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Heterometalation of 1,1′-bis(ortho-carborane)

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**ABSTRACT:** Deboronation of [8-(1′-clos o-1′,2′-C_{2}B_{10}H_{11})-closo-2,1,8-MC_{2}B_{9}H_{10}] affords diastereoisomeric mixtures of [8-(7′-nido-7′,8′-C_{2}B_{9}H_{11})-closo-2,1,8-MC_{2}B_{9}H_{10}] anions (1, M = Ru(p-cymene); 2, M = CoCp) isolated as [HNMe]⁺ salts. Deprotonation of 1 and reaction with CoCl₂/NaCp followed by oxidation yields [8-(1′-3′-Cp-closo-3′,1′,2′-CoC_{2}B_{9}H_{10})-2-(p-cymene)-closo-2,1,8-RuC_{2}B_{9}H_{10}] isolated as two separable diastereoisomers, 3α and 3β, the first examples of heterometalated derivatives of 1,1′-bis(ortho-carborane). Deprotonation of [7-(1′-clos o-1′,2′-C_{2}B_{10}H_{11})-nido-7,8-C_{2}B_{9}H_{11}]⁻, metatation with CoCl₂/NaCp⁺ and oxidation affords the isomers [1-(1′-clos o-1′,2′-C_{2}B_{10}H_{11})-3-Cp*-closo-3,1,2-CoC_{2}B_{9}H_{10}] (4) and [8-(1′-clos o-1′,2′-C_{2}B_{10}H_{11})-2-Cp*-closo-2,1,8-CoC_{2}B_{9}H_{10}] (5) as well as a trace amount of the 13-vertex/12-vertex species [12-(1′-clos o-1′,2′-C_{2}B_{10}H_{11})-4,5-Cp*-2-closo-4,5,1,12-CoC_{2}B_{9}H_{10}] (6). Reduction then re-oxidation of 4 converts it to 5. Deboronation of either 4 or 5 yields a diastereoisomeric mixture of [8-(7′-nido-7′,8′-C_{2}B_{9}H_{11})-2-Cp*-closo-2,1,8-CoC_{2}B_{9}H_{10}]⁻ (7), again isolated as the [HNMe]⁺ salt. Deprotonation of this followed by treatment with [RuCl₂(p-cymene)]₂ produces [8-(1′-3′-(p-cymene)-closo-3′,1′,2′-RuC_{2}B_{9}H_{10})-2-Cp*-closo-2,1,8-CoC_{2}B_{9}H_{10}] (8) as a mixture of two diastereoisomers in a 2:1 ratio which could not be separated. Diastereoisomers 8 are complementary to 3α and 3β in which {CoCp} and {Ru(p-cymene)} in 3 have been replaced by {Ru(p-cymene)} and {CoCp*}, respectively, in 8. Finally, thermolysis of mixture 8 in refluxing DME yields [8-(8′-2′-(p-cymene)-closo-2′,1′,8′-RuC_{2}B_{9}H_{10})-2-Cp*-closo-2,1,8-CoC_{2}B_{9}H_{10}] (9), again as a 2:1 diastereoisomeric mixture that could not be separated. All new species were characterised by multinuclear NMR spectroscopy and 3α, 3β, 4, 5, 6 and 9 were also characterised crystallographically.
INTRODUCTION
The principles of removal of a {BH} vertex from a closo carborane and its subsequent replacement by an isolobal metal fragment {MLn} to afford a metallacarborane (polyhedral subrogation) were established by Hawthorne and co-workers more than 50 years ago, and now a vast range of metallacarboranes of differing polyhedral shapes and sizes containing metal atoms from across a broad spectrum of the Periodic Table is known. Such species find application in catalysis, medicine, metal-ion extraction and advanced materials, amongst others.

The compound [1-(1′-closo-1′,2′-C2B10H11)-closo-1,2-C2B10H11], trivial name 1,1′-bis(ortho-carborane) (Figure 1), has a scaffold which offers extensive potential for derivatisation. In particular, products could be envisaged in which a metallacarborane is connected to a carborane by a \( C_{cage} - C_{cage} \) bond or in which two metallacarborane units are connected by a \( C_{cage} - C_{cage} \) bond. We have previously reported single cage metalation of 1,1′-bis(ortho-carborane) affording metallacarborane–carborane species, and double cage metalation yielding metallacarborane–metallacarborane compounds. In the latter case metalation followed double deboronation, so the final products were necessarily homometalated. However, the potential utility of double cage metalated derivatives of 1,1′-bis(ortho-carborane) would be greatly enhanced if controlled routes to heterometalated species were developed. In this contribution we report the stepwise deboronation and metalation of 1,1′-bis(ortho-carborane) to afford the first examples of heterometalated metallacarborane–metallacarborane species.

Figure 1. 1,1′-bis(ortho-carborane).
EXPERIMENTAL SECTION

Synthesis. Experiments were performed under dry, oxygen-free, N₂ using standard Schlenk techniques, although subsequent manipulations were sometimes performed in the open laboratory. Solvents were freshly distilled under nitrogen from the appropriate drying agent [THF and 40-60 petroleum ether (petrol); sodium wire: CH₂Cl₂ (DCM); calcium hydride] and were degassed (3×freeze-pump-thaw cycles) before use. Deuterated solvents for NMR spectroscopy [CDCl₃, (CD₃)₂CO, CD₂CN] were stored over 4 Å molecular sieves. Preparative TLC employed 20×20 cm Kieselgel F₂₅₄ glass plates and column chromatography used 60 Å silica as the stationary phase. Elemental analyses were conducted using an Exeter CE-440 elemental analyser. NMR spectra at 400.1 MHz (¹H) or 128.4 MHz (¹³C) were recorded on a Bruker DRX-400 spectrometer at room temperature. Electron ionisation mass spectrometry (EI-MS) was carried out using a Finnigan (Thermo) LCQ Classic ion trap mass spectrometer at the University of Edinburgh. The starting materials 1,1′-bis(ortho-carborane),⁸ [RuCl₂(p-cymene)]₂,⁹ [8-(1′-closo-1′,2′-C₂B₁₀H₁₁)-2-(p-cymene)-closo-2,1,8-RuC₂B₉H₁₀] (IIa),⁶ [8-(1′-closo-1,2′-C₂B₁₀H₁₁)-2-Cp-closo-2,1,8-CoC₂B₁₀H₁₁] (IIb)⁶ and [HNMe₃][7-(1′-closo-1′,2′-C₂B₁₀H₁₁)-nido-7,8-C₂B₉H₁₁] (III)⁶,¹⁰ were prepared by literature methods or slight variations thereof. All other reagents were supplied commercially.

[HNMe₃][8-(7′-nido-7,8′-C₂B₁₀H₁₁)-2-(p-cymene)-closo-2,1,8-RuC₂B₉H₁₀] (I). Compound IIa (0.200 g, 0.392 mmol) and KF (0.114 g, 1.962 mmol) was dissolved in a mixture of THF (50 mL) and deionised water (5 mL) and the solution heated to reflux overnight. Following cooling to room temperature solvents were removed in vacuo and the resultant white residue re-dissolved in deionised water (20 mL) and filtered. To the filtrate was added an aqueous solution of excess [HNMe₃]Cl which immediately resulted in the precipitation of a white solid, [HNMe₃][8-(7′-nido-7,8′-C₂B₁₀H₁₁)-2-(p-cymene)-closo-2,1,8-RuC₂B₉H₁₀] (I). This was collected by filtration, washed with water and dried in vacuo. Yield 0.188 g, 0.336 mmol, 86%. C₇H₁₂B₁₈NRu requires C 36.5, H 8.11, N 2.50; found C 35.6, H 8.23, N 3.06%. ¹H NMR [(CD₃)₂CO], essentially equimolar mixture of diastereoisomers; δ 6.00-5.87 [m, 4H+4H, CH₃C₆H₄CH(CH₃)₂], 3.21 [s, 18H, HN(CH₃)₃], 2.79 [overlapping app. septets, 1H+1H, CH₃C₆H₄CH(CH₃)₂], 2.64 (br. s, 1H+1H, C1H), 2.26 [s, 3H+3H, CH₃C₆H₄CH(CH₃)₂], 1.93 (br. s, 1H+1H, C8′H), 1.30-1.27 [overlapping pairs of d, 6H+6H, CH₃C₆H₄CH(CH₃)₂], -2.66 (1H) and -2.81 (1H) (overlapping br. singlets, μ-H). ¹³C[¹H] NMR [(CD₃)₂CO] (relative integrals given); δ -1.1 (1B), -2.8 (2B), -4.9 (1B), -7.9 (1B), -10.2 (3B), -13.8 (2B), -16.7 (2B), -19.5 (1B), -21.0 (2B), -25.5 (1B), -33.5 (1B), -35.9 (1B).

