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Carboranyl derivatives of amineboranes and boron analogs of esters: a synthetic investigation†

Geeta Rana[1], Kamesh Vyakaranam[1], Sarah C. Ledger[1], Shannon L. Delaney[1], John A. Maguire[2] and Narayan S. Hosmane[1]*

[1]Department of Chemistry and Biochemistry, Michael Faraday Laboratories, Northern Illinois University, DeKalb, IL 60115-2862, USA
[2]Department of Chemistry, Southern Methodist University, Dallas, TX 75275-0314, USA

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New functionalized carboranyl derivatives of amineboranes and boron analogs of esters are reported. The reaction of 1,12-(aminopropyl)-1,12-dicarbadodecaborane (2), 2-(aminopropyl)-1,2-dicarbadodecaborane (4), 1-methyl-2-(aminopropyl)-1,2-dicarbadodecaborane (6), 1-phenyl-2-(aminopropyl)-1,2-dicarbadodecaborane (8) with Me_3NBH_2X produced novel carboranylamineboranes of the general formula 1,12-[$(CH_2)_3NH_2BH_2X$]$_2$-1,12-$C_2B_{10}H_{10}$ [X = CN (2a), $COOCH_3$ (2b), CONHEt (2c), $CONHCH(CH_2C_6H_5)COOCH_3$ (2d), $CONHCH(CH_3)COOCH_3$ (2e), $CONHCH[CH(CH_3)_2]COOCH_3$ (2f), $CONHCH(CH_2C_6H_4OH)COOCH_3$ (2g), 1-$CH_2NH_2BH_2CN$ (2h)] or 1-R-2-[$(CH_2)_3NH_2BH_2X$]-1,2-$C_2B_{10}H_{10}$ {R = H, X = CN (4a), $COOCH_3$ (4b), CONHEt (4c), COOH (4d); R = CH_3, X = CN (6a), $COOCH_3$ (6b), $CONHCH(CH_2C_6H_5)COOCH_3$ (6c), $CONHCH(CH_3)COOCH_3$ (6d), $CONHCH[CH(CH_3)_2]COOCH_3$ (6e), $CONHCH(CH_2C_6H_4OH)COOCH_3$ (6f); R = C_6H_5, X = CN (8a), $COOCH_3$ (8b), $CONHCH(CH_2C_6H_5)COOCH_3$ (8c), $CONHCH(CH_3)COOCH_3$ (8d), $CONHCH[CH(CH_3)_2]COOCH_3$ (8e), $CONHCH(CH_2C_6H_4OH)COOCH_3$ (8f)} by the amine exchange reaction. The reaction of 1-(aminomethyl)-1,2-dicarbadodecaborane with Me_3NBH_2X (X = CN) produced 1-[$CH_2NH_2BH_2CN$]-1,2-$C_2B_{10}H_{10}$ (2h). Compounds 2a, 4a, 6a, and 8a were also synthesized by the reaction of 1,12-(aminopropyl)-1,12-dicarbadodecaborane hydrochloride (1), 2-(aminopropyl)-1,2-dicarbadodecaborane hydrochloride (3), 1-methyl-2-(aminopropyl)-1,2-dicarbadodecaborane hydrochloride (5), 1-phenyl-2-(aminopropyl)-1,2-dicarbadodecaborane hydrochloride (7) with sodium cyanoborohydride. The reaction of Li_2[1,2-CO_2-1,2-$C_2B_{10}H_{10}$] (9) or Li[1-R-2-CO_2-1,2-$C_2B_{10}H_{10}$], R = CH_3 (10), R = C_6H_5 (11), with Me_3NBH_2I gave 1,2-$CO_2BH_2NMe_3$-1,2-$C_2B_{10}H_{10}$ (9a) or 1-R-2-$CO_2BH_2NMe_3$-1,2-$C_2B_{10}H_{10}$, R = CH_3 (10a), R = C_6H_5 (11a), as new boron analogs of esters. All of these compounds were characterized by IR spectroscopy, ^1H, ^{13}C and ^{11}B NMR spectroscopy and chemical analyses. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: synthesis; BNCT; amineboranes; carborane; substituted carboranes

INTRODUCTION

Icosahedral carboranes (*o*-, *m*-, *p*-$C_2B_{10}H_{12}$) were first described in 1963,[1,2] and thereafter have been the subject of many studies,[3–5] more recently in the areas of materials chemistry[6] and medicinal chemistry.[7] Their thermal and chemical stabilities and high boron content have also made them attractive candidates for possible use in boron neutron capture therapy (BNCT).[8,9] In this regard, one of the major disadvantages of the icosahedral carboranes is their hydrophobicity and consequent low water solubility. Studies have shown that *p*-carborane isomers, the least

*Correspondence to: Narayan S. Hosmane, Department of Chemistry and Biochemistry, Michael Faraday Laboratories, Northern Illinois University, DeKalb, IL 60115-2862, USA.
E-mail: nhosmane@niu.edu
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toxic of the compounds, are also the least water soluble. From such solubility considerations, much of the research in this area has concentrated on the syntheses of derivatives of the *o*-carboranes. Our interest in these compounds, particularly amidecarboranylboranes, originates from our recent observation that, in a C6 gliosarcoma tumor implanted in a rat brain model, $Me_3NBH_2CONHCH(4\text{-}CH_2C_6H_5)COOMe$ showed *ca* 9 : 1 tumor : normal brain (T/N) ratios, compared with 3 : 1 for *p*-boronophenylalanine (BPA), whose B-10 enriched isomer is currently undergoing clinical trails as a BNCT agent.[10] Moreover, α-autoradiography showed that $Me_3NBH_2CONHCH(4\text{-}CH_2C_6H_5)COOMe$ was also found to incorporate into tumor cells that were infiltrating into normal brain tissue. This is important since such cells are thought to be a leading cause of tumor recurrence after radiation.[11] These results indicate that the amidecarboranylboranes might have potential therapeutic value and their syntheses and characterizations are well worth investigating. This is such a report on a series of neutral icosahedral carboranyl compounds produced from the reactions of carboranylamine hydrochlorides with a series of amineboranes, as outlined in Scheme 1.

EXPERIMENTAL

Materials and methods

All solvents, chemicals and reagents were of analytical grade and used without further purification unless otherwise noted. Baker analyzed silica gel (60–200 mesh) was used for flash column chromatography. 1,12-(Aminopropyl)-1,12-dicarbadodecaborane hydrochloride (**1**), 2-(aminopropyl)-1,2-dicarbadodecaborane hydrochloride (**3**), 1-methyl-2-(aminopropyl)-1,2-dicarbadodecaborane hydrochloride (**5**), and 1-phenyl-2-(aminopropyl)-1,2-dicarbadodecaborane hydrochloride (**7**) were synthesized by methods described by Soloway and coworkers.[12] The carboranylamines, 1,12-*bis*-(propylamine)-1,12-dicarbadodecaborane (**2**), 1-(propylamine)-1,2-dicarbadodecaborane (**4**), 1-methyl-2-(propylamine)-1,2-dicarbadodecaborane (**6**), and 1-phenyl-2-(propylamine)-1,2-dicarbadodecaborane (**8**) were synthesized by reacting the corresponding amine hydrochlorides with Et_3N followed by the removal of $Et_3N^+HCl^-$. The amineboranes of the formula Me_3NBH_2X [X = CN, $COOCH_3$, CONHEt, COOH, $CONHCH(CH_2C_6H_5)COOMe$, $CONHCH(4\text{-}CH_2C_6H_4OH)COOMe$, $CONHCH(CHMe_2)COOMe$, $CONHCH(CH_3)COOMe$, $CONHCH_2CH_3$] were made using the methods described by Spielvogel and coworkers.[13,14] 1,2-*Bis*-(carboxy)-1,2-dicarbadodecaborane (**9**), 1-methyl-2-(carboxy)-1,2-dicarbadodecaborane (**10**), and 1-phenyl-2-(carboxy)-1,2-dicarbadodecaborane (**11**) were synthesized by a procedure identical to the one described by Kahl and Kasar.[15] *closo*-1,2-$C_2B_{10}H_{12}$ (*o*-carborane), *closo*-1,12-$C_2B_{10}H_{12}$ (*p*-carborane), *closo*-1-Ph-1,2-$C_2B_{10}H_{11}$ (phenyl-*o*-carborane), and *closo*-1-Me-1,2-$C_2B_{10}H_{11}$ (methyl-*o*-carborane) were obtained from KATCHEM and used as received. Cyclohexane, 1,2-dimethoxyethane (DME) and benzene were dried over sodium metal and benzophenone and doubly distilled before use. *n*-BuLi (2.0 M in cyclohexane) was used as received.

Spectroscopic and analytical procedures

^1H, ^{11}B and ^{13}C NMR spectra were recorded on a Bruker Fourier-transform multinuclear magnetic resonance spectrometer at 200 MHz, 64.2 MHz and 50.3 MHz respectively. IR spectra were recorded using a Nicolet Magna 550 FT-IR spectrophotometer. Elemental analyses were obtained in house using a Perkin Elmer 2400 CHN elemental analyzer.

Syntheses

All experiments were carried out in 250 ml Pyrex glass round-bottom flasks, each one fitted with a nitrogen inlet and containing a magnetic stirring bar. The purities of all the known compounds were checked by comparing their IR and NMR spectra and melting points with authentic samples.

*1,12-[Propyl-*N*-(cyanoborane)amine]-1,12-dicarbadodecaborane (**2a**)*

A 3.85 mmol (1.00 g) sample of 1,12-(aminopropyl)-1,12-dicarbadodecaborane (**2**) and 7.71 mmol (0.76 g) of trimethylaminecyanoborane were dissolved in anhydrous tetrahydrofuran (THF) (20 ml) under nitrogen atmosphere. The mixture was heated to reflux and the extent of the reaction was monitored by ^{11}B NMR spectroscopy. After 12 h, the solvent was removed under reduced pressure, leaving a crude white solid product that was then recrystallized from dichloromethane : pentane (7 : 2) to produce off-white needles of 1,12-[propyl-*N*-(cyanoborane)amine]-1,12-dicarbadodecaborane (**2a**) (0.79 g, 78% yield, soluble in polar and slightly soluble in nonpolar organic solvents; m.p. 111–112 °C). Spectroscopic and analytical data for **2a**: ^1H NMR [dimethylsulfoxide (DMSO), relative to Me_4Si] δ 2.12 (4H, t, CH_2), 1.40 (4H, m, CH_2), 3.10 (4H, m, CH_2), 2.01 (10H, br, BH), 0.50–1.20 (4H, br, NH_2); ^{11}B NMR (DMSO, relative to $BF_3{\cdot}OEt_2$) δ −12.40 (10B, $J_{(BH)} = 143$ Hz), −14.82 (2B, exopolyhedral $J_{(BH)} = 143$ Hz); ^{13}C NMR (DMSO, relative to Me_4Si) δ 77.20 (C_{cage}), 114.00 (CN), 54.80 (CH_2); IR (KBr pellet, cm^{-1}) 2350, 2575 [ν(B–H)]. Elemental anal. Found: C, 35.84; H, 9.10; N, 16.75. Calc. for $C_{10}H_{30}B_{12}N_4$: C, 35.73; H, 8.99; N, 16.67%.

