Supplementary Material (ESI) for Chemical Communications

Supporting Information

Synthesis of Quadrupeds-Shaped Polyfunctionalized *o*-Carborane Synthons

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General Procedures. Elemental analyses were performed using a Carlo Erba EA1108 microanalyser. IR spectra were recorded from KBr pellets on a Shimadzu FTIR-8300 spectrophotometer. ^{1}H and $^{1}H\{^{11}B\}$ NMR (300.13 MHz), $^{13}C\{^{1}H\}$ NMR (75.47 MHz) and ^{11}B and $^{11}B\{^{1}H\}$ NMR (96.29 MHz) spectra were recorded with a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories. Chemical shift values for ^{11}B NMR spectra were referenced to external $BF_3{\leftarrow}OEt_2$ and those for ^{1}H, $^{1}H\{^{11}B\}$, $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectra were referenced to $SiMe_4$. Chemical shifts are reported in units of parts per million downfield from reference, and all coupling constants in Hz. MS spectra were recorded using a FIA-ES/MS (Shimadzu AD VP/ API 150) instrument for neutral species.

Materials: Unless otherwise noted, all manipulations were carried out under a nitrogen atmosphere using standard vacuum line techniques. Diethyl ether and THF were distilled from sodium benzophenone prior to use. Hexane was dried over molecular

sieves and deoxygenated before use. A 1.6 M solution of *n*-butyllithium in hexanes, allylmagnesium bromide, phenylmagnesium bromide, copper (I) iodide, borane-tetrahydrofuran complex, hydrogen peroxide and sulfur from Aldrich, and 1,2-*closo*-$C_2B_{10}H_{12}$ from Katchem Ltd. (Prague) were used as purchased. 8,9,10,12-I_4-1,2-*closo*-$C_2B_{10}H_8$ was synthesised according to the literature.[i]

8,9,10,12-tetraallyl-1,2-dicarba-*closo*-dodecaborane (3). To a stirring solution of 8,9,10,12-tetraiodo-1,2-dicarba-*closo*-dodecaborane (1.00 g, 1.54 mmol) in THF (25 mL) cooled to 0 ºC in an ice-water bath was added, dropwise, a solution of allylmagnesium chloride in THF (5 mL, 2M, 10 mmol). After stirring at room temperature for 30 minutes, $[PdCl_2(PPh_3)_2]$ (43.6 mg, 4% equiv.) and CuI (12.2 mg, 4% equiv.) were added in a single portion, following which the reaction was heated to reflux overnight. The solvent was removed and 25 mL of diethyl ether were added to the residue. The excess of Grignard reagent was destroyed by slow addition of dilute HCl. The organic layer was separated from the mixture, and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organic phase was dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The crude product was dissolved in hexane/chloroform mixture (5:1 by volume, *ca*. 5 mL) and passed through a bed of silica. The solvent was removed *in vacuo* to give 8,9,10,12-tetraallyl-1,2-dicarba-*closo*-dodecaborane as a yellowish oil (420 mg, 90 %). Elemental analysis calcd. (%) $C_{14}B_{10}H_{28}$: C, 55.22; H, 9.27. Found: C, 54.76; H, 9.26. FTIR (KBr), ν (cm^{-1}) = 3069 (w, $C_{cluster}$-H and $=CH_2$ st.), 2995, 2970, 2910, 2885 (w, =CH- and -CH_2- st.), 2592 (s, B-H st.), 1634 (vs, C=C st.), 997, 899 (vs, $=CH_2$ δ oop). ^{1}H NMR ($CDCl_3$): δ = 5.93 (2 H, m, CH_2=C*H*-CH_2), 5.77 (2 H, m, CH_2=C*H*-CH_2), 4.9-4.6 (8 H, m, C*H*$_2$=CH-CH_2), 3.37 (2 H, br s, $C_{cluster}$H), 3.1 – 1.0 (6 H, br m, BH), 1.67 (4 H, br s, CH_2=CH-

