APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2003; **17**: 518–524

Nickelation of $[3\text{-Et-}7,8\text{-Ph}_2\text{-}7,8\text{-}\textit{nido}\text{-C}_2\text{B}_9\text{H}_8]^{2-}$: synthesis and characterization of 1,2 → 1,2 and 1,2 → 1,7 isomerized products[†][§]

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Received 5 February 2003; Revised 20 February 2003; Accepted 27 February 2003

The reaction between $[3\text{-Et-}7,8\text{-Ph}_2\text{-}7,8\text{-}\textit{nido}\text{-C}_2\text{B}_9\text{H}_8]^{2-}$ and Ni(dppe)Cl_2 in tetrahydrofuran affords major and minor products, identified spectroscopically and crystallographically. The major species is $1,2\text{-Ph}_2\text{-}4\text{-dppe-}6\text{-Et-}4,1,2\text{-}\textit{closo}\text{-NiC}_2\text{B}_9\text{H}_8$, which arises from the presumed initial product $1,2\text{-Ph}_2\text{-}3\text{-dppe-}6\text{-Et-}3,1,2\text{-}\textit{closo}\text{-NiC}_2\text{B}_9\text{H}_8$ by a sterically induced 1,2 → 1,2 C atom isomerization, typical of overcrowded nickelacarboranes. The minor species is $1,8\text{-Ph}_2\text{-}2\text{-dppe-}4\text{-Et-}2,1,8\text{-}\textit{closo}\text{-NiC}_2\text{B}_9\text{H}_8$, arising from an unexpected 1,2 → 1,7 carbon-atom isomerization of the initial product. The fact that one boron atom is labelled with an Et group, coupled with the fact that these isomerizations occur at low temperatures, allows comment on the isomerization mechanisms. The minor isomer cannot be explained by reference to Wales' sequential diamond–square–diamond mechanism for $1,2\text{-}\textit{closo}\text{-C}_2\text{B}_{10}\text{H}_{12}$ → $1,7\text{-}\textit{closo}\text{-C}_2\text{B}_{10}\text{H}_{12}$. A simple rationalization of the formation of both major and minor isomers is available through triangle face rotation. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: carborane; isomerization; synthesis; spectroscopy; crystallographic study; vertex labelling

INTRODUCTION

Although the mechanism of isomerization of carboranes has been of interest for many years,[1–3] the high temperatures that are usually required have precluded experimental study of the mechanism *via* labelled vertices because the integrity of the vertex–label bond cannot be guaranteed under such conditions.[4]

Several years ago we showed that metallation of $[7,8\text{-Ph}_2\text{-}7,8\text{-}\textit{nido}\text{-C}_2\text{B}_9\text{H}_9]^{2-}$ with a $\{\text{PtL}_2\}$ metal–ligand fragment (L = phosphine) generates a $2,1,8\text{-PtC}_2\text{B}_9$ species at or near room temperature.[5] Assuming that the initial product of such metallation is a transient $3,1,2\text{-PtC}_2\text{B}_9$ species, this effectively represents low-temperature 1,2 → 1,7 carbon-atom isomerization (where the C–C connectivity is broken) of an icosahedral (hetero)carborane (Scheme 1). We later showed[6] that the identical reaction using $\{\text{NiL}_2\}$ metallating fragments produces $4,1,2\text{-NiC}_2\text{B}_9$ species by low-temperature '1,2 → 1,2' carbon-atom isomerization (where the C–C connectivity is retained), presumably via an intermediate analogous to that in the 1,2 → 1,7 carbon isomerization (Scheme 2).

Given such reliable low-temperature rearrangements, the possibility of tracking the (clearly different) 1,2 → 1,7 and 1,2 → 1,2 isomerization mechanisms becomes possible via vertex labelling studies, and to this end we have very recently[7] described several new labelled analogues of $[7,8\text{-Ph}_2\text{-}7,8\text{-}\textit{nido}\text{-C}_2\text{B}_9\text{H}_9]^{2-}$. We now report the nickelation of one of these, $[3\text{-Et-}7,8\text{-Ph}_2\text{-}7,8\text{-}\textit{nido}\text{-C}_2\text{B}_9\text{H}_8]^{2-}$, yielding, as expected, a labelled $4,1,2\text{-NiC}_2\text{B}_9$ species as major product, but also a labelled $2,1,8\text{-NiC}_2\text{B}_9$ species as minor co-product. Thus, mechanistic information on both the 1,2 → 1,7 and the 1,2 → 1,2 carbon-atom isomerizations is provided.

EXPERIMENTAL

General procedures

Experiments were performed under dry, oxygen-free nitrogen using standard Schlenk techniques, with some subsequent manipulation in the open laboratory. Solvents were

