

Remarkable cage deboronation and rearrangement of a *closo*-1,12-dicarbadoodecaborane to form a neutral *nido*-7,9-dicarbaundecaborane.

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Instrumentation

All ^1H , ^{11}B , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded at 300 K on a Bruker Avance III 400 MHz spectrometer (^1H at 400.1 MHz, ^{11}B at 128.4 MHz, ^{13}C at 100.6 MHz and ^{31}P at 162.0 MHz) or a Bruker Avance III 500 MHz spectrometer (^1H at 500.1 MHz, ^{11}B at 160.5 MHz, ^{13}C at 125.8 MHz and ^{31}P at 202.5 MHz). All NMR signals (δ) are reported in ppm. ^1H and ^{13}C NMR spectra were referenced to residual solvent peaks [(CD_3) $_2\text{CO}$, ^1H 2.05, ^{13}C 29.9 (CD_3); CDCl_3 , ^1H 7.24, ^{13}C 77.2; CD_3CN , ^1H 1.94, ^{13}C 118.7 (CN) ppm]. ^{11}B and ^{31}P NMR spectra were referenced according to the IUPAC unified scale (frequency ratios (Ξ) 32.083974 and 40.480742 for ^{11}B and ^{31}P nuclei, respectively).¹ Deuterated solvents of 99.5% isotopic purity or higher were obtained from Cambridge Isotopes Laboratories (USA) through Novachem (Australia).

Mass spectra were acquired in an appropriate solvent (flow rate 100 $\mu\text{L}/\text{min}$) on a Finnegan LCQ MS Detector (ESI). An ESI spray voltage of 5 kV was applied with a heated capillary temperature of 200 $^\circ\text{C}$ and a nitrogen sheath gas pressure of 60 psi. Elemental analyses were performed by Campbell Microanalytical Laboratory, University of Otago, New Zealand and by Chemical & Microanalytical Services Pty Ltd, Australia.

Synthesis and characterisation details

Organic solvents were purified prior to use according to Armarego and Chai.² THF was dried over sodium wire and freshly distilled from benzophenone ketyl before use. Anhydrous CH₃CN was freshly distilled from CaH₂ before use. All other solvents were used without purification.

The phosphines 1,7-*bis*(diphenylphosphino)-1,2-carborane **13**,³ 1,12-*bis*(diphenylphosphino)-1,12-carborane **14**⁴ and the phosphonium salt **6·2I**⁵ were prepared using reported procedures. [¹³C]-CH₃I and [¹³C]-CH₃OH (Cambridge Isotopes Laboratories, USA) were obtained from Novachem (Australia). All other reagents were available from Sigma-Aldrich Pty Ltd.

1,7-Bis(diphenylphosphino)-1,7-carborane **13**^{3,6}

¹H{¹¹B} NMR (CDCl₃) δ 7.66 (dd, ³J_{PH}, ³J_{HH} ~ 8.0 Hz, 8H, *ortho* CH), 7.32 (td, ³J_{HH} = 7.5 Hz, ⁵J_{PH} = 1.3 Hz, 4H, *para* CH), 7.78 (td, ³J_{HH}, ⁴J_{PH} ~ 6.6 Hz, 8H, *meta* CH), 2.57 (s, 2H, BH), 2.38 (s, 2H, BH), 2.26 (s, 4H, B4,6,8,11H), 2.15 (s, 2H, BH). ¹¹B NMR (CDCl₃) δ -3.4 (br d, 2B), -8.7 (br d, 6B), -12.8 (br d, 2B). ¹³C{¹H} NMR (CDCl₃) δ 135.3 (d, ²J_{PC} = 26.1 Hz, *ortho* C), 133.8 (d, ¹J_{PC} = 17.2 Hz, *ipso* C), 130.7 (d, ⁴J_{PC} = 0.7 Hz, *para* C), 128.5 (d, ³J_{PC} = 9.1 Hz, *meta* C), 74.0 (d, ¹J_{PC} = 66 Hz, cage C1,2). ³¹P{¹H} NMR (CDCl₃) δ 21.0 (s). Found C 60.87, H 5.96. Calc. for C₂₆H₃₀B₁₀P₂: C 60.92, H 5.90.

nido-7-[Methyldiphenylphosphonium]-7,9-dicarbaundecaborate **4**

A solution of **2.I** (1.67 g, 3.6 mmol) in DMF (100 ml) was stirred at 120 °C for 3 h. The solvent was removed in vacuo and the residue suspended in acetone (100mL). The mixture was triturated with water (100 mL) to precipitate the product. The acetone was removed from the aqueous solution *in vacuo* and the insoluble material isolated by centrifugation. This material was suspended in ethanol and collected by filtration. After drying *in vacuo*, a colourless powder was identified as **4** (0.87 g, 73 %). Crystals suitable for X-ray diffraction were obtained by slow evaporation from a concentrated solution of **4** in DMF. ¹H{¹¹B} NMR ((CD₃)₂CO) δ 7.87 (dd, ³J_{PH} = 12.6 Hz, ³J_{HH} = 8.1 Hz, 2H, *ortho* CH), 7.84 (dd, ³J_{PH} = 13.2 Hz, ³J_{HH} = 7.6 Hz, 2H, *ortho* CH), 7.75 (dt, ⁴J_{PH} = 6.4 Hz, ³J_{HH} = 5.7 Hz, 2H, *meta* CH), 7.73 (dt, ⁴J_{PH} = 6.2 Hz, ³J_{HH} = 6.9 Hz, 2H, *meta* CH), 7.70 (dt, ⁵J_{PH} = 3.6 Hz, ³J_{HH} = 7.7 Hz, 1H, *para*