*Alternate method for (**2a**)*

A 3.01 mmol (1.00 g) sample 1,12-(aminopropyl)-1,12-dicarbadodecaborane hydrochloride (**1**) and sodium cyanoborohydride (0.38 g, 6.02 mmol) were dissolved in anhydrous DME (25 ml) under nitrogen atmosphere. The resulting solution was refluxed and monitored by its ^{11}B NMR spectra. After 12 h of refluxing, the reaction flask was cooled to room temperature and then filtered through a glass frit to collect a clear filtrate. The white solid, collected on the frit (identified as NaCl) was discarded. The solvent, DME, was then removed

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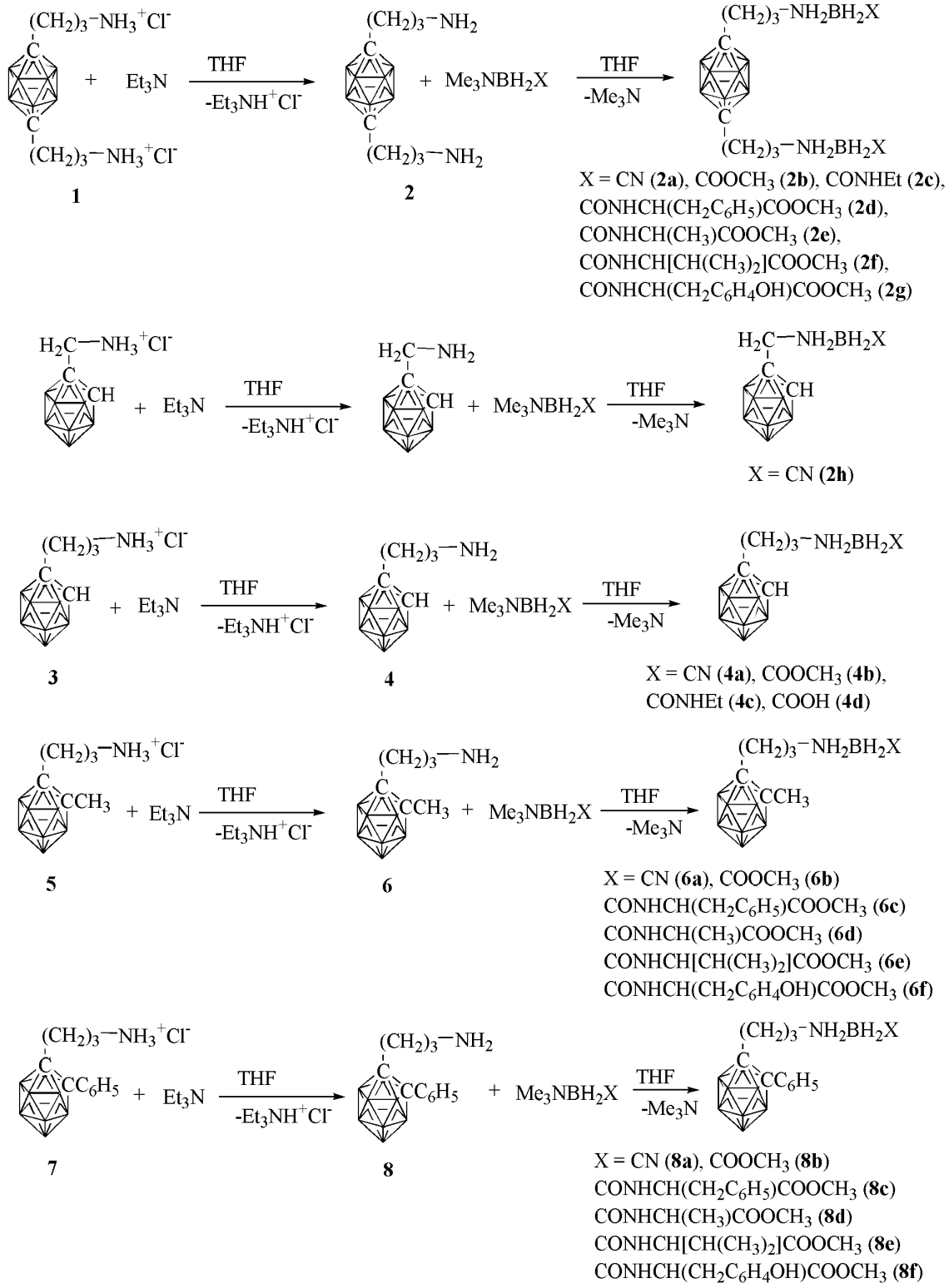

Scheme 1. Synthetic scheme for the preparation of carboranyl amineboranes.

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from the filtrate under reduced pressure. The resulting crude white residue was purified by column chromatography (8 : 2 $CHCl_3$: hexane) to isolate a white crystalline solid, identified as **2a**, in 86% yield (0.87 g, 2.58 mmol). Spectroscopic and analytical data were the same as above.

*1,12-[Propyl-*N*-(methoxycarbonylborane)amine]-1,12-dicarbadodecaborane (**2b**)*

A 3.85 mmol (1.00 g) sample of 1,12-(aminopropyl)-1,12-dicarbadodecaborane (**2**) and 7.71 mmol (0.87 g) of trimethylaminecarbomethoxyborane were dissolved in anhydrous THF (20 ml) under nitrogen atmosphere. The mixture was heated to reflux and the extent of the reaction was monitored by ^{11}B NMR spectroscopy. After 9 h, the solvent was removed under reduced pressure and the resulting crude white solid product was then recrystallized from ethylacetate : pentane (9 : 1) to produce off-white needles of 1,12-[propyl-*N*-(methoxycarbonylborane)amine]-1,12-dicarbadodecaborane (**2b**) (0.86 g, 72% yield, soluble in polar organic solvents; m.p. 126–129 °C). Spectroscopic and analytical data for **2b**: ^{1}H NMR (DMSO, relative to Me_4Si) δ 2.10 (4H, t, CH_2), 1.32 (4H, m, CH_2), 2.93 (4H, m, CH_2), 2.00 (10H, br, BH), 0.60–1.30 (4H, br, BH), 3.82 (6H, s, CH_3), 5.09 (4H, br, NH_2); ^{11}B NMR (DMSO, relative to $BF_3{\cdot}OEt_2$) δ −12.60 (10B, $J_{(BH)} = 144.2$ Hz), −11.37 (2B, exopolyhedral $J_{(BH)} = 100$ Hz); ^{13}C NMR (DMSO, relative to Me_4Si) δ 75.80 (C_{cage}), 179.20 (C═O), 54.00 (OCH_3); IR (KBr pellet, cm^{-1}) 2371, 2560 [ν(B–H)]. Elemental anal. Found: C, 35.96; H, 9.17; N, 7.02. Calc. for $C_{12}H_{36}B_{12}N_2O_4$: C, 35.84; H, 9.02; N, 6.97%.

*1,12-[Propyl-*N*-(carbamoylborane)amine]-1,12-dicarbadodecaborane (**2c**)*

A 3.92 mmol (1.02 g) sample of 1,12-(aminopropyl)-1,12-dicarbadodecaborane (**2**) and 7.72 mmol (1.11 g) of trimethylaminecarbamoylborane were dissolved in anhydrous THF (15 ml) under nitrogen atmosphere. The mixture was heated to reflux and the extent of the reaction was monitored by ^{11}B NMR spectroscopy. After 17 h, the solvent was removed under reduced pressure and the crude white solid product was then recrystallized from ethylacetate : pentane : hexane (9 : 1 : 1) to produce white crystals of 1,12-[propyl-*N*-(carbamoylborane)amine]-1,12-dicarbadodecaborane (**2c**) (0.91 g, 70% yield, m.p. 136–137 °C). Spectroscopic and analytical data for **2c**: ^{1}H NMR (DMSO, relative to Me_4Si) δ 2.13 (4H, t, CH_2), 1.41 (4H, m, CH_2), 3.11 (4H, m, CH_2), 2.02 (10H, br, BH), 0.50–1.10 (4H, br, BH), 2.76 (4H, q, CH_2), 1.02 (6H, t, CH_3), 5.11 (4H, br, NH_2); ^{11}B NMR (DMSO, relative to $BF_3{\cdot}OEt_2$) δ −11.90 (10B, $J_{(BH)} = 142.8$ Hz), −9.86 (2B, exopolyhedral $J_{(BH)} = 91.0$ Hz); ^{13}C NMR (DMSO, relative to Me_4Si) δ 76.20 (C_{cage}), 162.00 (C═O), 47.00 (NCH_2), 20.00 (CH_3); IR (KBr pellet, cm^{-1}) 2433, 2520 [ν(B–H)]. Elemental anal. Found: C, 39.30; H, 9.99; N, 13.15. Calc. for $C_{14}H_{42}B_{12}N_4O_2$: C, 39.26; H, 9.89; N, 13.09%.

*1,12-[Propyl-*N*-(methylcarbonyl-L-phenylalanine)amine]-1,12-dicarbadodecaborane (**2d**)*

A 3.88 mmol (1.01 g) sample of 1,12-(aminopropyl)-1,12-dicarbadodecaborane (**2**) and 7.72 mmol (2.15 g) of trimethylamineborylcarbonylphenylalanine methylester were dissolved in anhydrous THF (20 ml) under nitrogen atmosphere. The mixture was heated to reflux and the extent of the reaction was monitored by ^{11}B NMR spectroscopy. After 23 h, the solvent was removed under reduced pressure and the crude white solid product was then recrystallized from acetone : chloroform : pentane (7 : 2 : 1) to produce white crystals of 1,12-[propyl-*N*-(methylcarbonyl-L-phenylalanine)amine]-1,12-dicarbadodecaborane (**2d**) (1.21 g, 58% yield, soluble in polar organic solvents; m.p. >250 °C, decomposed). Spectroscopic and analytical data for **2d**: ^{1}H NMR (DMSO, relative to Me_4Si) δ 2.15 (4H, t, CH_2), 1.72 (4H, m, CH_2), 2.91 (4H, m, CH_2), 0.50–1.20 (4H, br, BH), 2.01 (10H, br, BH), 3.86 (6H, s, CH_3), 7.16–7.41 (10H, m, aromatic), 3.12 (4H, d, CH_2), 3.51 (2H, m, CH), 5.25 (4H, br, NH_2); ^{11}B NMR (DMSO, relative to $BF_3{\cdot}OEt_2$) δ −13.13 (10B, $J_{(BH)} = 136.0$ Hz), −7.76 (2B, exopolyhedral $J_{(BH)} = 126.4$ Hz); ^{13}C NMR (DMSO, relative to Me_4Si) δ 74.20 (C_{cage}), 164.00 (C═O), 129.5 (aromatic), 56.00 (OCH_3), 22.00 (CH_2), 42.60 (CH); IR (KBr pellet, cm^{-1}) 2268, 2570 [ν(B–H)]. Elemental anal. Found: C, 51.77; H, 7.88; N, 8.09. Calc. for $C_{30}H_{52}B_{12}N_4O_6$: C, 51.73; H, 7.81; N, 8.05%.