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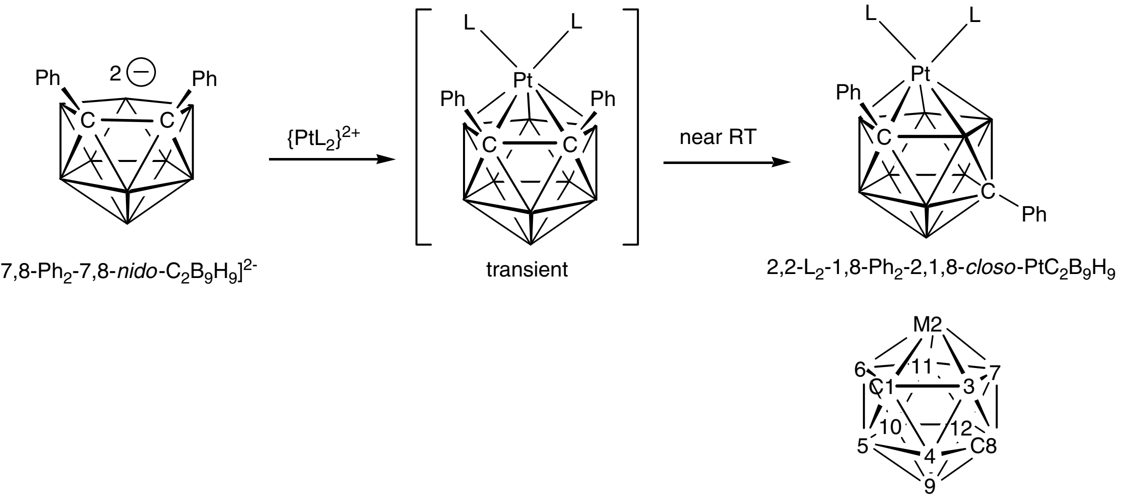
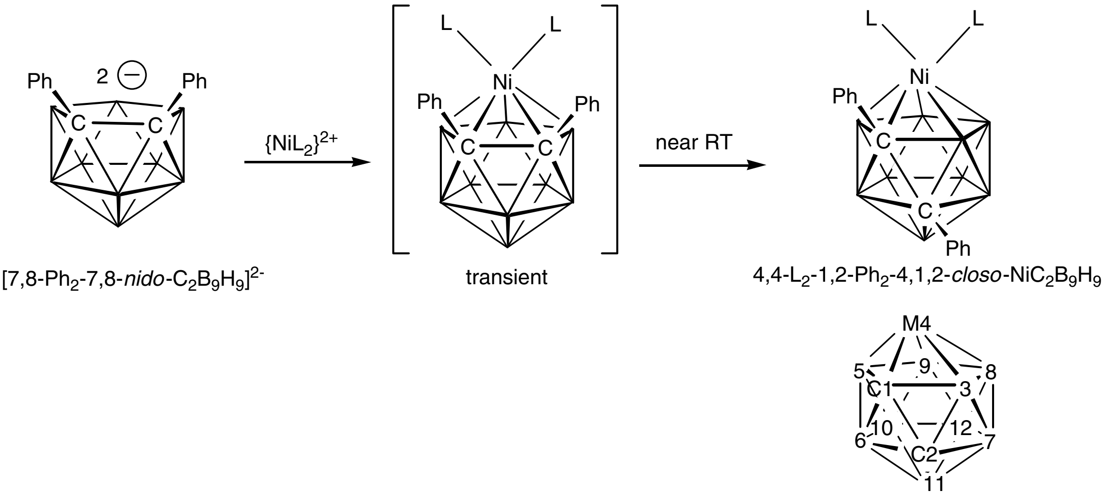
[†] Dedicated to Professor Thomas P. Fehlner on the occasion of his 65th birthday, in recognition of his outstanding contributions to organometallic and inorganic chemistry.

[§] Steric effects in heteroboranes. Part 28. For part 27 see Hodson BE, Ellis D, McGrath TD, Monaghan JJ, Rosair GM, Welch AJ. *Angew. Chem. Int. Ed. Engl.* 2001; **40**: 715.

Contract/grant sponsor: The Leverhulme Trust; Contract/grant number: F/00 276/A.



Scheme 1. Metallation of $[7,8\text{-Ph}_2\text{-}7,8\text{-}nido\text{-C}_2\text{B}_9\text{H}_9]^{2-}$ with a $\{\text{PtL}_2\}$ metal–ligand fragment generating a 1,7 carbon-atom isomerized $2,1,8\text{-PtC}_2\text{B}_9$ species at or near room temperature via a notional $3,1,2\text{-PtC}_2\text{B}_9$ intermediate. Shown below the final product is the conventional numbering scheme for a $2,1,8\text{-MC}_2\text{B}_9$ polyhedron.



Scheme 2. Metallation of $[7,8\text{-Ph}_2\text{-}7,8\text{-}nido\text{-C}_2\text{B}_9\text{H}_9]^{2-}$ with an $\{\text{NiL}_2\}$ metal–ligand fragment generating a 1,2 carbon-atom isomerized $4,1,2\text{-NiC}_2\text{B}_9$ species at or near room temperature via a notional $3,1,2\text{-NiC}_2\text{B}_9$ intermediate. Shown below the final product is the conventional numbering scheme for a $4,1,2\text{-MC}_2\text{B}_9$ polyhedron.

freshly distilled over CaH_2 (CH_2Cl_2, CHCl_3) or sodium wire (tetrahydrofuran (THF), Et_2O, 40–60 petroleum ether) or stored over 4 Å molecular sieves (CDCl_3). NMR spectra at 200.13 (^{1}H), 128.38 (^{11}B) or 161.98 MHz (^{31}P) were recorded on Bruker AC 200 or DPX 400 spectrometers from CDCl_3 solutions at ambient temperature, chemical shifts being recorded relative to SiMe_4 (^{1}H), $\text{BF}_3 \cdot \text{OEt}_2$ (^{11}B) or H_3PO_4 (^{31}P). IR spectra were recorded from CH_2Cl_2 solutions on a Perkin–Elmer Spectrum RX FTIR spectrophotometer. Elemental analyses were determined by the departmental service. The starting materials $[\text{HNMe}_3][3\text{-Et-}7,8\text{-Ph}_2\text{-}7,8\text{-}nido\text{-C}_2\text{B}_9\text{H}_9]$ [7] and Ni(dppe)Cl_2 [8] (dppe = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) were prepared by literature methods or slight variants thereof. All other reagents were used as supplied.

