Chapter 6

Experimental Section

6.1 General Experimental

Synthesis

All experiments were performed under dry, oxygen-free N₂, using standard Schlenk techniques, with some subsequent manipulations in the open laboratory. Solvents were freshly distilled over CaH₂ (CH₂Cl₂) or Na wire (THF, 40-60 petroleum ether, toluene) under nitrogen and were degassed (3 x freeze-pump-thaw cycles) prior to use, or were stored over 4 Å molecular sieves. Preparative TLC employed 20 x 20 cm Kieselgel 60 F₂₅₄ glass plates.

Analysis

NMR spectra at 400.1 MHz (¹H) or 128.4 MHz (¹¹B) were recorded on Bruker DPX-400 or AVIII-400 spectrometers at Heriot-Watt University from CDCl₃ solutions at room temperature. The internal reference compound used for ¹¹B spectroscopy is BF₃·OEt₂. Electron ionisation mass spectrometry (EIMS) was carried out using either a Kratos Concept mass spectrometer at Heriot-Watt University or a Finnigan (Thermo) LCQ Classic ion trap mass spectrometer at the University of Edinburgh. Elemental Analyses (CHN) were determined by the Chemistry Department services of Heriot-Watt University using an Exeter CE-440 elemental analyser.

Hazards

Standard principles of safe handling and good general laboratory practice were followed, including the wearing of protective clothing and safety glasses. Extra care and attention were employed when handling flammable solvents, volatile compounds, sodium, lithium and toxic carboranes.
Standard Preparations

1,2-µ-(CH₂SiMe₂CH₂)-1,2-closo-C₂B₁₀H₁₀,¹ [(p-cymene)RuCl₂]₂,² 1-Me-1,2-closo-C₂B₁₀H₁₁,³ 1,2-µ-(CH₂)₃-1,2-closo-C₂B₁₀H₁₀,⁴ 1,8-Me₂-4-Cp-4,1,8-closo-CoC₂B₁₀H₁₀,⁵ 1,12-Me₂-4-Cp-4,1,12-closo-CoC₂B₁₀H₁₀,⁵ 4-(η-C₉H₇)-4,1,12-closo-CoC₂B₁₀H₁₂,⁶ 4-Cp-4,1,6-closo-CoC₂B₁₀H₁₂,⁷ 4-Cp-4,1,8-closo-CoC₂B₁₀H₁₂,⁷ 4-Cp-4,1,10-closo-CoC₂B₁₀H₁₂,⁸ and 4-Cp-4,1,12-closo-CoC₂B₁₀H₁₂,⁷,⁸ were prepared using literature methods or slight variations thereof. 1,2-Me₂-1,2-closo-C₂B₁₀H₁₀ was prepared by treatment of Li₂[1,2-closo-C₂B₁₀H₁₀] with MeI in Et₂O.⁹ All other reagents and solvents were supplied commercially and used as received. A 2M solution of NaCp and 2.5 M solution of n-BuLi were used in the relevant syntheses.

Crystallography

Single crystals suitable for X-ray diffraction were grown by either solvent or vapour diffusion using a CH₂Cl₂/40-60 petroleum ether system (except compounds 6 and 17 which were grown using a THF/diethyl ether system at -30 °C and a THF/40-60 petroleum ether system at room temperature respectively) at -15 °C or -30 °C. Crystals were mounted in inert oil on a cryoloop and cooled to 100 K by an Oxford Cryosystems Cryostream. Intensity data were collected on a Bruker X8 APEX2 diffractometer using graphite-monochromated Mo-Kα X-radiation. Indexing, data collection and absorption correction were performed using the APEXII suite of programs.¹⁰ The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares (SHELXL-97).¹¹ Refinement was completed with all non-hydrogen atoms assigned anisotropic displacement parameters. Geometric measurements were made using Mercury software.¹²
6.2.1 Synthesis of 1,2-Me₂-4-Cp-4,1,2-closo-CoC₂B₁₀H₁₀ (1) and 1,6-Me₂-4-Cp-4,1,6-closo-CoC₂B₁₀H₁₀ (2)

A solution of 1,2-µ-(CH₂SiMe₂CH₂)-1,2-closo-C₂B₁₀H₁₀ (0.50 g, 2.19 mmol) in THF (30 ml) was stirred with lithium metal (0.15 g, 21.9 mmol) overnight at room temperature. The resulting dark orange solution was transferred via gas tight syringe to a second Schlenk tube and NaCp (6.6 ml, 13.2 mmol) followed by CoCl₂ (2.10 g, 16.2 mmol) added at 0 °C. The reaction mixture was left to stir overnight at room temperature to give a brown suspension which was subjected to aerial oxidation for 1 h followed by filtration through a short silica column eluting with CH₂Cl₂. Purification of the oily brown residue by preparative TLC on silica with a mixed eluent of CH₂Cl₂:40-60 petroleum ether (3:2) revealed two major mobile bands which were collected as solids:

- Orange  \( R_f = 0.35 \)  Yield = 28 mg, 4%  Compound 1
- Dark red  \( R_f = 0.58 \)  Yield = 20 mg, 3%  Compound 2
1,2-Me₂-4-Cp-4,1,2-closo-CoC₂B₁₀H₁₀ (1)

CHN

Required for C₉H₂₁B₁₀Co:  C 36.5, H 7.14%.
Found:  C 36.6, H 7.17%.

EIMS

m/ᵚ envelope centred on 296 (M⁺).

[MW = 296.29 g mol⁻¹].

¹¹B{¹H} NMR

δ 14.52 (2B), 10.83 (2B), 3.79 (2B), -6.09 (2B),
-8.89 (2B).

〈δ(¹¹B)〉 = 2.83 ppm.

¹H NMR

δ 5.39 (s, 5H, C₅H₅), 2.43 (s, 6H, C_cageCH₃).

X-Ray Diffraction

Solvent diffusion of 40-60 petroleum ether into a CH₂Cl₂ solution of 1 at -15 °C resulted in suitable quality crystals for X-ray diffraction.
1,6-Me₂-4-Cp-4,1,6-closo-CoC₂B₁₀H₁₀ (2)

CHN

Required for C₉H₂₁B₁₀Co:  C 36.5, H 7.14%.
Found:  C 36.7, H 7.18%.

EIMS

$m/z$ envelope centred on 296 (M⁺).

[MW = 296.29 g mol⁻¹].

¹¹B{¹H} NMR

δ 13.59 (1B), 3.00 (2B), 1.85 (1B), -1.63 (1B), -4.44 (2B), -5.78 (2B), -11.18 (1B).

⟨δ(¹¹B)⟩ = -1.18 ppm.

¹H NMR

δ 5.40 (s, 5H, C₅H₅), 2.34 (s, 6H, C_cageCH₃).

X-Ray Diffraction

Crystals were grown by solvent diffusion of 40-60 petroleum ether into a CH₂Cl₂ solution of 2 at -15 °C.
6.2.2 Preferred Synthesis of 1,6-Me₂-4-Cp-4,1,6-closo-CoC₂B₁₀H₁₀ (2)

1,2-Me₂-1,2-closo-C₂B₁₀H₁₀ (0.25 g, 1.45 mmol) was treated with sodium metal (0.074 g, 3.19 mmol) and naphthalene (ca. 15 mg) in THF (30 ml) at room temperature overnight. The resulting cloudy solution was transferred via cannula to a second Schlenk tube and cooled to 0 °C. NaCp (2.18 ml, 4.36 mmol) and CoCl₂ (0.70 g, 5.37 mmol) were added and the reaction mixture stirred overnight at room temperature. The crude mixture was then subjected to aerial oxidation (1 h) followed by filtration through silica and further purification by column chromatography on silica [CH₂Cl₂:40-60 petroleum ether (3:2)] to afford compound 2 as a dark red solid.

Yield = 240 mg, 56%.
6.2.3 Preparation of $^{1,8}$-Me$_2$-4-Cp-$^{4,1,8}$-closo-CoC$_2$B$_{10}$H$_{10}$ (3)

Compound 3 was attained from overnight thermolysis of 2 (0.24 g, 0.81 mmol) in refluxing THF (30 ml). Purification by column chromatography [CH$_2$Cl$_2$:40-60 petroleum ether (3:2)] afforded compound 3 as a light orange solid along with minor amounts of the corresponding 4,1,12- isomer and unchanged 3.

