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Synthesis and reactivity of 7,9-diphenyl-*nido*-carbaundecaboranes: rearrangement processes in carbaplatinaboranes revisited†

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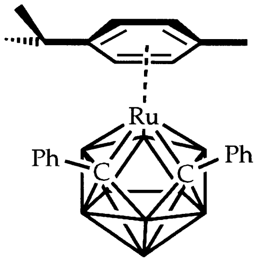
A number of synthetic routes towards diphenyl *nido*-carbaborane $[7,9\text{-}Ph_2\text{-}7,9\text{-}nido\text{-}C_2B_9H_{10}]^-$ have been elucidated. Base-induced degradation of $1,7\text{-}Ph_2\text{-}1,7\text{-}closo\text{-}C_2B_{10}H_{10}$ afforded two isolable products $[NEt_3H]$-$[7,9\text{-}Ph_2\text{-}x\text{-}OEt\text{-}7,9\text{-}nido\text{-}C_2B_9H_9]$ (x = 3 **1a** or 2 **1b**), both of which contain an ethoxide-substituted cage. The structural identity of **1a** was established by a single-crystal X-ray diffraction study. Fluoride-induced degradation gave a product assigned as $[NBu_4][7,9\text{-}Ph_2\text{-}10\text{-}OH\text{-}7,9\text{-}nido\text{-}C_2B_9H_9]$ **2**, also studied crystallographically. Heating a solid sample of $Cs[7,8\text{-}Ph_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_{10}]$ in a sealed tube under vacuum for 4 h at 300 °C afforded the target species $[NEt_3H][7,9\text{-}Ph_2\text{-}7,9\text{-}nido\text{-}C_2B_9H_{10}]$ **3**, after cation metathesis. Deprotonation of **3** and reaction with $[PtCl_2(PMe_2Ph)_2]$ afforded the new compound $1,1\text{-}(PMe_2Ph)_2\text{-}2,4\text{-}Ph_2\text{-}1,2,4\text{-}closo\text{-}PtC_2B_9H_9$ **4**. Compound **4** has been characterised by multinuclear (^1H, ^{11}B and $^{31}P\text{-}\{^1H\}$) NMR spectroscopy as well as a single-crystal X-ray diffraction study. The isolation of this stable (in refluxing toluene) compound having a $1,2,4\text{-}MC_2B_9$ cage architecture indicates that a hextuple-concerted diamond–square–diamond mechanism cannot be operating in the spontaneous isomerisation of $1,2\text{-}Ph_2\text{-}3,3\text{-}(PMe_2Ph)_2\text{-}3,1,2\text{-}closo\text{-}PtC_2B_9H_9$ below ambient temperature to afford $1,1\text{-}(PMe_2Ph)_2\text{-}2,8\text{-}Ph_2\text{-}1,2,8\text{-}closo\text{-}PtC_2B_9H_9$. The new compounds $1,1\text{-}(PR_3)_2\text{-}2,4\text{-}Ph_2\text{-}7\text{-}OEt\text{-}closo\text{-}1,2,4\text{-}PtC_2B_9H_8$ ($R_3 = Me_2Ph$ **5a** or Et_3 **5b**), both fully characterised by multinuclear NMR spectroscopy, have also been synthesized.

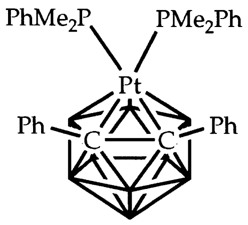
We are currently interested in crowded carbametallaboranes of the type $1\text{-}Ph\text{-}2\text{-}R\text{-}3\text{-}(\mu\text{-}L)\text{-}3,1,2\text{-}MC_2B_9H_9$ (R = H, Me or Ph; L = C_5H_5, C_6H_6 for example).[2] When R = Ph steric congestion between the adjacent phenyl groups results either in polyhedral distortion, leading to *pseudocloso* structures (*e.g.* **a**) in which the cage-carbon connectivity has been broken, or in cage-carbon isomerisation. An unusually facile example of the latter is the sterically induced low-temperature (<20 °C) polyhedral rearrangement of $1,2\text{-}Ph_2\text{-}3,3\text{-}(PMe_2Ph)_2\text{-}3,1,2\text{-}closo\text{-}PtC_2B_9H_9$[3] to afford $1,1\text{-}(PMe_2Ph)_2\text{-}2,8\text{-}Ph_2\text{-}1,2,8\text{-}closo\text{-}PtC_2B_9H_9$ (**b** and **c** respectively).

We noted[3] that generation of the $2,1,8\text{-}PtC_2B_9$ product was probably inconsistent with the elegant hextuple-concerted diamond–square–diamond (d.s.d.) mechanism for rearrangements of icosahedral heteroboranes. In such a mechanism, the C(1)–C(2) connectivity would be broken in the initial transition state and would result in a species with a $1,2,4\text{-}PtC_2B_9$ cage architecture (**d**). This compound would not be expected to have the severe intramolecular crowding between adjacent phenyl groups present in $3,1,2\text{-}closo\text{-}PtC_2B_9$, and thus could be stable to further isomerisation. Thus, the independent isolation of this $1,2,4\text{-}PtC_2B_9$ species would argue strongly against the d.s.d. mechanism operating in the above case.

In order to confirm this hypothesis, the synthesis of the $1,2,4\text{-}PtC_2B_9$ isomer was attempted directly starting from $[7,9\text{-}Ph_2\text{-}7,9\text{-}nido\text{-}C_2B_9H_{10}]^-$ (note the change in conventional numbering between *closo* and *nido* species). This paper describes a number of attempted synthetic routes towards $[7,9\text{-}Ph_2\text{-}7,9\text{-}nido\text{-}C_2B_9H_{10}]^-$ and the reaction between this carbaborane and $[PtCl_2(PMe_2Ph)_2]$. Also reported are the products of reactions between $[PtCl_2(PR_3)_2]$ ($R_3 = Et_3$ or Me_2Ph) and $[NEt_3H][3\text{-}OEt\text{-}7,9\text{-}Ph_2\text{-}nido\text{-}7,9\text{-}C_2B_9H_9]$.



a



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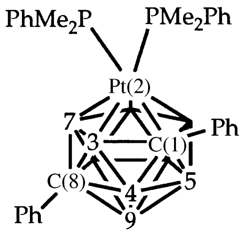

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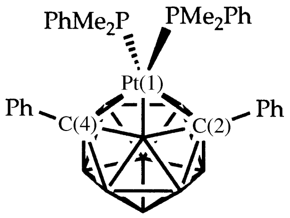

d

Experimental

General

All experiments, apart from fluoride decapitation reactions, were carried out under a dry, oxygen-free dinitrogen atmosphere, using Schlenk-line techniques, although all the new compounds reported are stable to the ambient atmosphere both as solids and as solutions. The fluoride decapitation reactions were performed as described recently by Wade and co-workers.[4] All solvents were dried over the appropriate drying agents immediately prior to use [CH_2Cl_2, CaH_2; tetrahydrofuran (thf) and diethyl ether, sodium wire–benzophenone; toluene, light petroleum (b.p. 40–60 and 60–80 °C), sodium wire]. Chromatography columns (3 × 15 cm) were packed with silica (Kieselgel 60, 200–400 mesh). The compounds $[PtCl_2(PMe_2Ph)_2]$,[5] $1,7\text{-}Ph_2\text{-}1,7\text{-}closo\text{-}C_2B_{10}H_{10}$[6] and $Cs[7,8\text{-}Ph_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_{10}]$[7] (similarly to $Cs[7\text{-}Ph\text{-}7,8\text{-}C_2B_9H_{11}]$[7]) were prepared as described previously.

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† Steric effects in heteroboranes. Part 17.[1]

Spectroscopy

Proton NMR spectra were recorded on a Brüker AC 200 spectrometer and ^{1}H, ^{11}B and ^{31}P spectra on a Brüker DPX 400 spectrometer at 297 K in $CDCl_3$ solutions unless otherwise stated. Proton chemical shifts are reported relative to residual protio solvent in the sample, ^{11}B relative to external $BF_3{\cdot}OEt_2$ at 128.0 MHz and ^{31}P relative to external H_3PO_4 at 162.0 MHz. Infrared spectra were recorded from CH_2Cl_2 or thf solutions, using 0.1 mm NaCl solution cells on a Nicolet Impact 400 FTIR spectrophotometer, unless otherwise stated.