[HNMe₃][8-(7′-nido-7,8′-C₂B₁₀H₁₁)-2-Cp-closo-2,1,8-CoC₂B₉H₁₀] (2). Similarly, compound IIb (0.200 g, 0.502 mmol) was deboronated with KF (0.146 g, 2.513 mmol) in THF/water and then methasised with [HNMe₃]Cl affording the product, [HNMe₃][8-(7′-nido-7,8′-C₂B₁₀H₁₁)-2-Cp-closo-2,1,8-CoC₂B₉H₁₀] (2), as a yellow solid. Yield 0.192 g, 0.429 mmol, 85%. C₁₂H₂₈B₁₅CoN requires C 32.2, H 8.11, N 3.13; found C 32.3, H 8.18, N 3.01%. ¹H NMR [(CD₃)₂CO], equimolar mixture of diastereoisomers; δ 5.50 (s, 5H, C₅H₅), 5.49 (s, 5H, C₅H₅), 3.19 [s, 18H, HN(CH₃)₃], 2.84 (br. s, 1H+1H, C1H), 1.88 (br. s, 1H+1H, C8′H), -2.70 (1H) and -2.85 (1H) (overlapping br. singlets, μ-H). ¹³C[¹H] NMR [(CD₃)₂CO] (relative integrals given); δ -0.4 (3B), -1.2 (1B), -5.9 (2B), -9.6 (1B), -10.1 (1B), -12.7 (1B), -14.1 (2B), -17.3 (2B), -18.3 (1B), -20.4 (1B), -23.4 (1B), -33.3 (1B), -35.7 (1B).

α-[8-(1′,3′-Cp-closo-3′,1′,2′-CoC₂B₁₀H₁₀)-2-(p-cymene)-closo-2,1,8-RuC₂B₉H₁₀] (3α) and β-[8-(1′,3′-Cp-closo-3′,1′,2′-CoC₂B₁₀H₁₀)-2-(p-cymene)-closo-2,1,8-RuC₂B₉H₁₀] (3β). BuLi (0.15 mL of a 2.5 M solution, 0.375 mmol) was added dropwise to a cooled (0 °C) solution of 1 (0.100 g, 0.179 mmol) in THF (20 mL) and the reagents stirred at room temperature for 0.5 h. The solution was then frozen at -196 °C and CoCl₂ (0.081 g, 0.624 mmol) and NaCp (0.27 mL of a 2.0 M solution, 0.540 mmol) were added. The reaction mixture was stirred overnight. Following aerial oxidation (0.5 h) and filtration through silica, solvents were removed in vacuo and the residue was purified by column chromatography using a...
as further purified by H_5H added sodium naphthalenide (1 mL of a 0.043 M solution in THF, 0.043 mmol). The reagents were warmed to 10.0 multiple overlapping resonances with maxima at -3.8, -5.2, -6.8, -8.5, -10.0 (total integral 11B), -14.6 (2B), -16.2 (1B), -17.9 (1B), -20.7 (1B). EIMS; envelope centred on m/z 622 (M^+).

β-[8-(1′-3′-Cp-closol-3′,1′,2′-CoC_B_8H_10]2-(p-cymene)-closo-2,1,8-RuC_B_8H_10] (3β). Rf 0.56. Yield 0.027 g, 0.043 mmol, 24%. C_{19}H_{30}Ru requires C 36.7, H 6.32; found C 35.9, H 6.65%. 1H NMR (CDCl_3); δ 5.93-5.82 [m, 4H, CH_2(CH(CH_3)_2)], 5.80 (s, 5H, C_5H_5), 4.27 (br. s, 1H, C_2′H), 2.81 [app. sept, 1H, CH_2(CH(CH_3)_2)], 2.63 (br. s, 1H, C_1H), 2.32 [s, 3H, CH_3CH_2CH(CH_3)_2]. 11B{^1H} NMR (CDCl_3); δ 5.0 (1B), 2.2 (1B), -0.9 to -10.4 multiple overlapping resonances with maxima at -0.9, -3.9, -5.6, -7.5, -8.7, -10.4 (total integral 11B), -14.6 (2B), -16.5 (1B), -17.4 (1B), -20.7 (1B). EIMS; envelope centred on m/z 622 (M^+).

[1-(1′-closo-1′,2′-C_6B_10H_11)-3-Cp*-closo-3,1,2-CoC_B_8H_10] (4) and [12-(1′-closo-1′,2′-C_6B_10H_11)-4,5-Cp*-closo-4,5,1,12-CoC_B_8H_10] (6). "BuLi (0.60 mL of a 2.5 M solution, 1.50 mmol) was added dropwise to an ice-cooled solution of III ([HNMe_3]^+ salt, 0.250 g, 0.745 mmol) in THF (25 mL) and the products stirred for 1 h at room temperature. The pale yellow solution was then frozen at -196°C, CoCl_2 (0.320 g, 2.465 mmol) and NaCp* (4.2 mL of a 0.5 M solution, 2.100 mmol) were added, and the reaction mixture was stirred overnight at room temperature. Following aerial oxidation (0.5 h) and filtration through silica, volatiles were removed in vacuo and the residue purified by column chromatography using a DCM:petrol eluent, 2:3, to afford red, yellow and green (trace) bands, compounds 4 and 6 respectively.

[1-(1′-closo-1′,2′-C_6B_10H_11)-3-Cp*-closo-3,1,2-CoC_B_8H_10] (4). Rf 0.41. Yield 0.120 g, 0.256 mmol, 34%. C_{14}H_{30}Co requires C 35.9, H 7.74; found C 35.8, H 7.83%. 1H NMR (CDCl_3); δ 4.10 (br. s, 1H, C_2′H), 3.37 [br. s, 1H, C_2H], 1.84 [s, 15H, C_5(CH_3)_5]. 11B{^1H} NMR (CDCl_3); δ 10.1 (1B), -1.9 (2B), -3.8 (4B), -6.0 (2B), -9.6 (6B), -12.4 (3B), -15.0 (1B). EIMS; envelope centred on m/z 469 (M^+).

[12-(1′-closo-1′,2′-C_6B_10H_11)-4,5-Cp*-closo-4,5,1,12-CoC_B_8H_10] (6). Rf 0.68. Yield 0.033 g, 0.070 mmol, 9%. C_{14}H_{30}Co requires C 35.9, H 7.74; found C 36.3, H 7.86%. 1H NMR (CHCl_3:CD_3CN; 1:10); δ 4.01 (br. s, 1H, C_2′H), 2.09 (br. s, 1H, C_1H), 1.84 [s, 15H, C_5(CH_3)_5]. 11B{^1H} NMR (CDCl_3); δ 3.2 (1B), 1.1 (2B), -2.6 (1B), -4.1 (2B), -4.9 (1B), -7.2 (2B), -9.9 (6B), -13.3 (2B), -13.9 (1B), -18.0 (1B), -18.6 (1B). EIMS; envelope centred on m/z 469 (M^+).

Redox isomerisation of 4 to 5. To a frozen solution of 4 (0.020 g, 0.043 mmol) in THF (10 mL) was added sodium naphthalenide (1 mL of a 0.043 M solution in THF, 0.043 mmol). The reagents were warmed to room temperature, stirred under nitrogen for 1 h and then aerially oxidised for 0.5 h. Purification by
preparative TLC using a DCM:petrol eluent, 2:3, afforded the starting material 4 (Rt 0.40, 0.008 g, 0.017 mmol, 40%) and a yellow product (Rt 0.65, 0.009 g, 0.019 mmol, 45%) identical to 5 by $^1$H and $^{13}$C NMR spectroscopies. 

