 1382, 723. EIMS $[M+H]^+$ m/z 203.2. Anal. calcd for $C_6H_{20}B_{10}$: C, 35.97; H, 10.06. Found: C, 36.31; H, 10.54.

*4.2.2. 1-(n-Pentyl)-1,2-dicarba-closo-dodecaborane (**4**).* Eluent: hexane. Yield 83% (90 mg). Colorless liquid. ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 3.48 (s, 1H), 2.11 (t, 2H, J=8.5 Hz), 1.41–1.35 (m, 2H), 1.25–1.15 (m, 4H), 0.81 (t, 3H, J=7.2 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 75.5, 60.9, 38.1, 31.0, 28.8, 22.2, 13.8. ^{11}B NMR ($CDCl_3$, 160 MHz, ppm): δ −2.3 (d, J=149.9 Hz, 1B), −5.8 (d, J=147.0 Hz, 1B), −8.8–(−13.6) (m, 8B). FTIR (KBr, cm^{-1}): ν 3066, 2958, 2932, 2864, 2593, 1465, 1380, 723. EIMS $[M+H]^+$ m/z 217.2. Anal. calcd for $C_7H_{22}B_{10}$: C, 39.22; H, 10.34. Found: C, 39.90; H, 10.26.

*4.2.3. 1-(n-Hexyl)-1,2-dicarba-closo-dodecaborane (**6**).*[7b] Eluent: hexane. Yield 80% (92 mg). Colorless liquid. ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 3.55 (s, 1H), 2.18 (t, 2H, J=8.5 Hz), 1.46–1.43 (m, 2H), 1.27–1.25 (m, 6H), 0.88 (t, 3H, J=6.8 Hz). ^{13}C NMR ($CDCl_3$, 125.7 MHz, ppm): δ 75.5, 60.9, 38.1, 31.3, 29.2, 28.6, 22.4, 13.9. ^{11}B NMR ($CDCl_3$, 160.5 MHz, ppm): δ −2.4 (d, J=148.7 Hz, 1B), −5.9 (d, J=147.4 Hz, 1B), −8.8–(−13.6) (m, 8B). FTIR (KBr, cm^{-1}): ν 3066, 2957, 2931, 2860, 2593, 1465, 1379, 723. EIMS $[M+H]^+$ m/z 231.2. Anal. calcd for $C_8H_{24}B_{10}$: C, 42.07; H, 10.59. Found: C, 41.60; H, 10.44.

*4.2.4. 1-(n-Nonyl)-1,2-dicarba-closo-dodecaborane (**8**).*[13] Eluent: hexane. Yield 73% (99 mg). Colorless liquid. ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 3.55 (s, 1H), 2.19–2.16 (m, 2H), 1.48–1.42 (m, 2H), 1.30–1.25 (m, 12H), 0.87 (t, 3H, J=6.7 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 75.5, 60.9, 38.1, 31.8, 29.3, 29.2, 29.1, 29.0, 28.9, 22.6, 14.0. ^{11}B NMR ($CDCl_3$, 160 MHz, ppm): δ −2.3 (d, J=148.6 Hz, 1B), −5.8 (d, J=144.2 Hz, 1B), −8.8–(−13.6) (m, 8B). FTIR (KBr, cm^{-1}): ν 3066, 2955, 2927, 2856, 2593, 1465, 1377, 723. EIMS $[M+H]^+$ m/z 273.3. Anal. calcd for $C_{11}H_{30}B_{10}$: C, 48.53; H, 11.03. Found: C, 48.47; H, 10.95.

*4.2.5. 1-(4-Methyl-1-pentyl)-1,2-dicarba-closo-dodecaborane (**10**).* Eluent: hexane. Yield 75% (86 mg). Colorless liquid. ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 3.55 (s, 1H), 2.17 (t, 2H, J=8.5 Hz), 1.55–1.49 (m, 1H), 1.48–1.41 (m, 2H), 1.15–1.11 (m, 2H), 0.87 (d, 6H, J=6.6 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 75.5, 60.9, 38.3, 38.0, 27.6, 27.1, 22.4. ^{11}B NMR ($CDCl_3$, 160 MHz, ppm): δ −2.4 (d, J=149.5 Hz, 1B), −5.9 (d, J=146.6 Hz, 1B), −8.8–(−13.6) (m, 8B). FTIR (KBr, cm^{-1}): ν 3066, 2957, 2930, 2870, 2593, 1465, 1386, 1368, 723. EIMS $[M+H]^+$ m/z 231.2. Anal. calcd for $C_8H_{24}B_{10}$: C, 42.10; H, 10.52. Found: C, 42.33; H, 10.63.

