Exploration of Bis(nickelation) of 1,1′-Bis(o-carborane)

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Abstract: The metalation of \([\text{Tl}]_2[1-(1′-3′,1′,2′-\text{closo}-\text{TlC}_2\text{B}_8\text{H}_{10})-3,1,2-\text{closo}-\text{TlC}_2\text{B}_8\text{H}_{10}]\), with the smaller \([\text{Ni}(\text{dmp})]\) fragment sourced from \([\text{Ni}(\text{dmpe})\text{Cl}_2]\), is explored. The bis(nickelated) products are obtained as a diastereoisomeric mixture. These isomers were separated, fully characterised spectroscopically and crystallographically and identified as \(\text{rac}-[1-(1′-3′-(\text{dmpe})-3′,1′,2′-\text{closo}-\text{NiC}_2\text{B}_8\text{H}_{10})-3-(\text{dmpe})-3,1,2-\text{closo}-\text{NiC}_2\text{B}_8\text{H}_{10}]\) (1) and \(\text{meso}-[1-(1′-3′-(\text{dmpe})-3′,1′,2′-\text{closo}-\text{NiC}_2\text{B}_8\text{H}_{10})-3-(\text{dmpe})-3,1,2-\text{closo}-\text{NiC}_2\text{B}_8\text{H}_{10}]\) (2). Previously, these 3,1,2-NiC\(_2\)B\(_8\)3′,1′,2′-NiC\(_2\)B\(_8\) architectures (where both cages are not isomerised), were inaccessible, and thus new structures can be achieved during bis(nickelation) with \([\text{Ni}(\text{dmpe})]\). Further, the metalation of the tetra-thallium salt with the bulky \([\text{Ni}(\text{dmp})]\) fragment sourced from \([\text{Ni}(\text{dmp})\text{Cl}_2]\) was also studied. These bis(nickelated) products were also fully characterised and are afforded as the stereospecific species \(\text{rac}-[1-(1′-3′-(\text{dmpe})-3′,1′,2′-\text{closo}-\text{NiC}_2\text{B}_8\text{H}_{10})-3-(\text{dmp})-3,1,2-\text{closo}-\text{NiC}_2\text{B}_8\text{H}_{10}]\) (3) and \([1-(2′-4′-(\text{dmp})-4′,1′,2′-\text{closo}-\text{NiC}_2\text{B}_8\text{H}_{10})-3-(\text{dmp})-3,1,2-\text{closo}-\text{NiC}_2\text{B}_8\text{H}_{10}]\) (4a). In the latter metalation, compound 3 shows intramolecular dihydrogen bonding, contributing to the stereospecificity, whereas isomerisation from 3,1,2 to 4,1,2-in the 4a is related to steric relief.

Keywords: 1,1′-bis(o-carborane); deboronation; metalation; bis(nickelation); diastereoisomers; stereospecific

1. Introduction

Since the discovery of bis(carboranes) in 1964, the chemistry of 1,1′-bis(o-carborane) (Scheme 1, a) has evolved rapidly, particularly once a high-yielding synthetic route was devised in 2003. Bis(carborane) offers a versatile building block in designing three-dimensional molecules, an array of homogeneous catalyst precursors, luminescent materials and organic derivatives via C\(_{\text{cage}}\)-H or B\(_{\text{cage}}\)-H functionalisation [1–6].

Since 2010, the Welch group have established many variations of the metalation chemistry of 1,1′-bis(o-carborane), one approach being cage expansion chemistry via reduction-metalation of this species [1], whilst another metalation strategy explored broadly within the group is deboronation/metalation of 1,1′-bis(o-carborane).

The single deboronation/metalation of 1,1′-bis(o-carborane) has been reported for cobalt, nickel and ruthenium metal fragments and afforded a wide range of mono-metallic-bis(carborane) isomers [7,8]. In further developments, double deboronation/metalation was achieved, such that both cages became metallacarboranes. The binmetallic metallacarboranes derived from the metalation of doubly deboronated 1,1′-bis(o-carborane) with both rhodium and ruthenium fragments are 3,1,2-MC\(_2\)B\(_9\)-2′,1′,8′-MC\(_2\)B\(_9\) \([M = \{\text{Rh}, \text{Ru}\}\] species, in which one of the cages has isomerised (Scheme 1, b and c). There are limited examples of the parent 3,1,2-MC\(_2\)B\(_9\)-3′,1′,2′-MC\(_2\)B\(_9\) form [9,10]. Variation in the isomer type with cobalt has been achieved by varying the metalation source, forming either 3,1,2-CoC\(_2\)B\(_9\)-3′,1′,2′-CoC\(_2\)B\(_9\) (non-isomerised) or 3,1,2-CoC\(_2\)B\(_9\)-2′,1′,8′-CoC\(_2\)B\(_9\) (isomerised) (Scheme 1, c) products [9]. Notably, an example of stepwise deboronation/metalation-deboronation/heterometalation is also reported [11]. Here we document an expansion
of the bimetallic metallacarboranes library via the double deboronation/nickelation of 1,1'-bis(o-carborane).