CH), 7.68 (dt, $^5J_{\text{PH}} = 3.6$ Hz, $^3J_{\text{HH}} = 7.5$ Hz, 1H, *para* CH), 2.62 (s, 1H, BH), 2.44 (d, $^2J_{\text{PH}} = 13.2$ Hz, 3H, Me), 2.37 (s, 1H, BH), 1.84 (2H, br s, C9H + BH), 1.59 (br s, 1H, B10H or B11H), 1.41 (s, 1H, BH), 1.39 (br s, 1H, B11H or B10H), 1.04 (s, 1H, B1H), 0.56 (s, 1H, B6H), -1.76 (t, $^3J_{\text{HH}} \sim 12.4$ Hz, 1H, H μ). $^{11}\text{B}\{^1\text{H}\}$ NMR ((CD₃)₂CO) δ 0.9 (br s, 1B), -0.5 (br s, 1B), -5.7 (br s, 1B), -18.4 (br s, 2B), -19.5 (br s, 1B), -20.9 (br s, 1B), -31.8 (br s, 2B). $^{13}\text{C}\{^1\text{H}\}$ NMR ((CD₃)₂CO) δ 134.8 (d, $^4J_{\text{PC}} = 2.7$ Hz, *para* C), 134.6 (d, $^4J_{\text{PC}} = 2.8$ Hz, *para* C), 133.8 (d, $^2J_{\text{PC}} = 9.2$ Hz, *ortho* C), 133.8 (d, $^2J_{\text{PC}} = 9.2$ Hz, *ortho* C), 130.4 (d, $^3J_{\text{PC}} = 12.5$ Hz, *meta* C), 130.2 (d, $^3J_{\text{PC}} = 10.7$ Hz, *meta* C), 125.8 (d, $^1J_{\text{PC}} = 89.8$ Hz, *ipso* C), 124.6 (d, $^1J_{\text{PC}} = 90.8$ Hz, *ipso* C), 36.5 (br, cage C9), 10.3 (d, $^1J_{\text{PC}} = 60.1$ Hz, PCH₃), cage C7 peak presumed hidden in solvent resonance at 29.7 ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR ((CD₃)₂CO) δ 30.4 (s). Found C 54.26, H 7.38. Calc. for C₁₅H₂₄B₉P: C 54.16, H 7.27.

nido-7,9-[Bis(methyldiphenylphosphonium)]-7,9-dicarbaundecaborate 7

A mixture of **6·2I** (0.31 g, 0.39 mmol) in CH₃OH (10 mL) was stirred and heated under reflux. The solid material slowly dissolved over *ca.* 1 h of heating to give a clear colourless solution. A yellow precipitate formed after 23 h, which did not re-dissolve after a further 30 h heating under reflux. The mixture was transferred to a screw-top pressure tube (Ace Glass Inc.) and stirred at 110 °C for 65 h, though the precipitate did not dissolve under these conditions. The yellow solid was isolated by filtration and recrystallised from hot CH₃CN (20 mL) to give pale yellow crystals (22 mg, 11%). $^1\text{H}\{^{11}\text{B}\}$ NMR (CDCl₃) δ 7.87 (dd, $^3J_{\text{PH}} = 11.8$ Hz, $^3J_{\text{HH}} = 8.0$ Hz, 4H, *ortho* CH), 7.75 (dd, $^3J_{\text{PH}} = 12.0$ Hz, $^3J_{\text{HH}} = 8.2$ Hz, 4H, *ortho* CH), 7.59 (t, $^3J_{\text{HH}} \sim 7.7$ Hz, 2H, *para* CH), 7.54 (t, $^3J_{\text{HH}} \sim 7.5$ Hz, 2H, *para* CH), 7.48 (t, $^3J_{\text{HH}} \sim 7.5$ Hz, 4H, *meta* CH), 7.41 (t, $^3J_{\text{HH}} \sim 7.5$ Hz, 4H, *meta* CH), 2.06 (d, $^2J_{\text{PH}} = 13.1$ Hz, 6H, Me), 1.64 (s, 2H, BH), 1.46 (s, 5H, BH), 1.28 (s, 1H, BH), 0.18 (s, 1H, B1H). ^{11}B NMR (CDCl₃) δ -12.5 (br, 2B, B2,5), -17.8 (d, 3B), -18.7 (d, 2B), -20.2 (d, 1B), -45.7 (d, 1B, $J_{\text{BH}} = 140$ Hz, B1). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃) δ 134.9 (d, $^2J_{\text{PC}} \sim 9.5$ Hz, *ortho* C), 134.8 (d, $^2J_{\text{PC}} \sim 9.5$ Hz, *ortho* C), 134.7 (d, $^4J_{\text{PC}} \sim 2.0$ Hz, *para* C), 134.7 (d, $^4J_{\text{PC}} \sim 2.0$ Hz, *para* C), 130.8 (d, $^3J_{\text{PC}} = 11.9$ Hz, *meta* C), 130.6 (d, $^3J_{\text{PC}} = 10.8$ Hz, *meta* C), 128.2 (d, $^1J_{\text{PC}} = 89.2$ Hz, *ipso* C), 128.0 (d, $^1J_{\text{PC}} = 89.6$ Hz, *ipso* C), 21.7 (br, C_{cage}), 12.9 (d, $^1J_{\text{PC}} = 60.9$ Hz, Me). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl₃) δ 27.5 (s).

Dimethyldiphenylphosphonium iodide 8•I⁻

The filtrate and supernatant solutions from the synthesis of **7** were combined and the solvent removed to give PPh₂(CH₃)₂•I as a colourless solid (0.17 g, 0.51 mmol, 65%). An analytically pure sample was obtained by recrystallisation from CH₃OH. ¹H NMR (CD₃CN) δ 7.84-7.67 (m, 10H, Ph), 2.48 (d, ²J_{PH} = 14.2 Hz, 6H, CH₃). ¹³C{¹H} NMR (CD₃CN) δ 136.0 (d, ⁴J_{PC} = 4.0 Hz, *para* C), 133.2 (d, ²J_{PC} = 10.6 Hz, *ortho* C), 131.3 (d, ³J_{PC} = 12.8 Hz, *meta* C), 122.1 (d, ¹J_{PC} = 88.1 Hz, *ipso* C), 9.8 (d, ¹J_{PC} = 57.4 Hz, PCH₃). ³¹P{¹H} (CD₃CN) NMR δ 21.9 (s). *m/z* (ESI-MS, +ve) 215.3 [PPh₂(CH₃)₂]⁺. *m/z* (ESI-MS, -ve) 127.3 [I]⁻. Found C 49.45, H 4.72. Calc. for C₁₄H₁₆PI: C 49.14, H 4.71%.