Syntheses

[NEt_3H][7,9-Ph_2-*x*-OEt-7,9-*nido*-$C_2B_9H_9$] (*x* = 3 1a or 2 1b). The compounds 1,7-Ph_2-1,7-*closo*-$C_2B_{10}H_{10}$ (0.78 g, 2.63 mmol) and KOH (0.36 g, 6.42 mmol) were dissolved in degassed ethanol (50 cm^3) in an autoclave (150 cm^3) equipped with a magnetic stirring bar and flushed with dinitrogen. The autoclave was heated to 200 °C for 18 h under autogenous pressure [*ca.* 12 bar (*ca.* 1.2 × 10^6 Pa)]. Once cooled, CO_2 was bubbled through the solution for 1 h. The white, sticky, precipitate of K_2CO_3 that formed was filtered off and the resulting pale yellow solution reduced *in vacuo* to leave an oily, pale yellow solid. This was redissolved in water (50 cm^3) and [NEt_3H]Cl (0.38 g, 2.76 mmol) in water (5 cm^3) was added to afford an off-white precipitate, which was filtered off and recrystallised from CH_2Cl_2–light petroleum (b.p. 60–80 °C) at 3 °C to afford white, needle-shaped crystals of compound **1a**. A second recrystallisation of the supernatant afforded a lower yield of pure **1a**. Total mass 0.61 g, 54%. A third recrystallisation precipitated a small amount of white solid that was a mixture of **1a** (*ca.* 20%) and **1b** (*ca.* 80%). A ^{1}H NMR spectrum of the mixture before any recrystallisation showed that the ratio of **1a** to **1b** was approximately 9 : 1.

Compound **1a** (Found: C, 59.5; H, 8.7; N, 3.0. Calc. for $C_{22}H_{40}B_9NO{\cdot}0.25CH_2Cl_2$: C, 58.9; H, 8.9, N, 3.0%). NMR: ^{1}H, δ 8.55 (s br, 1 H, *H*NEt_3), 7.51 (m, 4 H, Ph), 7.15 (m, 6 H, Ph), 3.67 [apparent q, 2 H, OCH_2, *J*(HH) 6], 2.95 [q, 6 H, NCH_2, *J*(HH) 7], 1.18 [t, 9 H, CH_3, *J*(HH) 7] and 1.07 [t, 3 H, CH_3, *J*(HH) 6]; ^{11}B, δ 2.00 (sharp, 1 B), 0.64 (br, 1 B), −1.75 (br, 1 B), −2.10 (br, 1 B), −17.13 (br, 1 B), −18.2 (br, 1 B), −22.37 (br, 1 B), −29.35 [d, 1 B, *J*(HB) 121] and −35.79 [d, 1 B, *J*(HB) 130 Hz]; ^{11}B-{^{1}H}, δ 2.00 (1 B), 0.64 (1 B), −1.75 (1 B), −2.10 (1 B), −17.13 (1 B), −18.2 (1 B), −22.37 (1 B), −29.35 (1 B) and −35.79 (1 B).

Compound **1b** (isolated as a 1 : 4 mixture of **1a** and **1b**): NMR ^{1}H, δ 7.56 (m, 4 H, Ph), 7.25–6.96 (m, 6 H, Ph), 3.59 [q, 1 H, OCH_2, *J*(HH) 7], 3.42 [q, 1 H, OCH_2, *J*(HH) 7], 2.97 [q, 6 H, NCH_2, *J*(HH) 7], 1.14 [t, 9 H, CH_3, *J*(HH) 7] and 0.93 [t, 3 H, CH_3, *J*(HH) 7 Hz]; ^{11}B-{^{1}H},[‡] δ 0.53 (br, 2 B), −2.84 (br, 3 B), −22.07 (br, 2 B), −30.62 (br, 1 B) and −39.05 (br, 1 B).

[NBu_4][7,9-Ph_2-10-OH-7,9-*nido*-$C_2B_9H_9$] 2. The compound 1,7-Ph_2-1,7-*closo*-$C_2B_{10}H_{10}$ (0.300 g, 1.01 mmol) was dissolved in thf (20 cm^3) and [NBu_4]F (5 cm^3 of a 1.0 mol dm^{-3} solution in thf ≡ 5.0 mmol) was added. The solution was heated to reflux overnight, after which the characteristic *closo* B–H stretch at 2600 cm^{-1} had been replaced by one at 2545 cm^{-1} characteristic of a *nido*-C_2B_9 cage. Dichloromethane (100 cm^3) was added, and the resulting solution washed with water (3 × 50 cm^3). The organic layer was dried over $MgSO_4$, following which removal of the solvent afforded a white solid, which on recrystallisation from hot ethanol gave white needles of [NBu_4][7,9-Ph_2-10-OH-7,9-*nido*-$C_2B_9H_9$] **2**, mass 0.40 g (78%). Positive-ion FAB mass spectrum: *m/z* 787 {[NBu_4]$_2$[$C_2B_9H_{10}OPh_2$]} (Found: C, 65.7; H, 10.4; N, 2.5. Calc. for $C_{30}H_{56}B_9NO$: C, 66.3; H, 10.3; N, 2.6%). IR (KBr disc): 3443 (vbr) (OH), 2539 (br) cm^{-1} (BH). NMR [$(CD_3)_2CO$]: ^{1}H, δ 7.38 (m, 4 H, Ph), 6.95–6.70 (m, 6 H, Ph), 3.25 (m, 8 H, NCH_2), 1.70 (m, 8 H, CH_2), 1.31 (m, 8 H, CH_2) and 0.87 [t, 12 H, CH_3, *J*(HH) 8]; ^{11}B, δ 3.67 (s, 1 B), 1.36 [d, 1 B, *J*(HB) 128], 0.79 [d, 1 B, *J*(HB) *ca.* 120], −0.70 [d, 1 B, *J*(HB) 141], −15.19 [d, 1 B, *J*(HB) 143], −18.30 [d br, 1 B, *J*(HB) 156], −22.30 [d, 1 B, *J*(HB) 165], −31.50 [d, 1 B, *J*(HB) 143] and −33.65 [d, 1 B, *J*(HB) 133 Hz]; ^{11}B-{^{1}H}, δ 3.67 (1 B), 1.36 (1 B), 0.79 (1 B), −0.70 (1 B), −15.19 (1 B), −18.30 (1 B), −22.30 (1 B), −31.5 (1 B) and −33.65 (1 B).

[NEt_3H][7,9-Ph_2-7,9-*nido*-$C_2B_9H_{10}$] 3. The compound Cs-[7,8-Ph_2-7,8-*nido*-$C_2B_9H_{10}$] (0.300 g, 0.717 mmol) was heated in a sealed tube for 4 h at 300 °C. The resulting pale yellow solid was dissolved in CH_2Cl_2 (40 cm^3) and [NEt_3H]Cl (0.15 g, 1.1 mmol) added to afford a white precipitate, which was filtered off to give [NEt_3H][7,9-Ph_2-7,9-*nido*-$C_2B_9H_{10}$] **3**. Mass 0.21 g (75%) (Found: C, 61.7; H, 9.95; N 2.9. Calc. for $C_{20}H_{36}B_9N$: C, 61.9; H, 9.9; N, 3.6%). NMR [$(CD_3)_2CO$]: ^{1}H, δ 7.45 (m, 4 H, Ph) and 7.05–6.82 (m, 6 H, Ph); ^{11}B, δ 0.72 [d, 3 B one coincident, *J*(HB) *ca.* 140], −15.25 [d, 2 B, *J*(HB) 139], −18.31 [d br, 2 B, *J*(HB) 97], −28.40 [d, 1 B, *J*(HB) 135] and −32.80 [d, 1 B, *J*(HB) 134 Hz]; ^{11}B-{^{1}H}, δ 0.72 (3 B, one coincident), −15.25 (2 B), −18.31 (2 B), −28.40 (1 B) and −32.80 (1 B).