$^{[1]}$H NMR [(CD$_3$)$_2$CO], essentially equimolar mixture of diastereoisomers; δ 3.18 (s, 18H, HN(CH$_3$)$_3$), 1.96 (br s, 1H+1H, C1H), 1.88 (br s, 1H+1H, C8'H), 1.85 [s, 15H, C$_5$(CH$_3$)$_5$], 1.84 [s, 15H, C$_5$(CH$_3$)$_5$], -2.68 (1H) and -2.84 (1H) (overlapping br. singlets, μ-H). $^{13}$C NMR [(CD$_3$)$_2$CO] (relative integrals given); δ 13.3 (3B), -4.2 (2B), -7.1 (1B), -9.4 (1B), -10.1 (1B), -13.9 (3B), -17.2 (1B), -18.0 (1B), -19.1 (1B), -20.5 (1B), -24.3 (1B), -33.4 (1B), -35.7 (1B).

$^{[8]}$-(1'-3'-s-(p-cymene)-closo-3',1',2'-RuC$_2$B$_8$H$_{10}$)-2-Cp*-closo-2,1,8-CoC$_2$B$_8$H$_{10}$ (8, major and minor diastereoisomers). BuLi (0.17 mL of a 2.5 M solution, 0.425 mmol) was added dropwise to a cooled (0 °C) solution of 7 (0.100 g, 0.193 mmol) in THF (20 mL). After warming to room temperature, the dark yellow solution was frozen at -196 °C and [RuCl$_2$(p-cymene)]$_2$ (0.059 g, 0.096 mmol) was added. The reaction mixture was rewarmed and stirred overnight. Following filtration through silica, volatiles were removed in vacuo and the residue was purified by column chromatography using a DCM:petrol eluent (3:7) to afford a mobile yellow band (Rt 0.34) which ultimately yielded [8-(1'-3'-s-(p-cymene)-closo-3',1',2'-RuC$_2$B$_8$H$_{10}$)-2-Cp*-closo-2,1,8-CoC$_2$B$_8$H$_{10}$] (8) as a yellow solid. NMR spectroscopy reveals 8 to be a mixture of the two diastereoisomers in an approximate 2:1 ratio. In spite of exhaustive chromatography these isomers could not be separated. Yield 0.032 g, 0.046 mmol, 24%. C$_{24}$H$_{30}$B$_{18}$CoRu requires: C 41.6, H 7.13. Found: C 41.0, H 7.16%.

$^1$H NMR (CDCl$_3$, major diastereoisomer); δ 6.04-5.78 [m, 4H, CH$_2$Cd$_{5}$CH(2')CH(3')$_2$], 3.75 (br s, 1H, C2'H), 3.03 [app. sept, 1H, CH$_2$Cd$_{5}$CH(2')CH(3')$_2$], 2.46 [s, 3H, CH$_2$Cd$_{5}$CH(2')CH(3')$_2$], 1.847 [s, 15H, C$_5$(CH$_3$)$_5$], 1.79 (br s, 1H, C1H), 1.35-1.26 [m, 6H, CH$_2$Cd$_{5}$CH(2')CH(3')$_2$].

$^{13}$C NMR (CDCl$_3$, minor diastereoisomer); δ 6.04-5.78 [m, 4H, CH$_2$Cd$_{5}$CH(2')CH(3')$_2$], 3.88 (br s, 1H, C2'H), 3.03 [app. sept, 1H, CH$_2$Cd$_{5}$CH(2')CH(3')$_2$], 2.44 [s, 3H, CH$_2$Cd$_{5}$CH(2')CH(3')$_2$], 1.852 [s, 15H, C$_5$(CH$_3$)$_5$], 1.79 (br s, 1H, C1H), 1.35-1.26 [m, 6H, CH$_2$Cd$_{5}$CH(2')CH(3')$_2$].

$^{13}$C NMR (CDCl$_3$); δ 2.7 to 0.3 multiple overlapping resonances with maxima at 2.7, 1.9, 0.3 (total 5B), -3.8 to -7.6 multiple overlapping resonances with maxima at -3.8, -6.1, -7.6 (total 7B), -13.1 to -19.6 multiple overlapping resonances with maxima at -13.1, -14.8, -17.2, -19.6 (total 6B). EIMS; envelope centred on m/z 692 (M$^+$).

**Thermal isomerisation of 8 to 9.** Mixture 8 (0.020 g, 0.029 mmol) was dissolved in dimethoxyethane (DME, 10 mL) and heated to reflux overnight. Following cooling, solvent was removed in vacuo and the residue was purified by preparative TLC using a DCM:petrol eluent (2:3) to afford a yellow band (Rt 0.36) from which [8-(8'-2'-s-(p-cymene)-closo-2',1',8'-RuC$_2$B$_8$H$_{10}$)-2-Cp*-closo-2,1,8-CoC$_2$B$_8$H$_{10}$] (9) was afforded as a yellow solid. By $^1$H NMR spectroscopy 9 was shown to be a mixture of two diastereoisomers in an approximate 2:1 ratio. Exhaustive chromatography failed to separate these components. Yield 0.017 g, 0.025 mmol, 85%. C$_{24}$H$_{30}$B$_{18}$CoRu requires: C 40.1, H 6.86. Found: C 40.1, H 6.98%. $^1$H NMR (CDCl$_3$, major diastereoisomer); δ 5.86-5.71 [m, 4H, CH$_2$Cd$_{5}$CH(2')CH(3')$_2$], 2.81 [app. sept, 1H, CH$_2$Cd$_{5}$CH(2')CH(3')$_2$], 2.59 (br s, 1H, C1'H), 2.30 [s, 3H, CH$_2$Cd$_{5}$CH(2')CH(3')$_2$], 1.84 [s, 15H, C$_5$(CH$_3$)$_5$], 1.74 (br s, 1H, C1'H), 1.29-1.26 [m, 6H, CH$_2$Cd$_{5}$CH(2')CH(3')$_2$].

$^{13}$C NMR (CDCl$_3$, minor diastereoisomer); δ 5.86-5.71 [m, 4H, CH$_2$Cd$_{5}$CH(2')CH(3')$_2$], 2.81 [app. sept, 1H, CH$_2$Cd$_{5}$CH(2')CH(3')$_2$], 2.62 (br s, 1H, C1'H), 2.30 [s, 3H,
$\text{CH}_2\text{C}_6\text{H}_4\text{CH}(\text{CH}_3)_2$, 1.83 [s, 15H, C$_3$(CH$_3$)$_2$], 1.77 (br. s, 1H, CH$\text{H}$), 1.29-1.26 [m, 6H, CH$_2$CH$_3$CH$_2$CH(CH$_3$)$_2$]. $^{11}$B{($^1$H)} NMR (CDCl$_3$): δ 2.4 to -7.9 multiple overlapping resonances with maxima at 2.4, 1.0, -1.7, -4.9, -6.6, -7.9 (total 12B), -14.3 to -20.5 multiple overlapping resonances with maxima at -14.3, -16.2, -19.1, -20.5 (total 6B). EIMS; envelope centred on m/z 692 (M$^+$).

**Crystallography.** Single crystals of 3α, 3β-0.5CH$_2$Cl$_2$, 4, 5 and 9-CH$_2$Cl$_2$ were grown by diffusion of a DCM solution of the appropriate compound and petrol at -20 °C, whilst single crystals of 6-CHCl$_3$ were afforded by slow evaporation of a CHCl$_3$ solution at room temperature. Diffraction data from 3α were collected at 100 K on a Rigaku 007-HF diffractometer equipped with Cu-$K\alpha$ X-radiation; data from 3β-0.5CH$_2$Cl$_2$ and 6-CHCl$_3$ were collected at 100 K on a Bruker X8 APEXII diffractometer operating with Mo-$K\alpha$ radiation; data from 4 and 5 were obtained at 120 K on a Rigaku Oxford Diffraction SuperNova diffractometer, using Mo-$K\alpha$ radiation; data from 9-CH$_2$Cl$_2$ were collected at 100 K on a Rigaku FR-E+ diffractometer, also using Mo-$K\alpha$ radiation. Compound 5 crystallises as a two-component twin, but all other samples were single crystals. Using OLEX2 11 structures were solved by direct methods using the SHELXS 12 or SHELXT 13 programme, and refined by full-matrix least-squares using SHELXL 14. In 3α the 'Pr group of the p-cymene of one of the two crystallographically-independent molecules is partially disordered and there is multiple disordering of the CHCl$_3$ molecule of solvation in 6-CHCl$_3$. In 9-CH$_2$Cl$_2$ application of the Vertex-Centroid Distance (VCD) and Boron-Hydrogen Distance (BHD) methods 15-17 revealed partial disorder between two cage (CH) and (BH) vertices in each metallacarborane cage since the two diastereoisomeric forms of 9 are both present, but in all other structures cage C atoms bearing only H substituents were clearly distinguished from B atoms by the VCD and BHD approaches. H atoms bound to cage B or cage C atoms were allowed positional refinement, but all other H atoms were treated as riding on their respective C atom, with C$_{\text{primary}}$–H 0.98 Å, C$_{\text{secondary}}$–H 0.99 Å, C$_{\text{tertiary}}$–H 1.00 Å, C$_{\text{arene}}$–H 1.00 Å and C$_{\text{C}}$–H 1.00 Å. H atom displacement parameters were constrained to 1.2×U$_{eq}$ (bound B or C) except for Me H atoms, 1.5×U$_{eq}$ (C$_{\text{methyl}}$). Table 1 contains unit cell data and further experimental details.

