Steric Effects in Heteroboranes. Part 9.[1] Cycloocta-1,5-diene Palladium and Platinum Complexes of Mono- and Di-phenyl C_2B_9 Ligands: Metal-mediated Polyhedral Rearrangement‡

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The compounds 1-Ph-3-(cod)-3,1,2-$PdC_2B_9H_{10}$ **1a**, 1,2-Ph_2-3-(cod)-3,1,2-$PdC_2B_9H_9$ **2a**, 1-Ph-3-(cod)-3,1,2-$PtC_2B_9H_{10}$ **3a**, and 1,11-Ph_2-3-(cod)-3,1,11-$PtC_2B_9H_9$ **4**, have been prepared from the reactions between Tl_2[7-Ph-*nido*-7,8-$C_2B_9H_{10}$] or Tl_2[7,8-Ph_2-*nido*-7,8-$C_2B_9H_9$] and [$PdCl_2$(cod)] or [$PtCl_2$(cod)] as appropriate (cod = cycloocta-1,5-diene). The platinum reactions are considerably cleaner than the palladium ones. Compound **2a** was subjected to a crystallographic study which reveals severe intramolecular overcrowding; the palladium atom is slipped by 0.56 Å away from the C-bound phenyl groups, the co-ordination of the cod ligand to the metal is distorted and the cage is deformed with extended C–B distances in the ligand face. Although **1a** and **3a** are structural analogues, **2a** and **4** are not. Rather, compound **4** is only isolated as the C-separated species defined by a 3,1,11-PtC_2B_9 architecture, thus illustrating that the nature of the metal atom can influence the ease with which carbametallaboranes undergo polyhedral rearrangement. Compound **1a** was recovered unchanged from refluxing toluene, but under the same conditions **2a** was converted into **2a'**, tentatively identified as the rearranged isomer 1,11-Ph_2-3-(cod)-3,1,11-$PdC_2B_9H_9$.

In previous papers in this series we have demonstrated that unusual molecular structures and interesting reactivities can result from deliberately making heteroboranes overcrowded. Thus, in 1,2-Ph_2-3-η-C_5Me_5-3,1,2-$RhC_2B_9H_9$ the cage adopts an unusual *pseudocloso* structure to relieve congestion between the adjacent phenyl rings, forced to lie nearly coplanar by the C_5Me_5 ligand.[2] Moreover, in 1-Ph-3,3-$(PMe_2Ph)_2$-3,1,2-$PtC_2B_9H_{10}$ the $\{PtL_2\}$ fragment is required to adopt a conformation relative to the carbaborane ligand face that is sterically and not electronically preferred; as such it is ground-state destabilised and isomerises to two C_{cage}-separated isomers at only 55 °C.[3] The analogous species 1,2-Ph_2-3,3-$(PMe_2Ph)_2$-3,1,2-$PtC_2B_9H_9$ cannot be isolated, rather it spontaneously rearranges to 1,11-Ph_2-3,3-$(PMe_2Ph)_2$-3,1,11-$PtC_2B_9H_9$ to avoid overcrowding between the phosphine ligands and cage-bound phenyl groups.[3] Finally, we have very recently shown[1] that *exo*-skeletal isomerisation occurs to separate the copper phosphine units in the dicupracarbaboranes $[(R_3P)Cu]_2Ph_2C_2B_9H_9$ as a direct consequence of intramolecular steric crowding, but that, interestingly, these distant copper phosphine fragments are still able to exchange in solution at ambient temperature.

Seeking further information on ML_2 complexes of sterically demanding carbaboranes we studied reactions in which [7-Ph-*nido*-7,8-$C_2B_9H_{10}]^{2-}$ and [7,8-Ph_2-*nido*-7,8-$C_2B_9H_9]^{2-}$ are treated with sources of $\{(cod)Pd\}^{2+}$ and $\{(cod)Pt\}^{2+}$ (cod = cycloocta-1,5-diene). As a result we detail the first isolation of a compound with formula 1,2-Ph_2-3,3-L_2-3,1,2-$MC_2B_9H_9$ and describe its very distorted molecular structure. We also demonstrate the metal dependence of polyhedral rearrangement for a pair of molecules which are otherwise identical.