R$_f$ = 0.75        Yield = 212 mg, 88%        Compound 3
1,8-Me₂-4-Cp-4,1,8-closo-CoC₂B₁₀H₁₀ (3)

CHN
Required for C₉H₂₁B₁₀Co:  C 36.5, H 7.14%.
Found:  C 36.2, H 7.18%.

EIMS
m/z envelope centred on 296 (M⁺).
[MW = 296.29 g mol⁻¹].

¹¹B{¹H} NMR
δ 18.77 (1B), 10.56 (1B), 9.83 (1B), 2.69 (1B),
2.26 (1B), -1.04 (1B), -2.11 (2B), -5.71 (1B),
-12.49 (1B).
⟨δ(¹¹B)⟩ = 2.07 ppm.

¹H NMR
δ 5.28 (s, 5H, C₅H₅), 2.47 (s, 3H, C_cageCH₃),
1.95 (s, 3H, C_cageCH₃).

X-Ray Diffraction

Crystals were grown by solvent diffusion of 40-60 petroleum ether into a CH₂Cl₂ solution of 3 at -15 °C.
6.2.4 Synthesis of 1,2-Me$_2$-4-(p-cymene)-4,1,2-closo-RuC$_2$B$_{10}$H$_{10}$ (4) and 1,6-Me$_2$-4-(p-cymene)-4,1,6-closo-RuC$_2$B$_{10}$H$_{10}$ (5)

A solution of 1,2-µ-(CH$_2$SiMe$_2$CH$_2$)-1,2-closo-C$_2$B$_{10}$H$_{10}$ (0.20 g, 0.88 mmol) in THF (20 ml) was stirred with sodium metal (0.045 g, 1.94 mmol) and naphthalene (ca. 15 mg) overnight at room temperature. The resulting dark orange solution was transferred via gas tight syringe to a second Schlenk tube containing a frozen suspension of [(p-cymene)RuCl$_2$]$_2$ (0.27 g, 0.44 mmol) in THF (10 ml). The reaction mixture was then frozen before being allowed to warm to room temperature and stirred for 48 h to give a brown suspension. Filtration of the crude suspension through silica resulted in an oily brown residue which was purified by TLC on silica [CH$_2$Cl$_2$:40-60 petroleum ether (4:1)] to afford two major products which were collected as solids:

<table>
<thead>
<tr>
<th>Color</th>
<th>R$_f$</th>
<th>Yield</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orange</td>
<td>0.54</td>
<td>16 mg, 4%</td>
<td>4</td>
</tr>
<tr>
<td>Yellow</td>
<td>0.86</td>
<td>21 mg, 6%</td>
<td>5</td>
</tr>
</tbody>
</table>
1,2-Me$_2$-4-(p-cymene)-4,1,2-closo-RuC$_2$B$_{10}$H$_{10}$ (4)

CHN

Required for C$_{14}$H$_{30}$B$_{10}$Ru:  C 41.3, H 7.42%.

Found:  C 39.9, H 7.17%.

EIMS

$m/z$ envelope centred on 408 (M$^+$_).

[MW = 407.58 g mol$^{-1}$].

$^{11}$B{$^1$H} NMR

$\delta$ 14.19 (2B), 11.52 (2B), 5.21 (1B), 3.21 (1B), -5.98 (2B), -11.96 (2B).

$\langle \delta(^{11}$B) $\rangle = 2.40$ ppm.

$^1$H NMR

$\delta$ 6.13-6.02 (m, 4H, CH$_3$C$_6$H$_4$CH(CH$_3$)$_2$),

2.80 (septet, 1H, CH$_3$C$_6$H$_4$CH(CH$_3$)$_2$),

2.19 (s, 3H, CH$_3$C$_6$H$_4$CH(CH$_3$)$_2$),

2.05 (s, 6H, C$_{cage}$CH$_3$),

1.19 (d, 6H, CH$_3$C$_6$H$_4$CH(CH$_3$)$_2$).

X-Ray Diffraction

Crystals were grown by solvent diffusion of 40-60 petroleum ether into a CH$_2$Cl$_2$ solution of 4 at -15 °C.
1,6-Me_2-4-(p-cymene)-4,1,6-closo-RuC_2B_{10}H_{10} (5)

CHN

Required for C_{14}H_{30}B_{10}Ru:  C 41.3, H 7.42%.
Found:  C 41.4, H 7.52%.

EIMS

m/z envelope centred on 407 (M^+).
[MW = 407.58 g mol^{-1}].

^{11}B\{^1H\} NMR

δ 13.97 (1B), 3.67 (1B), 2.13 (2B), -0.64 (1B),
-3.49 (2B), -5.94 (2B), -14.02 (1B).
⟨δ(^{11}B)⟩ = -1.16 ppm.

^1H NMR

δ 5.91-5.80 (m, 4H, CH_3C_6H_4CH(CH_3)_2),
2.85 (septet, 1H, CH_3C_6H_4CH(CH_3)_2),
2.28 (s, 3H, CH_3C_6H_4CH(CH_3)_2),
2.00 (s, 6H, C_{cage}CH_3),
1.23 (d, 6H, CH_3C_6H_4CH(CH_3)_2).

X-Ray Diffraction

Crystals were grown by solvent diffusion of 40-60 petroleum ether into a CH_2Cl_2 solution of 5 at -15 °C.
6.3.1 Synthesis of 4-(η-C₉H₇)-4,1,6-closo-CoC₂B₁₀H₁₂ (6)

1,2-closo-C₂B₁₀H₁₂ (0.70 g, 4.85 mmol) was stirred with sodium metal (0.28 g, 12.1 mmol) in degassed THF (30 ml) at room temperature overnight. In a second Schlenk tube a solution of Li[C₉H₇] was prepared by treating indene (1.69 ml, 14.55 mmol) with n-BuLi (6.40 ml, 16.0 mmol) in degassed THF (10 ml) at 0 °C followed by stirring for 1 h at room temperature then at reflux for 15 min. The reduced carborane solution was transferred via cannula to the dark red solution of Li[C₉H₇] and the resulting red solution cooled to 0 °C followed by addition of CoCl₂ (2.33 g, 17.95 mmol). The reaction mixture was then stirred at room temperature overnight and the crude suspension subjected to aerial oxidation for 0.5 h followed by filtration through a short silica column eluting with CH₂Cl₂. Further purification by column chromatography on silica [CH₂Cl₂:40-60 petroleum ether (3:2)] afforded compound 6 as a brown solid.

Rₜ = 0.62    Yield = 730 mg, 47.3%    Compound 6
4-(\(\eta\)-C\(_9\)H\(_7\))-4,1,6-closo-CoC\(_3\)B\(_{10}\)H\(_{12}\) (6)

**CHN**
- Required for C\(_{11}\)H\(_{19}\)B\(_{10}\)Co: C 41.5, H 6.02%.
- Found: C 41.6, H 6.18%.

**EIMS**
- \(m/z\) envelope centred on 316 (M\(^+\)).
- [MW = 318.29 g mol\(^{-1}\)].

**\(^{11}\)B\(^{1H}\) NMR**
- \(\delta\) 14.54 (1B), 1.95 (2B), -0.52 (1B), -3.80 (3B), -11.90 (2B), -16.89 (1B).
- \(\langle \delta(\(^{11}\)B) \rangle = -3.42\) ppm.

**\(^1\)H NMR**
- \(\delta\) 7.72 (m, 2H, C\(_6\)H\(_4\)), 7.60 (m, 2H, C\(_6\)H\(_4\)), 5.93 (d, 2H, C\(_5\)H\(_3\)), 5.60 (t, 1H, C\(_5\)H\(_3\)), 3.78 (br s, 2H, C\(_{cage}\)H).

**X-Ray Diffraction**

Crystals were grown by solvent diffusion of diethyl ether into a THF solution of 6 at -30 °C.
6.3.2 Synthesis of 1,6-Me₂-4-(η-C₉H₇)-4,1,6-closo-CoC₂B₁₀H₁₀ (7)

A degassed THF (30 ml) solution of 1,2-Me₂-1,2-closo-C₂B₁₀H₁₀ (0.50 g, 2.90 mmol) was stirred overnight with sodium metal (0.24 g, 10.4 mmol) and the resulting solution transferred via cannula to a second Schlenk tube containing a freshly prepared THF (10 ml) solution of Li[C₉H₇] (8.70 mmol) at 0 °C. CoCl₂ (1.39 g, 10.7 mmol) was then added and the mixture stirred overnight at room temperature. Aerial oxidation (0.5 h) of the brown suspension and subsequent filtration through a short silica column eluting with CH₂Cl₂ yielded an oily brown solid which was further purified by preparative TLC on silica [CH₂Cl₂:40-60 petroleum ether (3:2)] to afford compound 7 as a dark brown solid.