nido-7,9-[Bis(methyldiphenylphosphonium)]-7,9-dicarbaundecaborate chloride 9•Cl

A sample of **7** (25 mg, 0.047 mmol) suspended in acetonitrile (1 mL) was added with one drop of concentrated hydrochloric acid and left to stir at room temperature until all the solid had dissolved. The solution was slowly added with water (1 mL). The resulting precipitate was filtered, washed with hexanes and dried *in vacuo* to give an off-white solid **9•Cl** (18 mg, 67%). ¹H{¹¹B} NMR (CDCl₃) δ 7.73-7.62 (m, 8H, Ph), 7.56-7.48 (m, 12H, Ph), 2.27 (d, ²J_{PH} = 12.6 Hz, 6H, PCH₃), 2.54 (s, 2H, B2,5H), 2.41 (s, 1H, B8H), 1.89 (d, ²J_{HH} = 7.8 Hz, 2H, B10,11H), 1.55 (s, 2H, B3,4H), 0.65 (s, 1H, B1H), -1.55 (t, ²J_{HH} = 10.1 Hz, 1H, H_μ). ¹¹B NMR (CDCl₃) δ 4.1 (br, 2B, B2,5), -6.4 (d, 1B, J_{BH} = 127 Hz, B8), -16.5 (d, 2B, B3,4), -18.9 (d, 2B, B10,11), -30.3 (d, 1B, J_{BH} ~ 110 Hz, B1 or B6), -31.0 (d, 1B, J_{BH} ~ 130 Hz, B6 or B1). ¹³C{¹H} NMR (CDCl₃) δ 134.4 (d, ⁴J_{PC} = 2.2 Hz, *para* C), 134.4 (d, ⁴J_{PC} = 3.0 Hz, *para* C), 132.4 (d, ²J_{PC} = 9.5 Hz, *ortho* C), 132.4 (d, ²J_{PC} = 9.5 Hz, *ortho* C), 129.8 (d, ³J_{PC} = 12.6 Hz, *meta* C), 129.7 (d, ³J_{PC} = 12.7 Hz, *meta* C), 121.8 (d, ¹J_{PC} = 90.3 Hz, *ipso* C), 121.1 (d, ¹J_{PC} = 89.4 Hz, *ipso* C), 34.4 (br, C_{cage}), 10.7 (d, ¹J_{PC} = 40.8 Hz, Me). ³¹P{¹H} NMR (CDCl₃) δ 28.0 (s). *m/z* (ESI-accurate MS, +ve) Found 532.31687 [M-I]⁺ Calc. for C₂₈H₃₆B₉P₂ 532.31796.

Bis[methyldiphenylphosphonium]-1,7-carborane iodide 10•2I

A solution of **13** (0.50 g, 0.97 mmol) and CH₃I (5.0 mL, 80.1 mmol) in THF (6.0 mL) was stirred and heated under reflux for 11 h. The precipitate that formed was isolated by filtration, washed with THF (30 mL) and dried under vacuum over P₂O₅ to afford a colourless powder **10•2I** (0.77 g, 96 %). ¹³C NMR data for **10•2I** were not obtained

due to poor solubility in many organic solvents. ^1H NMR (CD_3CN) δ 8.10 (dd, $^3J_{\text{PH}} = 13.0$ Hz, $^3J_{\text{HH}} = 8.4$ Hz, 8H, *ortho* CH), 7.96 (t, $^3J_{\text{HH}} = 7.5$ Hz, 4H, *para* CH), 7.78 (td, $^3J_{\text{HH}} \sim 8.0$ Hz, $^5J_{\text{PH}} \sim 4.0$ Hz, 8H, *meta* CH), 2.96 (d, $^2J_{\text{PH}} = 12.8$ Hz, 6H, PCH_3), 2.89 (s, 2H, BH), 2.57 (s, 2H, BH), 2.47 (s, 4H, B4,6,8,11H), 2.38 (s, 2H, BH), 2.13 (s, 5H, 2.5 H_2O). $^{11}\text{B}\{^1\text{H}\}$ NMR (CD_3CN) δ -1.1 (br d, $J_{\text{BH}} \sim 128$ Hz, 2B), -7.8 (d, $J_{\text{BH}} = 136$ Hz, 2B), -9.6 (br d, $J_{\text{BH}} \sim 152$ Hz, 4B, B4,6,8,11), -13.8 (br d, $J_{\text{BH}} \sim 142$ Hz, 2B). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN) δ 27.4 (s). m/z (ESI-MS, +ve) 271.1 $[\text{M}-2\text{I}]^{2+}$. Found C 39.66, H 4.38. Calc. for $\text{C}_{28}\text{H}_{36}\text{B}_{10}\text{P}_2\text{I}_2(\text{H}_2\text{O})_{2.5}$: C 39.96, H 4.91%.

nido-7,9-[Bis(methyldiphenylphosphonium)]-10-methoxy-7,9-dicarbaundecaborate iodide 11•I

A sample of **10•2I** (200 mg, 0.25 mmol) suspended in methanol (5 mL) was stirred under reflux and the yellow precipitate that formed from this reaction was filtered. This solid was recrystallized from acetonitrile and dried in vacuo to give yellow crystals of **11•I** (114 mg, 66 %). $^1\text{H}\{^{11}\text{B}\}$ NMR (CD_3CN) δ 7.90-7.80 (m, 12H, Ph), 7.70-7.65 (m, 8H, Ph), 3.01 (s, 3H, OMe), 2.80 (s, 1H, B2H), 2.60 (s, 1H, B5H), 2.48 (d, $^2J_{\text{PH}} = 13.4$ Hz, 3H, PCH_3), 2.47 (d, $^2J_{\text{PH}} = 13.0$ Hz, 3H, PCH_3), 2.37 (s, 1H, B8H), 2.00 (d, 1H, B11H), 1.49 (d, $^3J_{\text{HH}} = 7.7$ Hz, 1H, B4H), 1.29 (d, $^3J_{\text{HH}} = 7.6$ Hz, 1H, B3H), 0.95 (s, 1H, B1H), 0.82 (s, 1H, B6H), 0.60 (d, $^2J_{\text{HH}} = 13.3$ Hz, 1H, H_μ). ^{11}B NMR (CD_3CN) δ 3.4 (s, 3B, B2,5,10), -8.9 (d, 1B, $J_{\text{BH}} = 142$ Hz, B8), -17.8 (d, 1B, $J_{\text{BH}} = 136$ Hz, B4), -22.7 (d, 1B, $J_{\text{BH}} \sim 161$ Hz, B3), -24.2 (d, 1B, $J_{\text{BH}} \sim 161$ Hz, B11), -33.6 (d, 1B, $J_{\text{BH}} \sim 136$ Hz, 2B, B1,6). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN) δ 136.0 (d, $^4J_{\text{PC}} = 3.0$ Hz, *para* C), 135.8 (d, $^4J_{\text{PC}} = 3.0$ Hz, *para* C), 134.4 (d, $^2J_{\text{PC}} = 8.7$ Hz, *ortho* C), 134.3 (d, $^2J_{\text{PC}} = 8.1$ Hz, *ortho* C), 131.2 (d, $^3J_{\text{PC}} = 12.5$ Hz, *meta* C), 131.1 (d, $^3J_{\text{PC}} = 12.5$ Hz, *meta* C), 131.0 (d, $^3J_{\text{PC}} = 12.7$ Hz, *meta* C), 131.0 (d, $^3J_{\text{PC}} = 12.7$ Hz, *meta* C), 123.8 (d, $^1J_{\text{PC}} = 89.9$ Hz, *ipso* C), 123.7 (d, $^1J_{\text{PC}} = 90.1$ Hz, *ipso* C), 123.1 (d, $^1J_{\text{PC}} = 90.3$ Hz, *ipso* C), 122.9 (d, $^1J_{\text{PC}} = 89.6$ Hz, *ipso* C), 58.3 (s, OMe), 12.0 (d, $^1J_{\text{PC}} = 42.6$ Hz, PMe), 11.4 (d, $^1J_{\text{PC}} = 43.2$ Hz, Me). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN) δ 28.7 (s, 1P), 28.4 (s, 1P). m/z (ESI-accurate MS, +ve) Found 562.32618 $[\text{M}-\text{I}]^+$ Calc. for $\text{C}_{29}\text{H}_{38}\text{B}_9\text{P}_2\text{O}$ 562.32077.

