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Isomerisation following the platination of $[7,8-Ph_2-9,11-I_2-7,8-nido-C_2B_9H_7]^{2-2}$

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Warmly dedicated to Professor Michael B. Hursthouse, a mentor and friend to A.J.W. for more than 35 years, on the occasion of his 65th birthday.

Abstract

The synthesis, by electrophilic substitution, and characterisation of two new B-substituted nido diphenylcarboranes is described. [HNMe₃][7,8-Ph₂-9-I-7,8-*nido*-C₂B₉H₉] (1) and [HNMe₃][7,8-Ph₂-9,11-I₂-7,8-*nido*-C₂B₉H₈] (2) were characterised spectroscopically with the structure of the latter additionally confirmed by a crystallographic study. [7,8-Ph₂-9,11-I₂-7,8-*nido*-C₂B₉H₈]²⁻ was treated with a source of {Pt(PMe₂Ph)₂}²⁺ and three new platinacarboranes isolated. All were characterised by a combination of ¹H, ¹¹B and ³¹P NMR spectroscopies and by single crystal X-ray diffraction, and all were found to have undergone a 1,2 \rightarrow 1,7 cage C atom isomerisation, relative to the presumed first product of the metallation. The major product **3** is 1,8-Ph₂-2,2-(PMe₂Ph)₂-6,7-I₂-2,1,8-*closo*-PtC₂B₉H₇ and 1,8-Ph₂-2,2-(PMe₂Ph)₂-6,12-I₂-2,1,8-*closo*-PtC₂B₉H₇ and 1,8-Ph₂-2,2-(PMe₂Ph)₂-10,12-I₂-2,1,8-*closo*-PtC₂B₉H₇, having one and two substituted boron vertices in the lower pentagonal belt. These structural results allow speculation on the mechanism of isomerisation of crowded platinacarboranes.

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1. Introduction

For many years there has been significant interest in the mechanism(s) of isomerisation of icosahedral carboranes [1]. Some attempts have been made to study the phenomenon experimentally using B-substituted species [2] but the high temperatures generally required to induce cage reorganisation have inevitably led to doubts about the integrity of the B-X bonds under such conditions [3].

We have shown [4] that metallation of $[7,8-Ph_2-7,8-nido-C_2B_9H_9]^{2-}$ with a sufficiently bulky metal-ligand fragment leads to isomerisation to 2,1,8-MC₂B₉ products (effectively a 1,2 \rightarrow 1,7 C-atom isomerisation) at room temperature,

presumably via a highly sterically hindered, transient, 3,1,2-MC₂B₉ species (Scheme 1, Step 1). Under the benign conditions of these reactions one could be confident that vertex-substituent bonds would remain intact. Moreover, with certain metal fragments, specifically {Mo(η -C₃H₅)(CO)₂⁺}, several intermediate species have actually been isolated [5] and resemble structures predicted [6] by ab initio computational studies of the isomerisation of 1,2-*closo*-C₂B₁₀H₁₂.

Thus, we subsequently embarked on a programme to map, experimentally, the mechanism(s) of carborane isomerisation via the synthesis and subsequent metallation of a series of B-substituted carboranes, identifying the ultimate products by crystallographic study [7]. Using $\{ML_2\}^{2+}$ fragments two general themes developed: addition of bulky $\{NiL_2\}^{2+}$ generally yields products with $4,1,2-NiC_2B_9$ architectures, representing " $1,2 \rightarrow 1,2$ " C atom isomerisation [7c,7d,8], although occasionally 2,1,8-NiC_2B_9 species

^{*} Steric effects in heteroboranes. Part 31. For part 30, see [7d].

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Scheme 1. Possible formation of platinacarboranes 3–5 by triangle face rotations (tfrs) starting from an implied transient species I. In each tfr the face highlighted in bold is assumed to rotate by 120°. In Steps 2' and 2" the B₃ and CB₂ tfrs could be sequential or synchronous. $P = PMe_2Ph$.

are also formed [7c,7d], whereas addition of bulky $\{PtL_2\}^{2+}$ always gives 2,1,8-PtC₂B₉ products [4,7b,7d], although in one case [7b] we were also able to isolate a 3,1,2-PtC₂B₉ species and show that it represented an intermediate by its isomerisation to 2,1,8-PtC₂B₉ on gentle warming.

In this paper, we extend these studies by describing the synthesis of new mono- and disubstituted nido-diphenylcarboranes and the results of subsequent metallation of the latter with a $\{PtL_2\}^{2+}$ fragment.