Rᵋ = 0.62 Yield = 340 mg, 33.8% Compound 7
1,6-Me₂-4-(η-C₅H₇)-4,1,6-closo-CoC₂B₁₀H₁₀ (7)

CHN
Required for C₁₃H₂₃B₁₀Co:  C 45.1, H 6.69%.
Found:  C 44.9, H 6.77%.

EIMS

$m/z$ envelope centred on 346 (M⁺).

$[MW = 346.34 \text{ g mol}^{-1}]$.

$^{11}\text{B}\{^1\text{H}\} \text{ NMR}$

$\delta$ 15.08 (1B), 4.87 (2B), 0.33 (1B), -0.47 (1B),
-4.79 (2B), -7.28 (2B), -12.05 (1B).

$\langle \delta(^{11}\text{B}) \rangle = -1.15 \text{ ppm.}$

$^1\text{H} \text{ NMR}$

$\delta$ 7.80 (m, 2H, $C₆H₄$), 7.60 (m, 2H, $C₆H₄$),
5.80 (d, 2H, $C₅H₃$), 5.75 (t, 1H, $C₅H₃$),
2.15 (s, 6H, $C_{cage}CH₃$).

X-Ray Diffraction

Crystals were grown by solvent diffusion of 40-60 petroleum ether into a CH₂Cl₂ solution of 7 at -30 °C.
6.3.3 Preparation of 4-(η-C₉H₇)-4,1,8-closo-CoC₂B₁₀H₁₂ (8)

A THF (25 ml) solution of 6 (0.21 g, 0.66 mmol) was stirred at reflux for 18 h to afford, after solvent removal, a bronze solid. Preparative TLC on silica [CH₂Cl₂:40-60 petroleum ether (3:2)] separated compound 8 as a bronze product from minor amounts of the corresponding 4,1,12- isomer 14 and unchanged 6.

Rᵣ = 0.77     Yield = 153 mg, 73.6%     Compound 8
4-(η-C₉H₇)-4,1,8-closo-CoC₂B₁₀H₁₂ (8)

CHN

Required for C₁₁H₁₉B₁₀Co:  C 41.5, H 6.02%.
Found: C 41.5, H 6.08%.

EIMS

m/z envelope centred on 317 (M⁺).
[MW = 318.29 g mol⁻¹].

¹¹B{¹H} NMR

δ 22.61 (1B), 9.32 (1B), 7.43 (1B), 6.34 (1B),
-0.92 (1B), -5.80 (1B), -7.23 (1B), -8.69 (1B),
-9.72 (1B), -12.52 (1B).
⟨δ(¹¹B)⟩ = 0.08 ppm.

¹H NMR

δ 7.57 (m, 2H, C₆H₄), 7.48 (m, 2H, C₆H₄),
5.86 (m, 1H, C₅H₃), 5.82 (m, 1H, C₅H₃),
5.09 (app t, 1H, C₅H₃), 3.75 (br s, 1H, C_cageH),
2.50 (br s, 1H, C_cageH).
6.3.4 Preparation of 1,8-Me$_2$-4-(\(\eta\)-C$_9$H$_7$)-4,1,8-closo-CoC$_2$B$_{10}$H$_{10}$ (9)

Compound 7 (0.20 g, 0.58 mmol) was heated to reflux in THF (25 ml) for 18 h. Purification by TLC on silica [CH$_2$Cl$_2$:40-60 petroleum ether (3:2)] afforded compound 9 as an orange solid along with a lesser amount of the corresponding 4,1,12- isomer 15 (57 mg, 28.5%).

R$_f$ = 0.75  Yield = 133 mg, 66.5%  Compound 9
1,8-Me₂-4-(η-C₅H₇)-4,1,8-closo-CoC₂B₁₀H₁₀ (9)

**CHN**
Required for C₁₃H₂₃B₁₀Co: C 45.1, H 6.69%.
Found: C 44.9, H 6.71%.

**EIMS**
m/z envelope centred on 346 (M⁺).
[MW = 346.34 g mol⁻¹].

**¹¹B{¹H} NMR**
δ 21.23 (1B), 13.23 (1B), 10.79 (1B), 5.22 (1B), 3.34 (1B), -2.11 (1B), -2.57 (1B), -2.97 (1B), -5.67 (1B), -13.19 (1B).
⟨δ(¹¹B)⟩ = 2.73 ppm.

**¹H NMR**
δ 7.56 (m, 2H, C₆H₄), 7.51 (m, 2H, C₆H₄), 5.65 (m, 1H, C₅H₃), 5.60 (m, 1H, C₅H₃), 5.25 (app t, 1H, C₅H₃), 2.60 (s, 3H, C₉C₅H₃), 1.75 (s, 3H, C₉C₅H₃).

**X-Ray Diffraction**

Crystals were grown by solvent diffusion of 40-60 petroleum ether into a CH₂Cl₂ solution of 9 at -30 °C.
6.3.5 Synthesis of 1(or 6)-Me-4-(η-C₉H₇)-4,1,6-closo-CoC₂B₁₀H₁₁ (10)

1-Me-1,2-closo-C₂B₁₀H₁₁ (0.25 g, 1.55 mmol) was stirred overnight with sodium metal (0.09 g, 3.90 mmol) in THF (30 ml). The reduced carborane was then treated with a freshly prepared THF solution of Li[Ç₉H₇] (4.65 mmol) and CoCl₂ (0.75 g, 5.74 mmol) at 0 °C and the mixture stirred overnight at room temperature. The resultant brown suspension was subjected to aerial oxidation (0.5 h), filtration through silica and further purification by column chromatography on silica [CH₂Cl₂:40-60 petroleum ether (1:4)] to afford compound 10 as a dark brown solid.

Rᵣ = 0.64  Yield = 208 mg, 40.4%  Compound 10
1(or 6)-Me-4-(η-C₉H₇)-4,1,6-closo-CoC₂B₁₀H₁₁ (10)

CHN

Required for C₁₂H₂₁B₁₀Co: C 43.4, H 6.37%.
Found: C 43.3, H 6.52%.

EIMS

\[ m/z \text{ envelope centred on } 332 (M^+). \]
[\( \text{MW} = 332.34 \text{ g mol}^{-1} \).]

\(^{11}\text{B}\{^1\text{H}\} \text{ NMR} \)
\( \delta 14.32 \text{ (1B), 8.20 (1B), -0.10 (1B), -2.38 (2B), -3.43 (1B), -4.59 (1B), -7.59 (1B), -10.21 (1B), -16.46 (1B).} \)
\( \langle \delta^{(11}\text{B}) \rangle = -2.46 \text{ ppm.} \)

\(^1\text{H} \text{ NMR} \)
\( \delta 7.86 \text{ (m, 1H, } C₆H₄), 7.66 \text{ (m, 2H, } C₆H₄), 7.33 \text{ (m, 1H, } C₅H₃), 6.12 \text{ (m, 1H, } C₅H₃), 5.73 \text{ (m, 1H, } C₅H₃), 5.61 \text{ (app t, 1H, } C₅H₃), 2.62 \text{ (s, 3H, } C_{\text{cage}}CH₃), 2.48 \text{ (br s, 1H, } C_{\text{cage}}H). \)
6.3.6 Preparation of 8-Me-4-(η-C₉H₇)-4,1,8-closo-CoC₂B₁₀H₁₁ (11) and 1-Me-4-(η-C₉H₇)-4,1,8-closo-CoC₂B₁₀H₁₁ (12)

A THF (25 ml) solution of 10 (0.10 g, 0.30 mmol) was stirred at reflux for 18 h. Preparative TLC on silica [CH₂Cl₂:40-60 petroleum ether (3:2)] revealed in order of elution, a brown band (R_f = 0.87, 21 mg, 21%, tentatively assigned from ¹¹B and ¹H NMR spectroscopies as a mixture of 1-Me-4-(η-C₉H₇)-4,1,12-closo-CoC₂B₁₀H₁₁ and 12-Me-4-(η-C₉H₇)-4,1,12-closo-CoC₂B₁₀H₁₁), an orange band and a lower brown band (5 mg, 5%, unchanged compound 10). The ¹¹B and ¹H NMR spectra of the orange band appeared to show a mixture of two isomers in approximately 2:1 ratio.

R_f = 0.80       Yield = 67 mg, 67%       Mixture of compounds 11 and 12

CHN

Required for C₁₂H₂₁B₁₀Co:   C 43.4, H 6.37%.