Synthesis

$[\text{HNMe}_3][3\text{-Et-}7,8\text{-Ph}_2\text{-}7,8\text{-}nido\text{-C}_2\text{B}_9\text{H}_9]$ (0.108 g, 0.29 mmol) in Et_2O (25 ml) was cooled to 0 °C and *n*-BuLi in hexanes (0.25 ml of 2.5 M solution ≡ 0.63 mmol) added. The solution was allowed to warm to room temperature and then heated to reflux for 1 h, affording the salt $\text{Li}_2[3\text{-Et-}7,8\text{-Ph}_2\text{-}7,8\text{-}nido\text{-C}_2\text{B}_9\text{H}_8]$. Solvent was removed from this product, which was then redissolved in THF (25 ml) and frozen to −196 °C. Solid Ni(dppe)Cl_2 (0.153 g, 0.29 mmol) was added, and the mixture allowed to warm to room temperature under constant stirring, affording a dark-brown product. The solvent was exchanged for CH_2Cl_2 and the product filtered through Celite®. Preparative thin-layer chromatography (TLC) on silica using CH_2Cl_2/40–60 petroleum ether as eluent (70 : 30) afforded two mobile red bands, subsequently collected as solids.

*1,2-Ph$_2$-4-dppe-6-Et-4,1,2-*closo*-NiC$_2$B$_9$H$_8$ (**1**)*

Yield 0.040 g, 17.9%. Anal. Found: C, 63.5; H, 6.09. Calc. for $C_{42}H_{47}B_9NiP_2$: C, 65.5; H, 6.15%. IR ν (cm^{-1}): 2523 (br). ^{1}H NMR δ (ppm): 7.9–6.2 (m, 30H, C_6H_5), 2.3–1.8 (m, 4H, CH_2CH_2), 1.05 (t, 3H, CH_2CH_3), 0.80 (app t, 2H, CH_2CH_3). ^{11}B–{^{1}H} NMR δ (ppm): 12.22 (1B), 1.38 (2B), −0.27 (1B), −3.24 (1B), −6.69 (1B), −7.94 (1B), −13.43 (2B). ^{31}P–{^{1}H} NMR δ (ppm): 56.72 (br d, 1P, $^2J_{PP}$ 27.0 Hz), 53.80 (br d, 1P, $^2J_{PP}$ 27.0 Hz).

*1,8-Ph$_2$-2-dppe-4-Et-2,1,8-*closo*-NiC$_2$B$_9$H$_8$ (**2**)*

Yield 0.005 g, 2.3%. Anal. Found: C, 58.9; H, 5.64. Calc. for $C_{42}H_{47}B_9NiP_2 \cdot CHCl_3$: C, 58.1; H, 5.44%. IR ν (cm^{-1}): 2564 (br). ^{1}H NMR δ (ppm): 7.9–6.7 (m, C_6H_5), spectrum poorly resolved at low frequency. ^{11}B–{^{1}H} NMR δ (ppm): −0.45 (4B), −4.06 (1B), −7.08 (1B), −12.05 (2B), −16.47 (1B). ^{31}P–{^{1}H} NMR δ (ppm): 58.56 (br d, 1P, $^2J_{PP}$ 31.0 Hz), 55.78 (br d, 1P, $^2J_{PP}$ 31.0 Hz).

Crystallography

Single crystals of compounds **1** and **2** were grown by diffusion of a CH_2Cl_2 or $CHCl_3$ solution of the compound, respectively, and a five fold excess of 40–60 petroleum ether at −30 °C. Crystals of **2** were ultimately found to contain one (partially disordered) molecule of $CHCl_3$ per molecule of nickelacarborane. Diffraction data were measured at 160(2) K on a Bruker AXS *P*4 diffractometer equipped with an Oxford Cryosystems Cryostream cooler. One asymmetric fraction of intensity data was collected[9] to $\theta_{max} = 25°$ with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å) using ω scans. Standard reflections were re-measured every 100 data and any crystal decay corrected. Data were corrected for absorption by ψ scans. Both structures were solved[10] by direct and difference Fourier methods and refined by full-matrix least-squares against F^2. Non-hydrogen atoms were assigned anisotropic displacement parameters. Phenyl, methylene and methyl hydrogen atom positions were calculated and treated as riding models (C–H distances 0.95 Å, 0.99 Å and 0.98 Å respectively) with displacement parameters calculated as 1.2, 1.2 and 1.5 times the bound carbon atom U_{eq} respectively. Cage hydrogen atoms were treated as riding on the appropriate boron atom (B–H = 1.12 Å) with U_H set at 1.2 U_B. Table 1 lists details of unit-cell data, intensity data collection and structure refinement.