Scheme 1. Line diagrams of a–c. Species a is 1,1'-bis(o-carborane), whereas b (α-form) and c (β-form) were derived via double deboronation/metalation of a. Unlabelled vertices are B.

2. Materials and Methods
2.1. General Considerations

Experiments were carried out under dry, oxygen-free N2, using standard Schlenk techniques, although subsequent manipulations were performed at ambient condition. Tetrahydrofuran (THF) was dried and distilled under sodium/benzophenone, whilst petrol was distilled from sodium wire before use. DCM was purified in an MBRAUN SPS-800 (Dieselstr. 31, D-85748 Garching,). Degassing of solvents was performed (3 × freeze-pump-thaw cycles) before reaction. Preparative TLC used Kieselgel F254 glass plates (20 × 20 cm), 1H (400.1 MHz), 31P (162.0 MHz) or 11B (128.4 MHz) NMR spectra and 1H,31P Heteronuclear Multiple Bond Correlation (HMBC) experiment (in Supplementary Materials) were run on a Bruker DPX-400 spectrometer (Bruker BioSpin AG, Fallenden, Switzerland). The precursors 1,1'-bis(o-carborane) [12], its deboronated derivative [Tl2[1-(1'-3',1',2'-closo-TIC2B9H10)-3,1,2-closo-TIC2B9H10]] (Tl4-salt) (WARNING: Thallium is extremely toxic, appropriate precautions are required when handling thallium compounds) [9] and [NiCl2(dmpe)] (dmpe = 1,2-bis(dimethylphosphino)ethane) [13] were prepared by modified literature methods. [NiCl2(dppe)] (dppe = 1,2-bis(diphenylphosphino)ethane) and the remaining reagents were purchased commercially.

2.1.1. Synthesis and Characterisation of rac-[1-(1'-3'- (dmpe)-3',1',2'-closo-NiC2B9H10)-3-(dmpe)-3,1,2-closo-NiC2B9H10] (1) and meso-[1-(1'-3'- (dmpe)-3',1',2'-closo-NiC2B9H10)-3-(dmpe)-3,1,2-closo-NiC2B9H10] (2)

The Tl4-salt (0.60 g, 0.56 mmol) was taken into THF (15 mL). The yellow suspension was degassed by freeze-pump-thaw (three cycles). [NiCl2(dmpe)] (0.31 g, 1.1 mmol) was transferred at −196 ºC. The reaction suspension was allowed to warm and was stirred at room temperature. After overnight stirring, the mixture turned dark green. All volatiles were removed in vacuo. The residue was dissolved in DCM and passed through a small pad of silica. The filtrate was reduced in volume under low pressure and purified by preparative TLC using DCM and petrol (80:20) to afford two dark green bands, which were collected as solids. The upper green band with Rf = 0.84 afforded rac-[1-(1'-3'- (dmpe)-3',1',2'-closo-NiC2B9H10)-3-(dmpe)-3,1,2-closo-NiC2B9H10] (1) (80 mg, 21%) and a lower green band with Rf = 0.63 gave meso-[1-(1'-3'- (dmpe)-3',1',2'-closo-NiC2B9H10)-3-(dmpe)-3,1,2-closo-NiC2B9H10] (2) (76 mg, 20%).

Compound 1: 1H NMR (CD2Cl2): δ 2.43 (d, J1/PH = 14.0 Hz, 2H, CHcage), 2.14–1.90 (m, 8H, P(CH2)2P), 1.83 (d, J2/PH = 10.0 Hz, 6H, CH3), 1.67 (d, J2/PH = 10.0 Hz, 6H, CH3), 1.55 (d, J2/PH = 10.0 Hz, 12H, CH3).

1H NMR (CD2Cl2): δ 2.43 (s, 2H, CHcage), 2.12–1.89 (m, 8H, P(CH2)2P), 1.83 (s, 6H, CH3), 1.67 (s, 6H, CH3), 1.56 (s, 12H, CH3). 31P[1H] NMR
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(CD₂Cl₂): δ 43.1 (d, ²J_{PP} = 29.2 Hz, 2P), 33.0 (d, ²J_{PP} = 29.2 Hz, 2P). ¹¹B[^1H] NMR (CD₂Cl₂): δ −2.7 (2B), −4.1 (2B), −7.3 (2B), −11.8 (2B), −13.6 (2B), −15.8 (4B), −21.1 (4B).