*1,12-[Propyl-*N*-(methylcarbonyl-L-alanine)amine]-1,12-dicarbadodecaborane (**2e**)*

A 3.96 mmol (1.03 g) sample of 1,12-(aminopropyl)-1,12-dicarbadodecaborane (**2**) and 7.70 mmol (2.15 g) of trimethylamineborylcarbonylalanine methylester were dissolved in anhydrous THF (20 ml) under nitrogen atmosphere. The mixture was heated to reflux and the extent of the reaction was monitored by ^{11}B NMR spectroscopy. After 23 h, the solvent was removed under reduced pressure and the crude white solid product was then recrystallized from acetone : chloroform : pentane (7 : 2 : 1) to produce white crystals of 1,12-[propyl-*N*-(methylcarbonyl-L-alanine)amine]-1,12-dicarbadodecaborane (**2e**) (1.21 g, 58% yield, soluble in polar organic solvents; m.p. >270 °C, decomposed). Spectroscopic and analytical data for **2e**: ^{1}H NMR (DMSO, relative to Me_4Si) δ 2.12 (4H, t, CH_2), 1.58 (4H, m, CH_2), 2.86 (4H, m, CH_2), 0.50–1.30 (4H, br, BH), 2.08 (10H, br, BH), 3.48 (2H, m, CH), 3.82 (6H, s, CH_3), 1.30 (6H, d, CH_3), 5.35 (4H, br, NH_2); ^{11}B NMR (DMSO, relative to $BF_3{\cdot}OEt_2$) δ −12.82 (10B, $J_{(BH)} = 141.0$ Hz), −7.84 (2B, exopolyhedral $J_{(BH)} = 130.6$ Hz); ^{13}C NMR (DMSO, relative to Me_4Si) δ 72.60 (C_{cage}), 165.60 (C═O), 54.50 (OCH_3), 38.00 (CH_3), 43.00 (CH); IR (KBr pellet, cm^{-1}) 2257, 2485 [ν(B–H)]. Elemental anal. Found: C, 39.75; H, 8.50; N, 10.33. Calc. for $C_{18}H_{46}B_{12}N_4O_6$: C, 39.72; H, 8.52; N, 10.30%.

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*1,12-[Propyl-*N*-(methylcarbonyl-L-valine)amine]-1,12-dicarbadodecaborane (**2f**)*

A 3.88 mmol (1.01 g) sample of 1,12-(aminopropyl)-1,12-dicarbadodecaborane (**2**) and 7.71 mmol (1.77 g) of trimethylamineborylcarbonylvaline methylester were dissolved in anhydrous THF (20 ml) under nitrogen atmosphere. The mixture was heated to reflux and the extent of the reaction was monitored by ^{11}B NMR spectroscopy. After 20 h, the solvent was removed under reduced pressure and the crude white solid product was then recrystallized from acetone : pentane (7 : 1) to produce white crystals of 1,12-[propyl-*N*-(methylcarbonyl-L-valine)amine]-1,12-dicarbadodecaborane (**2f**) (1.07 g, 57 % yield, m.p. >250 °C, decomposed). Spectroscopic and analytical data for **2f**: ^{1}H NMR (DMSO, relative to Me_4Si) δ 2.20 (4H, t, CH_2), 1.46 (4H, m, CH_2), 2.97 (4H, m, CH_2), 0.46–1.46 (4H, br, BH), 2.12 (10H, br, BH), 3.79 (6H, s, CH_3), 1.12 (12H, d, CH_3), 3.25 (2H, d, CH), 1.72 (2H, m, CH), 5.41 (4H, br, NH_2); ^{11}B NMR (DMSO, relative to $BF_3{\cdot}OEt_2$) δ −12.96 (10B, $J_{(BH)} = 143.0$ Hz), −7.92 (2B, exopolyhedral $J_{(BH)} = 128.7$ Hz); ^{13}C NMR (DMSO, relative to Me_4Si) δ 73.80 (C_{cage}), 166.30 (C═O), 52.00 (OCH_3), 21.00 (CH_3), 25.00, 43.90 (CH); IR (KBr pellet, cm^{-1}) 2281, 2513 [ν(B–H)]. Elemental anal. Found: C, 44.20; H, 9.15; N, 9.25. Calc. for $C_{22}H_{58}B_{12}N_4O_6$: C, 44.01; H, 9.07; N, 9.33%.

*1,12-[Propyl-*N*-(methylcarbonyl-L-tyrosine)amine]-1,12-dicarbadodecaborane (**2g**)*

A 4.01 mmol (1.04 g) sample of 1,12-(aminopropyl)-1,12-dicarbadodecaborane (**2**) and 7.75 mmol (2.27 g) of trimethylamineborylcarbonyltyrosine methylester were dissolved in anhydrous THF (20 ml) under nitrogen atmosphere. The mixture was heated to reflux and the extent of the reaction was monitored by ^{11}B NMR spectroscopy. After 15 h, the solvent was removed under reduced pressure and the crude white solid product was then recrystallized from acetone : chloroform : pentane (5 : 4 : 1) to produce white crystals of 1,12-[propyl-*N*-(methylcarbonyl-L-tyrosine)amine]-1,12-dicarbadodecaborane (**2g**) (1.20 g, 50% yield, m.p. >250 °C, decomposed). Spectroscopic and analytical data for **2g**: ^{1}H NMR (DMSO, relative to Me_4Si) δ 2.22 (4H, t, CH_2), 1.41 (4H, m, CH_2), 3.02 (4H, m, CH_2), 0.42–1.52 (4H, br, BH), 2.15 (10H, br, BH), 3.79 (6H, s, CH_3), 7.30–7.80 (10H, m, aromatic), 3.19 (2H, t, CH), 3.08 (4H, d, CH_2), 5.38 (4H, br, NH_2); ^{11}B NMR (DMSO, relative to $BF_3{\cdot}OEt_2$) δ −13.41 (10B, $J_{(BH)} = 134.0$ Hz), −7.62 (2B, exopolyhedral $J_{(BH)} = 126.4$ Hz); ^{13}C NMR (DMSO, relative to Me_4Si) δ 72.8 (C_{cage}), 164.30 (C═O), 128.00–131.00 (aromatic), 23.90 (CH_2), 44.00 (CH); IR (KBr pellet, cm^{-1}) 2399, 2538 [ν(B–H)]. Elemental anal. Found: C, 49.55; H, 7.53; N, 7.72. Calc. for $C_{30}H_{54}B_{12}N_4O_8$: C, 49.45; H, 7.47; N, 7.69%.

*1-[Methyl-*N*-(cyanoborane)amine]-1,2-dicarbadodecaborane (**2h**)*

A 4.70 mmol (0.82 g) sample of 1-(aminomethyl)-1,2-dicarbadodecaborane and 4.71 mmol (0.46 g) of trimethylaminecyanoborane were dissolved in anhydrous THF (20 ml) under nitrogen atmosphere. The mixture was heated to reflux and the extent of the reaction was monitored by ^{11}B NMR spectroscopy. After 8 h, the solvent was removed under reduced pressure and the crude white solid product was then recrystallized from acetone : chloroform : pentane (5 : 4 : 1) to produce white crystals of **2h** (0.62 g, 63% yield, m.p. >240 °C, decomposed). Spectroscopic and analytical data for **2h**: ^{1}H NMR (DMSO, relative to Me_4Si) δ 2.22 (2H, t, CH_2), 0.42–1.52 (12H, br, BH), 4.56 (1H, s, CH); ^{11}B NMR (DMSO, relative to $BF_3{\cdot}OEt_2$) δ −5.21 (1B, $J_{(BH)} = 129.6$ Hz), −8.18 (1B, $J_{(BH)} = 133.7$ Hz), −10.23 (2B, $J_{(BH)} = 140.3$ Hz), −12.18 (2B, $J_{(BH)}$ unresolved), −14.54 (4B, $J_{(BH)}$ unresolved), −13.88 (1B, $J_{(BH)} = 102.0$ Hz); ^{13}C NMR (DMSO, relative to Me_4Si) δ 73.8, 78.3 (C_{cage}), 23.90 (CH_2); IR (KBr pellet, cm^{-1}) 2400, 2269, 2389 [ν(B–H)]. Elemental anal. Found: C, 22.43; H, 7.98; N, 13.11. Calc. for $C_4H_{17}B_{11}N_2$: C, 22.65; H, 8.02; N, 13.21%.

*2-[Propyl-*N*-(cyanoborane)amine]-1,2-dicarbadodecaborane (**4a**)*

A 4.16 mmol (1.00 g) sample of 2-(aminopropyl)-1,2-dicarbadodecaborane (**4**) and 4.15 mmol (0.41 g) of trimethylaminecyanoborane were placed in a 100 ml round-bottom flask. Anhydrous THF was added to the reaction vessel and the contents were refluxed at 65 °C and monitored via ^{11}B NMR. After complete conversion (9.5 h), the solvent was removed and the solid obtained was recrystallized from methylene chloride to isolate a white crystalline solid, 2-[propyl-*N*-(cyanoborane)amine]-1,2-dicarbadodecaborane (**4a**) in 63% yield (0.61 g, m.p. 91–93 °C). Spectroscopic and analytical data for **4a**: ^{1}H NMR (DMSO, relative to Me_4Si) δ 2.21 (2H, t, CH_2), 1.60 (2H, m, CH_2), 3.21 (2H, m, CH_2), 5.19 (1H, s, CH), 0.60–1.48 (12H, br, BH), 4.98 (2H, m, NH_2), 5.25 (2H, br, NH_2); ^{11}B NMR (DMSO, relative to $BF_3{\cdot}OEt_2$) δ − 7.21 (1B, $J_{(BH)} = 129.6$ Hz), −9.38 (1B, $J_{(BH)} = 133.7$ Hz), −11.53 (2B, $J_{(BH)} = 140.3$ Hz), −13.68 (2B, $J_{(BH)}$ unresolved), −15.84 (4B, $J_{(BH)}$ unresolved), −14.68 (1B, $J_{(BH)} = 102.0$ Hz); ^{13}C NMR (DMSO, relative to Me_4Si) δ 72.80 (C_{cage}, CH not observed), 110.20 (CN); IR (KBr pellet, cm^{-1}) 2384, 2601 [ν(B–H)]. Elemental anal. Found: C, 30.21; H, 8.90; N, 11.77. Calc. for $C_6H_{21}B_{11}N_2$: C, 30.00; H, 8.81; N, 11.67%.