C*H*$_2$), 1.50 (4 H, br s, CH$_2$=CH-C*H*$_2$). ^{1}H{^{11}B} NMR (CDCl$_3$): δ = 5.93 (2 H, m, CH$_2$=C*H*-CH$_2$), 5.77 (2 H, m, CH$_2$=C*H*-CH$_2$), 4.9-4.6 (8 H, m, C*H*$_2$=CH-CH$_2$), 3.37 (2 H, br s, C$_{cluster}$H), 2.08 (2 H, br s, B(3,6)H), 1.95 (4 H, br s, B(4,5,7,11)H), 1.67 (4 H, d, ^{3}*J*(H,H) = 8.1, CH$_2$=CH-C*H*$_2$), 1.50 (4 H, d, ^{3}*J*(H,H) = 7.5, CH$_2$=CH-C*H*$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 139.9, 139.3 (s, CH$_2$=*C*H-CH$_2$), 112.3 (s, *C*H$_2$=CH-CH$_2$), 46.5 (s, C$_{cluster}$), 20.7 (br m, CH$_2$=CH-*C*H$_2$). ^{11}B NMR (CDCl$_3$): δ = 7.8 (2 B, s, B(9,12)), 1.9 (2 B, s, B(8,10)), -13.7 (4 B, d, ^{1}*J*(B,H) = 160, B(4,5,7,11)), -17.8 (2 B, d, ^{1}*J*(B,H) = 174, B(3,6)). ESI MS: *m*/*z* = 302.2 (M - H$^+$, 100%).

8,10-diphenyl-9,12-diiodo-1,2-dicarba-*closo*-dodecaborane (4). To a stirring solution of 8,9,10,12-tetraiodo-1,2-dicarba-*closo*-dodecaborane (150 mg, 0.23 mmol) in THF (4 mL) cooled to 0 ºC in an ice-water bath was added, dropwise, a solution of phenylmagnesium chloride in THF (0.81 mL, 2M, 1.62 mmol). After stirring at room temperature for 30 minutes, [PdCl$_2$(PPh$_3$)$_2$] (6.5 mg, 4% equiv.) and CuI (1.8 mg, 4% equiv.) were added in a single portion, following which the reaction was heated to reflux overnight. The solvent was removed and 5 mL of diethyl ether were added to the residue. The excess of Grignard reagent was destroyed by slow addition of dilute HCl. The organic layer was separated from the mixture, and the aqueous layer was extracted with diethyl ether (3 x 5 mL). The combined organic phase was dried over MgSO$_4$, filtered and the solvent removed under reduced pressure. The crude product was purified by flash silica gel chromatography, using chloroform as the eluting solvent, to give 8,10-diphenyl-9,12-diiodo-1,2-dicarba-*closo*-dodecaborane (103 mg, 81%) (Elemental analysis calcd. (%) C$_{14}$B$_{10}$H$_{18}$I$_2$: C, 30.67; H, 3.31. Found: C, 30.13; H, 2.93. FTIR (KBr), ν (cm^{-1}) = 3047 (s, C$_{cluster}$-H st.), 2600 (s, B-H st.). ^{1}H NMR (CD$_3$COCD$_3$): δ = 7.70 (4 H, m, C$_{phenyl}$H), 7.32 (6 H, m, C$_{phenyl}$H), 5.38 (2 H, br s, C$_{cluster}$H), 4.0 – 1.6

(6 H, br m, BH). $^{1}H\{^{11}B\}$ NMR (CD_3COCD_3): δ =7.70 (4 H, m, $C_{phenyl}H$), 7.32 (6 H, m, $C_{phenyl}H$), 5.38 (2 H, br s, $C_{cluster}H$), 3.04 (4 H, br s, B(4,5,7,11)H), 2.60 (2 H, br s, B(3,6)H). $^{13}C\{^{1}H\}$ NMR (CD_3COCD_3): δ = 135.4, 128.9, 128.1 (C_{phenyl}), 53.3 ($C_{cluster}$). ^{11}B NMR (CD_3COCD_3): δ = 2.1 (2 B, s, B(8,10)-Ph), -7.1 (2 B, s, B(9,12)-I), -11.9 (4 B, d, ^{1}J(B,H) = 169, B(4,5,7,11)), -14.8 (2 B, br, B(3,6)). ESI MS: *m*/*z* = 549.0 ($M - H^+$, 100%).