*4.2.6. 1-(4-Pentenyl)-1,2-dicarba-closo-dodecaborane (**12**).*[14] Eluent: hexane. Yield 63% (67 mg). Colorless liquid. ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 5.74–5.66 (m, 1H), 5.02–5.01 (m, 1H), 4.99 (s, 1H), 3.54 (s, 1H, $C_{cluster}$–H), 2.20–2.16 (m, 2H), 2.04–2.00 (m, 2H), 1.59–1.52 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 136.7, 116.0, 75.2, 61.0, 37.4, 32.7, 28.2. ^{11}B NMR ($CDCl_3$, 160 MHz, ppm): δ −2.3 (d, J=148.6 Hz, 1B), −5.7 (d, J=137.9 Hz, 1B), −8.8–(−13.6) (m, 8B). FTIR (KBr, cm^{-1}): ν 3065, 2979, 2957, 2935, 2866, 2594, 1459, 1440, 993, 917, 723. EIMS $[M+H]^+$ m/z 215.2. Anal. calcd for $C_7H_{20}B_{10}$: C, 39.59; H, 9.49. Found: C, 39.70; H, 9.66.

*4.2.7. 1-(2,2-Dimethyl-1-proyl)-1,2-dicarba-closo-dodecaborane (**14**).* Eluent: hexane. Yield 69% (74 mg). White solid, mp=66–67 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 3.56 (s, 1H), 2.26 (s, 2H), 1.03 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 74.32, 63.10, 51.75, 33.39, 29.39. ^{11}B NMR (160 MHz, $CDCl_3$) δ −2.12 (d, J=150.2 Hz, 1B), −5.02 (d, J=149.9 Hz, 1B), −7.90–−14.64 (m, 8B). FTIR (KBr, cm^{-1}): ν 3059, 2960, 2940, 2862, 2589, 1444, 1398, 1350, 722. EIMS $[M+H]^+$ m/z 217.3. Anal. calcd for $C_7H_{22}B_{10}$: C, 39.22; H, 10.34. Found: C, 39.38; H, 10.40.

*4.2.8. 1-[2-(2,4,6-Trimethylphenyl)-1-methyl]-1,2-dicarba-closo-dodecaborane (**16**).* Eluent: hexane. Yield 66% (91 mg). White solid, mp=105–106 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 6.87 (s, 2H), 3.60 (s, 2H), 3.41 (s, 1H), 2.30 (s, 6H), 2.27 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$)

δ 137.89, 137.43, 129.87, 129.82, 74.96, 58.93, 36.73, 20.99. ^{11}B NMR (160 MHz, $CDCl_3$) δ −1.94 (d, *J*=147.8 Hz, 1B), −5.39 (d, *J*=145.9 Hz, 1B), −8.82––14.32 (m, 8B). FTIR (KBr, cm^{-1}): ν 3064, 3005, 2970, 2919, 2858, 2621, 2578, 2565, 2549, 1613, 1581, 1482, 1464, 1446, 1376, 821. EIMS $[M+H]^+$ *m/z* 279.2. Anal. calcd for $C_{12}H_{24}B_{10}$: C, 52.14; H, 8.75. Found: C, 52.23; H, 8.83.

*4.2.9. 1-(4-Fluorophenylmethyl)-1,2-dicarba-closo-dodecaborane (**18**).* Eluent: hexane. Yield 71% (89 mg). White solid, mp=84–85 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15–7.09 (m, 2H), 7.06 (dd, *J*=11.8, 5.4 Hz, 2H), 3.50 (s, 2H), 3.23 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.81 (d, *J*=248.3 Hz), 131.67, 131.60, 130.32 (d, *J*=3.5 Hz), 116.30, 116.13, 74.42, 59.47, 42.91. ^{11}B NMR (160 MHz, $CDCl_3$) δ −2.28 (d, *J*=148.9 Hz, 1B), −5.46 (d, *J*=148.4 Hz, 1B), −7.80––14.70 (m, 8B). FTIR (KBr, cm^{-1}): ν 3063, 2940, 2870, 2615, 2581, 1601, 1509, 724. EIMS $[M+H]^+$ *m/z* 255.2. Anal. calcd for $C_9H_{17}B_{10}F$: C, 42.84; H, 6.79. Found: C, 43.10; H, 6.86.

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Supplementary data

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