| Crystallographic data. | 3α | 3β-0.5CH$_2$Cl$_2$ | 4 | 5 | 6-CHCl$_3$ | 9-CH$_2$Cl$_2$
|---|---|---|---|---|---|
| CCDC | 1828646 | 1828647 | 1828648 | 1828649 | 1828650 | 1828651
| Formula | C$_{20}$H$_{26}$CoRu | C$_{20}$H$_{26}$CoRu | C$_{20}$H$_{26}$CoRu | C$_{20}$H$_{26}$CoRu | C$_{20}$H$_{26}$CoRu | C$_{20}$H$_{26}$CoRu
| $M$ | 622.08 | 664.54 | 468.75 | 468.75 | 782.26 | 777.13
| Crystal system | triclinic | triclinic | orthorhombic | orthorhombic | triclinic | triclinic
| Space group | $P1$ | $P1$ | $Pbcn$ | $Pc$_{21} | $P1$ | $P1$
| $a/A$ | 9.0526(3) | 13.0896(9) | 14.0429(3) | 13.2177(3) | 8.3035(5) | 9.3895(2)
| $b/A$ | 16.0530(5) | 15.6050(11) | 18.3107(5) | 13.9889(4) | 15.0776(9) | 12.4982(2)
| $c/A$ | 19.5784(7) | 16.1374(11) | 19.0533(4) | 27.0886(7) | 16.2446(10) | 16.5176(3)
| $a^{\circ}$ | 82.385(3) | 64.491(3) | 90 | 90 | 72.909(4) | 97.171(2)
| $b^{\circ}$ | 87.118(3) | 85.635(4) | 90 | 90 | 75.995(4) | 98.157(2)
| $c^{\circ}$ | 78.086(3) | 85.818(4) | 90 | 90 | 89.479(4) | 110.914(2)
| $\alpha^{\circ}$ | 2758.55(16) | 2963.4(4) | 4899.27(19) | 5008.7(2) | 1882.0(2) | 1759.77(6)
| | 4.2 | 4.2 | 8.1 | 8.2 | 2.1 | 2.1
| $F(000)$/e | 1256 | 1340 | 1936 | 1936 | 804 | 792
| $D_{\text{calc}}$/Mg m$^{-3}$ | 1.498 | 1.490 | 1.271 | 1.243 | 1.380 | 1.467
| $X$-radiation | Cu-$K\alpha$ | Mo-$K\alpha$ | Mo-$K\alpha$ | Mo-$K\alpha$ | Mo-$K\alpha$ | Mo-$K\alpha$
| $\lambda/Å$ | 1.54178 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073
| $\mu$/mm$^{-1}$ | 9.190 | 1.174 | 0.705 | 0.690 | 1.116 | 1.073
| $\theta_{\text{max}}$/° | 68.24 | 33.10 | 29.79 | 32.84 | 27.05 | 27.48
| Data measured | 39206 | 77809 | 51637 | 67177 | 37219 | 39431
| Unique data | 10028 | 21546 | 6532 | 14322 | 8078 | 8068
| $R_{\text{int}}$ | 0.0414 | 0.0430 | 0.0479 | 0.0488 | 0.0588 | 0.0266
<p>| $R$, wR$_2$ (obs. data) | 0.0430, 0.1172 | 0.0367, 0.0810 | 0.0459, 0.1032 | 0.0512, 0.1145 | 0.0213, 0.0529 |</p>
<table>
<thead>
<tr>
<th></th>
<th>1.086</th>
<th>1.049</th>
<th>1.140</th>
<th>1.060</th>
<th>1.027</th>
<th>1.058</th>
</tr>
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<tbody>
<tr>
<td>Variables</td>
<td>850</td>
<td>856</td>
<td>375</td>
<td>750</td>
<td>539</td>
<td>494</td>
</tr>
<tr>
<td>$E_{max}, E_{min}$ Å$^{-3}$</td>
<td>1.32, −0.80</td>
<td>1.07, −1.32</td>
<td>0.61, −0.41</td>
<td>0.42, −0.32</td>
<td>0.77, −0.81</td>
<td>0.84, −0.75</td>
</tr>
<tr>
<td>Flack parameter</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.469(19)</td>
<td>-</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

Singly-metalated 1,1′-bis(ortho-carborane) is known in four isomeric forms,\(^6\),\(^8\),\(^9\) of which \([1-(1′-closo-1′,2′-C_2B_{10}H_{11})-closo-3,1,2-MC_2B_9H_{10}]\) (I) and \([8-(1′-closo-1′,2′-C_2B_{10}H_{11})-closo-2,1,8-MC_2B_9H_{10}]\) (II) (Figure 2) are the most common. We chose the latter as our starting point for the synthesis of heterometalated derivatives to minimise possible steric congestion between the two metal fragments. Deboronation of carboranes is classically performed by alkoxide,\(^1\),\(^2\) but this approach is unsuitable for II because of the limited solubility of II in EtOH. Although the parent species 1,1′-bis(ortho-carborane) has been successfully deboronated in MeCN/H_2O\(^10\) we have found that this approach affords only slow and incomplete deboronation of II. However, “wet” fluoride ion, also recognised as a mild and selective deboronating agent,\(^20\) proved to be successful. Thus compound II\(_a\) (\(M = Ru(p\text{-cymene})\))\(^6\) was successfully deboronated by KF in THF/water at reflux and metathesised to the trimethylammonium salt \([HNMe_3]^{8-}(7′-nido-7′,8′-C_2B_9H_{11})-2-(p\text{-cymene})-closo-2,1,8-RuC_2B_9H_{10}\) (1), obtained in 86% isolated yield (Scheme 1). Note that deboronation of II occurs exclusively at the C_2B_{10} cage and not the MC_2B_9 cage, and gives rise to a diastereoisomeric mixture since either B3′ or B6′ could be lost. Salt 1 was characterised by elemental analysis and NMR spectroscopy.

![Figure 2](image)

**Figure 2.** Two common isomers of singly-metalated 1,1′-bis(ortho-carborane) demonstrating the atom numbering schemes. Carbon vertices in blue, metal (M) vertices in red, boron vertices in black. I\(_a\) and II\(_a\), M = Ru(p-cymene). I\(_b\) and II\(_b\), M = CoCp.

Microanalytical results were consistent with the empirical formula C_{17}H_{45}B_{18}NRu. Although the existence of diastereoisomers could not be detected in the \(^{11}\)B\(^{\text{[1,1H]}}\) NMR spectrum (which consists of twelve resonances with relative integrals 1:2:1:3:2:2:1:2:1:1:1, total 18B, from \(\delta = -1\) to -36 ppm) nor from the two broad resonances in the \(^1\)H spectrum assigned to cage CH atoms (\(\delta = 2.64\) ppm, C1H; \(\delta = 1.93\) ppm, C8′H; assignments by reference to related species, see Table 2) clear evidence is found in the \(^1\)H resonances associated with the p-cymene ligand where the signal for the CH(CH_3)_2 proton appears as two overlapping apparent septets and the CH(CH_3)_2 protons give rise to two pairs of doublets. In addition the bridging protons on the nido carborane cages appears as two overlapping singlets at low frequency. Based on the integrals of these resonances the two diastereoisomers of 1 are formed in almost equal amounts.
Scheme 1. Deboronation of II to afford a diastereoisomeric mixture of either 1 or 2, and deboronation of 5 to afford a diastereoisomeric mixture of 7.

Table 2. Cage CH chemical shifts in 1-9 and related species.