Found:                     C 43.4, H 6.42%.

EIMS

m/z envelope centred on 332 (M⁺).

[MW = 332.34 g mol⁻¹].

241
8-Me-4-(η-C₉H₇)-4,1,8-closo-CoC₂B₁₀H₁₁ (11)

**X-Ray Diffraction**

Compound 11 preferentially crystallised by solvent diffusion of 40-60 petroleum ether into a CH₂Cl₂ solution of a mixture of 11 and 12 at -30 °C.

NMR spectra of redissolved crystals:

**¹¹B{¹H} NMR**

δ 20.44 (1B), 11.66 (1B), 8.71 (1B), 4.62 (1B), 2.09 (1B), -2.74 (1B), -3.52 (1B), -7.07 (2B), -12.63 (1B).

⟨δ(¹¹B)⟩ = 1.45 ppm.

**¹H NMR**

δ 7.53 (m, 4H, C₆H₄), 5.83 (m, 1H, C₃H₃), 5.79 (m, 1H, C₃H₃), 5.04 (app t, 1H, C₃H₃), 3.75 (br s, 1H, C₆C₆H₄), 1.75 (s, 3H, C₆C₆CH₃).
1-Me-4-(η-C₉H₇)-4,1,8-closo-CoC₂B₁₀H₁₁ (12)

NMR from difference spectroscopy:

$$^{11}B\{^1H\} \text{NMR}$$

$$\delta$$ 23.16 (1B), 11.23 (1B), 8.88 (1B), 6.77 (1B), 0.26 (1B), -5.20 (1B), -6.26 (2B), -7.30 (1B), -13.22 (1B).

$$\langle \delta^{(11)B} \rangle = 1.21 \text{ ppm.}$$

$$^1H \text{NMR}$$

$$\delta$$ 7.53 (m, 4H, C₆H₄), 5.67 (m, 1H, C₅H₃), 5.62 (m, 1H, C₅H₃), 5.27 (app t, 1H, C₅H₃), 2.42 (br s, 1H, C cageH), 1.53 (s, 3H, C cageCH₃).
6.3.7 Synthesis of 4-(η-C₉H₇)-4,1,10-closo-CoC₂B₁₀H₁₂ (13)

1,12-closo-C₂B₁₀H₁₂ (1.00 g, 6.93 mmol) was treated with sodium metal (1.16 g, 48.7 mmol) in liquid ammonia (30 ml) at -78 °C for 3 h with stirring. The reaction mixture was warmed to room temperature and the dry residue extracted into degassed THF (40 ml) and cooled to 0 °C. A THF solution of Li[C₉H₇] (20.79 mmol), freshly prepared from indene and n-BuLi, was added to the reduced carborane solution followed by CoCl₂ (3.33 g, 25.64 mmol). The reaction mixture was stirred overnight and the resultant brown suspension was subjected to aerial oxidation for 0.5 h followed by filtration under vacuum through silica. Column chromatography on silica [CH₂Cl₂:40-60 petroleum ether (3:2)] afforded a brown solid (minor, R₉ = 0.80, compound 14) and a red brown solid (major) which was identified as compound 13.

R₉ = 0.60       Yield = 1050 mg, 47.5%       Compound 13
4-(η-C₉H₇)-4,1,10-clos-CoC₂B₁₀H₁₂ (13)

CHN

Required for C₁₁H₁₉B₁₀Co:  C 41.5, H 6.02%.
Found:                    C 41.6, H 6.14%.

EIMS

m/z envelope centred on 318 (M⁺).
[MW = 318.29 g mol⁻¹].

¹¹B{¹H} NMR

δ 4.92 (2B), 3.86 (2B), -7.26 (1B), -9.01 (3B),
-12.77 (2B).
⟨δ(¹¹B)⟩ = -4.23 ppm.

¹H NMR

δ 7.71 (m, 2H, C₆H₄), 7.54 (m, 2H, C₆H₄),
5.81 (d, 2H, C₅H₃), 5.63 (t, 1H, C₅H₃),
5.05 (br s, 1H, C₅cageH), 1.93 (br s, 1H, C₅cageH).

X-Ray Diffraction

Crystals were grown by solvent diffusion of 40-60 petroleum ether into a CH₂Cl₂
solution of 13 at -30 °C.
6.3.8 Preparation of 4-(η-C₉H₇)-4,1,12-closo-CoC₂B₁₀H₁₂ (14)

A THF (30 ml) solution of 13 (0.85 g, 2.67 mmol) was heated to reflux for 18 h to afford, after column chromatography on silica [CH₂Cl₂:40–60 petroleum ether (3:2)], compound 14 as an orange brown solid along with a minor amount of unchanged 13.

Rₚ = 0.80      Yield = 775 mg, 91.2%      Compound 14
**4-(η-C₉H₇)-4,1,12-closo-CoC₂B₁₀H₁₂ (14)**

**CHN**
- Required for C₁₁H₁₉B₁₀Co: C 41.5, H 6.02%.
- Found: C 41.4, H 6.02%.

**EIMS**
- m/z envelope centred on 317 (M⁺).
- [MW = 318.29 g mol⁻¹].

**¹¹B{¹H} NMR**
- δ 8.78 (1B), 6.67 (1B), 3.99 (1B), 3.15 (1B),
- -2.78 (1B), -10.02 (2B), -14.32 (1B), -15.85 (1B),
- -17.32 (1B).
- ⟨δ(¹¹B)⟩ = -4.77 ppm.

**¹H NMR**
- δ 7.52 (m, 2H, C₆H₄), 7.47 (m, 2H, C₆H₄),
- 5.86 (m, 1H, C₃H₃), 5.78 (m, 1H, C₃H₃),
- 5.14 (app t, 1H, C₃H₃), 3.87 (br s, 1H, C_cageH)
- 3.15 (br s, 1H, C_cageH).

**X-Ray Diffraction**

Crystals were grown by solvent diffusion of 40-60 petroleum ether into a CH₂Cl₂ solution of 14 at -30 °C.
6.3.9 Preparation of 1,12-Me₂-4-(η-C₉H₇)-4,1,12-closo-CoC₂B₁₀H₁₀ (15)

Heating a toluene (25 ml) solution of compound 9 (0.075 g, 0.22 mmol) to reflux overnight affords, after preparative TLC on silica [CH₂Cl₂:40-60 petroleum ether (1:1)], dark brown 15 as the major product and unchanged 9 (13 mg) in 17.3% yield.

Rᵥ = 0.86  
Yield = 56 mg, 74.7%  
Compound 15
$1,12$-$\text{Me}_2$-$4$-($\eta$-$\text{C}_9\text{H}_7$)-$4,1,12$-$\text{closo}$-$\text{CoC}_2\text{B}_{10}\text{H}_{10}$ (15)

**CHN**

Required for $\text{C}_{13}\text{H}_{23}\text{B}_{10}\text{Co}$: C 45.1, H 6.69%.

Found: C 44.9, H 6.76%.

**EIMS**

$m/z$ envelope centred on 346 ($M^+$).

$[\text{MW} = 346.34 \text{ g mol}^{-1}]$.

**$^{11}\text{B}$-$^1\text{H}$ NMR**

$\delta$ 10.18 (1B), 8.97 (1B), 8.21 (1B), 4.23 (1B), 1.86 (1B), -5.19 (1B), -5.75 (1B), -8.02 (1B), -14.36 (2B).

$\langle \delta(11\text{B}) \rangle = -1.42$ ppm.

**$^1\text{H}$ NMR**

$\delta$ 7.55 (m, 4H, $C_6\text{H}_4$), 5.64 (m, 1H, $C_5\text{H}_3$), 5.55 (m, 1H, $C_5\text{H}_3$), 5.31 (app t, 1H, $C_5\text{H}_3$), 2.38 (s, 3H, $C_{\text{cage}}\text{CH}_3$), 1.72 (s, 3H, $C_{\text{cage}}\text{CH}_3$).