2. Experimental

2.1. Synthetic and spectroscopic studies

Experiments were performed under dry, oxygen-free N₂ using standard Schlenk techniques, with some subsequent manipulation in the open laboratory. Solvents were freshly distilled over CaH₂ (CH₂Cl₂) or Na wire (THF, Et₂O, 40–60 petroleum ether), or were stored over 4 Å molecular sieves [CDCl₃, (CD₃)₂CO]. Preparative thin layer chromatography (TLC) employed 20×20 cm Kieselgel 60 F₂₅₄

glass plates. NMR spectra at 200.13 (¹H), 400.13 MHz (¹H), 128.38 (¹¹B) or 161.98 MHz (³¹P) were recorded on Bruker AC 200 or DPX 400 spectrometers from CDCl₃ or (CD₃)₂CO solutions at ambient temperature, chemical shifts being recorded relative to SiMe₄ (¹H), BF₃ · OEt₂ (¹¹B) or H₃PO₄ (³¹P). IR spectra were recorded from KBr disks on a Perkin–Elmer Spectrum RX FT-IR spectrophotometer. Elemental analyses were determined by the EPS School service. The starting materials 1,2-Ph₂-1,2-*closo*-C₂B₁₀H₁₀ [9] and *cis*-PtCl₂(PMe₂Ph)₂ [10] were prepared by literature methods or slight variants thereof. All other reagents and solvents were supplied commercially and were used as received.

2.1.1. Synthesis of [HNMe₃][7,8-Ph₂-9-I-nido-C₂B₉H₉] (1)

1,2-Ph₂-C₂B₁₀H₁₀ (1.000 g, 3.38 mmol) and KOH (0.430 g; 8.45 mmol) were heated to reflux in EtOH (50 ml) for 72 h. Excess KOH was removed by reaction with CO₂ and filtering off the K₂CO₃ formed. To the clear colourless solution of K[7,8-Ph₂-*nido*-7,8-C₂B₉H₁₀] was added I₂ (0.870 g, 3.41 mmol) in ethanol (30 ml). The reaction

mixture was heated to reflux for 2 h, during which time the solution decolourised. The volume of solution was reduced to ca. 10 ml in vacuo and distilled water (50 ml) added. Filtration and addition of aqueous HNMe₃Cl (0.380 g, 4.00 mmol) gave a white precipitate which was filtered off and dried in vacuo. An alternative procedure involves extraction of the precipitate into CH_2Cl_2 (3 × 30 ml), drying over MgSO₄ and subsequent removal of the drying agents and solvents. An oily solid was recovered which was recrystallised from $CH_2Cl_2/40-60$ petroleum ether to give a white crystalline solid. Yield 1.000 g, (63% based on diphenylcarborane). Anal. Calc. for C₁₇H₂₉B₉IN: C, 43.3; H, 6.21; N, 2.97. Found: C, 43.3; H, 6.39; N, 2.56%. IR v_{max} (cm⁻¹): 2537 (B–H str). ¹H NMR δ (ppm): 7.2–6.8 (m, 10H, C_6H_5), 3.1 (s, 9H, NCH₃). ¹¹B-{¹H} NMR δ (ppm): -5.70 (1B), -14.42 (4B), -20.13 (1B), -23.96 (1B), -29.73 (1B), -35.68 (1B).

2.1.2. Synthesis of [HNMe₃][7,8-Ph₂-9,11-I₂-7,8-nido-C₂B₉H₈] (**2**)

To a solution of $K[7,8-Ph_2-nido-7,8-C_2B_9H_{10}]$ (1.69 mmol) in EtOH (50 ml) prepared as above, was added I_2 (1.080 g, 4.23 mmol) in ethanol (30 ml). The reaction mixture was heated to reflux for 18 h, during which time the solution decolourised. The volume of solution was reduced to ca. 10 ml in vacuo and distilled water (50 ml) added. Filtration and addition of aqueous HNMe₃Cl (0.173 g, 1.80 mmol) gave a white precipitate which was filtered off and dried in vacuo. Again, an alternative work-up involves extraction of the precipitate into CH2Cl2 $(3 \times 30 \text{ ml})$, drying over MgSO₄ and subsequent removal of the drying agents and solvents. A white solid was recovered which was recrystallised by evaporation of a dichloromethane solution to give colourless crystals. Yield 0.230 g (23% based on diphenylcarborane). Anal. Calc. for C₁₇H₂₈B₉I₂N: C, 34.2; H, 4.73; N, 2.34. Found: C, 34.1; H, 4.76; N, 2.27%. IR v_{max} (cm⁻¹): 2546 (B–H str). ¹H NMR δ (ppm): 7.2–6.8 (m, 10H, C₆H₅), 3.2 (s, 9H, NCH₃). ¹¹B–{¹H} NMR δ (ppm): -13.26 (3B), -16.55 (2B), -18.43 (2B, B9,11), -28.17 (1B), -35.30 (1B).