nido-7,9-[Bis(methyldiphenylphosphonium)]-10-methoxy-7,9-dicarbaundecaborate

12

A stirred solution of **11•I** (70 mg, 0.1 mmol) in acetonitrile (1 mL) was added with one drop of 0.1 M aqueous KOH solution. The resulting yellow solution was added with 3 mL of water to give a yellow solid. The aqueous solution was decanted and the solid was dissolved in chloroform (1 mL) followed by water (1 mL). The organic layer was separated and the solvents were removed *in vacuo* to leave a turgid yellow solid. This was washed with methanol and triturated with hexanes to form a light yellow powder identified as **12** (41 mg, 0.07 mmol, 72%). $^1\text{H}\{^{11}\text{B}\}$ NMR (CD_3CN) δ 8.03 (dd, $^3J_{\text{PH}} = 12.1$ Hz, $^3J_{\text{HH}} = 8.4$ Hz, 2H, *ortho* CH), 7.96 (dd, $^3J_{\text{PH}} = 12.4$ Hz, $^3J_{\text{HH}} = 8.3$ Hz, 2H, *ortho* CH), 7.77 (dd, $^3J_{\text{PH}} = 13.3$ Hz, $^3J_{\text{HH}} = 8.5$ Hz, 2H, *ortho* CH), 7.96 (dd, $^3J_{\text{PH}} = 12.0$ Hz, $^3J_{\text{HH}} = 8.5$ Hz, 2H, *ortho* CH), 7.70-7.44 (m, 12H, *para* CH + *meta* CH), 3.11 (s, 3H, OMe), 2.18 (d, $^2J_{\text{PH}} = 13.4$ Hz, 3H), 2.07 (d, $^2J_{\text{PH}} = 13.0$ Hz, 3H), 1.57 (s, 1H, BH), 1.18 (s, 5BH), 0.96 (d, $^3J_{\text{HH}} = 9.9$ Hz, 1H, B4H), 0.88 (d, $^3J_{\text{HH}} = 9.8$ Hz, 1H, B3H), -0.32 (s, 1H, B1H). ^{11}B NMR (CD_3CN) δ 7.3 (s, 1B, B10), -13.2 (d, 1B, $J_{\text{BH}} \sim 165$ Hz, B5), -15.3 (d, 1B, $J_{\text{BH}} \sim 145$ Hz, B2), -20.4 (d, 1B, $J_{\text{BH}} \sim 141$ Hz), -22.8 (d, 3B, $J_{\text{BH}} \sim 124$ Hz), -27.1 (s, 1B, $J_{\text{BH}} = 152$ Hz), -48.1 (d, 1B, $J_{\text{BH}} = 135$ Hz, B1). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN) δ 134.4 (d, $^2J_{\text{PC}} = 8.6$ Hz, *ortho* C), 134.3 (d, $^2J_{\text{PC}} = 9.0$ Hz, *ortho* C), 134.0 (d, $^2J_{\text{PC}} = 9.1$ Hz, *ortho* C), 133.9 (d, $^2J_{\text{PC}} = 8.7$ Hz, *ortho* C), 133.9 (*para* C), 133.6 (d, $^4J_{\text{PC}} = 2.3$ Hz, *para* C), 133.6 (d, $^1J_{\text{PC}} = 94.3$ Hz, *ipso* C), 133.5 (d, $^1J_{\text{PC}} = 96.0$ Hz, *ipso* C), 131.7 (d, $^1J_{\text{PC}} = 109.3$ Hz, *ipso* C), 131.6 (d, $^1J_{\text{PC}} = 113.3$ Hz, *ipso* C), 129.9 (d, $^3J_{\text{PC}} = 11.8$ Hz, *meta* C), 129.9 (d, $^3J_{\text{PC}} = 11.8$ Hz, *meta* C), 129.7 (d, $^3J_{\text{PC}} = 13.2$ Hz, *meta* C), 129.6 (d, $^3J_{\text{PC}} = 12.2$ Hz, *meta* C), 57.8 (s, OMe), 12.2 (d, $^1J_{\text{PC}} = 59.6$ Hz, PMe), 10.7 (d, $^1J_{\text{PC}} = 61.3$ Hz, PMe), cage carbon peaks were not observed. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN) δ 28.6 (s, 1P), 27.6 (s, 1P).