Experimental

Synthesis and Characterisation.—All reactions were performed under an atmosphere of dry, oxygen-free N_2 using standard Schlenk techniques, with some subsequent manipulations in the open laboratory. All solvents were dried and distilled under N_2 just prior to use. Infrared (difference) spectra were recorded as CH_2Cl_2 solutions in CaF_2 cells on a Perkin-Elmer 598 double-beam spectrophotometer, NMR spectra at 64.21 (^{11}B, ^{11}B-$\{^1H\}$) or 200.13 MHz (^1H) at 298 K from $CDCl_3$ solutions on a Bruker WP200SY spectrometer, chemical shifts being reported relative to external BF_3·OEt_2 and $SiMe_4$ respectively, positive shifts to high frequency. Preparative thin-layer chromatography (TLC) was performed using 20 x 20 cm glass plates with a 0.2 mm layer of silica (Merck). Microanalyses were by the departmental service. The starting materials Tl_2[7-Ph-*nido*-7,8-$C_2B_9H_{10}$],[4] Tl_2[7,8-Ph_2-*nido*-7,8-$C_2B_9H_9$],[2] [$PdCl_2$(cod)][5] and [$PtCl_2$(cod)][6] were prepared by literature methods or slight variants thereof, and their purities confirmed by microanalysis.

Synthesis of 1-Ph-3-(cod)-3,1,2-$PdC_2B_9H_{10}$ **1a**.—The salt Tl_2[7-Ph-7,8-$C_2B_9H_{10}$] (0.50 g, 0.81 mmol) and [$PdCl_2$(cod)] (0.18 g, 0.63 mmol) were stirred in CH_2Cl_2 (15 cm^3) in a foil-covered Schlenk tube for 2 h. The mixture was filtered and the filtrate concentrated to *ca.* 5 cm^3 *in vacuo*, before being applied to a Florisil column (20 x 2 cm, prewashed with CH_2Cl_2). Elution with CH_2Cl_2 revealed a dark red mobile band which was collected and evaporated to dryness to afford a dark red solid. Thin-layer chromatography (CH_2Cl_2–hexane, 1 : 1) yielded one major product (**1a**) and five minor ones (**1b**–**1f**).

Compound **1a**. 1-Ph-3-(cod)-3,1,2-$PdC_2B_9H_{10}$, purple, R_f = 0.5, yield = 0.05 g (19% based on Pd) (Found: C, 44.6; H, 6.55. Calc. for $C_{16}H_{27}B_9Pd$: C, 45.4; H, 6.40%). IR ν_{max} at 2515 cm^{-1} (B–H). NMR: ^{11}B-$\{^1H\}$, δ 20.06 (1B), 0.42 (1B), −2.41 (1B), −4.51 (1B), −7.67 (3B), −13.14 (1B) and −16.66 (1B); ^1H, δ 7.58 (d of d, *J* 7.8, 1.4 Hz, 2 H, C_6H_5), 7.32 (m, 3 H, C_6H_5), 5.81 (m, 2 H, cod CH), 4.93 (m, 2 H, cod CH), 4.73 (br s, 1 H, cage CH), 2.54 (m, 4 H, cod CH_2), 2.30 (m, 2 H, cod CH_2) and 2.09 (m, 2 H, cod CH_2).

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Compound **1b**. Dark red, $R_f = 0.6$. IR ν_{max} at 2860 (C–H) and 2530 cm^{-1} (B–H). NMR (decomposition apparent during spectral accumulation), ^{11}B-{^{1}H}, eight principal resonances at δ 20.2, 8.1, 0.0, −1.4, −4.6, −6.8, −12.4 and −16.2 plus a number of low-intensity peaks; ^{1}H, evidence for cod ligand (multiplets at δ 5.75, 2.6 and 2.0) and carbaborane ligand (multiplets centred on δ 7.6 and 7.3).