2.1.3. Syntheses of 1,8-Ph₂-2,2-(PMe₂Ph)₂-6,7-I₂-2,1,8-PtC₂B₉H₇ (**3**), 1,8-Ph₂-2,2-(PMe₂Ph)₂-6,12-I₂-2,1,8-PtC₂B₉H₇ (**4**) and 1,8-Ph₂-2,2-(PMe₂Ph)₂-10,12-I₂-2,1,8-PtC₂B₉H₇ (**5**)

Salt 2 (0.180 g; 0.30 mmol) was suspended in dry ether (30 ml) at 0 °C and ⁿBuLi (0.24 ml of a 2.5 M solution in hexanes, 0.60 mmol) was added dropwise. The solution was stirred at room temperature for 18 h. All volatiles were removed and THF (30 ml) added. The THF solution of Li₂[7,8-Ph₂-9,11-I₂-7,8-*nido*-C₂B₉H₇] was added to a frozen suspension of *cis*-PtCl₂(PMe₂Ph)₂ (0.163 g, 0.30 mmol) in THF (25 ml) at -196 °C. The mixture was refrozen, then slowly warmed to room temperature and stirred for 18 h. All volatiles were removed in vacuo and CH₂Cl₂ (20 ml) added. The yellow suspension was filtered and evacuated to dryness to yield a yellow solid. The product was purified by TLC, eluting with 50/50 CH₂Cl₂/40–60 petroleum ether to give three yellow bands, respectively, compounds **3** ($R_{\rm f} = 0.65$), **4** ($R_{\rm f} = 0.56$) and **5** ($R_{\rm f} = 0.45$).

3: yield 0.060 g (20%). *Anal.* Calc. for $C_{30}H_{39}B_9I_2P_2Pt$: C, 35.8; H, 3.91. Found: C, 34.9; H, 3.88%. IR v_{max} (cm⁻¹): 2575 (B–H str). ¹H NMR δ (ppm): 7.9–6.9 (m, 20H, C₆H₅), 2.2–1.2 (m, 12H, P–CH₃). ¹¹B–{¹H} NMR δ (ppm): -3.69 (1B), -8.61 (1B), -11.70 (1B), -15.44 (3B), -19.75 (2B), -23.93 (1B). ³¹P–{¹H} NMR δ (ppm): -15.80 (s, 1P, ¹J_{Pt–P} = 3284 Hz), -23.95 (s, 1P, ¹J_{Pt–P} = 3227 Hz).

4: yield 0.030 g (10%). *Anal.* Calc. for $C_{30}H_{39}B_9I_2P_2Pt$: C, 35.8; H, 3.91. Found: C, 35.1; H, 3.96%. IR v_{max} (cm⁻¹): 2544 (B–H str). ¹H NMR δ (ppm): 8.0–6.9 (m, 20H, C₆H₅), 2.1–1.2 (m, 12H, P–CH₃). ¹¹B–{¹H} NMR δ (ppm): -3.80 (2B), -11.38 (1B), -15.39 (4B), -18.09 (1B), -23.76 (1B). ³¹P–{¹H} NMR δ (ppm): -12.03 (s, 1P, ¹J_{Pt–P} = 3306 Hz), -21.36 (s, 1P, ¹J_{Pt–P} = 3217 Hz).

5: yield 0.030 g (10%). *Anal.* Calc. for $C_{30}H_{39}B_9I_2P_2Pt$: C, 35.8; H, 3.91. Found: C, 35.6; H, 3.85%. IR v_{max} (cm⁻¹): 2581 (B–H str). ¹H NMR δ (ppm): 7.5–7.0 (m, 20H, C₆H₅), 1.8–1.1 (m, 12H, P–CH₃). ¹¹B–{¹H} NMR δ (ppm): -6.74 (3B), -13.28 (3B), -14.91 (2B), -31.11 (1B). ³¹P–{¹H} NMR δ (ppm): -13.93 (s, 1P, ¹J_{Pt–P} = 3290 Hz), -15.32 (s, 1P, ¹J_{Pt–P} = 3347 Hz).