Compound 2: ¹¹H NMR (CD₂Cl₂): δ 2.48 (d, ²J_{PH} = 10.0 Hz, 2H, CH_{cage}), 2.16–1.79 (m, 8H, P(CH₂)₂P), 1.73 (d, ²J_{PH} = 10.0 Hz, 6H, CH₃), 1.70 (d, ²J_{PH} = 8.0 Hz, 6H, CH₃), 1.57 (d, ²J_{PH} = 10.0 Hz, 6H, CH₃), 1.55 (d, ²J_{PH} = 8.0 Hz, 6H, CH₃). ¹¹H[^1P] NMR (CD₂Cl₂): δ 2.49 (s, 2H, CH_{cage}), 2.14–1.78 (m, 8H, P(CH₂)₂P), 1.74 (s, 6H, CH₃), 1.70 (s, 6H, CH₃), 1.57 (s, 6H, CH₃), 1.55 (s, 6H, CH₃). ¹¹P[^1H] NMR (CD₂Cl₂): δ 43.7 (d, ²J_{PP} = 28.4 Hz, 2P), 33.4 (d, ²J_{PP} = 28.4 Hz, 2P). ¹¹B[^1H] NMR (CD₂Cl₂): δ −1.5 (2B), −4.0 (2B), −10.4 (2B), −11.5 (2B), −14.5 (3B), −15.9 (5B), −20.4 (2B).

2.1.2. Synthesis and Characterisation of rac-[1-(1′-3′-(dppe)-3′,1′,2′-closo-NiC₂B₉H₁₀)-3-(dppe)-3,1,2-closo-NiC₂B₉H₁₀] (3) and [1-(2′-4′-(dppe)-4′,1′,2′-closo-NiC₂B₉H₁₀)-3-(dppe)-3,1,2-closo-NiC₂B₉H₁₀] (4α)

A yellow suspension of Tl₂-salt (0.60 g, 0.56 mmol) in THF (20 mL) was frozen at −196 °C ([NiCl₂(dppe)] (0.59 g, 1.1 mmol) added to the frozen mixture. After overnight stirring, the reaction mixture gave a green suspension. All volatiles were evaporated off under reduced pressure. The mixture was taken into DCM and filtered through silica. The filtrate was reduced in a minimum amount under low pressure. All crystals were mounted in inert oil on a cryoloop and cooled to 100 K by an Oxford Cryosystems Cryostream. Indexing, data collection and absorption correction were obtained by solvent diffusion at 5 °C using DCM and petrol 40–60 as antisolvent. Intensity data for compounds 1–4 were collected on a Bruker X8 APEXII diffractometer, whereas for compound 4α on a Rigaku FRE+ equipped with VHF Varimax confocal mirrors and an AFC10 goniometer and HG Saturn 724+ detector using Mo-Kα X-radiation at the UK National Crystallography Service. All crystals were mounted in inert oil on a cryoloop and cooled to 100 K by an Oxford Cryosystems Cryostream. Indexing, data collection and absorption correction were performed using the APEXII suite of programmes [14]. Structures were solved with the SHELXS programme [15] and refined by full-matrix least-squares (SHELXL), using OLEX2 [16]. Table 1 summarises the crystallographic parameters. The location of the CH vertices in all cases was established by the Vertex to Centroid (VCD) method developed by the Welch group [17]. The VCD method is based on the fact that, in a carborane cage, the C vertices are closer to the cage centroid than the B vertices. The CH vertex’s location was corroborated by the Boron-to-Hydrogen distance method ("B"–H bond lengths for actual C atoms refined to ca. <0.8 Å) in all cases except 4α, where the positions of the H atoms could not be freely refined against the weak and twinned diffraction data. In this case, B-H distances were restrained to 1.10(2) Å.
Table 1. Crystallographic data for compounds 1–4α.