Compound **1c**. Green, $R_f = 0.65$. IR ν_{max} at 2900, 2840 (C–H) and 2530 cm^{-1} (B–H). NMR: ^{11}B-{^{1}H}, δ 20.4, 17.4, 6.7, 0.4, −2.4, −5.0, −6.8 (underlined resonances not coupled in ^{11}B spectrum), −10.3 and −15.0 (integrals unreliable); ^{1}H, evidence for cod ligand (multiplets at δ 5.75, 5.6, 2.5 and 2.25) and carbaborane ligand (multiplets at δ 7.6 and 7.4 and broad singlet at 4.9).

Compound **1d**. Purple, $R_f = 0.7$. IR ν_{max} at 2910 (C–H) and 2520 cm^{-1} (B–H). NMR: ^{11}B-{^{1}H}, δ 20.4, 10.2, 0.1, −2.4, −7.2, −8.3, −12.4 and −17.0 (integrals unreliable).

Compound **1e**. Yellow, $R_f = 0.75$. IR ν_{max} at 2560 cm^{-1} (B–H). NMR: ^{11}B-{^{1}H} (very poorly resolved), δ 20.2, 8.7, 0.1, −8.4 and −16.9.

Compound **1f**. Yellow, $R_f = 0.85$. IR ν_{max} at 2920 (C–H) and 2570 cm^{-1} (B–H). NMR: ^{11}B-{^{1}H}, nine principal resonances at δ 26.2, 15.7, 2.9, 1.6, −1.3, −3.6, −8.2, −10.2 and −12.1; ^{1}H, evidence for carbaborane ligand only (multiplets at δ 7.7 and 7.4, broad singlet at 3.1).

Thermolysis of Compound **1a**.—Compound **1a** (0.08 g, 0.19 mmol) was suspended in toluene (15 cm^3, degassed) and stirred at 55 °C for 1 h. Since there was no visible change the suspension was then heated to reflux for 0.5 h, again affording no apparent change. The toluene was removed *in vacuo* and the residue taken up in $CDCl_3$ and filtered. ^{11}B-{^{1}H} NMR: essentially the same as for **1a** except for the appearance of two additional resonances, δ −10.26 and −12.15.

Synthesis of 1,2-Ph$_2$-3-(cod)-3,1,2-PdC$_2$B$_9$H$_9$ **2a**.—Similarly, Tl$_2$[7,8-Ph$_2$-7,8-C$_2$B$_9$H$_9$] (0.50 g, 0.72 mmol) and [PdCl$_2$(cod)] (0.15 g, 0.53 mmol) were stirred in CH_2Cl_2 (15 cm^3) for 2 h. Filtration, concentration of the filtrate and column chromatography (Florisil, elution with CH_2Cl_2) afforded a dark red solid which again proved to be a mixture of species. Thin-layer chromatography (CH_2Cl_2–hexane, 3:2) produced one major product (**2a**) and four minor ones (**2b**–**2e**).

Compound **2a**. 1,2-Ph$_2$-3-(cod)-3,1,2-PdC$_2$B$_9$H$_9$, dark red, $R_f = 0.5$, yield = 0.04 g (15% based on Pd) (Found: C, 52.2; H, 6.60. Calc. for $C_{22}H_{31}B_9Pd$; C, 52.9; H, 6.25%). IR ν_{max} at 2900 (C–H) and 2515 cm^{-1} (B–H). NMR: ^{11}B-{^{1}H}, δ 25.21 (1B), 2.85 (2B), 0.85 (2B), −4.86 (3B) and −9.0 (1B); ^{1}H, δ 7.57 (d of d, *J* 8.1, 1.1 Hz, 4 H, C_6H_5), 7.16 (m, 6 H, C_6H_5), 5.58 (br, second order, 4 H, cod CH) and 2.52 (br, second order, 8 H, cod CH$_2$).