2.2. Crystallographic studies

Single crystals suitable for X-ray diffraction were grown by evaporation of a CH_2Cl_2 solution (salt 2), from diffusion of a CH_2Cl_2 solution and 40–60 petroleum ether at -30 °C (compounds 3 and 5) or from diffusion of a CH_2Cl_2 solution and diethylether at $-30 \,^{\circ}$ C (compound 4). Salt 2 crystallises with $1\frac{1}{2}$ equivalents of CH₂Cl₂ and compound 4 with 1 equivalent of Et₂O. Data were collected at 100 K (cold N₂ gas) on a Bruker AXS P4 diffractometer producing graphite-monochromated Mo K α radiation ($\lambda =$ 0.71069 Å) using ω scans to $\theta_{max} = 25^{\circ}$, and were corrected for absorption by psi scans. Structures were solved by direct and difference Fourier methods and refined [11] by full-matrix least-squares against F^2 . Refinement was completed with all non-hydrogen atoms assigned anisotropic displacement parameters. For the anion of 2 H_{exo} atoms were refined subject to a restrained B-H distance of 1.10(2) A, whilst the H_{endo} atom was freely refined. For 3-5 cage H atoms were allowed to ride on their bound boron with B-H constrained to 1.10 Å (1.12 Å for 3). In all structures CH atoms were similarly constrained, with C-H = 0.95 (phenyl), 0.98 (CH₃) or 0.99 (CH₂) Å. H atoms except methyl H atoms were assigned displacement parameters set at 1.2 times that of the U_{eq} of their bound atom, with methyl H atoms assigned displacement parameters calculated as 1.5 times the bound carbon atom U_{eq} . H atoms were included in all molecules of solvation. For 3 the maximum and minimum residual e-density are significant but both are within 1 Å of Pt2 and thus chemically

meaningless. Table 1 contains details of the crystallographic studies.

3. Results and discussion

3.1. B-substituted carboranes

Electrophilic iodination of $K[7,8-Ph_2-nido-7,8-C_2B_9H_{10}]$ with elemental I₂ proceeds smoothly in refluxing ethanol to generate, after metathesis with HNMe₃Cl, the new B-substituted nido diphenylcarboranes [HNMe₃][7,8-Ph₂-9-I-*nido*-7,8-C_2B_9H_9] (1) and [HNMe₃][7,8-Ph₂-9,11-I₂-7,8-*nido*-C_2B_9H_8] (2).

Use of one equivalent of I₂ affords a good yield of the monosubstituted 9-I species with <5% of the disubstituted 9,11-I₂ carborane also formed, as observed by ¹¹B spectroscopy. Addition of two equivalents of I₂ gives pure disubstituted compound, albeit in somewhat less good yield. Further substitution is not observed even with large excesses of I₂. The synthesis of salt 1 is analogous to that used by Hawthorne and Olsen to prepare the related species [NMe₄][9-I,-7,8-*nido*-C₂B₉H₁₁], although this early paper [12] does not report further substitution to the diiodo product. Both 1 and 2 are appreciably soluble in acetone and acetonitrile and sparingly soluble in halogenated solvents, but insoluble in 40/60 petroleum ether and toluene.

The compounds 1 and 2 were fully characterised by microanalysis, NMR and IR spectroscopies. In both cases the ¹H NMR spectra reveal signals due to cage phenyl and N-methyl hydrogen atoms in the correct relative integrals.

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Crystallographic	data	for	2-5	,a
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¹¹B NMR spectra are more informative. In the ¹¹B–{¹H} spectrum of **1** a 1:4:1:1:1:1 pattern, from high to low frequency, is observed, although the anticipated C_1 symmetry of the product requires the integral-4 signal to be a 1 + 1 + 1 + 1 coincidence. In the ¹¹B spectrum the uncoupled resonance due to the B atom bearing the iodine substituent is not obvious, and is presumed to lie within the envelope of these coincident signals. Compound **2** has a 3:2:2:1:1 pattern, its anticipated C_s symmetry requiring the highest frequency resonance to be a 2 + 1 coincidence. This time, however, the signal due to the two, symmetry equivalent, substituted B atoms is clear in the ¹¹B spectrum at δ –18.43.

Electrophilic attack on a nido carborane is expected to occur at the open face, but, to establish an unequivocal structure, a crystallographic determination of salt 2, as its $1\frac{1}{2}CH_2Cl_2$ solvate, was undertaken.

Fig. 1 shows a perspective view of a single anion and Table 2 lists selected interatomic distances and interbond angles. The 9,11-disubstitution by iodine is confirmed. The endo H atom H10a is semi-bridging the B10–B11 edge, B10–H10a 1.17(5) Å, B11–H10a 1.56(5) Å, consistent with the optimised structure of $[7,8-nido-C_2B_9H_{12}]^-$ [13]. As anticipated [14], the (H-bridged) B10–B11 edge, 1.842(7) Å, is consequently somewhat longer that the unbridged but otherwise equivalent B9–B10 edge, 1.805(8) Å. The C7–C8 distance in **2** is 1.610(6) Å, almost identical to that in the unsubstituted analogue $[7,8-nido-C_2B_9H_{10}]^-$ (1.590(5) Å for the [HNEt₃]⁺ salt and 1.602(3) Å in the $[C_6H_5CH_2NMe_3]^+$ salt) [15] and to that

