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# Towards the mechanism of heteroborane isomerisation: 1,2 → 1,2 and 1,2 → 1,7 low-temperature isomerisations from metallations of $[5\text{-I-}7,8\text{-Ph}_2\text{-}7,8\text{-}nido\text{-C}_2\text{B}_9\text{H}_8]^{2-}$ ☆

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**Abstract**

The reaction between $[5\text{-I-}7,8\text{-Ph}_2\text{-}7,8\text{-}nido\text{-C}_2\text{B}_9\text{H}_8]^{2-}$ and $\text{NiCl}_2(\text{dppe})$ affords $1,2\text{-Ph}_2\text{-}4,4\text{-dppe-}12\text{-I-}4,1,2\text{-}closo\text{-NiC}_2\text{B}_9\text{H}_8$ (**1**) and $1,8\text{-Ph}_2\text{-}2,2\text{-dppe-}10\text{-I-}2,1,8\text{-}closo\text{-NiC}_2\text{B}_9\text{H}_8$ (**2**). Reaction between the same carborane ligand and $cis\text{-PtCl}_2(\text{PMe}_2\text{Ph})_2$ yields three species, $1,8\text{-Ph}_2\text{-}2,2\text{-(PMe}_2\text{Ph)}_2\text{-}10\text{-I-}2,1,8\text{-}closo\text{-PtC}_2\text{B}_9\text{H}_8$ (**3**), $1,8\text{-Ph}_2\text{-}2,2\text{-(PMe}_2\text{Ph)}_2\text{-}12\text{-I-}2,1,8\text{-}closo\text{-PtC}_2\text{B}_9\text{H}_8$ (**4**), and $1,8\text{-Ph}_2\text{-}2,2\text{-(PMe}_2\text{Ph)}_2\text{-}7\text{-I-}2,1,8\text{-}closo\text{-PtC}_2\text{B}_9\text{H}_8$ (**5**). Compounds **1**–**5** have been characterised spectroscopically and crystallographically. The $4,1,2\text{-MC}_2\text{B}_9$ architecture of **1** constitutes a "1,2 → 1,2" cage C atom isomerisation, and the $2,1,8\text{-MC}_2\text{B}_9$ architectures of **2**–**5** a 1,2 → 1,7 cage C atom isomerisation, relative to the presumed first product of the metallations, $1,2\text{-Ph}_2\text{-}3,3\text{-L}_2\text{-}9\text{-I-}3,1,2\text{-}closo\text{-MC}_2\text{B}_9\text{H}_8$ [M = Ni, $\text{L}_2$ = dppe; M = Pt, $\text{L}_2 = (\text{PMe}_2\text{Ph})_2$]. The location of the (iodide) labelled boron vertex in the products allows speculation as to the mechanism of these isomerisations and the possible involvement of triangle face rotation is discussed.

*Keywords:* Metallacarborane; Synthesis; NMR spectroscopy; X-ray crystallography; Isomerisation mechanisms; Vertex labelling

## 1. Introduction

Sterically crowded transition metal metallacarboranes are analogues of carboranes with the potential to undergo low-temperature isomerisation. Thus, such compounds can be of value in experimental study of the mechanism(s) of isomerisation since the integrity of vertex-label bonds can be reasonably assured under the mild conditions of such isomerisations [1].

We have found that appropriate metallation of the 11-vertex nido carborane $[7,8\text{-Ph}_2\text{-}7,8\text{-}nido\text{-C}_2\text{B}_9\text{H}_9]^{2-}$ and its derivatives reliably affords isomerised products at or near room temperature. Use of a $\{\text{PtL}_2\}^{2+}$ metal–ligand fragment (L = phosphine) tends to give $2,1,8\text{-PtC}_2\text{B}_9$ products [2], this representing a net 1,2 → 1,7 C atom isomerisation. On the other hand, use of analogous $\{\text{NiL}_2\}^{2+}$ fragments tends to yield $4,1,2\text{-NiC}_2\text{B}_9$ species, by a "1,2 → 1,2" C atom rearrangement [3]. An unusual and significant result came from our use of the $\{\text{Mo}(\eta\text{-C}_3\text{H}_5)(\text{CO})_2\}^+$ fragment, giving a $2,1,8\text{-MoC}_2\text{B}_9$ product but via an isolable non-icosahedral intermediate [4], which affords a signpost to the rearrangement mechanism, at least in this case.