Compound **2b**. Orange, $R_f = 0.55$. IR ν_{max} at 3020, 2960 (C–H) and 2515 cm^{-1} (B–H). NMR: ^{11}B-{^{1}H}, δ 14.98 (1B), 1.48 (1B), −2.79 (2B), −6.25 (1B), −11.31 (2B), −17.25 (1B) and −19.57 (1B); ^{1}H, δ 7.41 (m, C_6H_5), 7.16 (m, C_6H_5), 5.58 (br m, cod CH) and 2.55 (br m, cod CH$_2$) (integrals unreliable).

Compound **2c**. Yellow, $R_f = 0.65$. IR ν_{max} at 2900 (C–H) and 2565 cm^{-1} (B–H). NMR: ^{11}B-{^{1}H}, five principal resonances at δ −4.2, −5.9, −12.1, −13.3 and −15.0 plus lower-intensity peaks at 7.3 (underlined resonances not coupled in ^{11}B spectrum) and 3.5; ^{1}H, convincing evidence for carbaborane ligand only (multiplets centred on δ 7.4 and 7.15).

Compound **2d**. Red, $R_f = 0.7$, trace amount. IR ν_{max} at 2900, 2850 (C–H) and 2560 cm^{-1} (B–H). NMR: ^{11}B-{^{1}H}, δ 25.8, 9.5, 3.5, 0.8, −5.1, −13.3, −14.7, −19.3 and −27.2 (integrals unreliable); ^{1}H, evidence for both cod ligand (broad resonances centred on δ 5.5 and 2.5) and carbaborane ligand (multiplets centred on δ 7.6 and 7.2).

Compound **2e**. Orange, $R_f = 0.8$, trace amount. IR ν_{max} at 2900 (C–H) and 2540 cm^{-1} (B–H). NMR: ^{11}B-{^{1}H} (very poorly resolved), δ 15.5, −1.9, −6.4, −14.7 and −19.6; ^{1}H, convincing evidence for carbaborane ligand only (aromatic region).

Thermolysis of **2a**. As for compound **1a**, a sample of **2a** (0.08 g, 0.16 mmol) was stirred in toluene (15 cm^3, degassed) at 55 °C for 1 h then heated to reflux for 0.5 h, the latter causing a colour change to yellow together with the deposition of a small amount of black solid. After filtration the solvent was removed from the filtrate to yield a yellow solid, **2a′**. NMR: ^{11}B-{^{1}H}, δ 1.07 (1B), −5.86 (4B) and −14.98 (4B); ^{1}H, δ 7.4–7.2 (m, 10 H, C_6H_5), 5.7 and 5.0 (m, 2 H, 2 H, both cod CH) and 2.6, 2.3 and 2.1 (m, 2 H, 2 H, 4 H, all cod CH$_2$).

Synthesis of 1-Ph-3-(cod)-3,1,2-PtC$_2$B$_9$H$_{10}$ **3a**.—Similarly, Tl$_2$[7-Ph-7,8-C$_2$B$_9$H$_{10}$] (0.50 g, 0.81 mmol) and [PtCl$_2$(cod)] (0.23 g, 0.61 mmol) were allowed to react in CH_2Cl_2 (15 cm^3) for 2 h. After filtration the red solution was concentrated and worked up by TLC (CH_2Cl_2–hexane, 2:1) affording one major band (**3a**) and one minor band (**3b**).

Compound **3a**. 1-Ph-3-(cod)-3,1,2-PtC$_2$B$_9$H$_{10}$, yellow, R_f = 0.85, yield = 0.13 g (42% based on Pt). NMR: ^{11}B-{^{1}H}, δ 10.26 (1 B, $^1J_{PtB}$ 280 Hz), −1.62 (1 B), −5.32 (1B), −7.94 (2B), −10.60 (1B), −12.42 (1B), −14.07 (1B) and −16.44 (1B); ^{1}H, δ 7.4–7.1 (m, 5 H, C_6H_5), 5.42 (m, 2 H, $^2J_{PtH}$ 65 Hz, cod CH), 4.58 (m, 2 H, evidence of $^2J_{PtH}$ coupling, cod CH), 3.74 (br s, 1 H, cage CH), 2.53 (m, 4 H, cod CH$_2$) and 2.11 (m, 4 H, cod CH$_2$).