Compound	2	3	4	5
Formula	$C_{17}H_{28}B_9I_2N \cdot 1\frac{1}{2}CH_2Cl_2$	$C_{30}H_{39}B_9I_2PPt$	$C_{30}H_{39}B_9I_2PPt \cdot C_2H_5O$	C ₃₀ H ₃₉ B ₉ I ₂ PPt
M_r	724.88	1007.73	1081.85	1007.73
Crystal size (mm)	$0.60 \times 0.50 \times 0.30$	$0.42 \times 0.22 \times 0.20$	$0.30 \times 0.50 \times 0.40$	$0.40 \times 0.60 \times 0.50$
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\overline{1}$	$P2_1/n$	$P2_1/n$	$P2_1/c$
<i>a</i> (Å)	8.7277(7)	12.003(4)	15.820(2)	10.9980(10)
b (Å)	11.0465(13)	17.308(6)	13.462(2)	25.352(3)
<i>c</i> (Å)	16.0255(19)	17.020(11)	20.210(2)	12.761(2)
α (°)	83.165(10)	90	90	90
β (°)	84.375(11)	93.17(4)	110.440(10)	95.950(10)
γ (°)	70.348(10)	90	90	90
$U(\text{\AA}^3)$	1441.9(3)	3530(3)	4033.1(9)	3538.9(8)
Z	2	4	4	4
F(000)	702	1912	2080	1912
μ (Mo K α) (mm ⁻¹)	2.47	5.84	5.12	5.82
Data measured	6088	7669	8597	7598
Unique data, n	5022	6203	7058	6209
R _{int}	0.0648	0.0404	0.0427	0.0340
R (all data)	0.0431	0.0482	0.0436	0.0378
wR_2 (all data)	0.0945	0.1056	0.1067	0.0956
S (all data)	1.074	1.063	0.735	0.953
Variables, p	332	397	442	398
$E_{\rm max}$ (e Å ⁻³)	1.663	3.213	0.880	0.847
E_{\min} (e Å ⁻³)	-1.467	-3.252	-1.118	-1.178

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|, wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2]^{1/2}, (w^{-1} = [\sigma^2(F_o)^2 + (aP)^2 + bP]$ where *a* and *b* are variables and *P* = [0.333(F_o)^2 + 0.667(F_c)^2]), S = [\sum [w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}, (where *n* is the number of data and *p* the number of parameters).



Fig. 1. Perspective view of the anion of $[HNMe_3]$ [7,8-Ph₂-9,11-I₂-7,8-*nido*-C₂B₉H₁₀] (2). Atoms are drawn as 50% probability ellipsoids except for H atoms.

Table 2 Selected interatomic distances (Å) and interbond angles (°) in $\mathbf{2}$

B1-B2	1.748(8)	B6-B11	1.770(7)
B1-B3	1.790(8)	C7–C8	1.610(6)
B1–B4	1.776(7)	C7-B11	1.620(7)
B1-B5	1.779(8)	C8–B9	1.610(7)
B1-B6	1.794(8)	B9-B10	1.805(8)
B2–B3	1.754(8)	B10-B11	1.842(7)
B2-C7	1.734(7)	C7-C71	1.510(6)
B2-B11	1.811(8)	C8-C81	1.509(6)
B2–B6	1.791(8)	B9–I9	2.210(5)
B3–B4	1.780(8)	B11–I11	2.195(5)
B3–C8	1.745(7)	B10–H10a	1.17(5)
B3-C7	1.733(7)	B11–H10a	1.56(5)
B4C8	1.745(7)	N1-C11	1.488(7)
B4–B9	1.774(8)	N1-C12	1.492(7)
B4–B5	1.762(8)	N1-C13	1.491(6)
B5–B9	1.741(7)	C1S-C11	1.730(6)
B5-B10	1.805(8)	C1S-C12	1.764(7)
B5-B6	1.823(8)	C2S-C13	1.661(11)
B6-B10	1.800(8)	C2S-C13 ^{#1}	1.743(11)
C71-C7-B11	121.2(4)	I9–B9–C8	121.7(3)
C71-C7-B2	121.6(4)	I9-B9-B4	117.5(3)
C71-C7-B3	116.3(4)	I9-B9-B5	121.2(3)
C71–C7–C8	117.6(4)	I9-B9-B10	121.1(3)
C81-C8-C7	116.4(4)	I11-B11-B10	123.2(3)
C81-C8-B3	115.2(4)	I11-B11-B6	120.5(3)
C81-C8-B4	120.2(4)	I11-B11-B2	116.8(3)
C81–C8–B9	121.6(4)	I11-B11-C7	121.2(3)

^{#1}atom generated by the operation 1 - x, -y, 1 + z.