1,1-$(PMe_2Ph)_2$-2,4-Ph_2-1,2,4-*closo*-$PtC_2B_9H_9$ 4. The compound [NEt_3H][7,9-Ph_2-7,9-*nido*-$C_2B_9H_{10}$] (0.100 g, 0.253 mmol) was deprotonated by reflux for 18 h with 2.5 equivalents of washed NaH in thf. This solution was added to a frozen (−196 °C) solution of [$PtCl_2(PMe_2Ph)_2$] (0.135 g, 0.253 mmol) in thf (10 cm^3). Warming to room temperature and stirring for 4 h resulted in an orange-brown solution. The solvent was removed *in vacuo* and the residue taken up in CH_2Cl_2. Filtration through a Celite pad afforded an orange-brown solution, which was reduced in volume *in vacuo* to *ca.* 2 cm^3. This was applied to the top of a chromatography column, and elution with CH_2Cl_2–light petroleum (b.p. 40–60 °C) (1 : 1) afforded a bright yellow band. Recrystallisation from CH_2Cl_2–light petroleum at 0 °C afforded bright yellow *crystals* of 1,1-$(PMe_2Ph)_2$-2,4-Ph_2-1,2,4-*closo*-$PtC_2B_9H_9$ **4**, mass 0.61 g (32%) (Found: C, 54.0; H, 5.15. Calc. for $C_{30}H_{41}B_9PtP_2$: C, 54.7; H, 5.55%). NMR: ^{1}H, δ 7.46–6.83 (m, 18 H, Ph), 5.97 (m, 2 H, Ph), 1.41 [d, 6 H, PMe, *J*(PH) 10, *J*(PtH) 42] and 0.72 [d, 6 H, PMe, *J*(PH) 10, *J*(PtH) 38]; ^{11}B,[§] δ −4.49 (br, 3 B, one coincident), −11.69 (br, 2 B), −15.84 (br, 2 B), −17.86 (br, 1 B) and −19.37 (br, 1 B); ^{11}B-{^{1}H}, δ −4.49 (3 B), −11.69 (2 B), −15.84 (2 B), −17.86 (1 B) and −19.37 (1 B); ^{31}P-{^{1}H}, δ −15.86 [d, *J*(PP) 14, *J*(PtP) 4758] and −20.00 [d br, *J*(PtP) 3792 Hz].

1,1-$(PMe_2Ph)_2$-2,4-Ph_2-7-OEt-1,2,4-*closo*-$PtC_2B_9H_8$ 5a. The compound [NEt_3H][7,9-Ph_2-3-OEt-7,9-*nido*-$C_2B_9H_9$] (0.100 g, 0.258 mmol) was deprotonated by reflux for 18 h with 2.5 equivalents of NaH in thf. This solution was added to a frozen (−196 °C) solution of [$PtCl_2(PMe_2Ph)_2$] (0.135 g, 0.248 mmol) in thf (10 cm^3). Warming to room temperature and stirring for 2 h resulted in an orange-brown solution. The solvent was removed *in vacuo* and the residue taken up in CH_2Cl_2. Filtration through a Celite pad afforded an orange-brown solution, which was reduced in volume *in vacuo* to *ca.* 2 cm^3. This was applied to the top of a column, and elution with CH_2Cl_2 afforded a bright yellow band. Recrystallisation from CH_2Cl_2–light petroleum (b.p. 60–80 °C) afforded bright yellow *microcrystals* of 1,1-$(PMe_2Ph)_2$-2,4-Ph_2-7-OEt-1,2,4-*closo*-$PtC_2B_9H_8$ **5a**, mass 0.060 g (29%) (Found: C, 46.9; H, 5.75. Calc. for $C_{32}H_{45}B_9OP_2Pt$: C, 48.0; H, 5.7%). NMR: ^{1}H, δ 7.62–6.96 (m, 18 H, Ph), 6.09 (m, 2 H, Ph), 3.67 [d of q, 1 H, OCH_2, *J*(HH) 10, 7], 3.25 [d of q, 1 H, OCH_2, *J*(HH) 10, 7], 1.46 [d, 3 H, PMe, *J*(PH) 11, *J*(PtH) 44], 1.44 [d, 3 H, PMe, *J*(PH) 11, *J*(PtH) 43], 1.10 [t, 3 H, CH_3,

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[‡] The resonances at δ −30.62 and −39.05 were observed as doublets in the ^{11}B NMR spectrum, *J*(HB) 116 and 135 Hz respectively; three overlapping resonances can be inferred from the asymmetry of the peak at δ −2.84.

[§] Broadness of peaks means that *J*(BH) was not resolved.

J(HH) 7], 0.90 [d, 3 H, PMe, J(PH) 10, J(PtH) 28] and 0.77 [d, 3 H, PMe, J(PH) 10, J(PtH) 28]; ^{11}B-{^{1}H},§ δ 0.47 (1 B), −4.61 (2 B), −6.50 (1 B), −15.67 (3 B) and −19.49 (2 B); ^{31}P-{^{1}H}, δ −16.39 [d, J(PP) 14, J(PtP) 4744] and −20.05 [d br, J(PP) 14, J(PtP) 3805 Hz.]

1,1-(PEt$_3$)$_2$-2,4-Ph$_2$-7-OEt-1,2,4-*closo*-PtC$_2$B$_9$H$_8$ 5b. In an identical manner to that described for compound **5a**; [NEt$_3$H][7,9-Ph$_2$-3-OEt-7,9-*nido*-C$_2$B$_9$H$_9$] (0.070 g, 0.162 mmol) was deprotonated and treated with [PtCl$_2$(PEt$_3$)$_2$] (0.082 g, 0.163 mmol). Chromatography afforded a fast moving minor yellow band which contained no B–H (by IR) and a subsequent major yellow band. Recrystallisation from CH$_2$Cl$_2$–light petroleum (b.p. 60–80 °C) at 3 °C afforded bright yellow *crystals* of 1,1-(PEt$_3$)$_2$-2,4-Ph$_2$-7-OEt-1,2,4-*closo*-PtC$_2$B$_9$H$_8$ **5b**, mass 0.047 g (38%) (Found: C, 43.3; H, 6 95. Calc. for C$_{28}$H$_{53}$B$_9$OP$_2$Pt: C, 44.3; H, 7.05%). NMR: ^{1}H, δ 7.38 (m, 4 H, Ph), 3.50 [d of q, 1 H, OCH$_2$, J(HH) 10, 6], 3.02 [d of q, 1 H, OCH$_2$, J(HH) 10, 6 Hz], 1.97 (m, 6 H, PCH$_2$), 1.58 (m, 6 H, PCH$_2$), 1.12–0.90 (m, 12 H, PCH$_2$CH_3 and CH$_3$) and 0.38 (m, 9 H, PCH$_2$CH_3); ^{11}B-{^{1}H},¶ δ 0.44 (1 B), −4.49 (2 B), −6.60 (1 B), −16.25 (3 B) and −20.05 (2 B); ^{31}P-{^{1}H}, δ 4.21 [d, J(PP) 7, J(PtP) 4707] and −7.52 [d br, J(PtP) 3678 Hz].

Crystallography

All measurements were carried out at room temperature on a Siemens P4 diffractometer, equipped with graphite-monochromated Mo-Kα X-radiation (λ = 0.710 73 Å). Crystallographic data are given in Table 1. Periodic remeasurement of three standard reflections revealed no significant crystal decay or electronic instability in each case. Intensity data were corrected for the effects of X-ray absorption by ψ scans.

The structures were solved without difficulty by direct methods and refined by full-matrix least squares, using SHELXTL.[8] For compound **1a** all cage H atoms were located and postionally refined with individual isotropic thermal parameters. One quarter of a molecule of CH$_2$Cl$_2$ cocrystallises per molecule of **1a**, with 0.5 of a Cl atom per asymmetric unit located *ca*. 1.5 Å from a centre of inversion; the associated C and H atoms could not be located. In **1a** the N–H distance was restrained to 0.90 Å and the thermal parameter of this H was fixed at 0.08 Å^2. For compounds **2** and **4** cage H atoms were placed in calculated positions, set 1.10 Å from B on a radial extension. Owing to the disorder present in **2**, the bridging H atom on the B(10)–B(11) edge and the hydroxyl hydrogen were not located. For all three structure determinations methyl, methylene and phenyl H atoms were constrained to idealised positions (C–H 0.97 for CH$_3$ and CH$_2$, 0.93 Å for aryl H) and given isotropic displacement parameters riding at 1.2U(C). All non-H atoms were refined with anisotropic displacement parameters. In the final stages of refinement data were weighted such that $w^{-1} = [\sigma^2(F_o) + (g_1P)^2 + g_2P]$ where $P = [\max(F_o^2$ or $0) + 2F_c^2]/3$.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/408.