Figure S1. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **7**

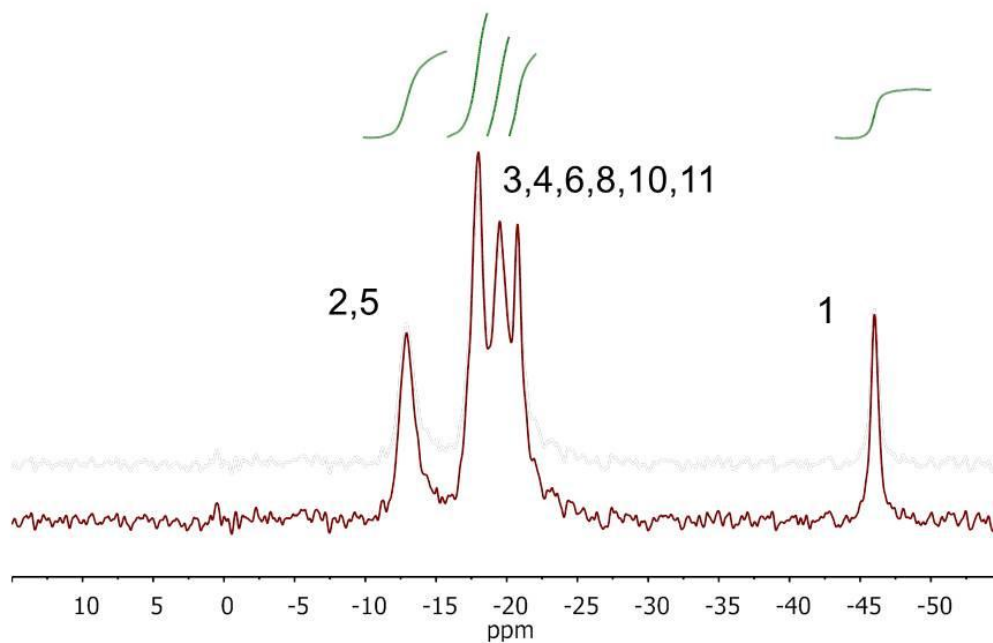


Figure S2. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **9·Cl**

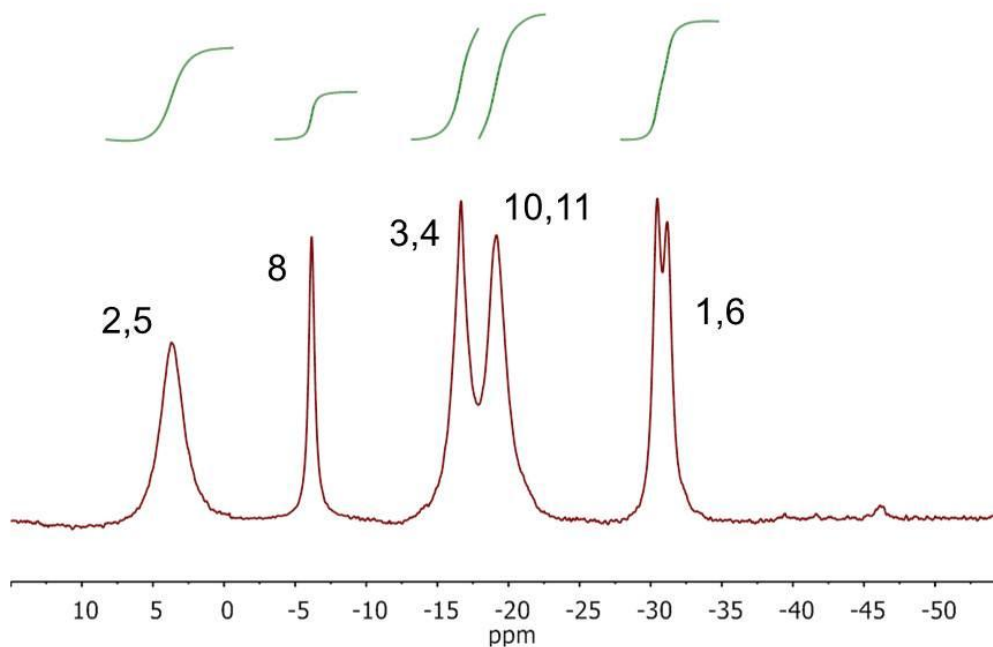


Figure S3. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **11**·I

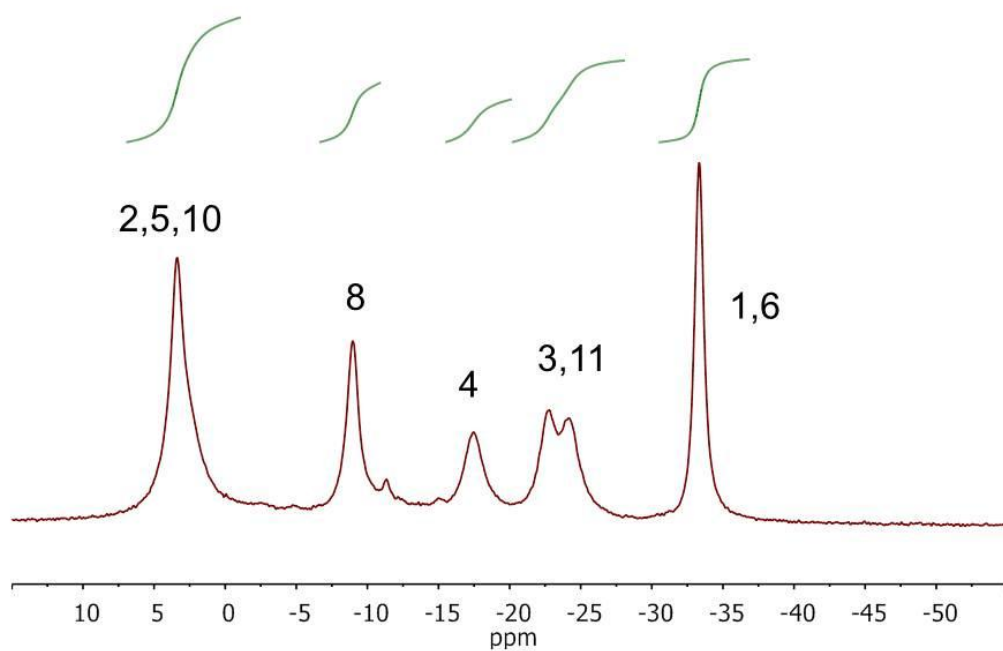
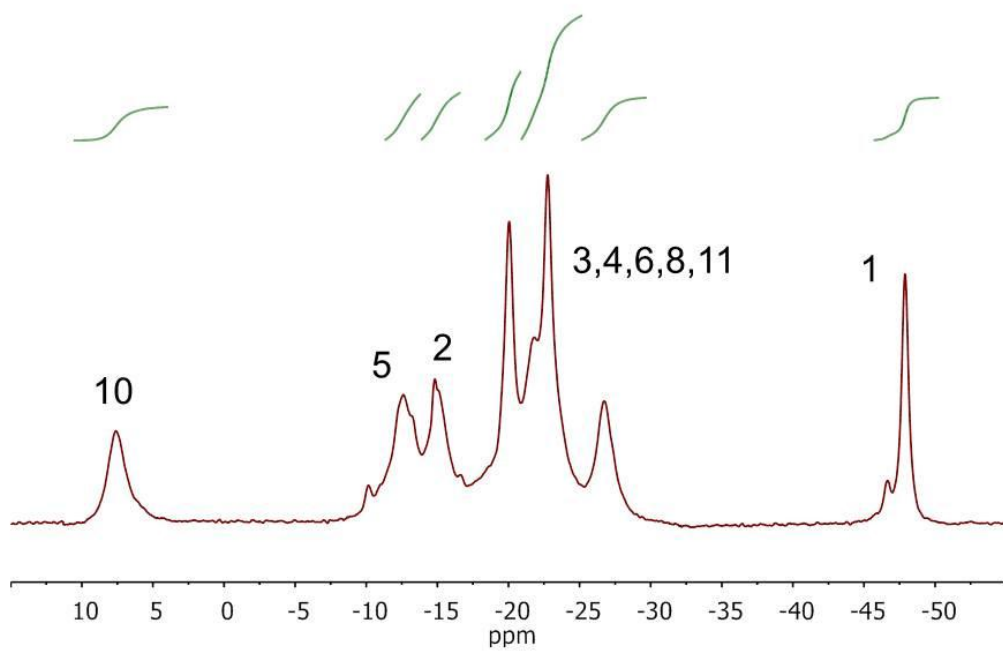