Table 1. Crystallographic data for compounds **1** and **2**

	1	**2**
Formula	$C_{42}H_{47}B_9NiP_2$	$C_{42}H_{47}B_9NiP_2 \cdot CHCl_3$
M_r	769.74	889.10
Colour	Red	Red
Habit	Cube	Rhombus
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	13.9733(19)	11.352(3)
b (Å)	19.572(3)	20.268(5)
c (Å)	14.4363(15)	18.767(5)
β (°)	90.158(9)	90.19(2)
U (Å^3)	3948.1(9)	4317.8(19)
Z	4	4
D_{calc} (Mg m^{-3})	1.295	1.368
μ(Mo Kα) (mm^{-1})	0.604	0.742
F(000)	1608	1840
Crystal size (mm^3)	0.12 × 0.18 × 0.46	0.28 × 0.38 × 0.68
Transmission factors	0.74–0.78	0.73–0.81
Data collected	8291	5080
Independent data, n	6900	4700
R_{int}	0.0938	0.1051
No. variables, p	488	528
R, wR_2 (all data)[a]	0.107, 0.156	0.082, 0.176
S (all data)[a]	1.07	1.06
a, b[a]	0.04, 8.51	0.08, 9.99
ρ_{max}, ρ_{min} (e$^-$ Å^{-3})	0.45, −0.58	0.56, −0.86

[a] $R = \sum \|\|F_o\| - \|F_c\|/\sum \|F_o\|$, $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{1/2}$ (where $w^{-1} = [\sigma^2(F_o)^2 + (aP)^2 + bP]$ 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).

RESULTS AND DISCUSSION

Synthesis and characterization

The reaction between [3-Et-7,8-Ph$_2$-7,8-*nido*-$C_2B_9H_8$]$^{2-}$ (as its Li$^+$ salt) and Ni(dppe)Cl_2 in THF affords two neutral products after work-up involving preparative TLC.

The major product, **1**, the slower moving of the two, is isolated in *ca* 18% yield, the low overall yield being ascribed to the relative insolubility of Ni(dppe)Cl_2 in THF. The ^{1}H NMR spectrum of **1** at 200 MHz reveals, in addition to the expected resonances from C_6H_5 and CH_2CH_2 bridge protons, two triplets at low frequency. That centred at 1.05 ppm is relatively sharp and integrates for three protons, whilst that centred at 0.08 ppm is broader and integrates for only two protons. The latter is, in reality, a quartet, assigned to the methylene protons of the ethyl label, broadened into an apparent triplet at 200 MHz by the adjacent heteroborane cage. The ^{11}B–{^{1}H} spectrum is typical of that of a closo MC_2B_9 cage, with resonances between +13 and −14 ppm. There are seven resonances, 1 : 2 : 1 : 1 : 1 : 1 : 2 (high to low frequency), indicating that the cluster is asymmetric. Unfortunately, it proved impossible unambiguously to assign the resonance due to the Et-substituted boron atom from the proton-coupled spectrum. A pair of mutual doublets, $^{2}J_{PP} = 27$ Hz, is observed in the ^{31}P–{^{1}H} NMR spectrum, indicating that rotation of the {Ni(dppe)} fragment about the nickel-cage axis is restricted at room temperature.

The results of a crystallographic study of **1** are fully consistent with the conclusions of the NMR experiments, albeit that the latter were not fully assigned. Figure 1 shows a perspective view of a single molecule and Table 2 hosts selected molecular parameters. Compound **1** is identified as $1,2\text{-Ph}_2\text{-}4\text{-dppe-}6\text{-Et-}4,1,2\text{-}closo\text{-NiC}_2\text{B}_9\text{H}_8$, nickelation of $[3\text{-Et-}7,8\text{-Ph}_2\text{-}7,8\text{-}nido\text{-C}_2\text{B}_9\text{H}_8]^{2-}$ having produced a product that has undergone a 1,2 → 1,2 carbon atom isomerization (Scheme 2). We have previously shown[6] that such isomerization is normal for nickelation of $[7,8\text{-Ph}_2\text{-}7,8\text{-}nido\text{-C}_2\text{B}_9\text{H}_9]^{2-}$ and have described $4,1,2\text{-}closo\text{-NiC}_2\text{B}_9$ products with {Ni(PEt$_3$)$_2$}, {Ni(PMe$_2$Ph)$_2$} and {Ni(dppe)} fragments. Compound **1** herein is, therefore, fully analogous to $1,2\text{-Ph}_2\text{-}4\text{-dppe-}4,1,2\text{-}closo\text{-NiC}_2\text{B}_9\text{H}_9$,[6] except that the present compound carries an Et label at B6 and, therefore, potentially provides information on the isomerization mechanism (*vide infra*).

Molecular parameters within **1** are broadly similar to the corresponding parameters in the unlabelled analogue $1,2\text{-Ph}_2\text{-}4\text{-dppe-}4,1,2\text{-}closo\text{-NiC}_2\text{B}_9\text{H}_9$.[6] The Ni–C1 distance is the longest of the Ni-cage distances, reflecting a buckling of the metalla-bonded B$_4$C face (C1 lies *ca* 0.17 Å below the best (least-squares) plane through B5B9B8B3) rather than a significant slip distortion[11] ($\Delta = 0.10$ Å). The {NiP$_2$} unit stands perpendicular to the polyhedron, making a dihedral angle of 87.2° with the (reference) C2B6B10B12B7 plane, and is oriented so as to minimise C1Ph···dppe contacts. A significant difference, however, exists between labelled and unlabelled nickelacarboranes in respect of the conformations of the cage Ph rings, θ_{Ph}, defined[12] as the modulus of the average $C_{cage}-C_{cage}-C_{phenyl}-C_{phenyl}$ torsion angles. In $1,2\text{-Ph}_2\text{-}4\text{-dppe-}4,1,2\text{-}closo\text{-NiC}_2\text{B}_9\text{H}_9$ the θ_{Ph} values are low, 11.6 and 7.9°, resembling the situation in the parent carborane $1,2\text{-Ph}_2\text{-}1,2\text{-}closo\text{-C}_2\text{B}_{10}\text{H}_{10}$.[13] In **1**, θ_{Ph2} is similarly low (4.4°), but θ_{Ph1} is much higher (32.4°), presumably to accommodate the steric demands of the adjacent Et substituent. In this respect the conformation of the cage Ph