**X-Ray Diffraction**

Crystals were grown by solvent diffusion of 40-60 petroleum ether into a $\text{CH}_2\text{Cl}_2$ solution of 15 at -30 °C.
6.3.10 Synthesis of 1,2-Me₂-4-(η-C₉H₇)-4,1,2-closo-CoC₂B₁₀H₁₀ (16)

1,2-μ-(CH₂SiMe₂CH₂)-1,2-closo-C₂B₁₀H₁₀ (0.25 g, 1.09 mmol) was treated with lithium metal (0.075 g, 10.90 mmol) in THF (25 ml) at room temperature for 24 h. The resulting yellow solution was transferred via cannula to a second Schlenk tube and cooled to 0 °C. A freshly prepared THF (10 ml) solution of Li[C₉H₇] (3.27 mmol) was then added followed by CoCl₂ (0.52 g, 4.03 mmol). The reaction mixture was stirred overnight and the resultant brown suspension subjected to aerial oxidation (0.5 h) followed by filtration through a short silica column. Preparative TLC on silica [CH₂Cl₂:40-60 petroleum ether (3:2)] yielded three products:

<table>
<thead>
<tr>
<th>Color</th>
<th>Rf</th>
<th>Yield</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orange</td>
<td>0.86</td>
<td>7 mg, 1.9%</td>
<td>9</td>
</tr>
<tr>
<td>Dark brown</td>
<td>0.74</td>
<td>36 mg, 9.5%</td>
<td>7</td>
</tr>
<tr>
<td>Brown</td>
<td>0.48</td>
<td>20 mg, 5.0%</td>
<td>16</td>
</tr>
</tbody>
</table>
1,2-Me₂-4-(η⁵-C₅H₇)-4,1,2-closos-CoC₂B₁₀H₁₀ (16)

CHN

Required for C₁₃H₂₃B₁₀Co:
C 45.1, H 6.69%.
Found:
C 45.2, H 6.81%.

EIMS

$m/z$ envelope centred on 345 (M⁺).

$[\text{MW} = 346.34 \text{ g mol}^{-1}]$.

$^{11}$B{$^1$H} NMR

$\delta$ 17.02 (2B), 11.93 (2B), 4.58 (1B), 2.28 (1B),
-6.72 (2B), -9.41 (2B).

$\langle \delta(^{11}\text{B}) \rangle = 3.25 \text{ ppm}$.

$^1$H NMR

$\delta$ 7.67 (m, 2H, C₆H₄), 7.48 (m, 2H, C₆H₄),
5.97 (d, 2H, C₅H₃), 5.37 (t, 1H, C₅H₃),
1.95 (s, 6H, C_{cage}CH₃).

X-Ray Diffraction

Crystals were grown by solvent diffusion of 40-60 petroleum ether into a CH₂Cl₂ solution of 16 at -30 °C.
6.3.11 Synthesis of $1,2-\mu-(\text{CH}_2)_3-4-(\eta-\text{C}_9\text{H}_7)-4,1,2$-closo-$\text{CoC}_2\text{B}_{10}\text{H}_{10}$ (17)

1,2-$\mu$-(CH$_2)_3$-1,2-closo-C$_2$B$_{10}$H$_{10}$ (0.33 g, 1.79 mmol) in THF (25 ml) was reduced with lithium metal (0.124 g, 17.90 mmol) and the resultant solution transferred to a THF (10 ml) solution of freshly prepared Li[C$_9$H$_7$] (5.37 mmol) at 0 °C, to which CoCl$_2$ (0.86 g, 6.62 mmol) was subsequently added. After aerial oxidation, filtration through silica and purification by preparative TLC on silica [CH$_2$Cl$_2$:40-60 petroleum ether (3:2)], compound 17 was isolated as a brown solid.

R$_f$ = 0.59    Yield = 150 mg, 23.4%    Compound 17
1,2-μ-(CH₂)₃-4-(η-C₉H₇)-4,1,2-closo-CoC₂B₁₀H₁₀ (17)

**CHN**

Required for C₁₄H₂₃B₁₀Co: C 46.9, H 6.47%.

Found: C 46.7, H 6.52%.

**EIMS**

\[ m/z \text{ envelope centred on } 357 (M^+) \].

\[ [\text{MW} = 358.35 \text{ g mol}^{-1}] \].

**¹¹B{¹H} NMR**

\[ \delta 16.24 (2B), 7.64 (2B), 5.54 (1B), 2.25 (1B), -4.67 (2B), -10.45 (2B). \]

\[ \langle \delta (¹¹B) \rangle = 2.53 \text{ ppm.} \]

**¹H NMR**

\[ \delta 7.66 (m, 2H, C₆H₄), 7.47 (m, 2H, C₆H₄), 5.92 (d, 2H, C₅H₃), 5.26 (t, 1H, C₅H₃), 2.69 (m, 2H, CH₂), 2.47 (m, 2H, CH₂), 2.08 (m, 1H, CH₂), 1.96 (m, 1H, CH₂). \]

**X-Ray Diffraction**

Crystals were grown by vapour diffusion of 40-60 petroleum ether into a THF solution of 17 at room temperature.
6.4.1 Synthesis of 1,14-Cp$_2$-1,14,2,9-closo-Co$_2$C$_2$B$_{10}$H$_{12}$ (18) and side products 1-Cp-14-C$_5$H$_4$CH(OH)CH$_2$CH$_2$CH$_3$-1,14,2,9-closo-Co$_2$C$_2$B$_{10}$H$_{12}$ (19) and 1,13-Cp$_2$-1,13,2,9-closo-Co$_2$C$_2$B$_{10}$H$_{12}$ (20)

A solution of 4,1,8- compound J (0.52 g, 1.94 mmol) in degassed THF (30 ml) was stirred with sodium (0.45 g, 19.4 mmol) and naphthalene (ca. 15 mg) overnight at room temperature. The solution was then transferred via cannula to a second Schlenk tube and cooled to 0 °C before the addition of NaCp (2.9 ml, 5.8 mmol) followed by CoCl$_2$ (0.93 g, 7.20 mmol). The reaction mixture was warmed to room temperature and left to stir overnight. The resultant brown suspension was subjected to aerial oxidation for 1 h followed by filtration through silica to give an oily brown solid which was initially purified by column chromatography [CH$_2$Cl$_2$:40-60 petroleum ether (2:3)]. Preparative TLC with a mixed eluent of CH$_2$Cl$_2$:40-60 petroleum ether (3:2) revealed a mixture of at least six mobile bands. In order of elution: pale yellow (trace), bright yellow (major), orange brown, green, dark blue and dark blue (minor). All mobile bands, except pale yellow, were collected and afforded solids.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$R_f$</th>
<th>Yield</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>pale yellow (trace)</td>
<td>0.94</td>
<td>negligible</td>
<td>Unidentified</td>
</tr>
<tr>
<td>bright yellow (major)</td>
<td>0.79</td>
<td>31 mg, 6%</td>
<td>J (SM)</td>
</tr>
<tr>
<td>orange brown</td>
<td>0.50</td>
<td>15 mg, 2%</td>
<td>20</td>
</tr>
<tr>
<td>green</td>
<td>0.36</td>
<td>25 mg, 4%</td>
<td>Q</td>
</tr>
<tr>
<td>dark blue</td>
<td>0.34</td>
<td>43 mg, 6%</td>
<td>18</td>
</tr>
<tr>
<td>dark blue (minor)</td>
<td>0.09</td>
<td>7 mg, 1%</td>
<td>19</td>
</tr>
</tbody>
</table>

The green and upper blue bands were collected together and subsequently separated using TLC with a mixed eluent of CH$_2$Cl$_2$:40-60 petroleum ether (3:1). The major bright yellow and green bands were identified by $^{11}$B and $^1$H NMR spectroscopies as starting material J and 4,5-Cp$_2$-4,5,1,6-closo-Co$_2$C$_2$B$_{9}$H$_{11}$ (Q$^{13}$) respectively.
1,14-Cp₂-1,14,2,9-closo-Co₂C₂B₁₀H₁₂ (18)

EIMS

\[ m/z \text{ envelope centred on 392 (M⁺).} \]
\[ [\text{MW} = 392.27 \text{ g mol}^{-1}] \]

\(^{11}\text{B}\{^{1}\text{H}\} \text{NMR}\)
\[ \delta -1.18 \text{ (2B), -2.30 (2B), -16.15 (2B),} \]
\[ -21.24 \text{ (2B), -25.99 (2B).} \]
\[ \langle \delta^{(11}\text{B}) \rangle = -13.37 \text{ ppm.} \]

\(^{1}\text{H NMR}\)
\[ \delta 4.78 \text{ (s, 10H, C}_5\text{H}_5\text{), 2.67 (br s, 2H, C}_{\text{cage}}\text{H).} \]
1-Cp-14-C₅H₄CH(OH)CH₂CH₂CH₃-1,14,2,9-closo-Co₂C₂B₁₀H₁₂ (19)

**EIMS**

\[ m/z \] envelope centred on 464 (M⁺).

\[ [MW = 464.37 \text{ g mol}^{-1}] \]

**¹¹B{¹H} NMR**

\[ \delta -1.10 \text{ (2B)}, -2.31 \text{ (2B)}, -15.96 \text{ (2B)}, -21.06 \text{ (2B)}, -25.82 \text{ (2B)}. \]

\[ \langle \delta^{(11)B} \rangle = -13.25 \text{ ppm.} \]

**¹H NMR**

\[ \delta 4.90 \text{ (m, 1H, } C₅H₄) \], \[ 4.80 \text{ (s, 5H, } C₅H₅) \], \[ 4.72 \text{ (m, 2H, } C₅H₄) \], \[ 4.48 \text{ (m, 1H, } C₅H₄) \], \[ 4.40 \text{ (m, 1H, } C₅H₄) \], \[ 2.68 \text{ (br s, 1H, } C_{cage}H) \], \[ 2.63 \text{ (br s, 1H, } C_{cage}H) \], \[ 1.45 \text{ (m, 2H, } CH₂) \], \[ 1.31 \text{ (m, 2H, } CH₂) \], \[ 0.85 \text{ (t, 3H, } CH₃) \].