Results and Discussion

Synthesis of [7,9-Ph$_2$-7,9-*nido*-C$_2$B$_9$H$_{10}$]$^-$

The target carbaborane fragment for the synthesis of 1,1-(PR$_3$)$_2$-2,4-Ph$_2$-1,2,4-*closo*-PtC$_2$B$_9$H$_9$ is [7,9-Ph$_2$-7,9-*nido*-C$_2$B$_9$H$_{10}$]$^-$, the synthesis of which was initially attempted by base degradation (KOH–EtOH) of 1,7-Ph$_2$-1,7-*closo*-C$_2$B$_{10}$H$_{10}$. Reactions in an autoclave between 160 and 200 °C afforded only two isolable products, neither of which was the anticipated [7,9-Ph$_2$-7,9-*nido*-C$_2$B$_9$H$_{10}$]$^-$ anion. Separation of these two products by fractional crystallisation afforded a major (**1a**) (*ca*. 54% yield) and a minor (**1b**) (*ca*. 5% yield) product. The ^{1}H NMR spectrum of **1a** at 400 MHz shows, as well as resonances due to phenyl groups and the triethylammonium counter ion, an apparent quartet centred at δ 3.67 of integral two and an apparent triplet at δ 1.07, integral three, suggesting the presence of a cage-bound ethoxide group. Nine inequivalent resonances (some overlapping) were observed in the ^{11}B-{^{1}H} NMR spectrum between δ 2.0 and −35.8, the region associated with {*nido*-C$_2$B$_9$} fragments. On retention of proton coupling the highest-frequency signal remained a clear singlet, indicating substitution was at one of the boron vertices. However, the site of substitution was unclear and a single-crystal X-ray diffraction experiment was performed on **1a**.

A perspective view of compound **1a**, demonstrating the atomic numbering scheme adopted, in shown in Fig. 1, whilst Table 2 lists selected bond distances and angles. Compound **1a** has a *nido* molecular architecture with an ethoxide group appended to B(3) on the lower pentagonal belt of the C$_2$B$_9$ cage. The carbaborane cage has B–B bond distances ranging between 1.746(9) and 1.833(8) Å and B–C bond lengths between 1.625(7) and 1.724(7) Å. These distances can be compared with those found in 8-SMe$_2$-7,9-*closo*-C$_2$B$_9$H$_{11}$,[9] 1.748(6)–1.841(6) and 1.583(5)–1.693(6) Å respectively.

The two phenyl substituents on the cage carbon atoms are in different orientations with respect to the cage. In *closo* 1,2-diphenylcarbaboranes (and derivatives thereof)[10] the phenyl ring conformation has been described by the parameter θ, the modulus of the average C$_{\text{cage}}$–C$_{\text{cage}}$–C$_{\text{phenyl}}$–C$_{\text{phenyl}}$ torsion angle. However, in the systems described here this parameter is no longer applicable as the cage carbon atoms are not adjacent. Instead, the twist of the phenyl rings is described by the parameter γ, the dihedral angle between the mean plane of the phenyl ring carbon atoms and the plane defined by the cage carbon atom and the two boron atoms directly in line with it when viewed down the C$_{\text{cage}}$–C$_{ipso\text{-P}}$ bond [*i.e.* C(9), B(1) and B(2)]. Using this notation values of γ may be loosely compared with values of θ. Thus, for the phenyl substituent on C(9), the aromatic ring is twisted with respect to the plane defined by C(9)–B(1)–B(2), to γ = 13.7°, lying essentially orthogonal to the open C$_2$B$_3$ face, as is the situation found in [NEt$_3$H][7,8-Ph$_2$-7,8-*nido*-C$_2$B$_9$H$_{10}$][11] where the θ value is 7.8° averaged over both phenyl rings. However, for the aryl ring attached to C(7) the proximity of the ethoxide group means that the ring is rotated to minimise steric interactions, the aromatic ring twisting with

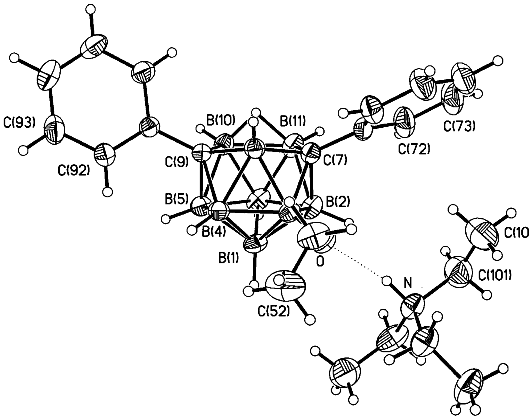

Fig. 1 Perspective view of compound **1a**. Thermal ellipsoids are drawn at the 30% probability level, except for H atoms which have an artificial radius of 0.1 Å for clarity. Phenyl rings are numbered cyclically and H atoms of the phenyl groups carry the same number as the atom to which they are attached

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¶ Broadness of peaks means that J(BH) was not resolved except for the resonance at δ −20.05 [J(BH) 109 Hz].

Table 1 Crystallographic data and details of data collection and structure refinement for compounds **1a**, **2** and **4**

	1a	**2**	**4**
Formula	$C_{22}H_{40}NO{\cdot}0.25CH_2Cl_2$	$C_{30}H_{56}B_9NO$	$C_{30}H_{41}B_9P_2Pt$
M	453.07	544.05	755.95
System	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
a/Å	15.806(2)	15.727(2)	10.2034(9)
b/Å	12.4146(14)	10.5290(11)	19.410(2)
c/Å	14.549(4)	20.479(3)	16.670(2)
β/°	98.691(11)	93.386(13)	94.160(7)
U/Å	2822.0(8)	3385.4(7)	3292.9(5)
Z	4	4	4
D_c/g cm^{-3}	1.066	1.067	1.525
μ(Mo-Kα)/mm^{-1}	0.104	0.058	4.379
F(000)	970	1184	1496
$\theta_{\text{orientation}}$/°	5.1–12.1	3.3–11.1	3.7–12.9
$\theta_{\text{data collection}}$/°	1–25	1–25	2–25
hkl Ranges	−18 to 18, 1 to −14, −1 to 17	−1 to 18, −1 to 12, −24 to 24	−1 to 12, −1 to 23, −19 to 19
ω-Scan speed/° min^{-1}	1.5–40	1.5–30	1.5–60
Data measured	6054	7359	7232
Unique data	4898	5902	5755
g_1	0.2494	0.1414	0.0385
g_2	0.66	4.31	10.52
R (all data)	0.1727	0.2301	0.0638
Data observed [$F_o > 4\sigma(F_o)$]	2682	2288	4329
R (observed data)	0.1130	0.0984	0.0396
$wR2$	0.3245	0.2472	0.0993
S	1.072	0.994	1.097
Variables	346	385	379
Maximum, minimum residue/e Å^{-3}	1.538, −0.260	0.831, −0.296	0.569, −1.169