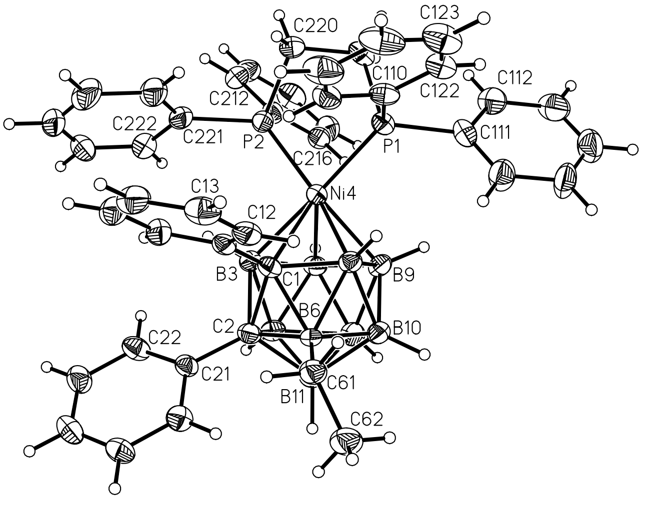


Figure 1. Perspective view of compound **1**. Thermal ellipsoids are drawn at the 50% probability level, except for hydrogen atoms.

Table 2. Selected interatomic distances (Å) and interbond angles (°) for **1**

Distances			
C(1)–C(2)	1.688(6)	B(7)–B(11)	1.790(8)
C(1)–B(3)	1.716(7)	B(8)–B(9)	1.764(8)
C(1)–Ni(4)	2.279(5)	B(8)–B(12)	1.788(8)
C(1)–B(5)	1.704(7)	B(9)–B(10)	1.778(8)
C(1)–B(6)	1.744(7)	B(9)–B(12)	1.779(8)
C(2)–B(3)	1.790(7)	B(10)–B(11)	1.786(8)
C(2)–B(7)	1.707(7)	B(10)–B(12)	1.784(8)
C(2)–B(11)	1.708(7)	B(11)–B(12)	1.766(8)
C(2)–B(6)	1.729(7)	Ni(4)–P(1)	2.1808(14)
B(3)–Ni(4)	2.086(5)	Ni(4)–P(2)	2.1938(14)
B(3)–B(8)	1.830(7)	C(1)–C(11)	1.509(6)
B(3)–B(7)	1.801(8)	C(2)–C(21)	1.518(6)
Ni(4)–B(8)	2.144(5)	B(6)–C(61)	1.590(7)
Ni(4)–B(9)	2.127(5)	C(61)–C(62)	1.542(7)
Ni(4)–B(5)	2.081(5)	P(1)–C(110)	1.839(5)
B(5)–B(9)	1.868(8)	P(1)–C(111)	1.814(5)
B(5)–B(10)	1.785(7)	P(1)–C(121)	1.845(5)
B(5)–B(6)	1.818(7)	P(2)–C(220)	1.848(5)
B(6)–B(10)	1.794(7)	P(2)–C(211)	1.837(5)
B(6)–B(11)	1.780(8)	P(2)–C(221)	1.822(5)
B(7)–B(8)	1.771(7)	C(110)–C(220)	1.522(7)
B(7)–B(12)	1.782(8)		
Angles			
C(11)–C(1)–C(2)	115.9(4)	Ni(4)–P(1)–C(110)	107.44(16)
C(11)–C(1)–B(3)	121.4(4)	Ni(4)–P(1)–C(111)	120.85(17)
C(11)–C(1)–Ni(4)	118.2(3)	Ni(4)–P(1)–C(121)	117.91(14)
C(11)–C(1)–B(5)	126.0(4)	C(110)–P(1)–C(111)	104.5(2)
C(11)–C(1)–B(6)	114.7(4)	C(110)–P(1)–C(121)	101.7(2)
C(21)–C(2)–C(1)	121.9(4)	C(111)–P(1)–C(121)	102.2(2)
C(21)–C(2)–B(3)	118.2(4)	Ni(4)–P(2)–C(220)	108.02(16)
C(21)–C(2)–B(7)	114.9(4)	Ni(4)–P(2)–C(211)	115.95(16)
C(21)–C(2)–B(11)	119.2(4)	Ni(4)–P(2)–C(221)	120.20(17)
C(21)–C(2)–B(6)	122.9(4)	C(220)–P(2)–C(211)	100.3(2)
C(61)–B(6)–C(1)	122.1(4)	C(220)–P(2)–C(221)	105.2(2)
C(61)–B(6)–C(2)	128.2(4)	C(211)–P(2)–C(221)	104.9(2)
C(61)–B(6)–B(11)	125.2(4)	P(1)–Ni(4)–P(2)	87.14(5)
C(61)–B(6)–B(10)	122.0(4)	P(1)–C(110)–C(220)	107.9(3)
C(61)–B(6)–B(5)	121.1(4)	P(2)–C(220)–C(110)	105.8(3)
B(6)–C(61)–C(62)	115.0(4)		

rings in **1** somewhat resembles that in 1,2-Ph_2-3-Me-1,2-*closo*-$C_2B_{10}H_9$,[7] although in the latter case the distortion is more symmetrical.