<table>
<thead>
<tr>
<th>Species</th>
<th>δ(CH)/ppm (assignment)</th>
<th>Solvent</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[closo-1,2-CB1nH12]</td>
<td>4.40 (C1H, C2H)</td>
<td>(CD)2:CO</td>
<td>21</td>
</tr>
<tr>
<td>[nido-7,8-CB2nH12]</td>
<td>1.88 (C7H, C8H)</td>
<td>CD2Cl2</td>
<td>22</td>
</tr>
<tr>
<td>[3-(p-cymene)-closo-3,1,2-RuCB2nH11]</td>
<td>3.70 (C1H, C2H)</td>
<td>CDCl3</td>
<td>23</td>
</tr>
<tr>
<td>[3-Cp-closo-3,1,2-CoCB2nH11]</td>
<td>4.26 (C1H, C2H)</td>
<td>CD2CN</td>
<td>4</td>
</tr>
<tr>
<td>[2-Cp-closo-2,1,8-CoCB2nH11]</td>
<td>2.73, 2.47 (not assigned)</td>
<td>CDCl3</td>
<td>18,24</td>
</tr>
<tr>
<td>[1(1' closo-1,2'-C2B9H11) closo-1,2'-C2B9H11]</td>
<td>5.05 (C2H, C2'H)</td>
<td>(CD)2:CO</td>
<td>25</td>
</tr>
<tr>
<td>[7(1' closo-1,2'-C2B9H11) nido-7,8-C2B9H11]</td>
<td>4.36 (C8H), 1.99 (C2'H)</td>
<td>(CD)2:CO</td>
<td>6</td>
</tr>
<tr>
<td>[1(1' closo-1,2'-C2B9H11)-3-(p-cymene)-closo-3,1,2-RuCB2nH10] (Ia)</td>
<td>4.03, 3.91 (not assigned)</td>
<td>CDCl3</td>
<td>6</td>
</tr>
<tr>
<td>[1(1' closo-1,2'-C2B9H11)-3-Cp-closo-3,1,2-CoCB2nH10] (Ib)</td>
<td>4.24, 4.03 (not assigned)</td>
<td>CDCl3</td>
<td>6</td>
</tr>
<tr>
<td>[8(1' closo-1,2'-C2B9H11)-2-(p-cymene)-closo-2,1,8-RuCB2nH10] (IIa)</td>
<td>3.64 (C2'H), 2.63 (C1H)</td>
<td>CDCl3</td>
<td>6</td>
</tr>
<tr>
<td>[8(1' closo-1,2'-C2B9H11)-2-Cp-closo-2,1,8-CoCB2nH10] (IIb)</td>
<td>3.59 (C2'H), 2.73 (C1H)</td>
<td>CDCl3</td>
<td>6</td>
</tr>
<tr>
<td>[8(7'-nido-7,8'-C2B9H11)-2-(p-cymene)-closo-2,1,8-RuCB2nH10]• (1)</td>
<td>2.64 (C1H), 1.93 (C8'H)</td>
<td>(CD)2:CO</td>
<td>this work</td>
</tr>
<tr>
<td>[8(7'-nido-7,8'-C2B9H11)-2-Cp-closo-2,1,8-CoCB2nH10] (2)</td>
<td>2.84 (C1H), 1.88 (C8'H)</td>
<td>(CD)2:CO</td>
<td>this work</td>
</tr>
<tr>
<td>α-[8(1'3'-Cp-closo-3'-1,2'-CoCB2nH10)-2-(p-cymene)-closo-2,1,8-RuCB2nH10] (3a)</td>
<td>4.27 (C2'H), 2.63 (C1H)</td>
<td>CDCl3</td>
<td>this work</td>
</tr>
<tr>
<td>β-[8(1'3'-Cp-closo-3'-1,2'-CoCB2nH10)-2-(p-cymene)-closo-2,1,8-CoCB2nH10] (3β)</td>
<td>4.12 (C2'H), 2.63 (C1H)</td>
<td>CDCl3</td>
<td>this work</td>
</tr>
<tr>
<td>[1(1' closo-1,2'-C2B9H11)-3-Cp*-closo-3,1,2-CoCB2nH10] (4)</td>
<td>4.10 (C2'H), 3.37 (C2'H)</td>
<td>CDCl3</td>
<td>this work</td>
</tr>
<tr>
<td>[8(1' closo-1,2'-C2B9H11)-2-Cp*-closo-2,1,8-CoCB2nH10] (5)</td>
<td>4.01 (C2'H), 2.09 (C1H)</td>
<td>CD-CN*</td>
<td>this work</td>
</tr>
<tr>
<td>[12(1' closo-1,2'-C2B9H11)-4,5-Cp*-closo-4,5,1,12-CoCB2nH10] (6)</td>
<td>3.80 (C2'H), 1.26 (C1H)</td>
<td>CDCl3</td>
<td>this work</td>
</tr>
<tr>
<td>[6(1' closo-1,2'-C2B9H11)-4-(p-cymene)-5-(mesitylene)-closo-4,5,1,6-RuCB2nH10]</td>
<td>4.10 (C2'H), 2.27 (C1H)</td>
<td>CDCl3</td>
<td>26</td>
</tr>
<tr>
<td>[HNMe3][4(7'-nido-7,8'-C2B9H11)-2-Cp*-closo-2,1,8-CoCB2nH10] (7)</td>
<td>1.96 (C1H), 1.88 (C8'H)</td>
<td>(CD)2:CO</td>
<td>this work</td>
</tr>
<tr>
<td>[8(1'3'-p-cymene)-closo-3'-1,2'-RuCB2nH10)-2-Cp*-closo-2,1,8-CoCB2nH10] (8, major)</td>
<td>3.75 (C2'H), 1.79 (C1H)</td>
<td>CDCl3</td>
<td>this work</td>
</tr>
<tr>
<td>[8(1'3'-p-cymene)-closo-3'-1,2'-RuCB2nH10)-2-Cp*-closo-2,1,8-CoCB2nH10] (8, minor)</td>
<td>3.88 (C2'H), 1.79 (C1H)</td>
<td>CDCl3</td>
<td>this work</td>
</tr>
<tr>
<td>[8(8'-2'-p-cymene)-closo-2'-1,8'-RuCB2nH10)-2-Cp*-closo-2,1,8-CoCB2nH10] (9, major)</td>
<td>2.59 (C1H), 1.74 (C1H)</td>
<td>CDCl3</td>
<td>this work</td>
</tr>
<tr>
<td>[8(8'-2'-p-cymene)-closo-2'-1,8'-RuCB2nH10)-2-Cp*-closo-2,1,8-CoCB2nH10] (9, minor)</td>
<td>2.62 (C1H), 1.77 (C1H)</td>
<td>CDCl3</td>
<td>this work</td>
</tr>
</tbody>
</table>

* CHCl3: CD2CN, 1:10
Similarly, deboronation of IIb (M = CoCp) and work-up led to the isolation of \([\text{HNMe}_3] [8-(7′-nido-7,8′-C_2B_{11}H_{11})-2\text{-Cp-closo}-2,1,8\text{-CoC}_2B_3H_9] \) (2) in 85% yield. Once again the presence of a diastereoisomeric mixture could not be detected from either the \(^{11}\text{B}\) NMR spectrum or the broad C\text{cage}H resonances in the \(^1\text{H}\) spectrum (\(\delta \) 2.84 ppm, C1H; \(\delta \) 1.93 ppm, C8\text{'}H; assignments based on Table 2), but is clearly evident from the existence in the latter of two very close (and equal integral) singlets at \(\delta \) 5.50 and 5.49 ppm due to the C\(_3\)H\(_5\) protons. As with 1 the B-H-B protons of the deboronated cage appear as broad overlapping singlets, this time at \(\delta \) -2.70 and -2.85 ppm.