Table 2 Bond lengths (Å) and selected interbond angles (°) in compound **1a**

O−C(51)	1.413(6)	O−B(3)	1.417(6)	B(5)−C(9)	1.670(7)	B(4)−B(8)	1.806(7)
B(1)−B(5)	1.750(8)	B(1)−B(2)	1.746(9)	B(5)−B(10)	1.824(8)	B(5)−B(6)	1.807(9)
B(1)−B(4)	1.799(8)	B(1)−B(6)	1.792(8)	B(6)−B(10)	1.799(8)	B(6)−B(11)	1.784(9)
B(2)−C(7)	1.686(7)	B(1)−B(3)	1.805(8)	C(7)−B(8)	1.626(7)	C(7)−C(71)	1.507(7)
B(2)−B(6)	1.775(8)	B(2)−B(3)	1.761(8)	B(8)−C(9)	1.625(7)	C(7)−B(11)	1.666(7)
B(3)−C(7)	1.724(7)	B(2)−B(11)	1.813(8)	C(9)−B(10)	1.647(7)	C(9)−C(91)	1.511(6)
B(3)−B(8)	1.815(7)	B(3)−B(4)	1.771(8)	C(51)−C(52)	1.454(9)	B(10)−B(11)	1.833(8)
B(4)−B(5)	1.766(8)	B(4)−C(9)	1.694(6)				
C(51)−O−B(3)	120.6(4)	B(2)−B(1)−B(6)	60.2(3)	B(2)−B(6)−B(1)	58.6(3)	B(11)−B(6)−B(10)	61.5(3)
B(5)−B(1)−B(6)	61.4(3)	B(5)−B(1)−B(4)	59.7(3)	B(1)−B(6)−B(5)	58.2(3)	B(10)−B(6)−B(5)	60.8(3)
B(2)−B(1)−B(3)	59.4(3)	B(4)−B(1)−B(3)	58.9(3)	C(71)−C(7)−B(8)	121.1(4)	C(71)−C(7)−B(11)	119.6(4)
C(7)−B(2)−B(3)	60.0(3)	B(1)−B(2)−B(3)	62.0(3)	C(71)−C(7)−B(2)	120.2(4)	B(11)−C(7)−B(2)	65.5(3)
B(1)−B(2)−B(6)	61.2(3)	C(7)−B(2)−B(11)	56.8(3)	C(71)−C(7)−B(3)	116.7(4)	B(8)−C(7)−B(3)	65.5(3)
B(6)−B(2)−B(11)	59.6(3)	O−B(3)−C(7)	121.5(4)	B(2)−C(7)−B(3)	62.2(3)	C(9)−B(8)−B(4)	58.9(3)
O−B(3)−B(2)	119.4(4)	C(7)−B(3)−B(2)	57.8(3)	C(7)−B(8)−B(3)	59.9(3)	B(4)−B(8)−B(3)	58.6(3)
O−B(3)−B(4)	125.3(4)	O−B(3)−B(1)	123.9(4)	C(91)−C(9)−B(8)	121.0(4)	C(91)−C(9)−B(10)	118.3(4)
B(2)−B(3)−B(1)	58.6(3)	B(4)−B(3)−B(1)	60.4(3)	C(91)C(9)−B(5)	119.1(4)	B(8)−C(9)−B(5)	113.5(4)
O−B(3)−B(8)	129.4(4)	C(7)−B(3)−B(8)	54.6(3)	B(10)−C(9)−B(5)	66.7(3)	C(91)−C(9)−B(4)	117.5(4)
B(4)−B(3)−B(8)	60.5(3)	C(9)−B(4)−B(5)	57.7(3)	B(8)−C(9)−B(4)	65.9(3)	B(5)−C(9)−B(4)	63.3(3)
B(3)−B(4)−B(1)	60.7(3)	B(5)−B(4)−B(1)	58.8(3)	C(9)−B(10)−B(5)	57.2(3)	B(6)−B(10)−B(5)	59.8(3)
C(9)−B(4)−B(8)	55.2(3)	B(3)−B(4)−B(8)	61.0(3)	B(6)−B(10)−B(11)	58.8(3)	C(7)−B(11)−B(2)	57.8(3)
C(9)−B(5)−B(4)	59.0(3)	B(1)−B(5)−B(4)	61.6(3)	B(6)−B(11)−B(2)	59.1(3)	B(6)−B(11)−B(10)	59.6(3)
B(1)−B(5)−B(6)	60.5(3)	C(9)−B(5)−B(10)	56.0(3)	O−C(51)−C(52)	114.0(5)		
B(6)−B(5)−B(10)	59.4(3)	B(2)−B(6)−B(11)	61.3(3)				

respect to C(7)−B(1)−B(5), to γ = 79.1°. The B(3)−O bond length is 1.417(6) Å, which is in the range for such bonds,[12] and the B−B connectivities to B(3) are not significantly distorted. The molecule crystallises with one close intermolecular contact with the $[NEt_3H]^+$ counter ion, a hydrogen bond being present in the solid state between O and H(90) at 1.915 Å.

With the result of the structure determination of compound **1a** thus established, re-examination of the ^1H NMR spectrum shows that, although the methylene protons on the ethoxide group are chemically inequivalent, they are apparently sufficiently magnetically similar to be observed as only one apparent quartet (even at 400 MHz). This is not the case, however, for the minor product, **1b**. For this species the ethoxide substituent is observed as two quartets at δ 3.59 and δ 3.42, both integrating to one proton each and a double of doublets (apparent triplet) at δ 0.93, equivalent to three protons. The ^{11}B-{^1H} NMR spectrum displays at least seven overlapping inequivalent boron environments between δ 0.53 and −39.05, suggesting that in **1b** the ethoxide is substituted at either B(2) or B(11), assuming that the cage carbons have not undergone rearrangement. However, the shielding pattern of a {7,9-Ph_2-7,9-*nido*-C_2B_9} fragment substituted at B(11) (see below) is different to that observed for **1b**. Thus we assign **1b** as [NEt_3H][2-OEt-7,9-Ph_2-7,9-*nido*-$C_2B_9H_9$].

It has previously been reported that, under similar conditions to those employed here, 1,7-Me_2-1,7-*closo*-$C_2B_{10}H_{10}$ undergoes base degradation to afford an alkoxy-substituted 7,9-Me_2-7,9-*nido*-C_2B_9 cage.[13] On the basis of chemical and NMR experiments, the position of the alkoxy substituent was determined to be at B(3), consistent with the solid-state structure reported here for compound **1a**. However, no other isomeric form (*e.g.* substitution in the 2 position) was reported.

Table 3 Bond lengths (Å) and selected interbond angles (°) in compound **2**

B(1)–B(2)	1.750(11)	B(1)–B(5)	1.754(10)	B(5)–B(6)	1.747(12)	B(5)–B(10)	1.789(12)
B(1)–B(3)	1.775(9)	B(1)–B(6)	1.783(13)	B(6)–B(10)	1.788(11)	B(6)–B(11)	1.813(11)
B(1)–B(4)	1.789(10)	B(2)–C(7)	1.676(9)	C(7)–C(71)	1.501(7)	C(7)–B(8)	1.607(10)
B(2)–B(3)	1.764(11)	B(2)–B(6)	1.786(10)	C(7)–B(11)	1.665(8)	B(8)–C(9)	1.580(9)
B(2)–B(11)	1.827(11)	B(3)–C(7)	1.684(9)	C(9)–C(91)	1.495(8)	C(9)–B(10)	1.659(9)
B(3)–B(4)	1.780(10)	B(3)–B(8)	1.830(12)	B(10)–O(1A)	1.375(9)	B(10)–B(11)	1.812(10)
B(4)–C(9)	1.702(9)	B(4)–B(5)	1.780(10)	B(11)–O(1B)	1.356(13)		
B(4)–B(8)	1.841(12)	B(5)–C(9)	1.665(9)				
B(2)–B(1)–B(3)	60.1(4)	B(2)–B(1)–B(6)	60.7(4)	C(71)–C(7)–B(8)	122.7(5)	C(71)–C(7)–B(11)	117.7(5)
B(5)–B(1)–B(6)	59.2(5)	B(5)–B(1)–B(4)	60.3(4)	C(71)–C(7)–B(2)	120.2(5)	B(11)–C(7)–B(2)	66.3(4)
B(3)–B(1)–B(4)	59.9(4)	C(7)–B(2)–B(3)	58.6(4)	B(8)–C(7)–B(3)	67.5(5)	B(2)–C(7)–B(3)	63.3(4)
B(1)–B(2)–B(3)	60.6(4)	B(1)–B(2)–B(6)	60.5(5)	C(7)–B(8)–B(3)	58.3(4)	C(9)–B(8)–B(4)	59.1(4)
C(7)–B(2)–B(11)	56.6(4)	B(6)–B(2)–B(11)	60.2(4)	B(3)–B(8)–B(4)	58.0(4)	C(91)–C(9)–B(8)	120.5(5)
C(7)–B(3)–B(2)	58.1(4)	B(2)–B(3)–B(1)	59.3(4)	C(91)–C(9)–B(10)	119.7(5)	C(91)–C(9)–B(5)	122.0(5)
B(1)–B(3)–B(4)	60.4(4)	C(7)–B(3)–B(8)	54.2(4)	B(10)–C(9)–B(5)	65.1(5)	C(91)–C(9)–B(4)	117.4(5)
B(4)–B(3)–B(8)	61.3(4)	C(9)–B(4)–B(5)	57.1(4)	B(8)–C(9)–B(4)	68.2(5)	B(5)–C(9)–B(4)	63.8(4)
B(5)–B(4)–B(1)	58.9(4)	B(3)–B(4)–B(1)	59.6(4)	O(1A)–B(10)–C(9)	119.1(6)	O(1A)–B(10)–B(6)	116.4(7)
C(9)–B(4)–B(8)	52.8(4)	B(3)–B(4)–B(8)	60.7(4)	O(1A)–B(10)–B(5)	108.7(7)	C(9)–B(10)–B(5)	57.6(4)
B(6)–B(5)–B(1)	61.2(5)	C(9)–B(5)–B(4)	59.1(4)	B(6)–B(10)–B(5)	58.5(5)	O(1A)–B(10)–B(11)	131.8(7)
B(1)–B(5)–B(4)	60.8(4)	C(9)–B(5)–B(10)	57.3(4)	B(6)–B(10)–B(11)	60.5(4)	O(1B)–B(11)–C(7)	122.8(7)
B(6)–B(5)–B(10)	60.7(5)	B(5)–B(6)–B(1)	59.6(5)	O(1B)–B(11)–B(6)	118.6(8)	O(1B)–B(11)–B(10)	128.1(7)
B(1)–B(6)–B(2)	58.7(5)	B(5)–B(6)–B(10)	60.8(4)	B(6)–B(11)–B(10)	59.1(4)	O(1B)–B(11)–B(2)	114.3(8)
B(2)–B(6)–B(11)	61.0(4)	B(10)–B(6)–B(11)	60.4(4)	C(7)–B(11)–B(2)	57.2(4)	B(6)–B(11)–B(2)	58.8(4)