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<td>C_{59}H_{74}B_{18}Ni_{2}P_{4}Cl_{6}</td>
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<td>P-1</td>
<td>C2/c</td>
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<td>25.0952(8)</td>
<td>10.2816(4)</td>
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<td>6758.4(4)</td>
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<tr>
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<td>1.407</td>
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<td><strong>μ(Mo-Kα)/mm⁻¹</strong></td>
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<td>5.584 to 58.27</td>
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<td>8989</td>
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<td>0.0752, 0.0996</td>
<td>0.0598, 0.0974</td>
<td>0.1200, 0.1892</td>
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<tr>
<td><strong>E_{max}, E_{min}/e Å⁻³</strong></td>
<td>0.29 / -0.26</td>
<td>0.87 / -0.79</td>
<td>0.65 / -1.01</td>
<td>0.52 / -0.72</td>
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<tr>
<td><strong>Flack parameter</strong></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.12(2)</td>
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</table>

1 was treated as a two-component crystal and refined with hkf 5 data. In 4α, disordered phenyl carbon atoms were constrained to have equal displacement parameters. The crystal of 4α was not single and refined as a two-component twin with the twin law 1 0 0 0 –1 0 0 0 –1 against HKLF 4 data, which were themselves treated with the solvent mask procedure implemented in OLEX2. HKLF 5 data were not available from the National crystallography service for this structure. A refinement model of the solvent showed approximately three molecules of highly disordered CH₂Cl₂ per bis carborane.

3. Results and Discussion

3.1. Characterisation of Compounds 1 and 2

Previously, the double deboronated [7-(7'-7',8'-nido-C₂B₉H₁₀)-7,8-nido-C₂B₉H₁₀]⁻⁴ tetraanion derived from [1-(1'-1',2'-closo-C₂B₁₀H₁₁),1,2-closo-C₂B₁₀H₁₁], commonly called 1,1'-bis(o-carborane), was isolated as [HNMe₃⁺] or [BTMA⁺] [BTMA = benzyltrimethylammonium] salts. Later, [TI⁺]⁺ salts were chosen for metalation because of their generally better yields [9]. We have reacted a suspension of [TI]₂[1-(1'-3',1',2'-closo-TIC₂B₉H₁₀)–3,1,2-closo-TIC₂B₉H₁₀] in THF with [Ni(dmpe)Cl₂] at room temperature. Workup and purification of the dark-green suspension involving preparative thin-layer chromatography (TLC) re-
sulted in two dark green bands, compounds 1 and 2, in moderate yield (Scheme 2). These were fully characterised by a variety of spectroscopic and crystallographic analyses.


An interesting feature of the double deboronation-metalation of 1,1′-bis(o-carborane) is that it gives diastereomeric metallcarborane products. Indeed, compound 1 turns out to be racemic, whilst compound 2 is in the meso form. These observations are also consistent with the NMR spectroscopic analysis. The 1H NMR spectrum of compound 1 reveals resonances arising from the methylene bridge of the two dmpe ligands, whilst the methyl groups of the dmpe ligands produce three doublet resonances. The first two are of integral-6 at δ 1.83, 1.67 ppm with coupling 2JPH = 10.0 Hz, and the last one is of integral-12 at δ 1.55, 2JPH = 10.0 Hz. On the contrary, the 1H NMR spectrum of compound 2 reveals, in addition to the signals for methylene bridge of the dmpe ligands, four doublets assigned to the methyl protons of the dmpe fragments at δ 1.73 (2JPH = 10.0 Hz), 1.70 (2JPH = 8.0 Hz), 1.57 (2JPH = 10.0 Hz) and 1.55 (2JPH = 8.0 Hz) ppm, each of integral-6. These resonances collapse to the corresponding singlets in the 1H[31P] spectrum. In the 1H NMR spectra there is also a single CHcage resonance of integral two for compound 1 appearing as a doublet δ 2.43 (2JPH = 14.0 Hz) ppm, confirmed as arising from coupling to phosphorus, since it collapses to a singlet on broad-band 31P decoupling, whilst the CHcage signal of integral two for compound 2 appears at a higher frequency, δ 2.48 (2JPH = 10.0 Hz) ppm, and collapses to a singlet on broad-band 31P decoupling. Therefore, these two isomers show slightly different characteristics in their proton NMR spectra. Moving to the 31P[1H] NMR spectrum of compound 1, this shows two mutual doublets with the integral ratio of 1:1 at δ 43.1 and 33.0 ppm and a coupling constant 2JPP = 29.2 Hz. This indicates that in each cage the two phosphorus atoms are magnetically inequivalent. Moreover, the two pairs of phosphorus atoms in different cages are also magnetically equivalent. This clearly shows that the metallacarborane cages are asymmetric. Similarly, the 31P[1H] NMR spectrum of compound 2 reveals two mutually coupled doublets of integral two at δ 43.7
and 33.4 ppm with coupling $^{2}J_{PP} = 28.4$ Hz, not very different from that of compound 1. Notably, from the $^{1}$H-$^{31}$P HMBC experiment, the splitting of $CH_{\text{cage}}$ arises from the trans phosphorus at δ 33.0 ppm for compound 1 and the trans phosphorus at δ 33.4 ppm for compound 2. Therefore, the resonances δ 43.1 ppm and δ 43.7 ppm correspond to the phosphorus atoms cis to the $CH_{\text{cage}}$ for compound 1 and compound 2, respectively. The $^{11}$B[$^{1}$H] NMR spectrum of compound 1 consists of seven resonances with relative integrals 2:2:2:2:4:4:4 from high frequency to low frequency, whereas compound 2 shows a distinctly different pattern comprising seven resonances in the integral ratio 2:2:2:3:5:2 from high frequency to low frequency. However, this spectroscopic information is not conclusive in determining the exact structures of the racemic and meso isomers.