**X-Ray Diffraction**

Crystals were grown by solvent diffusion of 40-60 petroleum ether into a CH₂Cl₂ solution of 19 at -30 °C.
1,13-Cp$_2$-1,13,2,9-closo-Co$_2$C$_2$B$_{10}$H$_{12}$ (20)

**EIMS**  
$m/z$ envelope centred on 392 (M$^+$).  
[MW = 392.27 g mol$^{-1}$].

$^{11}$B{$^1$H} NMR  
δ 18.16 (br, 1B), 8.80 (br, 1B),  
6.58 (br, 1B), 2.78 (1B), -2.47 (1B),  
-5.14 (br, 2B), -14.88 (2B), -30.07 (1B).  
$\langle \delta^{(11)B} \rangle = -3.63$ ppm.

$^1$H NMR  
δ 5.13 (br unresolved s, 10H, C$_5$H$_5$),  
2.60 (br s, 1H, C$_{cage}$H),  
2.11 (br s, 1H, C$_{cage}$H).

**X-Ray Diffraction**

Crystals were grown by solvent diffusion of 40-60 petroleum ether into a CH$_2$Cl$_2$ solution of 20 at -15 °C.
6.4.2 Synthesis of 2,9-Me\textsubscript{2}-1,14-Cp\textsubscript{2}-1,14,2,9-\textit{closo}-Co\textsubscript{2}C\textsubscript{2}B\textsubscript{10}H\textsubscript{10} (21)

A degassed THF (30 ml) solution of dimethyl 4,1,8- compound 3 (0.23 g, 0.78 mmol) was stirred overnight at room temperature with sodium metal (0.18 g, 7.80 mmol) and naphthalene \((ca. 15 \text{ mg})\). The resulting dark brown solution was transferred via cannula to a second Schlenk tube and cooled to \(-78^\circ\text{C}\) before treatment with NaCp (1.17 ml, 2.34 mmol) and CoCl\textsubscript{2} (0.375 g, 2.89 mmol). The reaction mixture was warmed to room temperature and left to stir overnight. The crude mixture was then subjected to aerial oxidation for 1 h followed by filtration through Celite\textsuperscript{®} and the dark residue purified by preparative TLC with a mixed eluent of CH\textsubscript{2}Cl\textsubscript{2}:40-60 petroleum ether (3:2) to reveal a mixture of at least five bands, including starting material and compound 21 which was collected as a dark blue solid.

\(R_f = 0.24\) \quad Yield = 50 mg, 15\% \quad \text{Compound 21}
2,9-Me$_2$-1,14-Cp$_2$-1,14,2,9-closo-Co$_2$C$_2$B$_{10}$H$_{10}$ (21)

**EIMS**

$m/z$ envelope centred on 420 (M$^+$).

[MW = 420.31 g mol$^{-1}$].

**$^{11}$B{$^1$H} NMR**

δ 1.20 (2B), -1.45 (2B), -10.01 (2B), -14.17 (2B), -18.10 (2B).

$\langle \delta^{(11}\text{B}) \rangle = -8.51$ ppm.

**$^1$H NMR**

δ 4.80 (s, 10H, C$_5$H$_5$), 2.01 (s, 6H, CH$_3$).

**X-Ray Diffraction**

Crystals were grown by vapour diffusion of 40-60 petroleum ether into a CH$_2$Cl$_2$ solution of 21 at -30 °C.
6.4.3 Synthesis of 2,10-Me₂-1,14-Cp₂-1,14,2,10-closo-Co₂C₂B₁₀H₁₀ (22)

A solution of dimethyl 4,1,12- compound E (0.32 g, 1.08 mmol) in degassed THF (30 ml) was stirred with sodium (0.25 g, 10.8 mmol) and naphthalene (ca. 15 mg) overnight at room temperature. The reduced cobaltacarborane solution was transferred via cannula to a second Schlenk tube and cooled to 0 °C followed by treatment with NaCp (1.62 ml, 3.24 mmol) and CoCl₂ (0.52 g, 4.0 mmol). The reaction mixture was warmed to room temperature, stirred overnight, aerially oxidised for 1 h and filtered through silica to give, on removal of solvent, an oily brown solid. Preparative TLC with a mixed eluent of CH₂Cl₂:40-60 petroleum ether (3:2) revealed a mixture of least nine mobile bands, three of which were collected and afforded solids. In order of elution: orange, purple and dark blue. The orange and dark blue bands were identified by ¹¹B and ¹H NMR spectroscopies as starting material compound E and 14-vertex 1,14,2,9- compound 21 respectively. The purple band corresponded to target compound 22.

<table>
<thead>
<tr>
<th>Compound</th>
<th>R_f</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>orange</td>
<td>0.80</td>
<td>108 mg, 34%</td>
</tr>
<tr>
<td>purple</td>
<td>0.45</td>
<td>15 mg, 3%</td>
</tr>
<tr>
<td>dark blue</td>
<td>0.25</td>
<td>8 mg, 2%</td>
</tr>
</tbody>
</table>

**EIMS**

m/z envelope centred on 420 (M⁺).  
[MW = 420.31 g mol⁻¹].

**¹¹B{¹H} NMR**

δ -4.89 (2B), -8.54 (4B), -12.54 (4B).  
⟨δ(¹¹B)⟩ = -9.41 ppm.

**¹H NMR**

δ 4.80 (s, 10H, C₅H₅), 1.77 (s, 6H, CH₃).
6.4.4 Synthesis of 1,14-(η-C₉H₇)₂-1,14,2,9-closo-Co₂C₂B₁₀H₁₂ (23)

4,1,8- indenyl compound 8 (0.36 g, 1.13 mmol) was stirred with sodium metal (0.18 g, 7.92 mmol) and naphthalene (ca. 15 mg) in degassed THF (30 ml) at room temperature overnight. The resulting dark brown solution was transferred via cannula to a second Schlenk tube containing a freshly prepared degassed THF (10 ml) solution of Li[C₉H₇] (3.39 mmol) cooled to 0 °C. CoCl₂ (0.54 g, 4.18 mmol) was added and the reaction mixture warmed to room temperature and left to stir overnight followed by aerial oxidation for 0.5 h and filtration through a short silica column eluting with CH₂Cl₂. Compound 23 was subsequently isolated as a brown-grey solid after preparative TLC [CH₂Cl₂:40-60 petroleum ether (3:2)].

R_f = 0.40 Yield = 10 mg, 2% Compound 23
1,14-(η-C₅H₇)₂-1,14,2,9-closo-Co₂C₂B₁₀H₁₂ (23)

**EIMS**  
\( m/z \) envelope centred on 492 (M⁺).  
[MW = 492.37 g mol⁻¹].

**\(^{11}\text{B}\{^1\text{H}\} \text{NMR}**  
\( \delta \) -0.76 (2B), -1.60 (2B), -14.23 (2B),  
-20.28 (2B), -23.83 (2B).  
\( \langle \delta(^{11}\text{B}) \rangle = -12.14 \text{ ppm}. \)

**\(^1\text{H} \text{NMR}**  
\( \delta \) 7.30 (m, 4H, \( \text{C}_6\text{H}_4 \)), 7.21 (m, 2H, \( \text{C}_6\text{H}_4 \)),  
7.03 (m, 2H, \( \text{C}_6\text{H}_4 \)), 5.38 (m, 2H, \( \text{C}_5\text{H}_3 \)),  
5.22 (m, 2H, \( \text{C}_5\text{H}_3 \)), 4.62 (t, 2H, \( \text{C}_5\text{H}_3 \)),  
1.19 (br s, 2H, \( \text{C}_{\text{cage}}\text{H} \)).