Figure S4. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **12**



¹³C Labelling studies

Bis[¹³C]-methylphenylphosphonium]-1,12-carborane iodide 6•2I

A solution of **14** (35 mg, 0.07 mmol) and [¹³C]-CH₃I (43 mg, 0.30 mmol) in THF (0.5 mL) in a closed vial was heated at 65 °C for 69 h. The vial was allowed to cool to room temperature. The precipitate that formed was isolated by centrifugation and the supernatant was discarded. The precipitate was washed by re-suspending the solid in THF (1 mL), isolating again by centrifugation and discarding the supernatant. This washing was repeated twice. Residual THF in the solid pellet was removed by a gentle stream of nitrogen gas and placing under vacuum for 20 h. The title compound was obtained as a colourless powder (52.1 mg, 97%). ¹H NMR (CD₃CN) δ 7.88 (m, 12H, Ph), 7.75 (m, 8H, Ph), 2.66 (dd, ²J_{CH} = 136.8 Hz, ²J_{PH} = 12.8 Hz, 6H, CH₃). ¹¹B{¹H} NMR (CD₃CN) δ -12.3 (br s, 10B). ¹³C{¹H} NMR (*d*₆-DMSO) δ 136.8 (s, *para* C), 134.4 (d, ²J_{PC} = 11 Hz, *ortho* C), 130.6 (d, ³J_{PC} = 13 Hz, *meta* C), 115.8 (d, ¹J_{PC} = 88 Hz, *ipso* C), 7.2 (d, ¹J_{PC} = 55 Hz, CH₃), cage carbon peak was not observed. ³¹P{¹H} NMR (CD₃CN) δ 26.8 (d, ¹J_{PC} = 58.1 Hz). *m/z* (ESI-MS, +ve) 272.1 [M-2I]²⁺. Found C 43.05, H 4.84. Calc. for C₂₆¹³C₂H₃₆B₁₀P₂I₂(C₄H₈O)_{0.5}: C 43.42, H 4.83%.

Degradation studies in CH₃OH and [¹³C]-CH₃OH

Entry 1. A mixture of [¹³C]-**6•2I** (7.8 mg, 0.01 mmol) in [¹³C]-CH₃OH (0.3 mL) was heated in a closed vial at 65 °C for 15 h. The solvent was removed by a gentle stream of nitrogen gas, followed by placing under vacuum for 12 h. Resonances corresponding to PPh₂(¹²CH₃)(¹³CH₃) salt were found in the NMR spectra of the crude material. ¹H NMR (CD₃CN) δ 2.45 (dd, ¹J_{CH} = 134.4 Hz, ²J_{PH} = 14.4 Hz, P¹³CH₃), 2.46 (dd, ³J_{CH} = 2.2 Hz, ²J_{PH} = 14.2 Hz, PCH₃). ¹³C{¹H} NMR (CD₃CN) δ 8.5 (d, ¹J_{PC} = 57 Hz, P¹³CH₃). ³¹P{¹H} NMR (CD₃CN) δ 20.7 (d, ¹J_{PC} = 57 Hz, P¹³CH₃). *m/z* (ESI-MS, +ve) Found 216.10243 [PPh₂(¹²CH₃)(¹³CH₃)]⁺. Calc. for C₁₃¹³C₁H₁₆P: 216.10177.

Entry 2. A mixture of **6•2I** (8.3 mg, 0.01 mmol) in [¹³C]-CH₃OH (0.3 mL) was heated in a closed vial at 65 °C for 15 h. The solvent was removed by a gentle stream of

nitrogen gas, followed by placing under vacuum for 12 h. Resonances corresponding to $\text{PPh}_2(\text{CH}_3)_2$ salt were found in the NMR spectra of the crude material. ^1H NMR (CD_3CN) δ 2.46 (d, $^2J_{\text{PH}} = 14.5$ Hz, PCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN) δ 8.6 (d, $^1J_{\text{PC}} = 58$ Hz, PCH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN) δ 20.7 (s). m/z (ESI-MS, +ve) Found 215.09918 [$\text{PPh}_2(^{12}\text{CH}_3)_2$] $^+$. Calc. for $\text{C}_{14}\text{H}_{16}\text{P}$: 215.09841.

Entry 3. A mixture of [^{13}C]-**6**•2I (8.2 mg, 0.01 mmol) in CH_3OH (0.3 mL) was heated in a closed vial at 65 °C for 15 h. The solvent was removed by a gentle stream of nitrogen gas, followed by placing under vacuum for 12 h. Resonances corresponding to $\text{PPh}_2(^{12}\text{CH}_3)(^{13}\text{CH}_3)$ salt were found in the NMR spectra of the crude material. ^1H NMR (CD_3CN) δ 2.46 (dd, $^1J_{\text{CH}} = 134.5$ Hz, $^2J_{\text{PH}} = 14.5$ Hz, P^{13}CH_3), (dd, $^3J_{\text{CH}} = 2.3$ Hz, $^2J_{\text{PH}} = 14.3$ Hz, PCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN) δ 8.5 (d, $^1J_{\text{PC}} = 57$ Hz, P^{13}CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN) δ 20.7 (d, $^1J_{\text{PC}} = 57$ Hz, P^{13}CH_3). m/z (ESI-MS, +ve) Found 216.10262 [$\text{PPh}_2(^{12}\text{CH}_3)(^{13}\text{CH}_3)$] $^+$. Calc. for $\text{C}_{13}^{13}\text{C}_1\text{H}_{16}\text{P}$: 216.10177.