*Alternative method for **4a***

A 3.62 mmol (1.00 g) sample of 2-(aminopropyl)-1,2-dicarbadodecaborane hydrochloride (**3**) and sodium cyanoborohydride (0.45 g, 7.24 mmol) were dissolved in anhydrous DME (35 ml) under nitrogen atmosphere. The resulting solution was refluxed and monitored by ^{11}B NMR spectra. After 22 h of refluxing, the reaction flask was cooled to room temperature and then filtered through a glass frit to collect a clear filtrate. The white solid, collected on the frit (identified as NaCl) was discarded. The solvent, DME, was then removed from the filtrate under reduced pressure. The resulting crude white residue was purified by column chromatography (9 : $CHCl_3$: hexane) to isolate a white crystalline

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solid, identified as **4a**, in 76% yield (0.66 g, 2.75 mmol). Spectroscopic and analytical data were the same as above.

*2-[Propyl-*N*-(carbomethoxyborane)amine]-1,2-dicarbadodecaborane (**4b**)*

A 4.24 mmol (1.02 g) sample of 2-(aminopropyl)-1,2-dicarbadodecaborane (**4**) and 4.16 mmol (0.55 g) of trimethylaminecarbomethoxyborane were placed in a 100 ml round-bottom flask. Anhydrous THF was added to the reaction vessel and the contents were refluxed at 65 °C and monitored via ^{11}B NMR. After complete conversion (9.5 h), the solvent was removed and the solid obtained was recrystallized from chloroform to isolate a white crystalline solid, 2-[propyl-*N*-(carbomethoxyborane)amine]-1,2-dicarbadodecaborane (**4b**) in 66% yield (0.72 g, m.p. 105–106 °C). Spectroscopic and analytical data for **4b**: ^{1}H NMR (DMSO, relative to Me_4Si) δ 1.98 (2H, t, CH_2), 1.56 (2H, m, CH_2), 3.16 (2H, m, CH_2), 5.08 (1H, s, CH), 0.50–1.37 (12H, br, BH), 3.78 (3H, s, CH_3), 5.26 (2H, br, NH_2); ^{11}B NMR (DMSO, relative to $BF_3{\cdot}OEt_2$) δ −7.42 (1B, $J_{(BH)}$ = 126.4 Hz), −8.92 (1B, $J_{(BH)}$ = 130.82 Hz), −10.68 (2B, $J_{(BH)}$ = 139.7 Hz), −13.94 (2B, $J_{(BH)}$ unresolved), −15.82 (4B, $J_{(BH)}$ unresolved), −10.23 (1B, $J_{(BH)}$ = 96.0 Hz); ^{13}C NMR (DMSO, relative to Me_4Si) δ 71.10 (C_{cage}, CH not observed), 176.40 (C═O), 55.00 (OCH_3); IR (KBr pellet, cm^{-1}) 2246, 2574 [ν(B–H)]. Elemental anal. Found: C, 30.55; H, 8.95; N, 5.15. Calc. for $C_7H_{24}B_{11}NO_2$: C, 30.77; H, 8.86; N, 5.13%.

*2-[Propyl-*N*-(carbamoylborane)amine]-1,2-dicarbadodecaborane (**4c**)*

A 4.28 mmol (1.03 g) sample of 2-(aminopropyl)-1,2-dicarbadodecaborane (**4**) and 4.16 mmol (0.60 g) of trimethylaminecyanoborane were placed in a 100 ml round-bottom flask. Anhydrous THF was added to the reaction vessel and the contents were refluxed at 65 °C and monitored via ^{11}B NMR. After complete conversion (17 h), the solvent was removed and the solid obtained was recrystallized from methylene chloride : pentane to isolate a off-white crystalline solid, 2-[propyl-*N*-(carbamoylborane)amine]-1,2-dicarbadodecaborane (**4c**) in 65% yield (0.74 g, m.p. 100 °C). Spectroscopic and analytical data for **4c**: ^{1}H NMR (DMSO, relative to Me_4Si) δ 1.96 (2H, t, CH_2), 1.42 (2H, m, CH_2), 3.12 (2H, m, CH_2), 5.12 (1H, s, CH), 0.52–1.20 (12H, br, BH), 2.76 (2H, q, CH_2), 1.22 (3H, t, CH_3), 5.30 (2H, br, NH_2); ^{11}B NMR (DMSO, relative to $BF_3{\cdot}OEt_2$) δ −7.38 (1B, $J_{(BH)}$ = 123.6 Hz), −9.42 (1B, $J_{(BH)}$ = 128.6 Hz), −11.22 (2B, $J_{(BH)}$ = 142.3 Hz), −14.01 (2B, $J_{(BH)}$ unresolved), −16.01 (4B, $J_{(BH)}$ unresolved), −8.2 (1B, $J_{(BH)}$ = 89.0 Hz); ^{13}C NMR (DMSO, relative to Me_4Si) δ 69.20 (C_{cage}, CH not observed), 164.00 (C═O), 44.00 (NCH_2), 21.00 (CH_3); IR (KBr pellet, cm^{-1}) 2393, 2591 [ν(B–H)]. Elemental anal. Found: C, 33.63; H, 9.53; N, 9.86. Calc. for $C_8H_{27}B_{11}N_2O$: C, 33.57; H, 9.51; N, 9.79%.

*2-[Propyl-*N*-(carboxyborane)amine]-1,2-dicarbadodecaborane (**4d**)*

A 4.20 mmol (1.01 g) sample of 2-(aminopropyl)-1,2-dicarbadodecaborane (**4**) and 4.16 mmol (0.49 g) of trimethylaminecarboxyborane were placed in a 100 ml round-bottom flask. Anhydrous THF was added to the reaction vessel and the contents were refluxed at 65 °C and monitored via ^{11}B NMR. After complete conversion (22 h), the solvent was removed and the solid obtained was recrystallized from THF to isolate a white crystalline solid, 2-[propyl-*N*-(carboxyborane)amine]-1,2-dicarbadodecaborane (**4d**) in 55% yield (0.57 g, m.p. 131–133 °C). Spectroscopic and analytical data for **4d**: ^{1}H NMR (DMSO, relative to Me_4Si) δ 1.99 (2H, t, CH_2), 1.39 (2H, m, CH_2), 3.18 (2H, m, CH_2), 5.14 (1H, s, CH), 0.61–1.39 (12H, br, BH), 5.29 (2H, br, NH_2); ^{11}B NMR (DMSO, relative to $BF_3{\cdot}OEt_2$) δ −7.62 (1B, $J_{(BH)}$ = 125.8 Hz), −10.21 (1B, $J_{(BH)}$ = 126.2 Hz), −10.98 (2B, $J_{(BH)}$ = 137.9 Hz), −13.88 (2B, $J_{(BH)}$ unresolved), −16.10 (4B, $J_{(BH)}$ unresolved), −9.40 (1B, $J_{(BH)}$ = 98.0 Hz); ^{13}C NMR (DMSO, relative to Me_4Si) δ 71.6 (C_{cage}, CH not observed), 182.00 (C═O); IR (KBr pellet, cm^{-1}) 2399, 2590 [ν(B–H)]. Elemental anal. Found: C, 27.69; H, 8.65; N, 5.40. Calc. for $C_6H_{22}B_{11}NO_2$: C, 27.81; H, 8.56; N, 5.41%.

*1-Methyl-2-[propyl-*N*-(cyanoborane)amine]-1,2-dicarbadodecaborane (**6a**)*

A 3.93 mmol (1.03 g) sample of 1-methyl-2-(aminopropyl)-1,2-dicarbadodecaborane (**6**) and 3.95 mmol (0.39 g) of trimethylaminecyanoborane were dissolved in anhydrous THF (15 ml) under nitrogen atmosphere. The mixture was heated to reflux and the extent of the reaction was monitored by ^{11}B NMR spectroscopy. After 5 h, the solvent was removed under reduced pressure and the crude white solid product was then recrystallized from methylene chloride : pentane (5 : 1) to produce white crystals of 1-methyl-2-[propyl-*N*-(cyanoborane)amine]-1,2-dicarbadodecaborane (**6a**) (0.76 g, 77% yield, soluble in polar organic solvents; m.p. 95–97 °C). Spectroscopic and analytical data for **6a**: ^{1}H NMR (DMSO, relative to Me_4Si) δ 2.11 (2H, t, CH_2), 1.42 (2H, m, CH_2), 2.91 (2H, m, CH_2), 0.58–1.42 (12H, br, BH), 2.24 (3H, s, CH_3), 5.21 (2H, br, NH_2); ^{11}B NMR (DMSO, relative to $BF_3{\cdot}OEt_2$) δ −7.82 (1B, $J_{(BH)}$ = 132.4 Hz), −9.91 (1B, $J_{(BH)}$ = 141.2 Hz), −12.01 (2B, $J_{(BH)}$ = 146.8 Hz), −14.41 (2B, $J_{(BH)}$ unresolved), −16.28 (4B, $J_{(BH)}$ unresolved), −12.82 (1B, $J_{(BH)}$ = 108.0 Hz); ^{13}C NMR (DMSO, relative to Me_4Si) δ 73.20, 65.40 (C_{cage}), 113.00 (CN); IR (KBr pellet, cm^{-1}) 2395, 2566 [ν(B–H)]. Elemental anal. Found: C, 33.14; H, 8.99; N, 11.32. Calc. for $C_7H_{23}B_{11}N_2$: C, 33.07; H, 9.12; N, 11.02.

*Alternative method for **6a***

A 3.44 mmol (1.00 g) sample of 1-methyl-2-(aminopropyl)-1,2-dicarbadodecaborane hydrochloride (**5**) and sodium cyanoborohydride (0.43 g, 6.88 mmol) were dissolved in anhydrous DME (30 ml) under nitrogen atmosphere. The resulting solution was refluxed and monitored by ^{11}B NMR spectra. After 20 h of refluxing, the reaction flask was cooled to room temperature and then filtered through a glass frit to collect a clear filtrate. The white solid, collected on the frit (identified as NaCl) was discarded. The solvent, DME, was then removed from the filtrate under reduced pressure. The resulting crude white residue was purified

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by column chromatography (9 : $CHCl_3$: hexane) to isolate a white crystalline solid, identified as **6a**, in 86% yield (0.75 g, 2.95 mmol). Spectroscopic and analytical data were the same as above.