As we are interested in the consequences of treating [7,9-Ph_2-7,9-*nido*-$C_2B_9H_9$]$^{2-}$ with [$PtCl_2(PMe_2Ph)_2$], the associated implications of cage phenyl-induced distortions and, specifically, comparison of the products of such a reaction with those from [7,8-Ph_2-7,8-*nido*-$C_2B_9H_9$]$^{2-}$, the presence of an appended ethoxide group on the cage of compounds **1a** and **1b** was unwanted, and an alternative route to cage degradation was sought.

Treatment of 1,7-Ph_2-1,7-*closo*-$C_2B_{10}H_{10}$ with 5 equivalents of [NBu_4] (thf solution, *ca*. 5% water) in thf at room temperature gave no reaction. However, heating the reaction mixture to reflux for 18 h resulted in complete conversion of the starting material into a *nido* product **2**. The ^{11}B-{^{1}H} NMR spectrum showed that the product was not the anticipated mirror symmetric [7,9-Ph_2-7,9-*nido*-$C_2B_9H_{10}$]$^-$ species, displaying nine inequivalent boron environments in the range δ 3.4 to −33.7, with a shielding pattern significantly different from that found in **1a** or **1b**. The ^{11}B NMR spectrum indicated substitution at one of the boron vertices, the resonance at δ 3.67 remaining a singlet on proton coupling. Positive-ion FAB mass spectrometry and microanalysis suggested the formulation of **2** to be [NBu_4][$C_2Ph_2B_9H_9X$], where X was either OH or F. Fluoride substitution on the cage (the opening of a *closo*-C_2B_6 cluster to afford a *nido*-species with fluoride incorporated having previously been reported[14]) was initially ruled out by the absence of a signal in the ^{19}F NMR spectrum. Additionally, a broad peak in the IR spectrum, centred at 3443 cm^{-1} was assigned to an OH group stretch. A single-crystal X-ray diffraction study was carried out on compound **2** in order to attempt to confirm the position and identity of this substituent.

A perspective view of a single molecule of compound **2** showing the atom labelling scheme is shown in Fig. 2, with salient bond lengths and angles given in Table 3. The molecular architecture is *nido*-C_2B_9, with a single hydroxyl group appended to one of the symmetry-equivalent boron atoms of the open C_2B_3 face. The hydroxyl group is crystallographically disordered between O(1A) and O(1B), the occupancy at O(1A) being 60.51(6)%. The aromatic cage substituents on C(7) and C(9) lie essentially orthogonal to the C_2B_3 face ($\gamma = 19.6$ and 6.1° respectively). The B–B bonds lengths range between 1.747(12) and 1.841(12) Å, with the C–B lengths 1.580(9)–1.702(9) Å. The B(10)–O(1A) and B(11)–O(1B) lengths are 1.375(9) and 1.356(13) Å respectively (average 1.365 Å). These compare with 1.384(5) Å in 6-Me_2S-4-OH-2-$(Me_3Si)_2CH$-*closo*-$CB_{10}H_8$,[15] 1.35(1) and 1.37(1) Å in 2,3-Me_2-4,7-$(OH)_2$-10-Br-2,3-*closo*-$C_2B_9H_6$[16] and 1.406(4) Å in 8-OH-9-Me-6-*nido*-$CB_{10}H_{10}$.[17] No indication of significant B–B connectivity lengthening around the B–OH bond was observed,[15,16] as has previously been noted in *closo*-hydroxyl-substituted carbaborane systems.

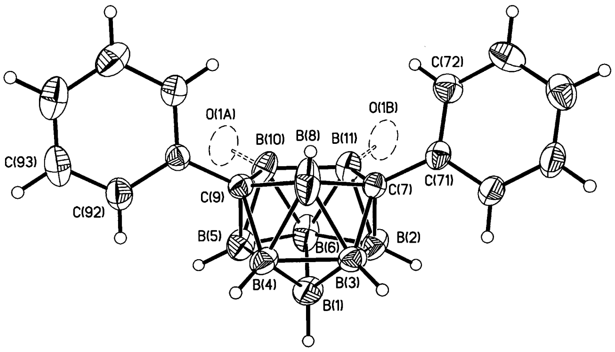


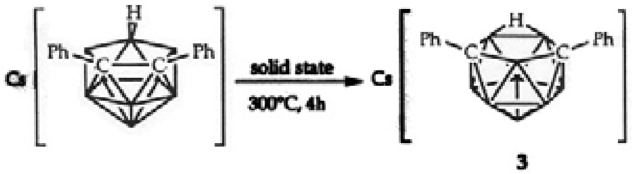
Fig. 2 Perspective view of the anion of compound **2**. Construction and labelling conventions as in Fig. 1

Unfortunately, the solid-state structural determination of compound **2** does not allow the distinction between OH and F, and a degree of caution must be employed in the assignment of the appended group. Noteworthy, though, is that water is strongly intimated in the mechanism of fluoride-induced deboronation.[14]

The inability of either base- or fluoride-induced deboronation to afford the required product led us to consider a different method.[18] Thus, we attempted to isomerise Cs[7,8-Ph_2-7,8-*nido*-$C_2B_9H_{10}$] by heating a sample in a sealed tube for 4 h at 300 °C, following a method described previously.[7] The product recovered displayed a ^{11}B-{^{1}H} NMR spectrum which demonstrated that the molecule possessed a mirror plane of symmetry, with only five resonances observed (δ 0.7 to −32.8) in the ratio 3:2:2:1:1 (the first signal coincident); this spectrum is clearly not that of the 7,8-C_2B_9 starting material. Analysis of a ^{11}B–^{11}B (correlation spectroscopy, COSY) spectrum confirmed the identity of the product as Cs[7,9-Ph_2-7,9-*nido*-$C_2B_9H_{10}$] (Scheme 1), which was converted into the required [NEt_3H]$^+$ salt **3** by simple metathesis.

Reaction with [$PtCl_2(PMe_2Ph)_2$]

Deprotonation of compound **3**, by heating to reflux in thf with an excess of sodium hydride, and subsequent reaction with



3

Scheme 1

1 equivalent of $[PtCl_2(PMe_2Ph)_2]$ affords compound **4**, 1,1-$(PMe_2Ph)_2$-2,4-Ph_2-1,2,4-*closo*-$PtC_2B_9H_9$, in moderate yield after chromatographic work-up. The ^{11}B-{^1H} NMR spectrum of **4** consists of five broad resonances between δ −4.5 and −19.4 in the ratio 3:2:2:1:1 (first resonance coincident), demonstrating that the molecule has a mirror plane of symmetry in solution. The ^1H NMR spectrum displays the expected aromatic resonances equivalent to four phenyl groups. In the alkyl region two doublets each of integral six, displaying coupling to phosphorus and platinum, are observed, at δ 1.41 and 0.72, due to the two pairs of equivalent methyl groups. The ^{31}P-{^1H} NMR spectrum shows two resonances both displaying ^{195}Pt satellites, a sharp doublet at δ −15.8 and a slightly broadened signal at δ −20.0 [*J*(PP) not resolved], demonstrating that the {PtP_2} fragment is static on the NMR time-scale, and not rotating with respect to the carbaborane cage. The NMR evidence strongly suggests that the molecule has not undergone rearrangement to give an asymmetric 2,1,8-PtC_2 cage architecture, but has instead retained a 1,2,4-PtC_2B_9 stereochemistry. Nevertheless, a single-crystal X-ray diffraction study was performed in order fully to confirm the positions of the cage carbon atoms.