A crystallographic study was carried out for both compounds 1 and 2. It is envisaged that the double deboronation-metalation of 1,1’-bis(o-carborane) with [Ni(dmpe)] fragments generates racemic and meso mixtures with 3,1,2-NiC₂B₉ architectures. Indeed, both cages of compounds 1 and 2 are singly-metalated and in the 3,1,2-NiC₂B₉ form. As regards the identification of the diastereoisomer, a crystallographic C₂ axis passes perpendicular to the C₁-C₁’ bond, leading to the same chirality for both cages and meaning that compound 1 is a racemic isomer, whereas a non-crystallographic inversion centre i can be imagined at the mid-point of the C₁-C₁’ bond in 2, meaning different chirality for each cage and showing that compound 2 is a meso isomer. Figure 1 shows a perspective view of a single molecule of racemic-[1-(1’-3’’-(dmpe)-3’’,1’’,2’’-closo-NiC₂B₉H₁₀)-3-(dmpe)-3,1,2-closo-NiC₂B₉H₁₀] (1), whereas a perspective view of a single molecule of meso-[1-(1’-3’’-(dmpe)-3’’,1’’,2’’-closo-NiC₂B₉H₁₀)-3-(dmpe)-3,1,2-closo-NiC₂B₉H₁₀] (2) is presented in Figure 2. These diastereoisomers are the first such examples in which both the metallacarborane moieties remain unisomerised, i.e., 1 and 2 are 3,1,2-NiC₂B₉ archites. The presence of the [(dmpe)NiC₂B₉] substituents on C₁ or C₁’ inhibit the free rotation of the [Ni(dmpe)] fragment on both the primed and non-primed cages. It is confirmed that in each cage the phosphorus atoms are inequivalent, giving rise to two doublets observed in the $^{31}$P NMR spectra (previously discussed). Since both cages are of the 3,1,2-NiC₂B₉ form, the two metallacarborane units at C₁ and C₁’ push each other away, so that the [Ni(dmpe)] fragment is bent away from its ideal orientation within the cages. In principle, the ideal orientation of the [NiP₁P₂] fragment in a NiC₂B₉ icosahedron is perpendicular to the vertical mirror plane through the C₂B₉ unit, conveniently defined by the interplane dihedral angle ($\theta$) of 90°. [8] For compound 1, $\theta$ is found to be 55.36(8)° for both the primed cage and non-primed cage, whilst for compound 2, $\theta$ is 57.59(15)° and 49.58(18)° for the primed cage and the non-primed cage, respectively. These calculations were carried using the planes through Ni₃P₁P₂ and Ni₃’P’₁P’₂ and through B₆B₈B₁₀ and B₆’B₈’B₁₀ for the non-primed and primed cages, respectively. Thus, the dihedral angles are clearly twisted away from the idealised 90°. We also note that in compound 1 the [NiPP] plane is bent away from the perpendicular to the bottom pentagonal B₅B₆B₁₁B₁₂B₉ plane by 6(7)°, whereas in compound 2 the corresponding angles are 6.1(12)° for the non-primed cage and 21.5(15)° for the primed cage. The internal steric crowding between two (dmpe)NiC₂B₉ units is also evidenced by the elongated Ni₃-C₁ distances compared to Ni₃-C₂ [compound 1 primed cage: 2.2977(19) Å versus 2.0657(18) Å]. This is also evidenced in compound 2, Ni₃-C₁: 2.326(4) Å [Ni₂-C₂: 2.066(4) Å] and Ni₃’-C₁’: 2.299(4) Å [Ni₂’-C₂’: 2.103(3) Å].
Figure 1. Molecular structure of rac-[1-(1′-3′-(dmpe)-3′,1′,2′-closo-NiC₂B₉H₁₀)-3-(dmpe)-3,1,2-closo-NiC₂B₉H₁₀] (1). Atoms with dashed suffixes are generated by the symmetry operation 1.5-x, y, 0.5-z.