*1-Methyl-2-[propyl-*N*-(carbomethoxyborane)amine]-1,2-dicarbadodecaborane (**6b**)*

A 4.05 mmol (1.02 g) sample of 1-methyl-2-(aminopropyl)-1,2-dicarbadodecaborane (**6**) and 3.93 mmol (0.52 g) of trimethylaminecarbomethoxyborane were dissolved in anhydrous THF (25 ml) under nitrogen atmosphere. The mixture was heated to reflux and the extent of the reaction was monitored by ^{11}B NMR spectroscopy. After 15 h, the solvent was removed under reduced pressure and the crude white solid product was then recrystallized from methylene chloride : pentane : toluene (5 : 1 : 3) to produce cream crystals of 1-methyl-2-[propyl-*N*-(carbomethoxyborane)amine]-1,2-dicarbadodecaborane (**6b**) (0.84 g, 75% yield, soluble in organic solvents; m.p. 125 °C). Spectroscopic and analytical data for **6b**: ^{1}H NMR (DMSO, relative to Me_4Si) δ 2.06 (2H, t, CH_2), 1.41 (2H, m, CH_2), 3.02 (2H, m, CH_2), 3.86 (3H, s, CH_3), 0.50–1.48 (12H, br, BH), 2.21 (3H, s, CH_3), 5.31 (2H, br, NH_2); ^{11}B NMR (DMSO, relative to $BF_3{\cdot}OEt_2$) δ −7.78 (1B, $J_{(BH)} = 133.6$ Hz), −10.12 (1B, $J_{(BH)} = 140.8$ Hz), −12.24 (2B, $J_{(BH)} = 144.6$ Hz), −14.38 (2B, $J_{(BH)}$ unresolved), −16.31 (4B, $J_{(BH)}$ unresolved), −8.27 (1B, $J_{(BH)} = 100.0$ Hz); ^{13}C NMR (DMSO, relative to Me_4Si) δ 72.91, 64.80 (C_{cage}), 175.60 (C═O), 52.90 (OCH_3); IR (KBr pellet, cm^{-1}) 2421, 2581 [ν(B–H)]; Elemental anal. Found: C, 33.20; H, 8.91; N, 4.90. Calc. for $C_8H_{26}B_{11}NO_2$: C, 33.45; H, 9.13; N, 4.88%.

*1-Methyl-2-[propyl-*N*-(methylcarbonyl-L-phenylalanine)amine]-1,2-dicarbadodecaborane (**6c**)*

A 3.96 mmol (1.01 g) sample of 1-methyl-2-(propylamine)-1,2-dicarbadodecaborane (**6**) and 3.93 mmol (1.09 g) of trimethylamineborylcarbonylphenylalanine methylester were dissolved in anhydrous THF (20 ml) under nitrogen atmosphere. The mixture was heated to reflux and the extent of the reaction was monitored by ^{11}B NMR spectroscopy. After 9 h, the solvent was removed under reduced pressure and the crude white solid product was then recrystallized from acetone : chloroform : pentane (5 : 4 : 1) to produce white crystals of 1-methyl-2-[propyl-*N*-(methylcarbonyl-L-phenylalanine)amine]-1,2-dicarbadodecaborane (**6c**) (1.01 g, 59% yield, m.p. >200 °C, decomposed). Spectroscopic and analytical data for **6c**: ^{1}H NMR (DMSO, relative to Me_4Si) δ 2.02 (2H, t, CH_2), 1.43 (2H, m, CH_2), 3.11 (2H, m, CH_2), 2.11 (3H, s, CH_3), 0.52–1.42 (12H, br, BH), 3.28 (1H, t, CH), 3.83 (3H, s, CH_3), 3.10 (2H, d, CH_2), 7.78 (5H, m, aromatic), 5.21 (2H, br, NH_2); ^{11}B NMR (DMSO, relative to $BF_3{\cdot}OEt_2$) δ −7.46 (1B, $J_{(BH)} = 128.4$ Hz), −9.02 (1B, $J_{(BH)} = 131.6$ Hz), −10.91 (2B, $J_{(BH)} = 143.1$ Hz), −14.21 (2B, $J_{(BH)}$ unresolved), −16.11 (4B, $J_{(BH)}$ unresolved), −9.90 (1B, $J_{(BH)} = 101.0$ Hz); ^{13}C NMR (DMSO, relative to Me_4Si) δ 76.40, 72.50 (C_{cage}), 55.10 (OCH_3), 129.60 (aromatic), 26.40 (CH_2), 41.30 (CH), 169.80 (C═O); IR (KBr pellet, cm^{-1}) 2379, 2612 [ν(B–H)]. Elemental anal. Found: C, 47.15; H, 7.90; N, 6.66. Calc. for $C_{17}H_{35}B_{11}N_2O_3$: C, 47.11; H, 7.91; N, 6.47%.

*1-Methyl-2-[propyl-*N*-(methylcarbonyl-L-alanine)amine]-1,2-dicarbadodecaborane (**6d**)*

A 4.04 mmol (1.03 g) sample of 1-methyl-2-(propylamine)-1,2-dicarbadodecaborane (**6**) and 3.93 mmol (0.80 g) of trimethylamineborylcarbonylalanine methylester were dissolved in anhydrous THF (25 ml) under nitrogen atmosphere. The mixture was heated to reflux and the extent of the reaction was monitored by ^{11}B NMR spectroscopy. After 21 h, the solvent was removed under reduced pressure and the crude white solid product was then recrystallized from chloroform : pentane (9 : 1) to produce white crystals of 1-methyl-2-[propyl-*N*-(methylcarbonyl-L-alanine)amine]-1,2-dicarbadodecaborane (**6d**) (0.80 g, 57% yield, m.p. >200 °C, decomposed). Spectroscopic and analytical data for **6d**: ^{1}H NMR (DMSO, relative to Me_4Si) δ 2.19 (2H, t, CH_2), 1.52 (2H, m, CH_2), 3.10 (2H, m, CH_2), 2.12 (3H, s, CH_3), 0.46–1.15 (12H, br, BH), 3.82 (3H, s, CH_3), 3.08 (1H, q, CH), 1.12 (3H, d, CH_3), 5.25 (2H, br, NH_2); ^{11}B NMR (DMSO, relative to $BF_3{\cdot}OEt_2$) δ −7.58 (1B, $J_{(BH)} = 133.7$ Hz), −10.22 (1B, $J_{(BH)} = 134.1$ Hz), −11.02 (2B, $J_{(BH)} = 142.9$ Hz), −14.40 (2B, $J_{(BH)}$ unresolved), −16.41 (4B, $J_{(BH)}$ unresolved), −10.02 (1B, $J_{(BH)} = 104.0$ Hz); ^{13}C NMR (DMSO, relative to Me_4Si) δ 76.00, 74.30 (C_{cage}), 54.30 (OCH_3), 22.00 (CH_3), 42.40 (CH), 166.80 (C═O); IR (KBr pellet, cm^{-1}) 2286, 2482 [ν(B–H)]. Elemental anal. Found: C, 37.05; H, 8.79; N, 7.91. Calc. for $C_{11}H_{31}B_{11}N_2O_3$: C, 36.85; H, 8.72; N, 7.82%.

*1-Methyl-2-[propyl-*N*-(methylcarbonyl-L-valine)amine]-1,2-dicarbadodecaborane (**6e**)*

A 3.96 mmol (1.01 g) sample of 1-methyl-2-(propylamine)-1,2-dicarbadodecaborane (**6**) and 3.93 mmol (0.91 g) of trimethylamineborylcarbonylvaline methylester were dissolved in anhydrous THF (20 ml) under nitrogen atmosphere. The mixture was heated to reflux and the extent of the reaction was monitored by ^{11}B NMR spectroscopy. After 21 h, the solvent was removed under reduced pressure and the crude white solid product was then recrystallized from acetone : pentane (7 : 3) to produce off-white crystals of 1-methyl-2-[propyl-*N*-(methylcarbonyl-L-valine)amine]-1,2-dicarbadodecaborane (**6e**) (0.81 g, 54% yield, m.p. >250 °C, decomposed). Spectroscopic and analytical data for **6e**: ^{1}H NMR (DMSO, relative to Me_4Si) δ 2.10 (2H, t, CH_2), 1.40 (2H, m, CH_2), 3.07 (2H, m, CH_2), 2.20 (3H, s, CH_3), 0.48–1.20 (12H, br, BH), 3.05 (1H, d, CH), 3.89 (3H, s, CH_3), 1.17 (6H, d, CH_3), 1.68 (1H, m, CH), 5.42 (2H, br, NH_2); ^{11}B NMR (DMSO, relative to $BF_3{\cdot}OEt_2$) δ −7.71 (1B, $J_{(BH)} = 134.8$ Hz), −10.16 (1B, $J_{(BH)} = 132.8$ Hz), −11.24 (2B, $J_{(BH)} = 143.2$ Hz), −14.26 (2B, $J_{(BH)}$ unresolved), −16.38 (4B, $J_{(BH)}$ unresolved), −10.41 (1B, $J_{(BH)} = 104.0$ Hz); ^{13}C NMR (DMSO, relative to Me_4Si) δ 72.80, 77.90 (C_{cage}), 54.30 (OCH_3), 44.00, 27.00 (CH), 22.00 (CH_3), 162.40 (C═O); IR (KBr pellet, cm^{-1}) 2277, 2528 [ν(B–H)]. Elemental anal. Found: C, 40.55;

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H, 9.21; N, 7.30. Calc. for $C_{13}H_{35}B_{11}N_2O_3$: C, 40.41; H, 9.13; N, 7.25%.

*1-Methyl-2-[propyl-*N*-(methylcarbonyl-L-tyrosine)amine]-1,2-dicarbadodecaborane (**6f**)*

A 4.08 mmol (1.04 g) sample of 1-methyl-2-(propylamine)-1,2-dicarbadodecaborane (**6**) and 3.94 mmol (1.16 g) of trimethylamineborylcarbonyltyrosine methylester were dissolved in anhydrous THF (35 ml) under nitrogen atmosphere. The mixture was heated to reflux and the extent of the reaction was monitored by ^{11}B NMR spectroscopy. After 25 h, the solvent was removed under reduced pressure and the crude white solid product was then recrystallized from dichloromethane : acetone : pentane (5 : 3 : 2) to produce yellowish-white crystals of 1-methyl-2-[propyl-*N*-(methylcarbonyl-L-tyrosine)amine]-1,2-dicarbadodecaborane (**6f**) (0.86 g, 49% yield, m.p. >250 °C, decomposed). Spectroscopic and analytical data for **6f**: ^{1}H NMR (DMSO, relative to Me_4Si) δ 2.14 (2H, t, CH_2), 1.42 (2H, m, CH_2), 3.19 (2H, m, CH_2), 2.07 (3H, s, CH_3), 0.40–1.16 (12H, br, BH), 3.81 (3H, s, CH_3), 3.01 (1H, t, CH), 2.99 (2H, d, CH_2), 7.65 (4H, m, aromatic), 5.39 (2H, br, NH_2); ^{11}B NMR (DMSO, relative to $BF_3{\cdot}OEt_2$) δ −7.76 (1B, $J_{(BH)}$ = 131.4 Hz), −11.01 (1B, $J_{(BH)}$ = 141.1 Hz), −13.26 (2B, $J_{(BH)}$ = 141.3 Hz), −15.61 (2B, $J_{(BH)}$ unresolved), −16.44 (4B, $J_{(BH)}$ unresolved), −9.24 (1B, $J_{(BH)}$ = 104.6 Hz); ^{13}C NMR (DMSO, relative to Me_4Si) δ 73.40, 76.80 (C_{cage}), 163.80 (C═O), 54.20 (OCH_3), 25.00 (CH_2), 46.00 (CH), 128.60–131.00 (aromatic); IR (KBr pellet, cm^{-1}) 2450, 2563 [ν(B–H)]. Elemental anal. Found: C, 45.35; H, 7.99; N, 6.44. Calc. for $C_{17}H_{35}B_{11}N_2O_4$: C, 45.33; H, 7.83; N, 6.22%.