A perspective view of a single molecule of compound **4**, showing the atom labelling scheme, is in Fig. 3, with bond lengths and selected interbond angles in Table 4. As can be clearly seen, cage-carbon isomerisation has not occurred and the 1,2,4-MC_2B_9 cage architecture predicted persists. The platinum atom lies 1.836 Å above the C_2B_3 face, with the phenyl rings adopting relatively high values of γ, due to the steric influence of the bis(phosphine)platinum unit.[3,19] Thus for the aryl ring C(21)–C(26) γ = 74.4° and for C(41)–C(46) γ = 80.9°. The Pt–B bonds lengths are 2.256(9), 2.278(9) and 2.316(9) Å, similar to those found in 1,1-$(PMe_2Ph)_2$-2,4-Me_2-1,2,4-*closo*-$PtC_2B_9H_9$[20] (compound **A**) although Pt–B(3) is slightly longer in **4** [2.316(9) *vs.* 2.270(9) Å]. The Pt–C bond lengths at 2.424(8) and 2.508(8) Å are comparable with those found in **A** at 2.452(8) and 2.442(7) Å, although Pt(1)–C(4) is somewhat longer and Pt(1)–C(2) shorter in **4**. The {PtP_2} fragment lies essentially coplanar with the plane defined by B(3), B(10) and B(12), as predicted by molecular orbital calculations,[21] the small twist of the {PtP_2} plane (9.8°) being attributed to a minimisation of steric interactions between the methyl group C(102) and the cage-carbon phenyl rings. That apart the only major deviations from C_s symmetry in the solid state arise from the orientation of the two PMe_2Ph groups, themselves related by an effective C_2 axis bisecting the P–Pt–P angle. The co-ordination around the platinum atom can best be described as approximately square planar [P(1)–Pt–P(2) 96.02(8), P(1)–Pt–B(3) 97.0(2)°]. The greater *trans* influence[20] of B(5)B(6) over B(3) is demonstrated clearly in the Pt–P bond lengths, Pt–P(1) being appreciably longer [2.307(2) Å] than Pt–P(2) [2.253(2) Å], a situation which mirrors that found in **A**. The B–B bond lengths are in the range 1.74(2)–1.86(2) Å, the C–B bond lengths in the range 1.679(12)–1.718(13) Å, both consistent with those found in other 1,2,4-*closo*-MC_2B_9 systems.[20,22] Previously, distortions of the metal fragment in carbametallaboranes have been described in terms of 'slip' and 'fold' parameters. In 3,1,2-PtC_2B_9 systems overlap of cage and metal molecular orbitals means the slip (Δ) is large and positive [that is towards B(4), B(5) and B(6)], whereas in 1,2,4-PtC_2B_9 systems it is significantly smaller and negative [towards B(3)]. Indeed, in compound **4** the metal is slipped by only Δ = −0.19 Å, which can be compared with −0.13 Å in 1,1-$(PMe_2Ph)_2$-2,4-Me_2-1,2,4-*closo*-$PtC_2B_9H_9$[20] and +0.42 Å in 3,3-$(PEt_3)_2$-3,1,2-*closo*-$PtC_2B_9H_{11}$.[21]

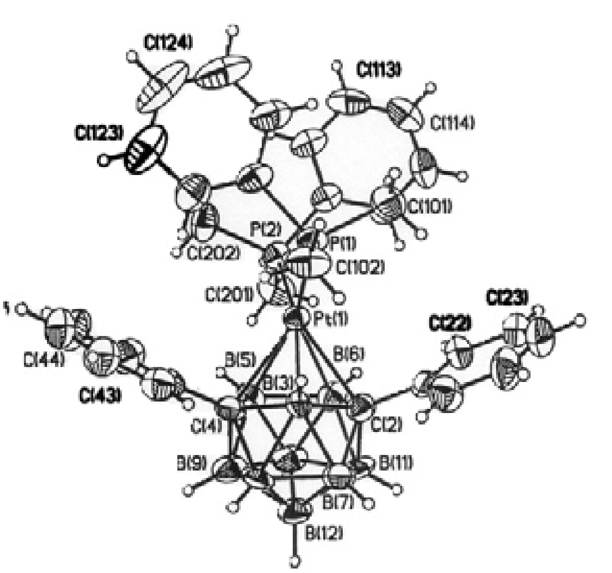


Fig. 3 Perspective view of compound **4**. Construction and labelling conventions as in Fig. 1

That one of the phosphorus atoms [P(1)] is transoid to the high-*trans*-influence boron atoms B(5) and B(6) is consistent with the ^{31}P-{^1H} NMR spectrum, the (broader) phosphorus signal which resonates at lower frequency showing a smaller ^{195}Pt–^{31}P coupling. Additionally, in the ^1H NMR spectrum, the lower-frequency alkyl signal displays a smaller magnitude of *J*(PtH) and thus is assigned to the equivalent methyl groups C(101) and C(102).

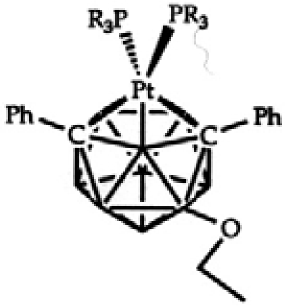
It has previously been observed that the monophenyl-substituted carbaplatinaborane 1-Ph-3,3-$(PMe_2Ph)_2$-3,1,2-*closo*-$PtC_2B_9H_{10}$ undergoes cage-carbon isomerisation to the 2,1,8-MC_2B_9 isomer at *ca.* 55 °C.[3] This facile isomerisation, in the absence of severe steric congestion from two adjacent phenyl groups, is attributed to 'ground-state destabilisation' of the {PtP_2} fragment, forced to adopt a non-preferred conformation by the presence of the single cage phenyl group. No such perturbations from the electronically preferred geometry are present in compound **4** and this was confirmed by no change observed (by NMR spectroscopy) on heating a toluene solution of **4** to reflux for 1 h.

Reaction between compound 1a and $[PtCl_2(PR_3)]$ (R_3 = Et_3 or Me_2Ph)

Under the same conditions as described for the synthesis of compound **4** $[PtCl_2(PMe_2Ph)_2]$ and $[PtCl_2(PEt_3)_2]$ were treated with Na_2[7,9-Ph_2-3-OEt-7,9-*nido*-$C_2B_9H_8$] to afford the new compounds 1,1-$(PMe_2Ph)_2$-2,4-Ph_2-7-OEt-1,2,4-*closo*-$PtC_2B_9H_8$ **5a** and 1,1-$(PEt_3)_2$-2,4-Ph_2-7-OEt-1,2,4-*closo*-$PtC_2B_9H_8$ **5b** in moderate yield. The NMR spectra of both **5a** and **5b** show the same salient features, and thus only those for **5a** are discussed, comments made also holding for **5b**. In the ^{31}P-{^1H} NMR spectrum two phosphorus environments are observed, demonstrating that the {PtP_2} fragment does not rotate on the NMR time-scale. Two doublets centred at δ −16.39 and −20.05 display the expected ^{31}P and ^{195}Pt couplings, the signal at lower frequency having the smaller ^{195}Pt–^{31}P coupling constant, as found for compound **4**. In the ^1H NMR spectrum two doublets of quartets corresponding to the ethoxide methylene protons are observed, centred at δ 3.67 and 3.25. An apparent triplet, integrating to three protons at δ 1.10, is assigned to the ethoxide methyl group. The four inequivalent phosphine methyl groups display the expected ^{31}P and ^{195}Pt couplings, the two signals at lower frequency again displaying smaller magnitudes of *J*(PtH).