Salts 1 and 2 are potential precursors for heterobimetallic 1,1′-bis(ortho-carborane) derivatives. Deprotonation of 1 with \(^{8}\text{BuLi}\) then reaction with a mixture of CoCl\(_2\) and NaCp followed by aerial oxidation afforded the ruthenacarborane–cobaltacarborane species 3 as a mixture of diastereoisomers, separated into components 3\(\alpha\) and 3\(\beta\) by TLC (Scheme 2). Compounds 3\(\alpha\) and 3\(\beta\) are orange solids isolated in yields of 22% and 24%, respectively, and affording satisfactory microanalytical results. Unsurprisingly as diastereoisomers their NMR spectra are very similar. In their \(^1\text{H}\) spectra, as well as the expected resonances for the \(p\)-cymene and Cp ligands, are one high frequency resonance (\(\delta \) ca. 4.2 ppm) and one relatively low frequency resonance (\(\delta \) ca. 2.6 ppm) assigned to C\text{cage}H atoms. By comparison with the C\text{cage}H resonances summarised in Table 2 we assign the high frequency signal to a (new) 3,1,2-CoC\(_2\)B\(_9\) cobaltacarborane cage and the low frequency signal to the (existing) 2,1,8-RuC\(_2\)B\(_9\) cage. We therefore formulate 3\(\alpha\) and 3\(\beta\) as diastereoisomers of \([8-(1′-3′-\text{Cp-closo}-3′,1′,2′-\text{CoC}_2B_3H_{10})-2-(p\text{-cymene})\text{-closo}-2,1,8-RuC_2B_9]\), the first examples of heterometalated derivatives of 1,1′-bis(ortho-carborane). The \(^{11}\text{B}\)\(^{1}\text{H}\) NMR spectra of 3\(\alpha\) and 3\(\beta\) suffer from multiple overlapping resonances which cannot easily be individually integrated, but nevertheless signals could be integrated at high frequency [\(\delta \) ca. 5 (1B) and 2 (1B) ppm] and at low frequency [\(\delta \) ca. -15 (2B), -16 (1B), -17 (1B) and -21 (1B) ppm], between which is a group of resonances integrating for a combined total of \(11\) B atoms.

Scheme 2. Formation of 3\(\alpha\) and 3\(\beta\) from 1.

![Scheme 2 Diagram](image)

The structures of 3\(\alpha\) and 3\(\beta\) were confirmed crystallographically. Crucial to the correct characterisation of these diastereoisomers was our ability to distinguish between cage \{CH\} fragments and \{BH\} fragments, but this was achieved unambiguously for both crystallographically-independent molecules of both species by application of the VCD and BHD methods.\(^{15-17}\) Perspective views of single molecules of 3\(\alpha\) and 3\(\beta\) are shown in Figure 3. These structural studies confirm that the ruthenacarborane cage is of 2,1,8-RuC\(_2\)B\(_9\) architecture whilst the cobaltacarborane cage is 3,1,2-CoC\(_2\)B\(_9\). This latter finding is somewhat surprising since we have previously shown that “in situ” metalation of singly-deboronated 1,1′-bis(ortho-carborane) (supplying the \{CoCp\} fragment from CoCl\(_2\)/NaCp followed by oxidation) affords predominantly the 2,1,8-
CoC₂B₉⁻1′,2′⁻C₂B₁₀ species II, the result of facile 3,1,2- to 2,1,8- isomerisation of the initially-formed [3,1,2-CoC₂B₉⁻1′,2′⁻C₂B₁₀]⁻ anion. Clearly in the case of 3α and 3β the presence of a 2,1,8-RuC₂B₉ substituent prevents isomerisation of the adjacent cobaltacarborane cage.

The two crystallographically-independent molecules of 3α effectively differ only in respect of the orientation of the p-cymene ligand on the ruthenacarborane cage relative to C2′ of the cobaltacarborane cage. In both molecules the p-cymene ligand is essentially parallel to the plane defined by atoms C8B4B5B₁₀B₁₂ (the lower pentagonal belt, the usual reference plane for icosahedral metallacarboranes) as expected given that the ruthenacarborane has a 2,1,8-RuC₂B₉ architecture. In contrast the Cp ligand on the 3′,1′,2′-CoC₂B₉ cage is clearly inclined away from the adjacent ruthenacarborane substituent to minimise steric crowding, subtending bend-back angles θ of 13.93(18)° and 13.97(18)° with the B₅′B₆′B₁₁′B₁₂′B₉′ lower pentagonal belt. In independent molecules of the related species [1-(1′-closo-1′,2′⁻C₂B₁₀H₁₁)-3-Cp-closo-3,1,2-CoC₂B₉H₁₀] the angles θ are 15.8 and 16.3°. The two independent molecules of 3β are practically superimposable, including the orientation of the p-cymene ligand. Once again this lies effectively parallel to its reference plane whilst the Cp ligand of the cobaltacarborane is inclined, by θ values of 13.57(8)° and 13.08(7)°.

Figure 3. Left; perspective view of one of the two crystallographically-independent molecules of compound 3α. Right; perspective view of one of the two crystallographically-independent molecules of compound 3β.

Having successfully prepared heterobimetallic Ru/Co derivatives of 1,1′-bis(ortho-carborane) by subrogating {BH} vertices firstly with a Ru-ligand fragment and secondly with a Co-ligand fragment, we then considered the reverse approach. However, treatment of salt 2 in THF with nBuLi resulted in considerable darkening of the solution, and no mobile products were afforded following subsequent reaction with [RuCl₂(p-cymene)]₂. Reasoning that this was probably the result of attack on the Cp ligand by nBuLi we switched attention to the Cp* analogue. The precursor II (M = CoC₉) is unknown so we attempted to prepare it in an analogous way to that which afforded IIb, namely deprotonation of the
[HNMe₂]⁺ salt of singly-deboronated 1,1′-bis(ortho-carborane) III, reaction with CoCl₂/NaCp⁺ and finally aerial oxidation (Scheme 3). Somewhat to our surprise, however, whilst the anticipated product [8-(1′-closo-1’,2′-C₂B₁₀H₁₁)-2-Cp⁰-closo-2,1,8-Co₂B₉H₁₀] (5) was afforded by this approach the major reaction product was, in fact, the isomeric species [1-(1′-closo-1’,2′-C₂B₁₀H₁₁)-3-Cp⁰-3,1,2-Co₂B₉H₁₀] (4). A trace amount of the 13-vertex bimetallicarborane/12-vertex carborane species [12-(1′-closo-1’,2′-C₂B₁₀H₁₁)-4,5-Cp⁰₂-closo-4,5,1,12-Co₂C₂B₉H₁₀] (6) was also isolated.

Compound 4 was isolated as a red solid in 34% yield and its chemical composition was established by elemental analysis and mass spectrometry. The ¹¹B{¹H} NMR spectrum is largely uninformative because of significant peak overlap between δ 0 and -16 ppm, but the presence of a single ¹B resonance at relatively high frequency (δ 10.1 ppm) is consistent with a 3,1,2-Co₂C₂B₉⁻1’,2’⁻C₂B₁₀ structure by reference to its Cp analogue I (M = CoCp). In the ¹H NMR spectrum, in addition to a singlet due to the Cp⁺ protons, are broad CcageH resonances at δ 4.10 and 3.37 ppm. In the Cp analogue the two CcageH resonances are very close and cannot be easily assigned (see Table 2) but in 4 the CcageH of the cobaltacarborane cage is shielded by the inductive effect of the Cp⁺ ligand and shifted ca. 0.6 ppm to lower frequency. The identity of compound 4 was confirmed crystallographically and a perspective view of a single molecule is shown in Figure 4 (left). The structure is directly comparable with that of its Cp analogue,⁶ albeit somewhat more distorted to accommodate the larger steric bulk of the Cp⁺ ligand. Thus Cp⁺ is more bent away from the C₂B₁₀ substituent with a θ value of 21.58(8)° (Cp analogue 15.8, 16.3°), the carborane substituent is less elevated with respect to the C₁C₂B₇B₈B₄ plane at 16.07(12)° (Cp analogue 19.1, 19.5°) and the C₁-Co₃ distance is extended at 2.1670(19) Å (Cp analogue 2.118, 2.124 Å).

Scheme 3. Formation of 4, 5 and 6 from deprotonation and metalation of III with {CoCp⁺}.

Yellow compound 5 was afforded in 9% isolated yield, and elemental analysis and mass spectrometry are fully consistent with 5 being an isomer of 4. There are two CcageH resonances in the ¹H NMR spectrum,
but in CDCl₃ the lower frequency one (due to the cobaltacarborane) is partially obscured by the signal due to the Cp* protons. Using a mixed solvent of CHCl₃:CD₃CN (1:10), however, shifts the C1H resonance somewhat such that it is now close to, but distinguished from, that of a trace of water. With a frequency of δ 2.09 ppm we again note that the C1H resonance in 5 is downfield shifted by ca. 0.6 ppm with respect to that in the Cp analogue II (Table 2). The structure of a single molecule of 5, established crystallographically, is shown in Figure 4 (right). In marked contrast to the situation in the 3,1,2-CoC₂B₉-1′,2′-C₂B₁₀ species 4, the Cp* ligand in the 2,1,8-CoC₂B₉-1′,2′-C₂B₁₀ isomer 5 is now essentially parallel with lower pentagonal belt of the cobaltacarborane since steric crowding with the carborane substituent is no longer a serious issue.