in the substituted species $[C_6H_5CH_2NMe_3][5-I-7,8-Ph_2-7,8-nido-C_2B_9H_9]$ (1.609(10) Å) [7a]. In C-adjacent diphenylcarborane derivatives we conveniently describe the conformation of the Ph rings with respect to the cage by parameter θ_{Ph} , the modulus of the average $C_{cage}-C_{cage}-C_{Ph}-C_{Ph}$ torsion angle [16]. The measured values in **2** are 10.0° for the ring on C7 and 8.0° for the ring on C8, these low values quantifying the clear conclusion from Fig. 1 that the Ph rings stand effectively perpendicular to the nido face of the carborane. The B–I bonds in **2** are 2.210(5) Å for B9–I9 and 2.195(5) Å for B11–I11, essentially the same as that in the anionic [5-I-7,8-Ph₂-7,8-*nido*-C₂B₉H₉]⁻, 2.211 (7) Å [7a], but slightly longer than those in the neutral compounds 9,12-I₂-1,2-*closo*-C₂B₁₀H₁₀, average 2.178(5) Å [17], 1,2-Ph₂-9,12-I₂-1,2-*closo*-C₂B₁₀H₈, 2.175(5) Å [7a], 1,2-Ph₂-9-I-1,2-*closo*-C₂B₁₀H₉, 2.178(4) Å [18], and 9,10-I₂-1,7-*closo*-C₂B₁₀H₁₀, average 2.153(14) Å [19].

3.2. Platincarboranes

We have previously noted that, as is logical, metallation of asymmetrically-substituted carboranes leads to a greater number of isomerised products than does metallation of symmetrically-substituted species. Thus, we have chosen to platinate the 9,11-disubstituted carborane **2** to promote isomerisation and track its mechanism. Deprotonation of **2** was effected with "BuLi in diethyl ether to produce Li₂[7,8-Ph₂-9,11-I₂-7,8-*nido*-C₂B₉H₇]. Addition of a THF solution of this to a suspension of *cis*-PtCl₂(PMe₂Ph)₂ in the same solvent at -196 °C, followed by warming to room temperature and stirring for 18 h afforded a yellow solution. On work-up by TLC three products were isolated. The fastest moving band **3** transpired to be the major component, being approximately twice as abundant as each of the two slower bands **4** and **5**.

Compound 3 was initially characterised by microanalysis and IR and multinuclear NMR spectroscopy. As is typical of such compounds the ¹H NMR spectrum proved relatively uninformative in terms of detailed structural information, simply revealing signals consistent with the presence of phenyl and methyl H atoms with the correct relative integrals. ${}^{11}B-{}^{1}H$ NMR spectroscopy was also of limited use: although the chemical shift range observed, δ -4 to -24, indicates a closo species (more consistent with an isomerised 2,1,8-PtC₂B₉ architecture that with a slipped $3,1,2-PtC_2B_9$ cage [7b,7d]), the relative broadness of the signals and the presence of significant signal overlap precludes definitive interpretation and, specifically, prevents identification of signals which remain uncoupled in the ^{11}B spectrum. The $^{31}P{-}\{^{1}H\}$ NMR spectrum reveals the presence of inequivalent phosphorus nuclei, each signal showing the expected ¹⁹⁵Pt satellites (average ${}^{1}J_{Pt-P} =$ 3256 Hz). Careful analysis also reveals residual ${}^{2}J_{P-P}$ coupling, however the value is too small to quote accurately.

The structure of **3** was established by crystallographic study. Fig. 2 shows a perspective view of one molecule while Table 3 lists selected interatomic distances and interbond angles. The compound is thus revealed to be 1,8-Ph₂-2,2-(PMe₂Ph)₂-6,7-I₂-2,1,8-*closo*-PtC₂B₉H₇, the cage having undergone a $1,2 \rightarrow 1,7$ C atom isomerisation (confirming the interpretation of the ¹¹B chemical shift range). The substituted (iodine-bearing) boron atoms are B6 and B7. The metal atom is bound to a CB₄ face which is folded into the usual envelope conformation (dihedral angle between B3C1B6 and B6B11B7B3 planes 14.0°) and, moreover,



Fig. 2. Perspective view of 1,8-Ph₂-2,2-(PMe₂Ph)₂-6,7-I₂-2,1,8-*closo*-PtC₂B₉H₇ (**3**). Atoms are drawn as 50% probability ellipsoids except for H atoms.

the Pt atom is slipped away from C1 ($\Delta = 0.47$ Å) resulting in a long Pt2–C1 distance, 2.666(7) Å, emphasised by its non-inclusion in Fig. 2. The (electronic) reasons underlying these slipping and folding distortions are well documented [20] but we believe that in the present case the slipping is enhanced by a (steric) contribution arising from the orientation of the Ph ring on C1. The presence of an adjacent I atom, I6, requires the plane of this Ph ring to lie perpendicular to the metal-bonded CB₄ plane (a convenient measure of this is ζ , the modulus of the average Pt2–C1–C11–C torsion angles, $\zeta = 66.3^{\circ}$) pushing back the {Pt(PMe₂Ph)₂} fragment.