**X-Ray Diffraction**

Crystals were grown by vapour diffusion of 40-60 petroleum ether into a CH₂Cl₂ solution of 23 at -30 °C.
6.4.5 Synthesis of $1,14-(\eta^3-C_9H_7)_2-1,14,2,10\text{-closo-Co}_2C_2B_{10}H_{12}$ (24)

A solution of 4,1,12- indenyl compound 14 (0.75 g, 2.36 mmol) in degassed THF (30 ml) was stirred with sodium (0.38 g, 16.5 mmol) and naphthalene (ca. 15 mg) overnight at room temperature. The reduced cobaltacarborane solution was transferred to a degassed THF (10 ml) solution of Li$[C_9H_7]$ (7.08 mmol) at 0 °C, to which CoCl$_2$ (1.13 g, 8.73 mmol) was added. The reaction mixture was warmed to room temperature and left to stir overnight. The resultant brown suspension was subjected to aerial oxidation for 0.5 h followed by filtration through a short silica column eluting with CH$_2$Cl$_2$. Preparative TLC [CH$_2$Cl$_2$:40-60 petroleum ether (3:2)] afforded compound 24 as a dark blue solid along with a trace amount of 1,14,2,9-isomer 23.

$R_f = 0.49$  Yield = 20 mg, 2%  Compound 24

$R_f = 0.38$  Yield = trace  Compound 23
**1,14-(η-\text{C}_5\text{H}_7)_{2-1,14,2,10-closo-\text{Co}_2\text{C}_2\text{B}_{10}\text{H}_{12}} (24)**

**EIMS**

\[ m/z \text{ envelope centred on } 493 \text{ (M}^+) \].

[\text{MW} = 492.37 \text{ g mol}^{-1}].

**$^{11}\text{B}\{^1\text{H}\} \text{ NMR}**

\[ \delta \text{ -6.17 (2B), -11.70 (2B), -13.19 (2B), -14.67 (2B), -18.74 (2B).} \]

\[ \langle \delta(^{11}\text{B}) \rangle = -12.89 \text{ ppm.} \]

**$^1\text{H} \text{ NMR}**

\[ \delta 7.32 \text{ (m, 4H, C}_6\text{H}_4), 7.10 \text{ (m, 4H, C}_6\text{H}_4), 5.25 \text{ (m, 4H, C}_3\text{H}_3), 4.63 \text{ (t, 2H, C}_5\text{H}_3), 0.94 \text{ (br s, 2H, C}_{\text{cage}}\text{H})]. \]

**X-Ray Diffraction**

Crystals were grown by vapour diffusion of 40-60 petroleum ether into a CH$_2$Cl$_2$ solution of 24 at -30°C.
6.5.1 Attempted Synthesis of \([K(18\text{-crown-6})][1,1'\text{-Co-closo-(14-Cp-14,2,10-CoC}_2\text{B}_{10}\text{H}_{12})_2]\) leading to the Synthesis of 2-OEt-4-Cp-4,1,12-closo-CoC\(_2\)B\(_{10}\)H\(_{11}\) (25) and 3-OEt-1,8-Cp\(_2\)-1,8,2,10-closo-Co\(_2\)C\(_2\)B\(_{10}\)H\(_{11}\) (26)

A solution of 4,1,12- compound \(K\) (0.50 g, 1.86 mmol) in THF (ca. 50 ml) was stirred with sodium (0.25 g, 10.9 mmol) and naphthalene (ca. 15 mg) overnight at room temperature. The resulting dark brown solution was transferred via cannula to a second Schlenk tube containing a frozen solution of CoCl\(_2\) (0.12 g, 0.93 mmol) in THF. The reaction mixture was warmed to room temperature and left to stir overnight followed by aerial oxidation for 1 h and subsequent filtration through Celite\(^\text{®}\). The solvent was removed in vacuo and the resultant oily brown residue dissolved in ethanol (20 ml). To this was added a solution of \([K(18\text{-crown-6})]\)Br which was prepared by dissolving KBr (0.11 g, 0.93 mmol) and 18-crown-6 (0.27 g, 1.03 mmol) in ethanol (10 ml). Purification of the crude mixture by TLC with a mixed eluent of CH\(_2\)Cl\(_2\):40-60 petroleum ether (3:2) revealed a complex mixture of 6 mobile bands.

<table>
<thead>
<tr>
<th>R(_f)</th>
<th>Yield</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>yellow (trace)</td>
<td>0.88</td>
<td>negligible</td>
</tr>
<tr>
<td>orange (major)</td>
<td>0.86</td>
<td>96 mg, 19%</td>
</tr>
<tr>
<td>brown</td>
<td>0.75</td>
<td>10 mg, 1%</td>
</tr>
<tr>
<td>brown</td>
<td>0.53</td>
<td>~2 mg</td>
</tr>
<tr>
<td>orange</td>
<td>0.39</td>
<td>33 mg, 6%</td>
</tr>
<tr>
<td>brown</td>
<td>0.21</td>
<td>6 mg, ~1%</td>
</tr>
</tbody>
</table>

All mobile bands, except yellow, were collected and afforded solids. The first major orange band was identified by \(^{11}\text{B}\) and \(^1\text{H}\) NMR spectroscopies as starting material \(K\). The first brown band was identified by mass spectrometry, \(^{11}\text{B}\) and \(^1\text{H}\) NMR spectroscopies as compound \(S\), the asymmetric 14-vertex 1,13,2,10- isomer. The second brown band was unidentified. The second orange band and the third brown band correspond to compounds 25 and 26 respectively.
2-OEt-4-Cp-4,1,12-closo-CoC\textsubscript{2}B\textsubscript{10}H\textsubscript{11} (25)

**EIMS**

\[ m/z \text{ envelope centred on } 312 (M^+) \]
\[ [\text{MW} = 312.30 \text{ g mol}^{-1}] \]

**\textsuperscript{11}B{\textsuperscript{1}H} NMR**

\[ \delta 13.57 \text{ (1B), 7.01 (1B), 4.99 (1B), 0.37 (1B), -2.86 (1B), -5.97 (1B), -7.33 (1B), -10.55 (1B), -12.38 (1B), -18.31 (1B).} \]
\[ \langle \delta(\textsuperscript{11}B) \rangle = -3.15 \text{ ppm.} \]

**\textsuperscript{1}H NMR**

\[ \delta 5.26 \text{ (s, 5H, } \text{CsH}_5\text{), 4.23 (q, 2H, O-CH}_2\text{CH}_3\text{),} \]
\[ 3.38 \text{ (br s, 1H, } \text{C}_{\text{cage}}H\text{), 2.49 (br s, 1H, } \text{C}_{\text{cage}}H\text{),} \]
\[ 1.38 \text{ (t, 3H, O-CH}_2\text{CH}_3\text{).} \]

**X-Ray Diffraction**

Crystals were grown by solvent diffusion of 40-60 petroleum ether into a CH\textsubscript{2}Cl\textsubscript{2} solution of 25 at -30 °C.
3-OEt-1,8-Cp₂-1,8,2,10-closo-Co₂C₂B₁₀H₁₁ (26)

**EIMS**

$m/z$ envelope centred on 437 (M$^+$).

$[\text{MW} = 436.33 \text{ g mol}^{-1}]$.

**X-Ray Diffraction**

Crystals were grown by solvent diffusion of 40-60 petroleum ether into a CH₂Cl₂ solution of 26 at -30 °C.
6.5.2 One-Electron Reduction of 4-Cp-4,1,6-closo-CoC\(_2\)B\(_{10}\)H\(_{12}\):
Direct Synthesis of 1,13-Cp\(_2\)-1,13,2,4-closo-Co\(_2\)C\(_2\)B\(_{10}\)H\(_{12}\) (27) and
1,8-Cp\(_2\)-1,8,2,4-closo-Co\(_2\)C\(_2\)B\(_{10}\)H\(_{12}\) (28)

A solution of naphthalene (0.143 g, 1.12 mmol) in THF (ca. 20 ml) was stirred with
excess sodium (0.13 g, 5.59 mol) for 1 h and the resulting dark green Na[naphthalenide]
solution transferred via filter stick to a frozen solution of 4,1,6 compound D (0.300 g,
1.12 mmol) in THF (ca. 10 ml). As the mixture warmed to room temperature a dark red
solution was produced, this was then left to stir overnight. NaCp (2.9 ml, 5.8 mmol) and
CoCl\(_2\) (0.93 g, 7.2 mmol) were then added at 0 °C and the reaction mixture left to stir
overnight at room temperature. The resultant brown suspension was filtered through
silica and initially purified by column chromatography [CH\(_2\)Cl\(_2\):40-60 petroleum ether
(2:3)] to afford starting material D (181 mg, 67%) and a slow moving brown fraction.
Preparative TLC of the oily brown fraction with a mixed eluent of CH\(_2\)Cl\(_2\):40-60
petroleum ether (4:1) revealed two mobile brown bands which afforded 27 and 28 as
brown solids in low yields.