The second product of the reaction, the faster moving compound **2**, is very much a minor product, being afforded in only 2% yield (a minor co-product was also reported[6] during the synthesis of 1,2-Ph_2-4-dppe-4,1,2-*closo*-$NiC_2B_9H_9$ but was not characterized). Compound **2** was partially characterized spectroscopically. It displays five resonances (4 : 1 : 1 : 2 : 1) in the $^{11}B-\{^1H\}$ NMR spectrum (again, that due to the labelled boron atom could not be distinguished) and a pair of mutual doublets in the $^{31}P-\{^1H\}$ spectrum, $^2J_{PP} = 31$ Hz. The 200 MHz ^1H spectrum, however, is uninformative at low frequency. Ultimately, the structural identity of **2** was revealed by a crystallographic study. Compound **2** crystallizes from $CHCl_3$ as the 1 : 1 solvate (fully consistent with microanalytical data) and a perspective view of the nickelacarborane is shown in Fig. 2. Key molecular parameters are listed in Table 3.

Compound **2** is thus shown to be 1,8-Ph_2-2-dppe-4-Et-2,1,8-*closo*-$NiC_2B_9H_8$, presumably the result of a 1,2 → 1,7 carbon-atom isomerization of the transient species 1,2-Ph_2-3-dppe-6-Et-2,1,8-*closo*-$NiC_2B_9H_8$ first formed (this process is shown for an unlabelled platinacarborane in Scheme 1). 1,2 → 1,7 carbon-atom isomerization on nickelation of a nido diphenylcarborane is rare[6] but not unknown,[14] being much more typical on platination of such species. The overall structure of **2**, therefore, resembles that typified by 1,8-Ph_2-2,2-$(PMe_2Ph)_2$-2,1,8-*closo*-$PtC_2B_9H_9$,[5] except that now an Et label is appended to B4, adjacent to both (non-adjacent) cage carbon atoms. Ni–C1 is again the longest Ni–cage atom connectivity. Although the nickel atom is slipped (relative to the B4B5B10B12C8 plane) by 0.23 Å, a relatively large amount for a nickelacarborane,[6] this value is small compared with that of analogous platinacarboranes.[5] C1 lies *ca* 0.19 Å below the B3B7B11B6 plane and almost in the plane of the perpendicular bisector of the $\{NiP_2\}$ fragment. The non-adjacency of the cage carbon atoms means that it is not possible to define the conformations of the cage phenyl rings in the standard way, but clearly that on C1 is oriented to minimize interaction with the dppe ligand.

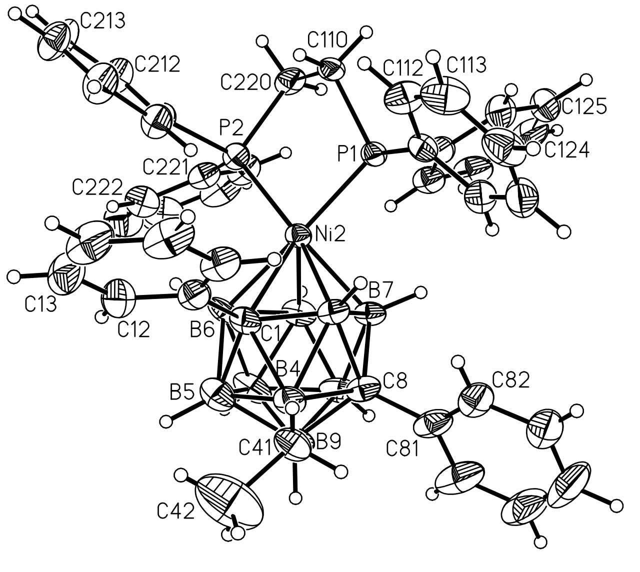


Figure 2. Perspective view of compound **2**. Thermal ellipsoids are drawn at the 50% probability level, except for hydrogen atoms.