Compound 4 was similarly initially characterised by microanalysis and IR and multinuclear NMR spectroscopy, and ultimately by X-ray diffraction. The ¹H NMR spectrum was broadly similar to that of **3**, showing Ph and Me resonances with the correct relative integrals. The ¹¹B–{¹H} NMR spectrum again revealed resonances between δ –4 and –24, indicative of a 2,1,8-*closo*-PtC₂B₉ cage. Once more the resonance(s) due to B–I could not clearly be discerned in the corresponding ¹¹B spectrum. In the ³¹P–{¹H} spectrum once more were two signals, each with Pt satellites (average ¹J_{Pt-Pt} = 3262 Hz) and showing small residual J_{P-P} coupling.

The crystallographic study of **4** (Fig. 3 and Table 3) reveals a very similar molecular structure to that established for **3** except that the second substituted **B** atom is now B12 as opposed to B7. Thus, compound **4** is 1,8-Ph₂-2,2-(PMe₂Ph)₂-6,12-I₂-2,1,8-*closo*-PtC₂B₉H₇. The PtC₂B₉ cage of **4** resembles that of **3** in many respects: the Pt-bonded CB₄ face is envelope-folded by 15.6°, and

Table 3 Selected interatomic distances (Å) and interbond angles (°) in 3–5 $\,$

	3	4	5
Pt2–C1	2.666(7)	2.671(5)	2.609(5)
Pt2–B3	2.217(8)	2.234(7)	2.251(6)
Pt2–B7	2.202(7)	2.190(6)	2.217(6)
Pt2-B11	2.245(8)	2.247(7)	2.246(6)
Pt2–B6	2.365(7)	2.355(7)	2.266(6)
Pt2–P1	2.326(2)	2.3003(15)	2.3055(14)
Pt2–P2	2.298(2)	2.3105(15)	2.2887(14)
C1–B3	1.705(10)	1.705(9)	1.686(8)
C1–B4	1.647(10)	1.655(9)	1.657(8)
C1-B5	1.707(10)	1.689(9)	1.661(8)
C1–B6	1.666(10)	1.682(9)	1.733(8)
C1C11	1.505(10)	1.507(8)	1.495(7)
B3–B4	1.821(11)	1.829(9)	1.831(8)
B3–C8	1.772(10)	1.761(8)	1.764(8)
B3–B7	1.864(11)	1.896(9)	1.871(8)
B4–B5	1.738(11)	1.733(9)	1.749(8)
B4–C8	1.747(11)	1.725(9)	1.731(8)
B4–B9	1.759(11)	1.765(9)	1.761(8)
B5–B6	1.844(11)	1.845(10)	1.829(8)
B5–B9	1.743(11)	1.742(9)	1.776(9)
B5-B10	1.775(11)	1.785(9)	1.799(9)
B6-B10	1.789(1)	1.810(9)	1.813(9)
B6-B11	1.875(11)	1.886(9)	1.879(9)
B7–C8	1.716(9)	1.710(9)	1.721(8)
B7-B12	1.790(10)	1.752(9)	1.748(8)
B7–B11	1.817(10)	1.792(9)	1.807(9)
C8–B9	1.744(10)	1.774(9)	1.767(8)
C8-B12	1.713(10)	1.745(9)	1.715(8)
C8–C81	1.496(9)	1.518(8)	1.511(7)
B9-B10	1.780(11)	1.792(9)	1.792(9)
B9-B12	1.741(11)	1.758(9)	1.788(9)
B10-B11	1.795(10)	1.783(9)	1.751(8)
B10-B12	1.774(11)	1.760(9)	1.774(9)
B11-B12	1.774(10)	1.757(9)	1.745(9)
B–I			
B6–I6	2.231(8)		
B7–I7	2.173(7)		
B6–I6		2.215(7)	
B12–I12		2.165(6)	
B10–I10			2.181(6)
B12–I12			2.169(6)
P1-Pt1-P2	93.05(7)	96.71(5)	96.61(5)

the Ph group on C1 subtends a high ζ angle, 84.8°, thus extending the slip distortion of the {Pt(PMe₂Ph)₂} fragment to $\Delta = 0.48$ Å, Pt2–C1 = 2.666(7) Å.

The final product of the metallation, compound 5, moves slowest on the TLC plate. ¹H NMR spectroscopy revealed the expected phenyl and methyl resonances and the ¹¹B–{¹H} NMR spectrum showed only four peaks, δ –6 to –32, presumably reflecting significant coincidences. Once more, it was not possible to assign those resonance(s) due to the substituted B atoms. Asymmetrically disposed phosphorus atoms were again evident from the observation of two signals (with attendant Pt satellites) in the ³¹P–{¹H} NMR spectrum, the average ¹J_{Pt–P} being 3319 Hz.