Figure 2. Molecular structure of meso-[1-(1′-3′-(dmpe)-3′,1′,2′-closo-NiC₂B₉H₁₀)-3-(dmpe)-3,1,2-closo-NiC₂B₉H₁₀] (2).
3.2. Characterisation of Compounds 3 and 4α

The treatment of [Tl]_2[1-(1′-3′,1′,2′-closo-TlC_2B_9H_{10})]-3,1,2-closo-TlC_2B_9H_{10}] in THF with [Ni(dppe)Cl_2] at room temperature followed by work up and purification involving preparative TLC afforded two army-green bands, compounds 3 and 4α (Scheme 3). The compounds were characterised spectroscopically as well as by single crystal XRD.

![Scheme 3](image_url)

Scheme 3. Synthesis of 3 and 4α from the nickelation of [Tl]_2[1-(1′-3′,1′,2′-closo-TlC_2B_9H_{10})]-3,1,2-closo-TlC_2B_9H_{10}]. NiPP = [Ni(dppe)].

Earlier we noted a diastereoisomeric mixture resulting from the deboronation-metalation of 1,1′-bis(o-carborane) with the [Ni(dmpe)] fragment. However, with the [Ni(dppe)] fragment, additionally, isomerisation occurred in the case of a mono-metalated [3,1,2-(dppe)-NiC_2B_9-1,2-C_2B_{10}] species which transformed to [4,1,2-(dppe)-NiC_2B_9-1,2-C_2B_{10}] due to the stereo-electronic nature of the dppe. Therefore, with double metalation using the[Ni(dppe)] fragment, the products could be diastereoisomers, stereospecific products and other isomers thereof. Although the \(^1\)H NMR spectra of 3 and 4α are more complex than those of compounds 1 and 2, there are resonances from phenyl protons and methylene bridge protons of the dppe. In the proton spectrum of 3, there is also a \(CH_{cage}\) resonance of integral two which appears at \(\delta 1.84\) ppm as a doublet \(J = 11.6\) Hz, whilst in the proton spectrum of 4α, there are two \(CH_{cage}\) resonances, each of integral-1, one at \(\delta 1.94\) ppm appearing as a singlet and the other at \(\delta 1.67\) ppm appearing as a doublet \(J = 11.2\) Hz. The doublets collapse to singlets in the \(^1\)H\(^{31}\)P) spectra. Notably the \(CH_{cage}\) resonance of 3 appears at a lower frequency than that of 1 (\(\delta 2.43\) ppm) or 2 (\(\delta 2.48\) ppm). The two doublet \(CH_{cage}\) resonances clearly indicate that both cages of compound 3 are nickellated and could be of 3,1,2-NiC_2B_9-3′,1′,2′-NiC_2B_9 architecture with reference to the proton spectra of compounds 1 and 2. The doublet and singlet \(CH_{cage}\) resonances indicate that nickelation occurred for both cages of compound 4α where one cage could be unisomerised, i.e., the [3,1,2-NiC_2B_9] form and another cage could be isomerised to either a [4,1,2-NiC_2B_9] or a [2,1,8-NiC_2B_9] form. These inferences are further supported by the \(^3\)P NMR spectra.
of compounds 3 and 4α. The $^{31}$P$[^1$H$] NMR spectrum of compound 3 consists of two mutual doublets with integral ratio 1:1 at δ 51.6 and 39.2 ppm with coupling $J = 19.1$ Hz; on the contrary, the $^{31}$P$[^1$H$] NMR spectrum of 4α consists of a singlet of integral-2 at δ 62.9 ppm and two mutual doublets, each of integral-1 at δ 49.4 and 47.5 ppm, with a coupling $J = 16.6$ Hz. This signifies the asymmetric nature of each metallacarborane cage but the symmetric nature of the whole molecule. The $^{11}$B$[^1$H$] NMR spectrum of compound 3 reveals five resonances with the relative integrals 2:4:2:5:5 from high frequency to low frequency, a different pattern to that for compounds 1 or 2, whilst the $^{11}$B$[^1$H$] NMR spectrum of 4α consists of multiple overlapping resonances with a total integral of 18B and is different in pattern to that of compounds 1, 2 and 3, thus preventing the identification of the exact isomer present and thereby requiring single crystal XRD analysis.