*1-Phenyl-2-[propyl-*N*-(cyanoborane)amine]-1,2-dicarbadodecaborane (**8a**)*

A 3.14 mmol (1.01 g) sample of 1-phenyl-2-(aminopropyl)-1,2-dicarbadodecaborane (**8**) and 3.15 mmol (0.32 g) of trimethylaminecyanoborane were dissolved in anhydrous THF (20 ml) under nitrogen atmosphere. The mixture was heated to reflux and the extent of the reaction was monitored by ^{11}B NMR spectroscopy. After 11 h, the solvent was removed under reduced pressure and the crude white solid product was then recrystallized from methylene chloride : pentane (7 : 1) to produce white crystals of 1-phenyl-2-[propyl-*N*-(cyanoborane)amine]-1,2-dicarbadodecaborane (**8a**) (0.68 g, 67% yield; m.p. 105–106 °C). Spectroscopic and analytical data for **8a**: ^{1}H NMR (DMSO, relative to Me_4Si) δ 2.12 (2H, t, CH_2), 1.39 (2H, m, CH_2), 3.03 (2H, m, CH_2), 0.46–1.48 (12H, br, BH), 7.80–8.10 (5H, m, phenyl), 5.12 (2H, br, NH_2); ^{11}B NMR (DMSO, relative to $BF_3{\cdot}OEt_2$) δ −7.18 (1B, $J_{(BH)}$ = 129.8 Hz), −9.25 (1B, $J_{(BH)}$ = 133.8 Hz), −11.32 (2B, $J_{(BH)}$ = 140.28 Hz), −13.36 (2B, $J_{(BH)}$ unresolved), −15.71 (4B, $J_{(BH)}$ unresolved), −12.26 (1B, $J_{(BH)}$ = 110.0 Hz); ^{13}C NMR (DMSO, relative to Me_4Si) δ 89.20, 85.00 (C_{cage}), 127.80 (aromatic), 118.00 (CN); IR (KBr pellet, cm^{-1}) 2429, 2380 [ν(B–H)]. Elemental anal. Found: C, 45.59; H, 8.18; N, 8.91. Calc. for $C_{12}H_{25}B_{11}N_2$: C, 45.57; H, 7.97; N, 8.86%.

*Alternative method for **8a***

A 2.82 mmol (1.00 g) sample of 1-phenyl-2-(aminopropyl)-1,2-dicarbadodecaborane hydrochloride (**7**) and sodium cyanoborohydride (0.35 g, 5.64 mmol) were dissolved in anhydrous DME (15 ml) under nitrogen atmosphere. The resulting solution was refluxed and monitored by ^{11}B NMR spectra. After 16.5 h of refluxing, the reaction flask was cooled to room temperature and then filtered through a glass frit to collect a clear filtrate. The white solid, collected on the frit (identified as NaCl) was discarded. The solvent, DME, was then removed from the filtrate under reduced pressure. The resulting crude white residue was purified by column chromatography (7.3 : EtOAc : hexane) to isolate a white crystalline solid, identified as **8a**, in 84% yield (0.75 g, 2.36 mmol). Spectroscopic and analytical data were the same as above.

*1-Phenyl-2-[propyl-*N*-(carbomethoxyborane)amine]-1,2-dicarbadodecaborane (**8b**)*

A 3.20 mmol (1.02 g) sample of 1-phenyl-2-(aminopropyl)-1,2-dicarbadodecaborane (**8**) and 3.14 mmol (0.41 g) of trimethylaminecarbomethoxyborane were dissolved in anhydrous THF (25 ml) under nitrogen atmosphere. The mixture was heated to reflux and the extent of the reaction was monitored by ^{11}B NMR spectroscopy. After 11 h, the solvent was removed under reduced pressure and the crude white solid product was then recrystallized from chloroform : pentane (3 : 1) to produce white crystals of 1-phenyl-2-[propyl-*N*-(carbomethoxyborane)amine]-1,2-dicarbadodecaborane (**8b**) (0.76 g, 68% yield; m.p. 125 °C). Spectroscopic and analytical data for **8b**: ^{1}H NMR (DMSO, relative to Me_4Si) δ 2.20 (2H, t, m, CH_2), 1.43 (2H, m, CH_2), 3.12 (2H, m, CH_2), 3.73 (3H, s, CH_3), 0.60–1.43 (12H, br, BH), 7.82–7.98 (5H, m, phenyl), 5.17 (2H, br, NH_2); ^{11}B NMR (DMSO, relative to $BF_3{\cdot}OEt_2$) δ −7.21 (1B, $J_{(BH)}$ = 126.3 Hz), −9.18 (1B, $J_{(BH)}$ = 130.8 Hz), −10.23 (2B, $J_{(BH)}$ = 139.62 Hz), −13.13 (2B, $J_{(BH)}$ unresolved), −15.58 (4B, $J_{(BH)}$ unresolved), −9.02 (1B, $J_{(BH)}$ 98.0 Hz); ^{13}C NMR (DMSO, relative to Me_4Si) δ 88.40, 86.10 (C_{cage}), 129.50 (aromatic), 172.00 (C═O), 53.4 (OCH_3); IR (KBr pellet, cm^{-1}) 2412, 2592 [ν(B–H)]. Elemental anal. Found: C, 44.74; H, 8.22; N, 3.95. Calc. for $C_{13}H_{28}B_{11}NO_2$: C, 44.72; H, 8.04; N, 4.01%.

*1-Phenyl-2-[propyl-*N*-(methylcarbonyl-L-phenylalanine)amine]-1,2-dicarbadodecaborane (**8c**)*

A 3.17 mmol (1.01 g) sample of 1-phenyl-2-(propylamine)-1,2-dicarbadodecaborane (**8**) and 3.14 mmol (0.87 g) of trimethylamineborylcarbonylphenylalanine methylester were dissolved in anhydrous THF (15 ml) under nitrogen atmosphere. The mixture was heated to reflux and the extent of the reaction was monitored by ^{11}B NMR spectroscopy. After 12 h, the solvent was removed under reduced pressure and the crude white solid product was then recrystallized from acetone : chloroform : pentane (7 : 2 : 1) to produce white crystals of 1-phenyl-2-[propyl-*N*-(methylcarbonyl-L-phenylalanine)amine]-1,2-dicarbadodecaborane (**8c**) (0.95 g, 60% yield, m.p. >250 °C, decomposed). Spectroscopic and

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analytical data for **8c**: ^{1}H NMR (DMSO, relative to Me_4Si) δ 2.19 (2H, t, CH_2), 1.38 (2H, m, CH_2), 3.01 (2H, m, CH_2), 0.75–1.33 (12H, br, BH), 3.78 (3H, s, CH_3), 3.01 (1H, t, CH), 3.12 (2H, d, CH_2), 7.26–7.90 (10H, m, aromatic), 5.15 (2H, br, NH_2); ^{11}B NMR (DMSO, relative to $BF_3 \cdot OEt_2$) δ −7.10 (1B, $J_{(BH)} = 126.7$ Hz), −9.31 (1B, $J_{(BH)} = 135.1$ Hz), −11.28 (2B, $J_{(BH)} = 141.62$ Hz), −13.72 (2B, $J_{(BH)}$ unresolved), −15.52 (4B, $J_{(BH)}$ unresolved), −8.30 (1B, $J_{(BH)} = 94.0$ Hz); ^{13}C NMR (DMSO, relative to Me_4Si) δ 89.20 (C_{cage}), 168.00 (C═O), 128.6 (aromatic), 53.9 (OCH_3), 24.00 (CH_2), 42.00 (CH); IR (KBr pellet, cm^{-1}) 2444, 2573 (ν(B–H)). Elemental anal. Found: C, 53.25; H, 7.55; N, 5.42. Calc. for $C_{22}H_{37}B_{11}N_2O_3$: C, 53.22; H, 7.51; N, 5.64%.

*1-Phenyl-2-[propyl-*N*-(methylcarbonyl-L-alanine)amine]-1,2-dicarbadodecaborane (**8d**)*

A 3.26 mmol (1.04 g) sample of 1-phenyl-2-(propylamine)-1,2-dicarbadodecaborane (**8**) and 3.14 mmol (0.64 g) of trimethylamineborylcarbonylalanine methylester were dissolved in anhydrous THF (25 ml) under nitrogen atmosphere. The mixture was heated to reflux and the extent of the reaction was monitored by ^{11}B NMR spectroscopy. After 8 h, the solvent was removed under reduced pressure and the crude yellow solid product was then recrystallized from acetone : pentane (7 : 1) to produce yellow crystals of 1-phenyl-2-[propyl-*N*-(methylcarbonyl-L-alanine)amine]-1,2-dicarbadodecaborane (**8d**) (0.79 g, 59% yield, m.p. >200 °C, decomposed). Spectroscopic and analytical data for **8d**: ^{1}H NMR (DMSO, relative to Me_4Si) δ 2.21 (2H, t, CH_2), 1.41 (2H, m, CH_2), 3.11 (2H, m, CH_2), 0.46–1.28 (12H, br, BH), 1.12 (3H, d, CH_3), 3.82 (3H, s, CH_3), 3.10 (1H, q, CH), 7.82 (5H, m, aromatic), 5.25 (2H, br, NH_2); ^{11}B NMR (DMSO, relative to $BF_3 \cdot OEt_2$) δ −7.24 (1B, $J_{(BH)} = 129.2$ Hz), −10.01 (1B, $J_{(BH)} = 136.8$ Hz), −11.76 (2B, $J_{(BH)} = 138.8$ Hz), −13.68 (2B, $J_{(BH)}$ unresolved), −15.84 (4B, $J_{(BH)}$ unresolved), −10.01 (1B, $J_{(BH)} = 94.6$ Hz); ^{13}C NMR (DMSO, relative to Me_4Si) δ 88.70, 84.30 (C_{cage}), 166.40 (C═O), 128.0 (aromatic), 52.00 (OCH_3), 42.00 (CH); IR (KBr pellet, cm^{-1}) 2449, 2375 [ν(B–H)]. Elemental anal. Found: C, 45.75; H, 8.00; N, 6.67. Calc. for $C_{16}H_{33}B_{11}N_2O_3$: C, 45.71; H, 7.91; N, 6.70%.