As previously noted it is somewhat surprising (based on precedence with CoCp⁶) that a significant amount of the 3,1,2-CoC₂B₉-1′,2′-C₂B₁₀ species 4 was afforded by “in situ” metalation of singly-deboronated 1,1′-bis(ortho-carborane). Nevertheless, 4 may be converted to 5 by a simple redox process. After a 1 h stir of 4 with one equivalent of Na[C₁₀H₈] in THF at ambient temperature followed by aerial oxidation conversion is ca. 50%. Note that under the same conditions the Cp analogue of 4 is completely converted to the Cp analogue of 5.⁶

![Figure 4. Left; perspective view of compound 4. Right; perspective view of one of the two crystallographically-independent molecules of compound 5.](image)

A minor co-product in the initial synthesis of 4 and 5 is green compound 6, whose limited availability (4 mg) resulted in characterisation only by mass spectrometry, NMR spectroscopy and single-crystal X-ray diffraction (Figure 5). Compound 6 consists of a 13-vertex docosahedral dicobaltacarborane in which the metal atoms occupy vertices 4 and 5 and the carbon atoms vertices 1 and 12, with a 1′,2′-C₂B₁₀H₁₁ substituent bound at C12. A handful (<20) of docosahedral MM′C₂B₉ metallacarboranes are known and in all structurally-established cases ²¹,²₈,₃₀ the metal atoms occupy the degree-6 vertices 4 and 5, with the carbon atoms either at vertices 1 and 6 or at vertices 2 and 3. Compound 6 is therefore the first proven example of a 13-vertex bimetalcarboranes with a 4,5,1,12-M₂C₂B₉ architecture, although this motif has previously been suggested for one isomer of (CoCp)₂C₂B₉H₁₁.³¹ We suggest that the origin of the unexpected product 6 is Direct Electrophilic Insertion (DEI) of a {CoCp*}⁺ fragment into the anionic species [4]⁻ or, more likely, [5]⁻ prior to aerial oxidation. DEI was first recognised as a route to
bimetallacarboranes by Kudinov and co-workers,\textsuperscript{29} and we have previously used it to deliberately prepare 14-vertex bimetallacarboranes from 13-vertex monometallacarborane anions.\textsuperscript{16,26,32} In the \textsuperscript{1}H NMR spectrum of 6 there are, in addition to the singlet arising from the 30 Cp\textsuperscript{*} protons, two broad integral-1 C\textsubscript{cage}H resonances at \( \delta \) 3.80 and 1.26 ppm. By analogy with [6-(1\textsuperscript{'-closo}-1\textsuperscript{'},2\textsuperscript{'}-C\textsubscript{2}B\textsubscript{10}H\textsubscript{11})-4-(p-cymene)-5-(mesitylene)-closo-4,5,1,6-Ru\textsubscript{2}C\textsubscript{2}B\textsubscript{9}H\textsubscript{10}],\textsuperscript{29} the closest fully-characterised compound in the literature, we assign the lower frequency C\textsubscript{cage}H resonance in 6 to C\textsubscript{1}H.

Deboronation of 5 with KF in THF/water followed by metathesis afforded the yellow solid [HNMe\textsubscript{3}][8-(7\textsuperscript{'}-nido-7\textsuperscript{'},8\textsuperscript{'}-C\textsubscript{2}B\textsubscript{9}H\textsubscript{11})-2-Cp\textsuperscript{*}-closo-2,1,8-CoC\textsubscript{2}B\textsubscript{9}H\textsubscript{10}] (7) as an equal mixture of diastereoisomers (Scheme 1). Salt 7 gave satisfactory elemental analysis. In the \textsuperscript{1}H NMR spectrum the C1H resonances of the diastereoisomers cannot be resolved, neither can the C8\textsuperscript{'}H resonances. By analogy with the C\textsubscript{cage}H chemical shifts for anion 2 (Table 2), the most similar species, we tentatively assign the resonance at \( \delta \) 1.96 ppm to C1H (shielded relative to that in 2 by the presence of the Cp\textsuperscript{*} ligand) and that at \( \delta \) 1.88 ppm to C8\textsuperscript{'}H. Evidence for a diastereoisomeric mixture is provided by the observation of two close and equal singlets assigned to the Cp\textsuperscript{*} protons at \( \delta \) 1.85 and 1.84 ppm, and a broad low-frequency signal due to the bridging protons of the deboronated cage which clearly shows partial resolution, with maxima at \( \delta \) -2.68 and -2.84 ppm.

![Figure 5](https://example.com/figure5.png)

**Figure 5.** Perspective view of compound 6.

Interestingly, KF/H\textsubscript{2}O deboronation of compound 4 followed by metathesis yields an orange-solid which, spectroscopically, appears to be a mixture of salt 7 and another species. We tentatively identify this second species as [HNMe\textsubscript{3}][1-(7\textsuperscript{'}-nido-7\textsuperscript{'},8\textsuperscript{'}-C\textsubscript{2}B\textsubscript{9}H\textsubscript{11})-3-Cp\textsuperscript{*}-closo-3,1,2-CoC\textsubscript{2}B\textsubscript{9}H\textsubscript{10}], i.e. the simple B3\textsuperscript{'} (or B6\textsuperscript{'}) deboronated variant of 4. Presumably partial isomerisation of the cobaltacarborane cage from 3,1,2-CoC\textsubscript{2}B\textsubscript{9} to 2,1,8-CoC\textsubscript{2}B\textsubscript{9}, yielding 7, accompanies deboronation. When this mixture is treated with \textsuperscript{"}BuLi and then metalated with [RuCl\textsubscript{2}(p-cymene)]\textsubscript{2} a diastereoisomeric mixture of a single species 8 is afforded, exactly the same mixture that is produced by deprotonation/metalation of salt 7 alone. This
suggests that deprotonation of \([1-(7'-nido-7',8'-C_2B_9H_{11})-3-Cp^*-closo-3,1,2-CoC_2B_9H_{10}]^-\) results in its complete isomerisation to the 2,1,8-CoC_2B_9 isomer, a conclusion that is fully consistent with the reduction-induced isomerisation of 3,1,2-MC_2B_9 species we have observed previously.\(^6\)

When prepared from salt 7 (Scheme 4), compound 8, \([8-(1'-3'-\text{p-cymene})-closo-3',1',2'-\text{RuC}_2B_9H_{10})-2-Cp^*-closo-2,1,8-\text{CoC}_2B_9H_{10}]\), is afforded (as a yellow solid) in 24\% isolated yield. Elemental analysis and mass spectrometry are fully consistent with the molecular formula \(C_{24}H_{20}B_{18}CoRu\). As anticipated from the fact that precursor 7 exists as two diastereoisomers, compound 8 is also a diastereoisomeric mixture, but, somewhat to our surprise, not an equal one. Although the \(^{13}\)B\{\(^1\)H\} NMR spectrum is largely uninformative due to multiple overlapping resonances, in the \(^1\)H spectrum are clear resonances for two high frequency \(C_{\text{cage}}H\) atoms, two CH\(_2\) groups of the p-cymene ligand and two separate resonances for the Cp\(^*\) protons (although the chemical shifts here are only distinguished in the third place of decimals). In all cases these pairs of resonances suggest that the two diastereoisomers are present in a ratio of ca. 2:1. The identity of compound 8 is revealed from the \(^1\)H NMR spectrum. We know that the cobaltacarborane cage is of 2,1,8-CoC_2B_9 architecture since that is what it was in precursor 7, but the ruthenacarborane cage in 8 must be 3',1',2'-RuC\(_2\)B\(_9\) since the high-frequency \(C_{\text{cage}}H\) resonances present (major isomer \(\delta\) 3.75 ppm, minor isomer \(\delta\) 3.88 ppm) are much more reminiscent of that in \([1-(1'-'closo-1',2'-3B_10H_{11})-3-(p-cymene)-closo-3,1,2-\text{RuC}_2B_9H_{10}]\) (Ia, \(\delta\) 4.03 or 3.91 ppm) than that in \([8-(1'-'closo-1',2'-C_2B_{10}H_{11})-2-(p-cymene)-closo-2,1,8-\text{RuC}_2B_9H_{10}]\) (IIa, \(\delta\) 2.63 ppm). See Table 2. Note that 8 is the complement of 3 in which \{CoC\} in 3 has been replaced by \{Ru(p-cymene)\} and \{Ru(p-cymene)\} in 3 has been replaced by \{CoC\(^*\)\}. Unlike 3, however, the diastereoisomeric components of 8 could not be separated in spite of exhaustive attempts by TLC, and neither could crystals of either diastereoisomer be grown from the mixture. The final experiment, thermal isomerisation of 8, was therefore performed on the isomeric mixture.