\(R_f = 0.65\) Yield = ~2 mg, 0.5% Compound 27
\(R_f = 0.58\) Yield = ~2 mg, 0.5% Compound 28
1,13-Cp₂-1,13,2,4-closo-Co₂C₂B₁₀H₁₂ (27)

EIMS  

\[ m/z \text{ envelope centred on 392 (M⁺), 268 (M⁺ - CpCo).} \] 
\[ \text{[MW} = 392.27 \text{ g mol}^{-1}\text{].} \]

\(^{11}\text{B}[^{1}\text{H}] \text{ NMR} \]
\[ \delta \text{ 13.69 (1B), 11.50 (1B), 1.96 (1B), -0.73 (1B),} \]
\[ -5.25 (1B), -8.20 (1B), -13.81 (1B), -17.95 (1B), \]
\[ -21.19 (1B), -26.36 (1B). \]
\[ \langle \delta(^{11}\text{B}) \rangle = -6.63 \text{ ppm.} \]

\(^{1}\text{H} \text{ NMR} \]
\[ \delta \text{ 5.20 (s, 5H, C₅H₅), 5.02 (s, 5H, C₅H₅),} \]
\[ 2.96 (\text{br s, 1H, C₅cageH}), 2.67 (\text{br s, 1H, C₅cageH}). \]

X-Ray Diffraction

Crystals were grown by solvent diffusion of 40-60 petroleum ether into a CH₂Cl₂ solution of 27 at -30 °C.
1,8-Cp₂-1,8,2,4-closo-Co₂C₂B₁₀H₁₂ (28)

**EIMS**

$m/z$ envelope centred on 392 ($M^+$), 268 ($M^+ - \text{CpCo}$).

$[\text{MW} = 392.27 \text{ g mol}^{-1}]$.

**$^{11}\text{B}\{}^{1}\text{H}\} \text{NMR}$**

$\delta$ 7.01 (1B), 3.58 (1B), 1.96 (2B),

-4.18 (1B), -5.50 (1B), -10.23 (1B),

-18.27 (1B), -19.94 (1B), -27.72 (1B).

$\langle \delta(^{11}\text{B}) \rangle = -7.13$ ppm.

**$^1\text{H} \text{NMR}$**

$\delta$ 5.46 (s, 5H, C₅H₅), 5.07 (s, 5H, C₅H₅),

3.80 (br s, 1H, C_{cage}H), 2.89 (br s, 1H, C_{cage}H).

**X-Ray Diffraction**

Crystals were grown by solvent diffusion of 40-60 petroleum ether into a CH₂Cl₂ solution of 28 at $-30 \degree \text{C}$.
6.5.3 One-Electron Reduction of 4-Cp-4,1,10-closo-CoC₂B₁₀H₁₂:

Direct Synthesis of 1,8-Cp₂-1,8,2,5-closo-Co₂C₂B₁₀H₁₂ (29)

A solution of naphthalene (0.143 g, 1.12 mmol) in THF (ca. 20 ml) was stirred with excess sodium (0.13 g, 5.59 mol) for 1 h and the resultant Na[naphthalenide] solution transferred via filter stick to a frozen solution of 4,1,10-compound P (0.300 g, 1.12 mmol) in THF (ca. 10 ml). The mixture was warmed to room temperature and stirred overnight. NaCp (2.9 ml, 5.8 mmol) and CoCl₂ (0.93 g, 7.2 mmol) were then added at 0 °C and the reaction mixture left to stir overnight at room temperature. The resultant brown suspension was filtered through silica and initially purified by column chromatography [CH₂Cl₂:40-60 petroleum ether (2:3)] to afford starting material P (150 mg, 50%) and a slow moving brown fraction. Preparative TLC of the oily brown fraction with a mixed eluent of CH₂Cl₂:40-60 petroleum ether (3:2) revealed a brown mobile band which afforded 29 as a brown solid in low yield.

R₁ = 0.51       Yield = 10 mg, 2%       Compound 29
1,8-Cp₂-1,8,2,5-closo-Co₂C₂B₁₀H₁₂ (29)

**EIMS**  
m/z envelope centred on 392 (M⁺), 268 (M⁺ - CpCo).  
[MW = 392.27 g mol⁻¹].

**¹¹B{¹H} NMR**  
δ 8.39 (1B), 2.95 (2B), -0.67 (1B),  
-2.38 (1B), -9.91 (1B), -14.77 (1B),  
-17.70 (1B), -21.20 (1B), -28.25 (1B).  
⟨δ(¹¹B)⟩ = -8.06 ppm.

**¹H NMR**  
δ 5.21 (s, 5H, C₅H₅), 5.04 (s, 5H, C₅H₅),  
2.71 (br s, 1H, C₈H₈), 2.25 (br s, 1H, C₈H₈).

**X-Ray Diffraction**

Crystals were grown by solvent diffusion of 40-60 petroleum ether into a CH₂Cl₂ solution of 29 at -30 °C.
6.5.4 One-Electron Reduction of 4-Cp-4,1,12-closo-CoC₂B₁₀H₁₂:
Direct Synthesis of 1,13-Cp₂-1,13,2,10-closo-Co₂C₂B₁₀H₁₂ (S)

Naphthalene (0.143 g, 1.12 mmol) was treated with excess sodium (0.13 g, 5.59 mol) in THF (ca. 20 ml) at room temperature for 1 h. The Na[naphthalenide] solution was then transferred via filter stick to a frozen solution of 4,1,12- compound K (0.300 g, 1.12 mmol) in THF (ca. 10 ml) and the mixture left to warm to room temperature and stirred overnight. NaCp (2.9 ml, 5.8 mmol) and CoCl₂ (0.93 g, 7.2 mmol) were then added at 0 °C and the reaction mixture left to stir overnight at room temperature to give a brown suspension which was filtered through silica. Initial purification by column chromatography [CH₂Cl₂:40-60 petroleum ether (3:2)] afforded starting material K (230 mg, 77%) and a slow moving brown fraction. Preparative TLC of the oily brown fraction with a mixed eluent of CH₂Cl₂:40-60 petroleum ether (3:2) revealed two brown mobile bands ((Rᵣ = 0.51/0.40). The upper band afforded S as a brown solid in low yield. The lower band was unidentified as only an impure trace amount was collected.

Rᵣ = 0.51  Yield = 5 mg, 1%  Compound S
6.5.5 One-Electron Reduction of 4-Cp-4,1,8-closo-CoC₂B₁₀H₁₂

A Na[naphthalenide] solution was prepared by treating naphthalene (0.143 g, 1.12 mmol) with excess sodium (0.13 g, 5.59 mol) in THF (ca. 20 ml) at room temperature for 1 h. The solution was transferred to a frozen solution of 4,1,8-compound J (0.300 g, 1.12 mmol) in THF (ca. 10 ml) and the mixture stirred overnight at room temperature. NaCp (2.9 ml, 5.8 mmol) and CoCl₂ (0.93 g, 7.2 mmol) were then added at 0 °C and the reaction mixture left to stir overnight at room temperature to give a brown suspension which was filtered through silica. Purification by column chromatography [40-60 petroleum ether: CH₂Cl₂ (4:1)] afforded an orange and a brown fraction. The orange fraction was found to be predominantly recovered starting material J (175 mg, 58%). Preparative TLC of the brown fraction with a mixed eluent of CH₂Cl₂:40-60 petroleum ether (3:2) revealed two discernible mobile bands: faint brown (Rᵣ = 0.56) and major green (Rᵣ = 0.39). The green band afforded 13-vertex bimetallic compound Q¹³ (33 mg, 8%). The faint brown band yielded an unidentified impure trace.
6.6 References