Entry 4. A mixture of **6**•2I (8.0 mg, 0.01 mmol) in CH_3OH (0.3 mL) was heated in a closed vial at 65 °C for 15 h. The solvent was removed by a gentle stream of nitrogen gas, followed by placing under vacuum for 12 h. Resonances corresponding to $\text{PPh}_2(\text{CH}_3)_2$ salt were found in the NMR spectra of the crude material. ^1H NMR (CD_3CN) δ 2.46 (d, $^2J_{\text{PH}} = 14.5$ Hz, PCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN) δ 8.6 (d, $^1J_{\text{PC}} = 57$ Hz, PCH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN) δ 20.7 (s). m/z (ESI-MS, +ve) Found 215.09897 [$\text{PPh}_2(^{12}\text{CH}_3)_2$] $^+$. Calc. for $\text{C}_{14}\text{H}_{16}\text{P}$: 215.09841.

Table S1: Results of the ^{13}C -labelling studies.

Entry	Reagents	ESI-MS (<i>m/z</i>)	^1H NMR (δ)	$^{13}\text{C}\{^1\text{H}\}$ NMR (δ)	$^{31}\text{P}\{^1\text{H}\}$ NMR (δ)
1	$[^{13}\text{C}]\text{-6}\bullet\text{2I}$ in $[^{13}\text{C}]\text{-CH}_3\text{OH}$	216.10243	2.45 (dd, $^1J_{\text{CH}} = 134.4$ Hz, $^2J_{\text{PH}} = 14.4$ Hz, P^{13}CH_3), 2.46 (dd, $^3J_{\text{CH}} = 2.2$ Hz, $^2J_{\text{PH}} = 14.2$ Hz, PCH_3)	8.5 (d, $^1J_{\text{PC}} = 57$ Hz)	20.7 (d, $^1J_{\text{PC}} = 57$ Hz, P^{13}CH_3)
2	$\text{6}\bullet\text{2I}$ in $[^{13}\text{C}]\text{-CH}_3\text{OH}$	215.09918	2.46 (d, $^2J_{\text{PH}} = 14.5$ Hz, PCH_3)	8.6 (d, $^1J_{\text{PC}} = 58$ Hz)	20.7 (s)
3	$[^{13}\text{C}]\text{-6}\bullet\text{2I}$ in CH_3OH	216.10262	2.46 (dd, $^1J_{\text{CH}} = 134.5$ Hz, $^2J_{\text{PH}} = 14.5$ Hz, P^{13}CH_3), (dd, $^3J_{\text{CH}} = 2.3$ Hz, $^2J_{\text{PH}} = 14.3$ Hz, PCH_3)	8.5 (d, $^1J_{\text{PC}} = 57$ Hz)	20.7 (d, $^1J_{\text{PC}} = 57$ Hz, P^{13}CH_3)
4	$\text{6}\bullet\text{2I}$ in CH_3OH	215.09897	2.46 (d, $^2J_{\text{PH}} = 14.5$ Hz, PCH_3)	8.6 (d, $^1J_{\text{PC}} = 57$ Hz)	20.7 (s)

Crystallographic details

X-ray diffraction measurements for **4** (CCDC 924176) and **7** (CCDC 924177) were carried out on a Bruker kappa-II CCD diffractometer at 150 K by using graphite-monochromated Mo-K α radiation ($\lambda = 0.710723$ Å). Crystals of **4** and **7** were mounted on the goniometer using cryo loops for intensity measurements, were coated with paraffin oil and then quickly transferred to the cold stream using Oxford Cryostream attachment. Symmetry related absorption corrections using the program SADABS⁸ were applied and the data were corrected for Lorentz and polarization effects using Bruker APEX2 software.⁹ The structures were solved by direct methods and the full-matrix least-squares refinements were carried out using SHELXL.¹⁰ The non-hydrogen atoms were refined anisotropically. The hydrogen atoms, located in the difference Fourier maps, were refined isotropically using riding model option in SHELXL.

There are intermolecular phenyl C-H...H-B interactions with C...B1 and C...B2 distances of 3.64 and 3.87 Å respectively with two close C-H...H-B distances at 2.26 Å in the crystal structure of **7**. The latter values suggest ‘dihydrogen bonds’ involving acidic CH and hydridic BH hydrogens are present in the crystal.¹¹ Such C-H...H-B contacts are also observed in the structures of **2**¹² and **4** with H...H distances measured at 2.26-2.36 Å.

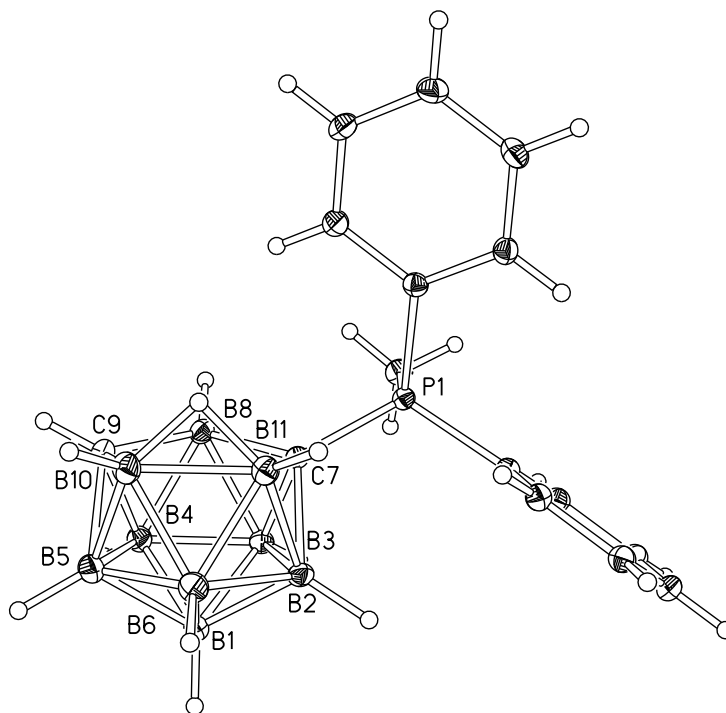


Figure S5. The molecular structure of **4**. Selected bond lengths in Å: C7-P1 1.775(2), C7-B8 1.644(3), C7-B11 1.661(3), C9-B8 1.623(3), C9-B10 1.650(3), B10-B11 1.828(3).