The precise natures of 3 and 4α were confirmed by crystallographic analysis. The racemic form of compound 3 is confirmed by a crystallographic C2 axis passing through the mid-point of the Cl-C1′ bond, and thus requiring both cages to be of the same chirality. Figure 3 shows a perspective view of a single molecule of rac-[1-(1′-3′-(dppe)-3′,1′,2′-closo-NiC$_2$B$_9$H$_{10}$)-3-(dppe)-3,1,2-closo-NiC$_2$B$_9$H$_{10}$] (3). However, it is clear that for compound 4α one of the cages has isomerised. A perspective view of a single molecule of [1-(2′-4′-(dppe)-4′,1′,2′-closo-NiC$_2$B$_9$H$_{10}$)-3-(dppe)-3,1,2-closo-NiC$_2$B$_9$H$_{10}$] (4α) is shown in Figure 4. For compound 3, both cages are nickellated by [Ni(dppe)] fragments and are of 3,1,2-NiC$_2$B$_9$ architecture. As noted, the midpoint of the Cl-C1′ bond lies on a crystallographic 2-fold axis. This leads to two bulky [(dppe)NiC$_2$B$_9$] units, connected at Cl and Cl′, pushing each other apart. There is a clear indication of internal crowding which is obvious from the orientation of the [NiP1P2] fragment in the NiC$_2$B$_9$ icosahedra. In 3 (for the non-primed cage), the θ (previously discussed) between the plane containing Ni3P1P2 and the plane through B6B8B10 is 60.72(9)°, which deviates significantly from 90°. Further evidence of steric congestion is demonstrated by the fact that the plane of the [NiP1P2] fragment deviates from perpendicularly to the plane through B5B6B11B12B9 vertices by 6.6(8)°. Additionally, the longer Ni3–C1 distance compared to Ni3–C2: 2.129(9) Å. This leads to two bulky {(dppe)NiC$_2$B$_9$′} fragments and are of 3,1,2-NiC$_2$B$_9$′ architecture. As noted, the midpoint of the Cl-C1′ bond lies on a crystallographic 2-fold axis. This leads to two bulky [{(dppe)NiC$_2$B$_9$}] units, connected at Cl and Cl′, pushing each other apart. There is a clear indication of internal crowding which is obvious from the orientation of the [NiP1P2] fragment in the NiC$_2$B$_9$′ icosahedra. In 3 (for the non-primed cage), the θ (previously discussed) between the plane containing Ni3P1P2 and the plane through B6B8B10 is 60.72(9)°, which deviates significantly from 90°. Further evidence of steric congestion is demonstrated by the fact that the plane of the [NiP1P2] fragment deviates from perpendicularly to the plane through B5B6B11B12B9 vertices by 6.6(8)°. Additionally, the longer Ni3–C1 distance compared to Ni3–C2: 2.129(9) Å. The relaxation of steric congestion in the (4′,1′,2′-NiC$_2$B$_9$′ cage) of 4α is reflected in the slightly shorter distance Ni4′–C1′ is 2.167(8) Å. Furthermore the dihedral angle between the Ni4′P1′P2′ and Cl′B11′B12′ planes for the primed cage is 86.1(4)°. Thus, the metalation of doubly deboronated species from 1,1′-bis(o-carborane) with [Ni(dppe)] results in bis-nickelated products, and although in principle both racemic and meso products were anticipated, only stereospecific racemic-3 and 4α were observed. The meso form was not found. The rationale for the formation of the rac form is discussed below.
Figure 3. A perspective view of rac-[1-(1′′-3′′-(dppe)-3′′,1′′,2′′-closo-NiC$_2$B$_9$H$_{10}$)-3-(dppe)-3,1,2-closo-NiC$_2$B$_9$H$_{10}$] (3) (all phenyls and the –CH$_2$–CH$_2$– bridge of dppe are in wireframe for clarity). Atoms with dashed suffixes are generated by the symmetry operation 1 – x, y, 0.5 – z.

Figure 4. Molecular structure of [1-(2′′-4′′-(dppe)-4′′,1′′,2′′-closo-NiC$_2$B$_9$H$_{10}$)-3-(dppe)-3,1,2-closo-NiC$_2$B$_9$H$_{10}$] (4α) (all phenyls and the –CH$_2$–CH$_2$– bridge of dppe are in wireframe for clarity).
3.3. Dihydrogen Interaction in 3 and Isomerisation in 4a