Table 3. Selected interatomic distances (Å) and interbond angles (°) for **2**

Distances			
C(1)–Ni(2)	2.288(8)	B(7)–B(11)	1.771(10)
C(1)–B(3)	1.655(9)	C(8)–B(9)	1.734(10)
C(1)–B(4)	1.728(9)	C(8)–B(12)	1.726(9)
C(1)–B(5)	1.696(9)	B(9)–B(10)	1.750(13)
C(1)–B(6)	1.712(10)	B(9)–B(12)	1.724(13)
Ni(2)–B(3)	2.071(8)	B(10)–B(11)	1.781(13)
Ni(2)–B(7)	2.088(5)	B(10)–B(12)	1.735(11)
Ni(2)–B(11)	2.109(5)	B(11)–B(12)	1.771(11)
Ni(2)–B(6)	2.092(8)	Ni(2)–P(1)	2.1726(18)
B(3)–B(4)	1.856(12)	Ni(2)–P(2)	2.1892(18)
B(3)–C(8)	1.744(7)	C(1)–C(11)	1.524(7)
B(3)–B(7)	1.836(10)	C(8)–C(81)	1.519(8)
B(4)–C(8)	1.758(10)	B(4)–C(41)	1.546(12)
B(4)–B(9)	1.781(9)	C(41)–C(42)	1.523(16)
B(4)–B(5)	1.767(10)	P(1)–C(110)	1.842(6)
B(5)–B(9)	1.767(10)	P(1)–C(111)	1.815(6)
B(5)–B(10)	1.780(13)	P(1)–C(121)	1.835(7)
B(5)–B(6)	1.809(14)	P(2)–C(220)	1.840(8)
B(6)–B(10)	1.803(9)	P(2)–C(211)	1.834(5)
B(6)–B(11)	1.843(11)	P(2)–C(221)	1.829(6)
B(7)–C(8)	1.710(11)	C(110)–C(220)	1.530(8)
B(7)–B(12)	1.786(9)		
Angles			
C(11)–C(1)–Ni(2)	116.6(4)	Ni(2)–P(1)–C(110)	108.28(19)
C(11)–C(1)–B(3)	122.5(5)	Ni(2)–P(1)–C(111)	121.1(3)
C(11)–C(1)–B(4)	113.6(6)	Ni(2)–P(1)–C(121)	113.6(2)
C(11)–C(1)–B(5)	114.2(6)	C(110)–P(1)–C(111)	107.5(3)
C(11)–C(1)–B(6)	121.6(5)	C(110)–P(1)–C(121)	100.2(3)
C(81)–C(8)–B(3)	120.1(5)	C(111)–P(1)–C(121)	104.1(3)
C(81)–C(8)–B(4)	116.8(6)	Ni(2)–P(2)–C(220)	107.14(19)
C(81)–C(8)–B(9)	119.9(5)	Ni(2)–P(2)–C(211)	118.6(2)
C(81)–C(8)–B(12)	118.8(4)	Ni(2)–P(2)–C(221)	117.50(19)
C(81)–C(8)–B(7)	115.9(6)	C(220)–P(2)–C(211)	100.4(3)
C(41)–B(4)–C(1)	126.5(5)	C(220)–P(2)–C(221)	106.6(4)
C(41)–B(4)–B(3)	122.9(5)	C(211)–P(2)–C(221)	104.7(2)
C(41)–B(4)–C(8)	123.1(5)	P(1)–Ni(2)–P(2)	87.04(7)
C(41)–B(4)–B(9)	123.9(6)	P(1)–C(110)–C(220)	105.4(3)
C(41)–B(4)–B(5)	127.0(7)	P(2)–C(220)–C(110)	106.8(5)
B(4)–C(41)–C(42)	116.2(7)		

Mechanistic considerations

The present study was undertaken in the expectation that nickelation of [3-Et-7,8-Ph_2-7,8-*nido*-$C_2B_9H_8$]$^{2-}$ would result in low-temperature 1,2 → 1,2 carbon-atom isomerization (Scheme 2), the location of the ethyl-labelled boron atom in the isomerized product affording mechanistic information. Whilst the major product of the reaction, **1**, is indeed 1,2 isomerized, it is not the only product. The minor product **2** is found unexpectedly to result from 1,2 → 1,7 carbon-atom isomerization of the assumed initial (transient) species (we have very recently isolated this initial species in a platination reaction, and confirmed its 3,1,2-MC_2B_9 architecture).[15] Since we have shown that compound **1** does not convert to **2** on thermolysis (toluene reflux for 4 h), it is clear that the 1,2 → 1,2 and 1,2 → 1,7 isomerizations of the assumed intermediate are separate events. Thus, the location of the Et-labelled boron atom in both **1** and **2** allows comment on both isomerization processes.

1,2 → 1,2 isomerization

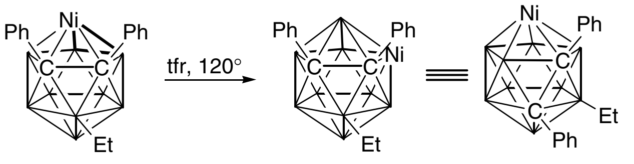
A 1,2 → 1,2 isomerization process, in which the two cage carbon atoms retain adjacency, immediately eliminates mechanisms based on either concerted or sequential diamond–square–diamond (DSD) processes, since these involve breaking the C–C connectivity at some point. Carbon-separated (hetero)boranes are thermodynamically preferred to carbon-adjacent analogues; so, once separated, it is difficult to envisage the cage carbon atoms becoming adjacent again. Moreover, in **1**, not only do the cage carbon atoms remain adjacent, but also the labelled boron atom remains adjacent to both. This suggests a relatively simple isomerization process, the most attractive of which is a single triangle face rotation (TFR) process. The transient species 1,2-Ph_2-3-dppe-6-Et-3,1,2-*closo*-$NiC_2B_9H_8$ and the isomerized product 1,2-Ph_2-4-dppe-6-Et-2,1,8-*closo*-$NiC_2B_9H_8$ (**1**) differ only in the relative position of the nickel vertex, meaning that the TFR of an NiB_2 face is required. Scheme 3 shows how a single TFR through 120° of the NiB_2 face highlighted leads to **1** (TFR applied to the symmetry-equivalent NiB_2 face leads to the enantiomer of **1**).