*1-Phenyl-2-[propyl-*N*-(methylcarbonyl-L-valine)amine]-1,2-dicarbadodecaborane (**8e**)*

A 3.14 mmol (1.01 g) sample of 1-phenyl-2-(propylamine)-1,2-dicarbadodecaborane (**8**) and 3.19 mmol (0.73 g) of trimethylamineborylcarbonylvaline methylester were dissolved in anhydrous THF (25 ml) under nitrogen atmosphere. The mixture was heated to reflux and the extent of the reaction was monitored by ^{11}B NMR spectroscopy. After 33 h, the solvent was removed under reduced pressure and the crude white solid product was then recrystallized from dichloromethane : chloroform : pentane (5 : 4 : 1) to produce yellow crystals of 1-phenyl-2-[propyl-*N*-(methylcarbonyl-L-valine)amine]-1,2-dicarbadodecaborane (**8e**) (0.83 g, 58% yield, m.p. >200 °C, decomposed). Spectroscopic and analytical data for **8e**: ^{1}H NMR (DMSO, relative to Me_4Si) δ 2.16 (2H, t, CH_2), 1.44 (2H, m, CH_2), 3.08 (2H, m, CH_2), 0.5–1.20 (12H, br, BH), 3.76 (3H, s, CH_3), 3.07 (1H, d, CH), 1.71 (1H, m, CH), 1.16 (6H, d, CH_3), 7.78 (5H, m, aromatic), 5.42 (2H, br, NH_2); ^{11}B NMR (DMSO, relative to $BF_3 \cdot OEt_2$) δ − 7.18 (1B, $J_{(BH)} = 127.3$ Hz), −9.42 (1B, $J_{(BH)} = 137.2$ Hz), −11.42 (2B, $J_{(BH)} = 143.4$ Hz), −14.07 (2B, $J_{(BH)}$ unresolved), −15.98 (4B, $J_{(BH)}$ unresolved), −8.90 (1B, $J_{(BH)} = 89.0$ Hz); ^{13}C NMR (DMSO, relative to Me_4Si) δ 86.42, 83.40 (C_{cage}), 168.20 (C═O), 129.5 (aromatic), 54.00 (OCH_3), 21.00 (CH_3), 44.26 (CH); IR (KBr pellet, cm^{-1}) 2456, 2532 [ν(B–H)]. Elemental anal. Found: C, 48.33; H, 8.42; N, 6.27. Calc. for $C_{18}H_{37}B_{11}N_2O_3$: C, 48.21; H, 8.31; N, 6.25%.

*1-Phenyl-2-[propyl-*N*-(methylcarbonyl-L-tyrosine)amine]-1,2-dicarbadodecaborane (**8f**)*

A 3.23 mmol (1.03 g) sample of 1-phenyl-2-(propylamine)-1,2-dicarbadodecaborane (**8**) and 3.14 mmol (0.92 g) of trimethylamineboryltyrosine methylester were dissolved in anhydrous THF (15 ml) under nitrogen atmosphere. The mixture was heated to reflux and the extent of the reaction was monitored by ^{11}B NMR spectroscopy. After 12 h, the solvent was removed under reduced pressure and the crude white solid product was then recrystallized from chloroform : pentane (9 : 1) to produce white crystals of 1-phenyl-2-[propyl-*N*-(methylcarbonyl-L-tyrosine)amine]-1,2-dicarbadodecaborane (**8f**) (0.85 g, 52% yield, m.p. >250 °C, decomposed). Spectroscopic and analytical data for **8f**: ^{1}H NMR (DMSO, relative to Me_4Si) δ 2.11 (2H, t, CH_2), 1.47 (2H, m, CH_2), 3.09 (2H, m, CH_2), 0.50–1.30 (12H, br, BH), 2.98 (2H, d, CH_2), 3.81 (3H, s, CH_3), 3.01 (1H, t, CH), 7.30–7.90 (9H, m, aromatic), 5.30 (2H, br, NH_2); ^{11}B NMR (DMSO, relative to $BF_3 \cdot OEt_2$) δ −7.22 (1B, $J_{(BH)} = 125.6$ Hz), −8.89 (1B, $J_{(BH)} = 129.6$ Hz), −10.92 (2B, $J_{(BH)} = 136.4$ Hz), −13.48 (2B, $J_{(BH)}$ unresolved, −15.94 4B, $J_{(BH)}$ unresolved), −9.20 (1B, $J_{(BH)} = 99.0$ Hz); ^{13}C NMR (DMSO, relative to Me_4Si) δ 89.80, 85.60 (C_{cage}), 168.40 (C═O), 129.00–131.50 (aromatic), 54.20 (OCH_3), 24.80 (CH_2), 44.00 (CH); IR (KBr pellet, cm^{-1}) 2552, 2386 [ν(B–H)]. Elemental anal. Found: C, 51.66; H, 7.32; N, 5.49. Calc. for $C_{22}H_{37}B_{11}N_2O_4$: C, 51.56; H, 7.28; N, 5.47%.

*1,2-[*N*-(Trimethylamineborane)carboxyl]-1,2-dicarbadodecaborane (**9a**)*

An 8.55 mmol (5.0 ml of 1.7 M in cyclohexane) sample of *n*-BuLi was syringed into a cold solution of 1,2-bis-(carboxy)-1,2-dicarbadodecaborane (1.00 g, 4.27 mmol) in DME. After warming to room temperature, a DME solution (1.60 g, 8.57 mmol) of trimethylaminemonoiodoborane (Me_3NBH_2I) was added and then refluxed for 10 h and was monitored by running ^{11}B NMR spectra of the products. After cooling the flask to room temperature, the solvent was removed *in vacuo* and the resulting crude white solid residue was purified by column chromatography (ethylacetate (90%)/hexane(10%)) to isolate white crystals, identified as 1,2-[*N*-(trimethylamineborane)carboxyl]-1,2-dicarbadodecaborane (**9a**), in 58% (0.84 g) yield. Spectroscopic and analytical data for **9a**: ^{1}H NMR (DMSO,

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relative to Me_4Si) δ 0.50–1.53 (14H, br, BH), 2.20 (18H, s, CH_3); ^{11}B NMR (DMSO, relative to $BF_3{\cdot}OEt_2$) δ −5.86 (2B, $J_{(BH)} = 144.0$ Hz), −9.21 (2B, $J_{(BH)} = 151.0$ Hz), −12.82 (4B, $J_{(BH)} = 160.0$ Hz), −14.01 (2B, $J_{(BH)} = 172.0$ Hz), −10.21 (2B, $J_{(BH)} = 100.0$ Hz); ^{13}C NMR (DMSO, relative to Me_4Si) δ 72.60 (C_{cage}), 178.00 (C═O), 40.4 (NCH_3); IR (KBr pellet, cm^{-1}) 2571, 2399 [ν(B–H)]. Elemental anal. Found: C, 32.30; H, 8.66; N, 7.79. Calc. for $C_{10}H_{32}B_{12}N_2O_4$: C, 32.10; H, 8.62; N, 7.49%.

*1-Methyl-2-[*N*-(trimethylamineborane)carboxyl]-1,2-dicarbadodecaborane (**10a**)*

A 4.93 mmol (3.0 ml of 1.7 M in cyclohexane) sample of *n*-BuLi was syringed into a cold solution of 1-methyl-2-(carboxy)-1,2-dicarbadodecaborane (1.00 g, 4.98 mmol) in DME. After warming to room temperature, a DME solution (0.92 g, 4.95 mmol) of trimethylaminemonoiodoborane (Me_3NBH_2I) was added and then refluxed for 7 h and was monitored by running ^{11}B NMR spectra of the products. After cooling the flask to room temperature, the solvent was removed *in vacuo* and the resulting crude off-white solid residue was purified by column chromatography (ethylacetate (70%)/hexane(30%)) to isolate off-white crystals, identified as 1-methyl-2-[*N*-(trimethylamineborane)carboxyl]-1,2-dicarbadodecaborane (**10a**), in 56% (0.73 g) yield. Spectroscopic and analytical data for **10a**: ^1H NMR (DMSO, relative to Me_4Si) δ 0.46–1.58 (12H, br, BH), 2.26 (3H, s, CH_3), 2.08 (9H, s, CH_3); ^{11}B NMR (DMSO, relative to $BF_3 \cdot OEt_2$) δ −7.72 (1B, $J_{(BH)} = 125.8$ Hz), −9.48 (1B, $J_{(BH)} = 141.8$ Hz), −12.24 (2B, $J_{(BH)} = 145.8$ Hz), −14.15 (2B, $J_{(BH)}$ unresolved), −15.98 (4B, $J_{(BH)}$ unresolved), −10.41 (1B, $J_{(BH)} = 97.0$ Hz); ^{13}C NMR (DMSO, relative to Me_4Si) δ 68.40, 72.68 (C_{cage}), 176.00 (C═O), 41.60 (NCH_3); IR (KBr pellet, cm^{-1}) 2479, 2386 [ν(B–H)]. Elemental anal. Found: C, 30.59; H, 8.88; N, 5.37. Calc. for $C_7H_{24}B_{11}NO_2$: C, 30.77; H, 8.86; N, 5.13%.

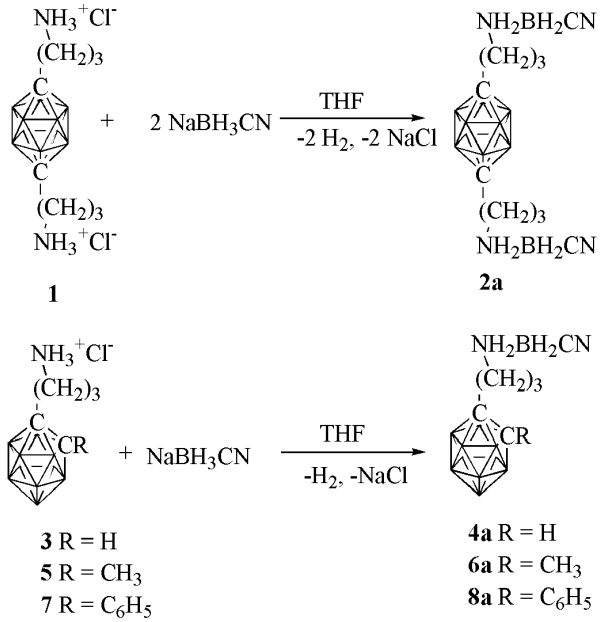
*1-Phenyl-2-[*N*-(trimethylamineborane)carboxyl]-1,2-dicarbadodecaborane (**11a**)*

A 3.78 mmol (2.7 ml of 1.7 M in cyclohexane) sample of *n*-BuLi was syringed into a cold solution of 1-phenyl-2-(carboxy)-1,2-dicarbadodecaborane (1.00 g, 3.79 mmol) in DME. After warming to room temperature, a DME solution (0.70 g, 3.81 mmol) of trimethylaminemonoiodoborane (Me_3NBH_2I) was added and then refluxed for 15 h and was monitored by running ^{11}B NMR spectra of the products. After cooling the flask to room temperature, the solvent was removed *in vacuo* and the resulting crude off-white solid residue was purified by column chromatography [ethylacetate (70%)/hexane (20%)/dichloromethane(10%)] to isolate cream crystals, identified as 1-phenyl-2-[*N*-(trimethylamineborane)carboxyl]-1,2-dicarbadodecaborane (**11a**), in 54% (0.65 g) yield. Spectroscopic and analytical data for **11a**: ^1H NMR (DMSO, relative to Me_4Si) δ 0.53–1.46 (12H, br, BH), 2.12 (9H, s, CH_3), 7.60–8.00 (5H, m, phenyl); ^{11}B NMR (DMSO, relative to $BF_3 \cdot OEt_2$) δ −7.18 (1B, $J_{(BH)} = 131.8$ Hz), −9.62 (1B, $J_{(BH)} = 132.9$ Hz), −11.48 (2B, $J_{(BH)} = 142.7$ Hz), −13.68 (2B, $J_{(BH)}$ unresolved), −15.89 (4B, $J_{(BH)}$), −11.02 (1B, $J_{(BH)} = 90.0$ Hz); ^{13}C NMR (DMSO, relative to Me_4Si) δ 75.80, 85.60 (C_{cage}), 128.60 (aromatic), 182.00 (C═O), 42.20 [NCH_3]; IR (KBr pellet, cm^{-1}) 2488, 2389 [ν(B–H)]. Elemental anal. Found: C, 43.11; H, 7.88; N, 4.28.Calc. for $C_{12}H_{26}B_{11}NO_2$: C, 42.99; H, 7.82; N, 4.18%.