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☆ Steric effects in heteroboranes. Part 30. For part 29, see [9].

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Developing these early studies by labelling specific boron vertices in the nido carborane ligand led to interesting results. The use of $SMe_2$ labels at positions 9 [5] and 10 [6] gave neutral products with $\{Mo(\eta\text{-}C_3H_5)(CO)_2\}^+$ (again, via non-icosahedral intermediates), and analysis of these led us to conclude broad (but not perfect) support for the sequential diamond–square–diamond (dsd) mechanism of Wales [7]. Nickelation of carborane labelled with Et at vertex 3 gave two products, a 4,1,2-$NiC_2B_9$ species and (unusually for nickel) a 2,1,8-$NiC_2B_9$ species [8]. A similar 2,1,8 species was afforded by platination of the same carborane, and of its analogue with an F label, but also isolated was a slipped, non-isomerised intermediate in the Et case [9]. The position of the label in the 2,1,8-Ni/$PtC_2B_9$ species, on vertex 4 of the closo icosahedron, does not accord with that predicted by the sequential dsd process. On the other hand, all the Ni and Pt products could be rationalised by a single triangle face rotation (tfr) of the presumed first product of the metallation, a crowded 3,1,2-$MC_2B_9$ species.

Seeking further insight into the mechanism of isomerisation of heteroboranes, we now report the results of both nickelation and platination of a further labelled carborane, $[5\text{-I-}7,8\text{-Ph}_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_8]^{2-}$.

## 2. Results and discussion

### 2.1. Nickelacarboranes

The reaction between $[5\text{-I-}7,8\text{-Ph}_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_8]^{2-}$, prepared by deprotonation of $[5\text{-I-}7,8\text{-Ph}_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_9]^-$ with *n*-BuLi under THF (THF = tetrahydrofuran) reflux, and $Ni(dppe)Cl_2$ [dppe = 1,2-bis(diphenylphosphino)ethane] in THF affords red $1,2\text{-Ph}_2\text{-}4,4\text{-dppe-}12\text{-I-}4,1,2\text{-}closo\text{-}NiC_2B_9H_8$ (**1**), and purple $1,8\text{-Ph}_2\text{-}2,2\text{-dppe-}10\text{-I-}2,1,8\text{-}closo\text{-}NiC_2B_9H_8$ (**2**), in modest yields (not optimised) following work-up involving thin layer chromatography. Compounds **1** and **2** were initially characterised by microanalysis, and IR and NMR spectroscopies, and ultimately by X-ray diffraction studies.