With the indication that the ruthenacarborane cage of 8 was of 3',1',2'-RuC\(_2\)B\(_9\) form, we investigated its possible thermal isomerisation. Compound 8 was recovered unchanged from heating to reflux in THF, but in refluxing DME for 1 h there was clear evidence from \(^1\)H NMR spectroscopy of a change and isomerisation was complete after overnight reflux (Scheme 4). The product, compound 9, was obtained as a yellow solid and was shown to be an isomer of 8 by elemental analysis and mass spectrometry. As was the case with 8, compound 9 is a mixture of two diastereoisomers (approximate ratio 2:1) that unfortunately we could not separate in spite of exhaustive attempts to do so.

Compound 9 is \([8-(8'-2'-\text{p-cymene})-closo-2',1',3'-C_2B_9H_{10})-2-Cp^*-closo-2,1,8-\text{CoC}_2B_9H_{10}]\), i.e. an isomer of 8 in which the ruthenacarborane cage has isomerised from 3',1',2'-RuC\(_2\)B\(_9\) to 2',1',8'-RuC\(_2\)B\(_9\). This is clear from the chemical shift of the higher frequency \(C_{\text{cage}}H\) resonances in the \(^1\)H NMR spectrum assigned to the ruthenacarborane cage (major isomer \(\delta\) 2.59 ppm, minor isomer \(\delta\) 2.62 ppm) which is in accord with the \(C_{\text{cage}}H\) chemical shift in \([8-(1'-'closo-1',2'-C_2B_{10}H_{11})-2-(p-cymene)-closo-2,1,8-\text{RuC}_2B_9H_{10}]\) (IIa), \(\delta\) 2.63 ppm (Table 2). In contrast the lower frequency \(C_{\text{cage}}H\) resonances in 9, assigned to the 2,1,8-CoC\(_2\)B\(_9\) cage, is barely changed from those in 8. A clear indication of the approximate 2:1 ratio of the two diastereoisomers of 9 comes from the well-resolved resonances due to the Cp\(^*\) protons at \(\delta\) 1.84 (major) and \(\delta\) 1.83 (minor) ppm. This ratio is effectively the same as that in 8.
Scheme 4. Formation of 8 and then 9 from deprotonation and metalation of 7 with \{Ru(p-cymene)\} followed by thermolysis. 7, 8 and 9 are all mixtures of two diastereoisomers; for 7 this mixture is 1:1 but for 8 and 9 the mixture is 2:1 although in these cases the identities of the major and minor components are not known.

\[\text{[Co']} + \text{[Ru]} \rightarrow \text{[Co']} + \text{[Co']} \]

7

\(i, ii\)

\[\text{[Co']} \rightarrow \text{[Co']} \]

8

24% isolated yield

\[\text{[Co']} \rightarrow \text{[Co']} \]

9

85% isolated yield

\([\text{Co'}] = \text{CoCp}^+, [\text{Ru}] = \text{Ru(p-cymene)}\)

\(i \text{ } \text{n}^3\text{BuLi}; ii \text{ } [\text{RuCl}_2(p\text{-cymene})]_2\)
Crystallisation of 9 from DCM/petrol affords yellow block crystals of 9·CH₂Cl₂, and crystallographic study reveals that the two diastereoisomers crystallise together to give a partially disordered structure. Initially this was evident from both VCD and BHD analysis of the prostructure,¹⁵⁻¹⁷ and was ultimately confirmed by successful refinement. In the cobaltacarborane cage vertices 1 and 11 are essentially 50:50 C:B disordered [occupancy factors of 0.52(2) for C1 and 0.48(2) for B1, with complementary occupancy factors for vertex 11] whilst in the ruthenacarborane cage vertex 1′ is 0.69(2):0.31(2) C:B and vertex 11′ is 0.31(2):0.69(2) C:B. The 50:50 disorder in the cobaltacarbo
crane cage means that both diastereoisomers are present in the crystal in equal amounts. Several crystals were successively mounted on the diffractometer but the unit cell dimensions of all were identical within experimental error. Figure 6 shows a perspective view of one arbitrary diastereoisomer of 9.

Notwithstanding the disorder, the crystallographic study confirms that in 9 the ruthenacarborane cage has isomerised from the 3′,1′,2′-RuC₂B₉ in 8 to 2′,1′,8′-RuC₂B₉ in 9, as inferred by analysis of the ¹H NMR spectrum. Just as compound 3α and 3β are the first examples of heterobimetallic derivatives of 1,1′-bis(ortho-carborane) with 2,1,8-MC₂B₉-3′,1′,2′-M′C₂B₉ structures, so compound 9 is the first heterobimetallic derivative with a 2,1,8-MC₂B₉-2′,1′,8′-M′C₂B₉ structure. Exopolyhedral ligand bend-back angles θ in 9 are 1.32(6)° (cobaltacarborane) and 5.54(7)° (ruthenacarborane), close to zero as expected for 2,1,8-MC₂B₉ cages.

CONCLUSIONS

Stepwise deboronation-metallation-deboronation-metallation has allowed isolation of the first examples of heterometalated derivatives of 1,1′-bis(ortho-carborane) with both 2,1,8-MC₂B₉-3′,1′,2′-M′C₂B₉ and 2,1,8-MC₂B₉-2′,1′,8′-M′C₂B₉ architectures. Critical to the success of this approach has been the use of the relatively mild reagent KF in THF/H₂O for the second deboronation step. Products are afforded as a mixture of diastereoisomers since the second deboronation occurs at both the 3′ and 6′ positions of the C₃B₁₀ cage. In one case these diastereoisomers could be separated by chromatography.

Figure 6. Perspective view of one arbitrary diastereoisomer of compound 9.
ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.xxxxxxx. This information comprises NMR spectra of all new products.

Accession Codes
CCDC 1828646-1828651 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes
The authors declare no competing financial interest.

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REFERENCES
(2) Hawthorne, M. F.; Young, D. C.; Garrett, P. M.; Owen, D. A.; Schwerin, S. G.; Tebbe, F. N.; Wegner, P. A. Preparation and characterization of the (3)-1,2- and (3)-1,7-dicarbadodecahydrondecaborate(-1) ions. J. Am. Chem. Soc., 1968, 90, 862-868.
(8) Ren, S.; Xie, Z. A Facile and Practical Synthetic Route to 1,1′-Bis(o-carborane). Organometallics, 2008, 27, 5167-5168. The ¹H NMR chemical shift (δ = 5.51 ppm) reported in this paper for the C2H and
C2'H atoms of 1,1'-bis(ortho-carborane) in (CD3)2CO is at variance with the value (δ = 5.05 ppm) that we and others (e.g. reference 25) record.


(19) Mandal, D.; Man, W. Y.; Rosair, G. M; Welch, A. J. Steric versus electronic factors in metallacarborane isomerisation: nickelacarboranes with 3,1,2-, 4,1,2- and 2,1,8-NiC3B7 architectures and pendant carborane groups, derived from 1,1'-bis(o-carborane). Dalton Trans., 2016, 45, 15013-15025.


The first examples of heterometalated derivatives of 1,1′-bis(ortho-carborane) are reported. Stepwise deboronation-metalation-deboronation-metalation with, firstly, [Ru] then [Co] and, secondly, [Co] then [Ru] metal-ligand fragments affords species with both 2,1,8-MC\textsubscript{2}B\textsubscript{9}-3′,1′,2′-M′C\textsubscript{2}B\textsubscript{9} and 2,1,8-MC\textsubscript{2}B\textsubscript{9}-2′,1′,8′-M′C\textsubscript{2}B\textsubscript{9} architectures, formed as mixtures of diastereoisomers.