8,9,10,12-tetra(3-hydroxypropyl)-1,2-dicarba-*closo*-dodecaborane (5). To a stirring solution of 8,9,10,12-tetraallyl-1,2-dicarba-*closo*-dodecaborane (61 mg, 0.20 mmol) in THF (2 mL) at 0 ºC, was added, dropwise, a solution of BH_3·THF in THF (0.8 mL, 1M, 0.80 mmol). The resulting suspension was stirred at 0 ºC for 30 minutes and at room temperature for further 30 minutes. Then, the reaction mixture was cooled again to 0 ºC in an ice-water bath and water (1 mL) was slowly added. When gas evolution had stopped, an aqueous NaOH solution (0.28 mL, 3M, 0.84 mmol) and subsequently, H_2O_2 in water (0.09 mL, 35%, 1.04 mmol), were added. Stirring was maintained at room temperature for 1.5 h, after which two liquid phases were observed. The upper organic layer was separated from the mixture, and the aqueous layer and washed with THF (3 x 2 mL). The combined organic phase was dried over $MgSO_4$, filtered and the solvent removed *in vacuo* to give 8,9,10,12-tetra(3-hydroxypropyl)-1,2-dicarba-*closo*-dodecaborane (65 mg, 86%). Elemental analysis calcd. (%) $C_{14}B_{10}H_{36}O_4$: C, 44.66; H, 9.64. Found: C, 44.47; H, 9.32. FTIR (KBr), ν (cm^{-1}) = 3327 (vs, O-H st.), 3065, 3034 (w, $C_{cluster}$-H st.), 2930, 2887 (s, C_{alkyl}-H st.), 2613, 2578 (s, B-H st.), 1057, 1005 (s, C-O st.). ^{1}H NMR (CD_3SOCD_3): δ = 4.51 (2 H, br s, $C_{cluster}H$), 4.34 (2 H, m, $HOCH_2CH_2CH_2$), 4.27 (2 H, m, $HOCH_2CH_2CH_2$), 3.36 (4 H, m, $HOCH_2CH_2CH_2$), 3.26 (4 H, m, $HOCH_2CH_2CH_2$), 2.4 – 0.8 (6 H, br m, BH), 1.50 (4 H, m, $HOCH_2CH_2CH_2$),

1.30 (4 H, m, $HOCH_2CH_2CH_2$), 0.53 (4 H, m, $HOCH_2CH_2CH_2$), 0.32 (4 H, m, $HOCH_2CH_2CH_2$). $^1H\{^{11}B\}$ NMR (CD_3SOCD_3): δ = 4.51 (2 H, br s, $C_{cluster}H$), 4.34 (4 H, m, $HOCH_2CH_2CH_2$), 4.27 (2 H, m, $HOCH_2CH_2CH_2$), 3.36 (4 H, m, $HOCH_2CH_2CH_2$), 3.26 (4 H, m, $HOCH_2CH_2CH_2$), 1.95 (2 H, br s, B(3,6)H), 1.78 (4 H, br s, B(4,5,7,11)H), 1.50 (4 H, m, $HOCH_2CH_2CH_2$), 1.30 (4 H, m, $HOCH_2CH_2CH_2$), 0.53 (4 H, m, $HOCH_2CH_2CH_2$), 0.32 (4 H, m, $HOCH_2CH_2CH_2$). $^{13}C\{^1H\}$ NMR (CD_3SOCD_3): δ = 63.6, 63.4 (s, $HOCH_2CH_2CH_2$), 47.2 (s, $C_{cluster}$), 33.1, 31.9 (s, $HOCH_2CH_2CH_2$), 9.7 (br s, $HOCH_2CH_2CH_2$). ^{11}B NMR (CD_3COCD_3): δ = 9.9 (2 B, s, B(9,12)), 3.6 (2 B, s, B(8,10)), -12.6 (4 B, d, ^1J(B,H) = 151, B(4,5,7,11)), -16.7 (2 B, d, ^1J(B,H) = 166, B(3,6)). ESI MS: m/z = 376.2 (M^+, 100%).

X-ray Structure Determinations of $[NMe_4]$5 and $[NMe_4]$6:

Single-crystal data collections for **4** and **5** were performed at –100º with an Enraf Nonius KappaCCD diffractometer using graphite monochromatized Mo K_α radiation. The structures were solved by direct methods and refined on F^2 by the SHELXL97 program.[ii] The non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were treated as riding atoms using the SHELXL97 default parameters. The crystallographic, structure refinement and bond parameters for **4** and **5** are reported in CIF-files deposited at CCDC with the reference numbers CCDC 804982 and 804983. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: (+44) 1223-336033; or e-mail: deposit@ccdc.cam.ac.uk).

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[ii] Sheldrick, G.M. *Acta Cryst*. **2008,** A64, 112