The reaction of the [7-(7′-7′,8′-nido-C2B9H10)-7,8-nido-C2B9H10]4− tetraanion with [Ni(dmpe)] fragments affords diastereomeric mixture products, i.e., rac (1) and meso (2) forms of 3,1,2-NiC2B9-3′,1′,2′-NiC2B9, whereas the same reaction with the more bulky [Ni(dppe)] fragment results in two isolable stereospecific products, i.e., rac 3,1,2-NiC2B9-3′,1′,2′-NiC2B9 and 3,1,2-NiC2B9-4′,1′,2′-NiC2B9, in compound 4α. The isolated rac-3 displays intramolecular dihydrogen bonding, as was found previously during the rationalisation of the stereospecific [CoCp] fragment metatation reaction with the [7-(7′-7′,8′-nido-C2B9H10)-7,8-nido-C2B9H10]4− tetraanion to form the only racemic form of the product 3,1,2-CoC2B9-3′,1′,2′-CoC2B9 [9]. The formation of intramolecular dihydrogen bonding associated with CH atoms of one cage and BH atoms of the other cage results from the relatively protonic and hydridic nature of the CH and BH atoms, respectively. 11B NMR analysis of individual vertices for 3,1,2-MC2B9 compounds established that the most hydridic BH atoms are H5 and H6 [18]. In the case of rac-3, the orientation of two [(dppe)NiC2B9] cages enables two sets of intramolecular dihydrogen bonds, CH2⋯BH6′ 2.07(3) Å (where i = 1 − x, y, 0.5 − z) and its symmetry equivalent, CH2⋯BH6′. Notably, the hypothetical analogous meso form could only allow for one set of such intramolecular dihydrogen bonding, whatever the rotameric arrangement, thereby rendering the meso isomer less favourable.

Crowding between the bulky [(dppe)(3,1,2-NiC2B9)] substituent on C1′ and the dppe ligand on Ni3 of an unisomerised 3,1,2-NiC2B9-3′,1′,2′-NiC2B9 species is likely to be the major cause of the isomerisation observed in compound 4α. Isomerisation moves the [(dppe)(3,1,2-NiC2B9)] substituent down to the lower pentagonal belt further away from the [Ni(dppe)] on the other cage. Indeed, we have already observed steric crowding in the unisomerised compound 3. In regards to the [3′,1′,2′-NiC2B9] to [4′,1′,2′-NiC2B9] isomerisation, this can likely be related to electronic factors, specifically the electron withdrawing nature of the dppe ligand. A similar 3,1,2- to 4,1,2- isomerisation of mono-metalated nickelacarboranes with dppe and PPh2Me ligands has been previously established [8].

4. Conclusions

Four new bis(nickelated) species are documented from the metatation of doubly deboronated 1,1′-bis(o-carborane), and their identity was confirmed by both spectroscopic and crystallographic means. The metatation of the [Ni(dmpe)] fragment with the Ti₄-salt gives diastereoisomeric products with the unusual crowded architecture of 3,1,2-NiC2B9-3′,1′,2′-NiC2B9 as racemic and meso forms. In contrast, metatation with the [Ni(dppe)] fragment results in the 3,1,2-NiC2B9-4′,1′,2′-NiC2B9 species, a stereospecific racemic product. The racemic product in the latter case shows intramolecular dihydrogen bonding, hence explaining the stereospecific reaction, whereas the stereo-electronic nature of the bis(phosphine) ligand influences the formation of the isomerised 3,1,2-NiC2B9-4′,1′,2′-NiC2B9 species.

Supplementary Materials: The following are available online at https://www.mdpi.com/2073-4352/11/1/16/s1, NMR spectra of all new compounds are available online along with the crystallographic data, free of charge. Crystallographic information for all compounds here has been deposited in the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC 2048463, 2048465, 2048466 and 2048464 (compounds 1, 2, 3 and 4α).

Author Contributions: Syntheses and original draft preparation, and editing, D.M.; final structure analysis and manuscript editing, G.M.R. All authors have read and agreed to the published version of the manuscript.

Funding: D.M. is grateful to the Heriot-Watt University for financial assistance; a James-Watt Ph.D. studentship was awarded to D.M. from 2013 to 2016. We thank EPSRC for funding the Bruker X8Apex2 diffractometer.

Institutional Review Board Statement: Not applicable.
Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: This work is taken from the Ph.D. thesis (2016) of D.M., supervised by Alan J. Welch at Heriot-Watt University. We thank EPSRC for funding the Bruker X8Apex2 diffractometer and the U.K. National Crystallography Service for data collection of compound 4α.

Conflicts of Interest: The authors declare no conflict of interest.

References

8. 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-NiC2B9 architectures and pendant carborane groups, derived from 1,1'-bis(o-carborane). Dalton Trans. 2016, 45, 15013–15025. [CrossRef] [PubMed]
12. Ren, S.; Xie, Z. A facile and practical synthetic route to 1,1'-bis (o-carborane). Organometallics 2008, 27, 5167–5168. [CrossRef]