Table S2. X-ray crystallographic data for **4** and **7**

Crystal data	4	7
Chemical formula	C ₁₅ H ₂₄ B ₉ P	C _{29.50} H ₃₅ B ₉ OP ₂
<i>M</i> _r	332.60	564.80
Crystal system, space group	Monoclinic, C2/c	Monoclinic, P2 ₁ /c
Temperature (K)	150	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	26.8733 (17), 7.2742 (6), 19.5342 (14)	15.2083 (5), 11.6030 (4), 17.4061 (6)
<i>b</i> (°)	106.280 (2)	93.844 (2)
<i>V</i> (Å ³)	3665.5 (5)	3064.60 (18)
<i>Z</i>	8	4
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
<i>μ</i> (mm ⁻¹)	0.14	0.17
Crystal size (mm)	0.18 × 0.17 × 0.05	0.26 × 0.13 × 0.06
Data collection		
<i>T</i> _{min} , <i>T</i> _{max}	0.974, 0.993	0.957, 0.990
No. of measured, independent and observed [<i>I</i> > 2 <i>s</i> (<i>I</i>)] reflections	12765, 3218, 2675	22964, 5374, 3914
<i>R</i> _{int}	0.056	0.075
Refinement		
<i>R</i> [<i>F</i> ² > 2 <i>s</i> (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.039, 0.105, 1.03	0.046, 0.118, 1.00
No. of reflections	3218	5374
No. of parameters	248	393
No. of restraints	0	0
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
Δ <i>ρ</i> _{max} , Δ <i>ρ</i> _{min} (e Å ⁻³)	0.32, -0.29	0.34, -0.29

Computational details

All computations were carried out with the Gaussian 09 package.¹³ The model geometries from various starting conformers were fully optimized with the B3LYP functional¹⁴ with no symmetry constraints using the 6-31G* basis set¹⁵ for all atoms. Frequency calculations on all optimized geometries revealed no imaginary frequencies. Frequency calculations on transition-state geometries from computed intrinsic reaction coordinate pathways revealed one imaginary frequency for each geometry. Calculated ¹¹B NMR chemical shifts obtained at the GIAO¹⁶-B3LYP/6-31G*//B3LYP/6-31G* level on the optimized geometries were referenced to BF₃.OEt₂ for ¹¹B: $\delta(^{11}\text{B}) = 111.7 - \sigma(^{11}\text{B})$. The combined observed and computed ¹¹B NMR method has been successfully used to determine carborane geometries elsewhere.¹⁷

Animations of the cage rearrangement pathways can be found at:

<http://www.dur.ac.uk/m.a.fox/ioppolo.ppt>

Table S3. Comparison between computed and observed ^{11}B NMR shifts in ppm for carboranes **4**, **7**, and **9⁺**-**12**.

	Calculated	Observed		Calculated	Observed
4			10²⁺		
B5	3.6	0.9 (1)	B5,12	0.9	-1.1 (2)
B2	-0.2	-0.5 (1)	B9,10	-6.7	-7.8 (2)
B8	-6.3	-5.7 (1)	B4,6,8,11	-9.4	-9.6 (4)
B3	-15.7	-18.4 (2)	B2,3	-14.4	-13.8 (2)
B4	-17.0				
B10	-17.6	-19.5 (1)	11⁺		
B11	-21.0	-20.9 (1)	B2	6.4	
B6	-29.4	-31.8 (2)	B5	5.8	3.4 (3)
B1	-30.1		B10	1.9	
			B8	-9.8	-8.9 (1)
7			B4	-14.2	-17.8 (1)
B2,5	-9.4	-12.5 (1)	B3	-20.4	-22.7 (1)
B6	-14.8		B11	-21.8	-24.2 (1)
B10,11	-15.2	-17.8 (3)	B6	-30.3	-33.6 (2)
B3,4	-17.5	-18.7 (2)	B1	-31.0	
B8	-19.5	-20.2 (1)			
B1	-42.7	-45.7 (1)	12		
			B10	8.0	7.3 (1)
9⁺			B5	-9.0	-13.2 (1)
B2,5	5.6	4.1 (2)	B2	-13.2	-15.3 (1)
B8	-7.1	-6.4 (1)	B6	-17.7	-20.4 (1)
B3,4	-13.9	-16.5 (2)	B4	-17.9	
B10,11	-18.2	-18.9 (2)	B8	-21.5	-22.8 (3)
B6	-27.3	-30.3 (1)	B3	-23.8	
B1	-29.6	-31.0 (1)	B11	-24.1	-27.1 (1)
			B1	-45.2	-48.1 (1)

Table S4. Total and relative energies for optimised geometries of isomeric neutral species $(PPh_2Me)_2C_2B_9H_9$ and $(PPh_2Me)_2C_2B_9H_{10}$ cations.

	Energy (a.u.)	Relative Energy (kcal mol ⁻¹)
<i>(PPh₂Me)₂C₂B₉H₉ isomers</i>		
7,9-(PPh ₂ Me) ₂ -7,9-C ₂ B ₉ H ₉	7 -1994.53270	0
2,9-(PPh ₂ Me) ₂ -2,9-C ₂ B ₉ H ₉	A -1994.48202	31.8
1,7-(PPh ₂ Me) ₂ -1,7-C ₂ B ₉ H ₉	B -1994.44654	54.1
2,8-(PPh ₂ Me) ₂ -2,8-C ₂ B ₉ H ₉	C -1994.46904	39.9
7,8-(PPh ₂ Me) ₂ -7,8-C ₂ B ₉ H ₉	-1994.44858	52.8
<i>(PPh₂Me)₂C₂B₉H₁₀ cations</i>		
[7,9-(PPh ₂ Me) ₂ -7,9-C ₂ B ₉ H ₁₀] ⁺	9⁺ -1994.97399	0
[2,9-(PPh ₂ Me) ₂ -2,9-C ₂ B ₉ H ₁₀] ⁺	-1994.92751	29.2
[7,8-(PPh ₂ Me) ₂ -7,8-C ₂ B ₉ H ₁₀] ⁺	-1994.89864	47.3

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