Table 4 Bond lengths (Å) and selected interbond angles (°) in compound **4**

Pt(1)–P(2)	2.253(2)	Pt(1)–B(6)	2.256(9)	B(3)–B(8)	1.829(12)	C(4)–C(41)	1.514(13)
Pt(1)–B(5)	2.278(9)	Pt(1)–P(1)	2.307(2)	C(4)–B(5)	1.679(12)	C(4)–B(8)	1.684(12)
Pt(1)–B(3)	2.316(9)	Pt(1)–C(2)	2.424(8)	C(4)–B(9)	1.694(12)	B(5)–B(9)	1.758(14)
Pt(1)–C(4)	2.508(8)	P(1)–C(121)	1.811(9)	B(5)–B(10)	1.763(14)	B(5)–B(6)	1.862(14)
P(1)–C(101)	1.813(10)	P(1)–C(102)	1.814(9)	B(6)–B(10)	1.77(2)	B(6)–B(11)	1.780(14)
P(2)–C(201)	1.808(8)	P(2)–C(111)	1.810(9)	B(7)–B(8)	1.76(2)	B(7)–B(12)	1.763(14)
P(2)–C(202)	1.813(9)	C(2)–C(21)	1.510(11)	B(7)–B(11)	1.79(2)	B(8)–B(9)	1.75(2)
C(2)–B(7)	1.680(13)	C(2)–B(6)	1.699(12)	B(8)–B(12)	1.75(2)	B(9)–B(12)	1.74(2)
C(2)–B(11)	1.716(12)	C(2)–B(3)	1.718(13)	B(9)–B(10)	1.77(2)	B(10)–B(11)	1.786(14)
B(3)–C(4)	1.705(11)	B(3)–B(7)	1.797(13)	B(10)–B(12)	1.79(2)	B(11)–B(12)	1.76(2)
P(2)–Pt(1)–B(6)	99.6(3)	P(2)–Pt(1)–B(5)	93.5(2)	C(41)–C(4)–B(5)	123.2(7)	C(41)–C(4)–B(8)	117.5(7)
B(6)–Pt(1)–B(5)	48.5(4)	P(2)–Pt(1)–P(1)	96.02(8)	B(5)–C(4)–B(9)	62.8(6)	B(8)–C(4)–B(9)	62.3(6)
B(6)–Pt(1)–P(1)	148.8(3)	B(5)–Pt(1)–P(1)	156.6(3)	B(8)–C(4)–B(3)	65.3(5)	B(9)–C(4)–B(3)	112.4(7)
P(2)–Pt(1)–B(3)	164.3(2)	B(6)–Pt(1)–B(3)	73.2(4)	B(5)–C(4)–Pt(1)	62.3(4)	B(3)–C(4)–Pt(1)	63.4(4)
B(5)–Pt(1)–B(3)	71.2(3)	P(1)–Pt(1)–B(3)	97.0(2)	C(4)–B(5)–B(9)	59.0(5)	B(9)–B(5)–B(10)	60.5(6)
P(2)–Pt(1)–C(2)	137.9(2)	B(6)–Pt(1)–C(2)	42.4(3)	B(10)–B(5)–B(6)	58.4(6)	C(4)–B(5)–Pt(1)	77.0(4)
B(5)–Pt(1)–C(2)	74.0(3)	P(1)–Pt(1)–C(2)	111.4(2)	B(6)–B(5)–Pt(1)	65.1(4)	C(2)–B(6)–B(11)	59.1(5)
B(3)–Pt(1)–C(2)	42.4(3)	P(2)–Pt(1)–C(4)	123.9(2)	B(10)–B(6)–B(11)	60.4(6)	B(10)–B(6)–B(5)	58.0(6)
B(6)–Pt(1)–C(4)	74.4(4)	B(5)–Pt(1)–C(4)	40.7(3)	C(2)–B(6)–Pt(1)	74.1(4)	B(5)–B(6)–Pt(1)	66.4(4)
P(1)–Pt(1)–C(4)	117.9(2)	B(3)–Pt(1)–C(4)	41.1(3)	B(8)–B(7)–B(12)	59.6(6)	C(2)–B(7)–B(11)	59.3(5)
C(2)–Pt(1)–C(4)	70.8(3)	C(121)–P(1)–C(101)	106.4(5)	B(12)–B(7)–B(11)	59.6(6)	C(2)–B(7)–B(3)	59.1(5)
C(121)–P(1)–C(102)	100.8(4)	C(101)–P(1)–C(102)	101.5(5)	B(8)–B(7)–B(3)	62.0(5)	C(4)–B(8)–B(9)	59.1(5)
C(121)–P(1)–Pt(1)	114.0(3)	C(101)–P(1)–Pt(1)	115.4(3)	B(9)–B(8)–B(12)	59.7(6)	B(12)–B(8)–B(7)	60.4(6)
C(102)–P(1)–Pt(1)	116.9(3)	C(201)–P(2)–C(111)	100.4(4)	C(4)–B(8)–B(3)	57.9(5)	B(7)–B(8)–B(3)	60.1(5)
C(201)–P(2)–C(202)	101.0(5)	C(111)–P(2)–C(202)	106.3(4)	C(4)–B(9)–B(8)	58.6(5)	B(12)–B(9)–B(8)	60.3(6)
C(201)–P(2)–Pt(1)	115.7(3)	C(111)–P(2)–Pt(1)	116.8(3)	C(4)–B(9)–B(5)	58.2(5)	B(12)–B(9)–B(10)	61.1(7)
C(202)–P(2)–Pt(1)	114.5(3)	C(21)–C(2)–B(7)	115.4(7)	B(5)–B(9)–B(10)	59.9(6)	B(5)–B(10)–B(6)	63.6(5)
C(21)–C(2)–B(6)	124.2(8)	C(21)–C(2)–B(11)	119.4(7)	B(5)–B(10)–B(9)	59.6(6)	B(6)–B(10)–B(11)	60.1(6)
B(7)–C(2)–B(11)	63.4(6)	B(6)–C(2)–B(11)	62.8(5)	B(9)–B(10)–B(12)	58.5(6)	B(11)–B(10)–B(12)	59.1(6)
C(21)–C(2)–B(3)	119.0(7)	B(7)–C(2)–B(3)	63.9(6)	C(2)–B(11)–B(6)	58.1(5)	C(2)–B(11)–B(7)	57.3(5)
C(21)–C(2)–Pt(1)	106.2(5)	B(6)–C(2)–Pt(1)	63.5(4)	B(12)–B(11)–B(7)	59.6(6)	B(12)–B(11)–B(10)	60.4(7)
B(3)–C(2)–Pt(1)	65.4(4)	C(2)–B(3)–B(7)	57.1(5)	B(6)–B(11)–B(10)	59.5(6)	B(9)–B(12)–B(8)	60.1(6)
C(4)–B(3)–B(8)	56.8(5)	B(7)–B(3)–B(8)	57.9(5)	B(8)–B(12)–B(7)	60.0(6)	B(11)–B(12)–B(7)	60.8(6)
C(4)–B(3)–Pt(1)	75.5(4)	C(2)–B(3)–Pt(1)	72.1(4)	B(9)–B(12)–B(10)	60.4(7)	B(11)–B(12)–B(10)	60.4(6)



5a $R_3 = Me_2Ph$

5b $R_3 = Et_3$

The $^{11}B-\{^1H\}$ NMR spectrum is relatively uninformative and consists of five broad resonances between δ 0.47 and −19.49 in the ratio 1:2:1:3:2. A preliminary X-ray structural determination on compound **5b**[23] shows that the molecule is essentially isostructural with **4**, apart from the appended ethoxide group, and that no cage-carbon isomerisation has occurred.

Conclusion

The isolation of complex **4** has clear implications for the mechanism of cage-carbon isomerisation in this class of compound. To restate, 1,2-Ph_2-3,3-$(PMe_2Ph)_2$-3,1,2-*closo*-$PtC_2B_9H_9$ cannot be isolated, affording 1,1-$(PMe_2Ph)_2$-2,8-Ph_2-1,2,8-*closo*-$PtC_2B_9H_9$ by a sterically induced rearrangement at temperatures below 20 °C.[3] The hextuple-concerted d.s.d. mechanism,[24] *via* a cuboctahedral intermediate, cannot be operating in this particular system since, in such a mechanism, the first product of rearrangement (which would have a 1,2,4-PtC_2B_9 substitution pattern) must necessarily be unstable and rearrange immediately to give the observed 2,1,8-PtC_2B_9 cage architecture. We have isolated this 'intermediate', compound **4** and the related **5a** and **5b**, and shown **4** to be stable to rearrangement in boiling toluene.

Over the years a number of alternative rearrangement mechanisms for *closo*-C_2B_{10} systems have been suggested, including rotation of two fused pentagonal-pyramid cluster halves,[25] (extended) triangular face rotation[26] and involvement of a 12-vertex *nido* intermediate.[27] As to which, if any, of these mechanisms is operating in the carbaplatinaborane system is not clear. Noteworthy is the fact that the majority of carba(metalla)borane isomerisations take place at elevated temperature, there being relatively few reports of low (ambient or lower)-temperature isomerisations,[3,22a] and that any mechanism postulated for the rearrangement must pass through a low-energy intermediate. Experiments are currently underway to help us elucidate the mechanism(s) of cage-carbon isomerisation operating in heteroborane systems and preliminary results have shown that intermediate species may, under certain conditions, be amenable to isolation.[1]

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