RESULTS AND DISCUSSION

Synthesis and characterization

A number of carboranylamineboranes and esters were synthesized by the amine exchange reaction of the bis(C_{cage}–amine) carborane, 1,12-$[(CH_2)_3NH_2]_2$-1,12-$C_2B_{10}H_{10}$ (**2**) with the amineboranes of the type Me_3NBH_2X to produce a series of new carboranylamineboranes of the form 1,12-$[(CH_2)_3NH_2BH_2X]_2$-1,12-$C_2B_{10}H_{10}$ [X = CN (**2a**), $COOCH_3$ (**2b**), CONHEt (**2c**), $CONHCH(CH_2C_6H_5)COOMe$ (**2d**), $CONHCH(CH_3)COOMe$ (**2e**), $CONHCH(CHMe_2)COOMe$ (**2f**), $CONHCH(4\text{-}CH_2C_6H_4OH)COOMe$ (**2g**)], as shown in Scheme 1. The yields ranged from 78% for **2a** to 50% for **2g**. In general, the reaction with the amineboranes, to produce **2a–2c**, gave yields in the region of 70%, whereas the amideborane products, **2d–2g**, had yields in the region of 50%. Since the X groups associated with the amideboranes are substantially larger than those of the amineboranes (see Scheme 1), it is not known whether the consistently lower yields for the former are due to steric effects or the influence of the amide linkage. The reaction of 1,12-$[(CH_2)_3NH_3Cl]_2$-1,12-$C_2B_{10}H_{10}$ (**1**) with $NaBH_3CN$ (commercially available from Aldrich Chemical Company) provided an alternate route to **2a** at a higher yield (86%) (see Scheme 2). However, the method outlined in Scheme 1 is a more general synthetic route with only slightly lower yields. We also synthesized **2h** (C_{cage}–amine) carborane, 1-$(CH_2NH_2BH_2CN)$-1,2-$C_2B_{10}H_{10}$ shown in Scheme 1 to



Scheme 2. Synthetic of carboranyl amineboranes.

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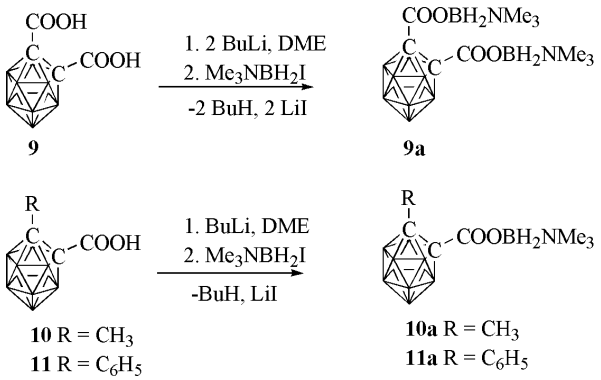
show that methyl derivatives of aminecarbonylboranes can also be synthesized in good yields.

An additional series of novel amine and amide carboranylboranes, **4a–4d**, **6a–6f**, and **8a–8f**, could be synthesized from the reaction of the monoamine carboranes, 1-[$(CH_2)_3NH_2$]-2-R-1,2-$C_2B_{10}H_{10}$ [R = H (**4**), CH_3 (**6**) and C_6H_5 (**8**)] with the trimethyl amine boranes, Me_3NBH_2X, where X spans the same substituent groups as used with the bis(amine)-*p*-carborane (**2**). The formulations and methods of preparation are summarized in Schemes 1 and 2. In general, the yields for these reactions are in the range of 77% (**6a**) to 52% (**8f**) and parallel those found for the bis-*p*-carboranes, **2a–2g**. As with the bis(amine)-*p*-carboranes, the amideboranes gave lower yields than did the amineboranes. The mono- and bis-amine carboranes are also similar, in that the use of $NaBH_3CN$ rather than Me_3NBH_2CN gave improved yields of **4a, 5a** and **6a**.

Schemes 1 and 2 show the different routes to the carboranylamineboranes; it is also possible to synthesize a series of carboranyl boronesters, as shown in Scheme 3. As shown in the scheme, the reaction of either 1,2-$(COOH)_2$-1,2-$C_2B_{10}H_{10}$ (**9**) or 1-(COOH)-2-(R)-1,2-$C_2B_{10}H_{10}$ [R = CH_3 (**10**), C_6H_5 (**11**)] with BuLi followed by treatment with Me_3NBH_2I produced the corresponding boranoesters, 1,2-$(COOBH_2NMe_3)_2$-1,2-$C_2B_{10}H_{10}$ (**9a**) or 1-$(COOBH_2NMe_3)$-2-(R)-1,2-$C_2B_{10}H_{10}$ [R = CH_3 (**10a**), C_6H_5 (**11a**)]. The yields of these reactions are quite similar being 58%, 56% and 54% for **9a, 10a** and **11a** respectively. The low yields for these compounds are due to loss of the product during work up. Although these yields are only modest, they are sufficiently high so as to provide a path for compounds that could be tested for therapeutic behavior.

All the compounds were characterized by ^1H, ^{11}B, ^{13}C NMR and IR spectroscopy. The IR spectra of all the products show the expected absorptions for the carborane B–H stretching in the region 2500–2615 cm^{-1}, with the exopolyhedral borane bands appearing at slightly lower energies (2238–2491 cm^{-1}). In the same way, the ^1H, ^{11}B, ^{13}C NMR spectra show resonances that are consistent with the formulations given in Schemes 1–3. For example, the ^{13}C NMR spectra of



Scheme 3. Synthesis of carboranyl esters.

compounds containing cyano functionality (**2a, 4a, 6a, 8a**) showed a peak in the range of 110–116 ppm and peaks between 75 and 88 ppm due to the cage carbon atoms of the carborane. For compounds containing a carbomethoxy group (**2b, 4b, 6b, 8b**), ^{13}C NMR spectra showed a peak in the range of 174–182 ppm (carbonyl), a peak at 54–58 ppm for the OCH_3 group and peaks between 76 and 87 ppm due to the cage carbon atoms of the carborane. For compounds containing a carbamoyl group (**2c, 4c**), ^{13}C NMR spectra showed a peak in the range of 162–176 ppm (carbonyl), a peak at 42–48 ppm for the NCH_2 group and peaks between 77 and 86 ppm due to the cage carbon atoms of the carborane. For compounds containing amino acids (**2d–g, 6c–f, 8c–f**), ^{13}C NMR spectra showed peaks corresponding to the side chain of the phenylalanine, alanine, valine and tyrosine amino acids and peaks between 76 and 89 ppm due to the cage carbon atoms of the carborane. For compounds **9a, 10a** and **11a**, ^{13}C NMR spectra showed a peak in the range of 176–182 ppm for the carbonyl group and peaks between 75 and 87 ppm due to the cage carbon atoms of the carborane. The ^{11}B NMR spectra showed peaks in the range of −7 to −16 ppm corresponding to the carborane present in all the compounds. For disubstituted amino *p*-carborane (**2a–2g**), two peaks were observed in the region −6.5 to −16.34 ppm. For monosubstituted amino *o*-, methyl- and phenyl-carboranes (**4a–d, 6a–f, 8a–f**), ^{11}B NMR spectra showed five peaks in the range of −6.67 to −16.00 ppm corresponding to the carborane cage. For compounds **9a, 10a, and 11a**, five peaks in the range of −5.86 to −15.97 ppm were observed in ^{11}B NMR spectra.

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REFERENCES

1. Heying TL, Ager Jr JW, Clark SL, Mangold DJ, Goldstein HL, Hillman M, Polak RJ, Szymanski JW. *Inorg. Chem.* 1963; **2**: 1089.
2. Fein MM, Bobinski J, Mayes N, Schwartz N, Cohen MS. *Inorg. Chem.* 1963; **2**: 1111.
3. Grimes RN. *Carboranes*. Academic Press: New York, 1970.
4. Bregadze VI. *Chem. Rev.* 1992; **92**: 209.
5. Hawthorne MF. *Advances in Boron Chemistry*, Siebert W, Ed. The Royal Society of Chemistry: UK, 1997; 261.
6. Hawthorne MF. *Contemporary Boron Chemistry*, Davidson M, Hughes AK, Marder TB, Wade K (eds). The Royal Society of Chemistry: UK, 2000; 197.
7. Soloway AH, Zhuo J-C, Rong F-G, Lunato AL, Ives DH, Barth RF, Anisuzzaman AKM, Barth CD, Barnum BA. *J. Organometal. Chem.* 1999; **581**: 150.
8. Zhuo J-C, Tjarks W, Soloway AH, Cai J, Wang J, Barth RF, Adams DM, Eriksson S, Lunato AJ, Ji W. In *Contemporary Boron Chemistry*, Davidson M, Hughes AK, Marder TB, Wade K (eds). The Royal Society of Chemistry: UK, 2000; 127.

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9. Endo Y. In *Contemporary Boron Chemistry*, Davidson M, Hughes AK, Marder TB, Wade K (eds). The Royal Society of Chemistry: UK, 2000; 139.
10. Takagaki M, Powell W, Sood A, Spielvogel BF, Hosmane NS, Kirihata M, Ono K, Masunaga SI, Kinashi Y, Miyatake SI, Hashimoto N. *Radiat. Res.* 2001; **156**: 118.
11. Giese A, Westphal M. *Neurosurgery* 1996; **39**: 235.
12. Wilson JG, Anisuzzaman AKM, Alam F, Soloway AH. *Inorg. Chem.* 1992; **31**: 1955.
13. Spielvogel BF, Ahmed FU, McPhail AT. *Inorg. Synth.* 1989; **25**: 79.
14. Sood A, Sood CK, Spielvogel BF, Hall IH. *Eur. J. Med. Chem.* 1989; **24**: 67.
15. Kahl SB, Kasar RA. *J. Am. Chem. Soc.* 1996; **118**: 1223.

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