The $^1H$ NMR spectra of both compounds are relatively uninformative, save confirming the expected relative integrals of phenyl and methylene protons. The $^{31}P\text{–}\{^1H\}$ spectra reveal that in both compounds rotation of the {Ni(dppe)} fragment about the nickel-cage axis is restricted since two resonances are observed (with two-bond P–P coupling resolved only for **1**). The $^{11}B\text{–}\{^1H\}$ NMR spectra, on the other hand, offer strong clues as to the structural identity of these molecules. For **1** there are five resonances between +12 and −17 ppm, with relative integrals (high to low frequency) 1:1:1:4:2. The middle resonance, −7.30 ppm, remains a singlet on retention of proton coupling and is therefore assigned to the labelled B atom. This chemical shift range is reminiscent of 4,1,2-$NiC_2B_9$ species afforded by the "1,2 → 1,2" C atom isomerisation of bis(phosphine)nickelacarboranes, viz. +12 to −16 ppm in $1,2\text{-Ph}_2\text{-}4,4\text{-}(PMe_2Ph)_2\text{-}4,1,2\text{-}closo\text{-}NiC_2B_9H_9$ [3], +12 to −17 ppm in $1,2\text{-Ph}_2\text{-}4,4\text{-}(PEt_3)_2\text{-}4,1,2\text{-}closo\text{-}NiC_2B_9H_9$ [3], +14 to −15 ppm in $1,2\text{-Ph}_2\text{-}4,4\text{-dppe-}4,1,2\text{-}closo\text{-}NiC_2B_9H_9$ [3] and +13 to −14 ppm in $1,2\text{-Ph}_2\text{-}4,4\text{-dppe-}6\text{-Et-}4,1,2\text{-}closo\text{-}NiC_2B_9H_8$ [8]. In compound **2** are six resonances, 1:3:1:1:2:1 from high to low frequency, spanning the chemical shift range −1 to −28 ppm. The absence of a high frequency resonance is inconsistent with a 4,1,2-$NiC_2B_9$ architecture but much more in keeping with a 2,1,8-heteroatom pattern (arising from net 1,2 → 1,7 C atom isomerisation). Except for the lowest frequency resonance (shown from an $^{11}B$ spectrum to be due to the I-labelled B atom) the $^{11}B$ chemical shift range in **2** is −1 to −17 ppm, exactly the same as in $1,8\text{-Ph}_2\text{-}2,2\text{-dppe-}4\text{-Et-}2,1,8\text{-}closo\text{-}NiC_2B_9H_8$ [8]. That the iodide label causes a pronounced upfield shift in the $^{11}B$ resonance of the attached boron atom has been previously observed; compare the chemical shifts of B9 in $1,2\text{-Ph}_2\text{-}9\text{-I-}1,2\text{-}closo\text{-}C_2B_{10}H_9$ [10] (−15.2 ppm) and B9/B12 in $1,2\text{-Ph}_2\text{-}9,12\text{-I}_2\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_8$ [11] (−10.0 ppm) with B9/B12 in $1,2\text{-Ph}_2\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10}$ [12] (−2.6 ppm).

Although these NMR studies strongly suggested, therefore, that **1** and **2** had, respectively, 4,1,2-$NiC_2B_9$ and 2,1,8-$NiC_2B_9$ geometries, definitive structural characterisations, and the important location of the iodide labels, were only realised by single crystal X-ray diffraction studies.

A perspective view of a single molecule of **1** is shown in Fig. 1, and Table 1 hosts selected molecular parameters. Although the study is of relatively poor precision (a consequence of poor crystal quality) the heteroatom pattern is confirmed as 4,1,2-$NiC_2$ and the iodide label is attached to B12. The Ni atom is slightly slipped [13] away from C1 ($\Delta$ = 0.11 Å) and the metal-bonded $B_4C$ face is slightly folded (5.9°) about B3···B5 into an envelope conformation; these distortions result in Ni4–C1 being the longest Ni–cage distance. The plane of the $\{NiP_2\}$ fragment is somewhat twisted from perpendicularity to the perpendicular bisector of the metal-bonded $B_4C$ ring (dihedral angle 72.4°). The cage-bound phenyl rings are orientated with low $\theta_{Ph}$ values [14] (9.2° for C101–C106 and 4.8° for C201–C206). Similar structural features to all those above have been noted in $1,2\text{-Ph}_2\text{-}4,4\text{-L}_2\text{-}4,1,2\text{-}closo\text{-}NiC_2B_9$ species studied previously [3,8]. The B–I distance, 2.225(19) Å, compares well with that in the precursors. [1]

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[1] B–I = 2.178(4) Å in $1,2\text{-Ph}_2\text{-}9\text{-I-}1,2\text{-}closo\text{-}C_2B_{10}H_9$ [10]. Unfortunately, the B–I distance in $[5\text{-I-}7,8\text{-Ph}_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_9]^-$, 2.211(7) Å, was omitted from Table 4 of [11].