The result of a crystallographic study of compound 5 is shown in Fig. 4, and Table 3 again lists key molecular parameters. This time *both* substituted B atoms (B10



Fig. 3. Perspective view of 1,8-Ph₂-2,2-(PMe₂Ph)₂-6,12-I₂-2,1,8-*closo*-PtC₂B₉H₇ (**4**). Atoms are drawn as 50% probability ellipsoids except for H atoms.

and B12) are in the lower half of the molecule, which is thus identified as $1,8-Ph_2-2,2-(PMe_2Ph)_2-10,12-I_2-2,1,8$ *closo*-PtC₂B₉H₇. Although the upper CB₄ face is still envelope-folded, this time by 15.6°, the non-adjacency of a substituted B atom to C1 means that the Ph ring on this



Fig. 4. Perspective view of $1,8-Ph_2-2,2-(PMe_2Ph)_2-10,12-I_2-2,1,8-closo-PtC_2B_9H_7$ (5). Atoms are drawn as 50% probability ellipsoids except for H atoms.

last atom can adopt an orientation which simply minimises steric repulsion between it and the phosphine ligands. Thus, ζ is only 10.9°, as a result of which both the slip parameter Δ , 0.36 Å, and the Pt2–C1 distance, 2.609(5) Å, are reduced in 5 relative to equivalent values in 3 and 4.

In compounds 3–5 collectively, the six B–I distances span the range 2.165(6)–2.231(8) Å. The two B6–I6 distances (compounds 3 and 4) are the two longest, but it is not obvious why this should be. Certainly the four distances measured here to B7, B10 and B12, 2.169(6)–2.181(6) Å, correspond well with those, 2.169(9)–2.204(12) Å, previously found in 1,8-Ph₂-2,2-(PMe₂Ph)₂-X-I-2,1,8-*closo*-PtC₂B₉H₈, X = 7, 10, 12 [7d].

3.3. Possible mechanistic implications

In several recent contributions [7] we have interpreted the results of both $1,2 \rightarrow 1,2$ and $1,2 \rightarrow 1,7$ C atom isomerisations in B-substituted nickel- and platinacarboranes in terms of either one or two triangle face rotations (tfrs), starting from a crowded, transient, 3,1,2-MC₂B₉ species (in one case [7b] this intermediate was actually isolated).

In Scheme 1 we show how the formation of the platinacarboranes 3 could also be explained by a tfr. In Step 1 the overcrowded, transient species I is formed by simple complexation of the metal fragment and carborane ligand. To relieve this overcrowding, a CB₂ face in I undergoes a tfr (Step 2) affording the major product 3. (note that since I has C_s symmetry either one of two equivalent CB₂ faces could rotate).

The formations of the minor products **4** and **5** cannot be so simply rationalised, but two factors appear relevant here. Firstly, we are fully confident that isomerisation only occurs following metallation since "BuLi deprotonation of **2** as described in Section 2.1.3 followed by reprotonation on addition of aqueous HNMe₃Cl regenerates only **2** as shown by ¹¹B NMR spectroscopy. Secondly, it is likely that **3–5** are formed via parallel rather than sequential isomerisation steps given the mild conditions under which they are prepared and our subsequent inability to convert from one to another by heating (either nothing happens or we observe substantial decomposition).

We thus suggest Step 2', as an alternative to Step 2, in which one of two possible B_3 triangle faces in I rotates to position one iodine substituent antipodal to a cage C atom, synchronous with, or followed immediately by, a CB₂ tfr analogous to that in Step 2, this overall process generating product 4. Moreover, Step 2", with both iodine substituents moving antipodal to cage C atoms, synchronous with or followed by CB₂ tfr, affords product 5.

We acknowledge that above mechanism is highly speculative, and that it raises several issues. Firstly, we have previously [7d] considered rotation of a CB_2 face involving two B vertices from the lower pentagon (shown in Step 2) as less likely than one involving one upper and one lower B atom. Secondly, with regard to Step 2', one could equally reasonably anticipate the combination of one of the tfrs shown with the symmetry-equivalent of the other, affording a further product $1,8-Ph_2-2,2-(PMe_2Ph)_2-7,10-I_2-2,1,8-closo-PtC_2B_9H_7$ (II) but this has not yet been identified.

Clearly a number of questions about the mechanism(s) of isomerisation that afford(s) compounds 3-5 remain, and studies designed to answer these are in hand. This is entirely consistent with the approach to chemical crystallography that Michael Hursthouse instilled in one of us as a postgraduate student – that molecular structure determination by crystallography should not be regarded simply as the end of one chemical investigation but, equally, based upon what that structure may mean in terms of chemical bonding or chemical reactivity, the beginning of another.



4. Supplementary material

Crystallographic data for the structure analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 281522–281525 for **2–5**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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