1,2 → 1,7 isomerization

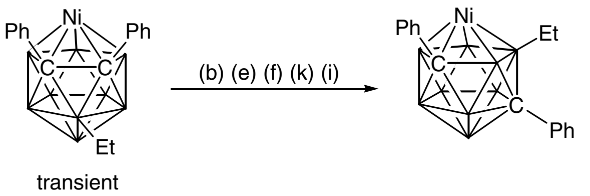
1,2 → 1,7 carbon-atom isomerization in (hetero)carboranes has been studied much more extensively than 1,2 → 1,2 isomerization (of course, for carboranes the 1,2 → 1,2 isomerization represents no net change). Of numerous suggested isomerization mechanisms,[16–21] that proposed by Wales,[22] involving a series of sequential DSD steps, has received experimental support from the results of recent work in our laboratories. On metallation of [7,8-Ph_2-7,8-*nido*-$C_2B_9H_9$]$^{2-}$ with {Mo(η-C_3H_5)(CO)$_2$$^+$} we were fortunate to isolate an isomerization intermediate,[23] thus providing an important signpost to the isomerization mechanism. The intermediate has the same gross architecture as one of the intermediates (in fact, the most stable intermediate) predicted by Wales in the isomerization of 1,2-*closo*-$C_2B_{10}H_{12}$ to 1,7-*closo*-$C_2B_{10}H_{12}$. Moreover, the relative positions of all three heteroatoms (M + 2C) in transient initial product, isolated intermediate and final 1,7 carbon-atom isomerized metallacarborane agree fully with those predicted.

Unfortunately, later studies starting from 9- and 10-labelled nido diphenylcarboranes afforded only limited agreement between theory and experiment.[24,25] Although the intermediates isolated from the reactions of [7,8-Ph_2-9-SMe_2-7,8-*nido*-$C_2B_9H_8$]$^-$ and [7,8-Ph_2-10-SMe_2-7,8-*nido*-$C_2B_9H_8$]$^-$ with {Mo(η-C_3H_5)(CO)$_2$$^+$} had the SMe_2 label at the correct position, one of the final products of the former reaction and the single final product of the latter reaction did not. This poor agreement is repeated in the present study. Because [3-Et-7,8-Ph_2-7,8-*nido*-$C_2B_9H_8$]$^{2-}$ is labelled on its mirror plane, Wales predicts only a single 1,7 carbon-atom isomerized product, 1,8-Ph_2-2-dppe-7-Et-2,1,8-*closo*-$NiC_2B_9H_8$ (Scheme 4) via sequential DSD processes (b) (e) (f) (k) (i) (see Ref. 22 for a description of these terms). The alternative route (b) (e) (j) (i) has been discounted by virtue of it predicting the wrong relative position of the metal vertex.

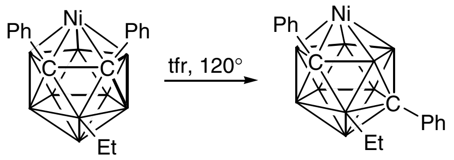
Clearly, the formation of compound **2** cannot be explained by such a process. Unlike the reactions of nido diphenylcarboranes with {Mo(η-C_3H_5)(CO)$_2$$^+$}, the nickelation of [3-Et-7,8-Ph_2-7,8-*nido*-$C_2B_9H_8$]$^{2-}$ does not afford an isolatable intermediate, and the nature of the rearrangement mechanism is consequently more uncertain. Nevertheless, having speculated on a single TFR mechanism for the formation of **1**, we note that an alternate TFR (shown in Scheme 5), this time involving a CB_2 face, satisfactorily accounts for the formation of product **2**. Again, TFR applied to the mirror image CB_2 face leads to the enantiomer of **2**.



Scheme 3. How the transient species 1,2-Ph_2-3-dppe-6-Et-3,1,2-*closo*-$NiC_2B_9H_8$ might isomerize to product **1** by rotation of the NiB_2 triangle face shown in bold.



Scheme 4. Application of the sequential DSD process (b) (e) (f) (k) (i) (see Ref. 22) to the transient species 1,2-Ph_2-3-dppe-6-Et-3,1,2-*closo*-$NiC_2B_9H_8$ producing 1,8-Ph_2-2-dppe-7-Et-3,1,2-*closo*-$NiC_2B_9H_8$.



transient **2**

Scheme 5. Rotation of a CB_2 triangular face (bold) affording product **2** from the transient species 1,2-Ph$_2$-3-dppe-6-Et-3,1,2-*closo*-$NiC_2B_9H_8$.

CONCLUSIONS

Nickelation of the labelled carborane dianion [3-Et-7,8-Ph$_2$-7,8-*nido*-$C_2B_9H_8$]$^{2-}$ yields two products. The major product, 1,2-Ph$_2$-4-dppe-6-Et-4,1,2-*closo*-$NiC_2B_9H_8$, arises from the expected 1,2 → 1,2 carbon-atom isomerization of the transient species assumed first to form. This product is most easily rationalized by a single 120° rotation of the NiB_2 face of the transient species. The minor product is 1,8-Ph$_2$-2-dppe-4-Et-2,1,8-*closo*-$NiC_2B_9H_8$, which has (unexpectedly) undergone a 1,2 → 1,7 carbon-atom isomerization. This species, too, can be rationalized by a TFR mechanism, this time of a CB_2 face.

Clearly, much more work needs to be done in this area, possibly using multiply labelled nido diphenylcarboranes, before the mechanisms of sterically induced 1,2 → 1,2 and 1,2 → 1,7 isomerizations can be firmly established. These studies are currently underway in our laboratories.

SUPPLEMENTARY MATERIAL

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos CCDC-200896 (**1**) and CCDC-200897 (**2**). Copies of these data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1233-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http//www.ccdc.cam.ac.uk).

Acknowledgements

We thank the Leverhulme Trust (DE) and Heriot-Watt University (SR) for support, Mr G. Evans and Mrs C. Graham for microanalysis, and Dr A.S.F. Boyd for NMR spectra. AJW acknowledges the receipt of a Royal Society Leverhulme Trust Senior Research Fellowship, 2002–03.

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