Compound **3b**. Rust, $R_f = 0.95$, estimated yield < 1%. NMR: ^{11}B-{^{1}H}, six principal resonances at δ 12.9, −1.3, −2.8, −5.2, −8.0 and −12.2 plus a number of low-intensity peaks, principally at 23.3 and 10.2; ^{1}H, convincing evidence for carbaborane ligand only (aromatic region).

Synthesis of 1,11-Ph$_2$-3-(cod)-3,1,11-PtC$_2$B$_9$H$_9$ **4**.—The salt Tl$_2$[7,8-Ph$_2$-7,8-C$_2$B$_9$H$_9$] (0.50 g, 0.72 mmol) and [PtCl$_2$(cod)] (0.21 g, 0.56 mmol) were stirred in CH_2Cl_2 (15 cm^3) for 2 h. The resulting mixture was filtered and the filtrate concentrated to *ca.* 5 cm^3 *in vacuo*. Column chromatography (alumina, 20 × 2 cm, elution with CH_2Cl_2) afforded a single mobile band from which was recovered an orange solid on removal of solvent. Yield 0.19 g (58% based on Pt). NMR: ^{11}B-{^{1}H}, δ −1.72 (1B), −4.11 (1B), −6.88 (1B), −8.39 (1B), −9.62 (1B), −13.15 (1B), −15.23 (1B), −16.94 (1B) and −17.80 (1B); ^{1}H, δ 7.5–7.1 (m, 10 H, C_6H_5), 5.3–5.0 (br m, 4 H, cod CH) and 2.6–2.2 (br m, 8 H, cod CH$_2$).

Crystallography.—Diffraction-quality single crystals of compound **2a** were obtained by slow diffusion of Et$_2$O into a CH_2Cl_2 solution of it at −30 °C.

Crystal data. $C_{22}H_{31}B_9Pd$, M = 499.18, monoclinic, space group $P2_1/n$, a = 10.946(2), b = 12.077(3), c = 17.680(3) Å, β = 91.2340(14)°, U = 2336.7 Å^3 from the least-squares refinement of the setting angles of 25 strong reflections ($11 < \theta < 12°$), Z = 4, D_c = 1.419 g cm^{-3}, μ(Mo-Kα) = 7.92 cm^{-1}.

Data collection and processing. A CAD4 diffractometer was employed at room temperature with graphite-monochromated Mo-Kα X-radiation ($\bar{\lambda}$ = 0.710 69 Å), ω–2θ scans in 96 steps with ω scan width 0.8 + 0.34 tan θ and scan speeds 0.82–2.35° min^{-1}. 6778 Independent reflections measured to θ_{max} = 30° and h −15 to 15, k 0–17, l 0–24, over the data collection period. No detectable decay or movement.

Structure solution and refinement. The metal atom was located by analysis of the Patterson function, and B, C, cage H and cod CH atoms from Fourier-difference syntheses. All these atoms were positionally refined. Phenyl H and cod CH$_2$ atoms were set in idealised positions, C–H 1.08 Å. An empirical absorption correction was applied after isotropic convergence, following which all non-H atoms refined with anisotropic thermal parameters. Hydrogen atoms were assigned a common isotropic thermal parameter, 0.0684(21) Å^2, at convergence. Data weighted according to $w^{-1} = \sigma^2(F) + 0.000\,815F^2$. At convergence R = 0.0422, R' = 0.0478 and S = 0.914 for 5412 observed data [$F \geqslant 2.0\sigma(F)$]. Maximum and minimum residues in final ΔF map +0.47 and −0.72 e Å^{-3} respectively. Programs used: CADABS,[7] SHELX 76,[8] DIFABS,[9] CALC[10]

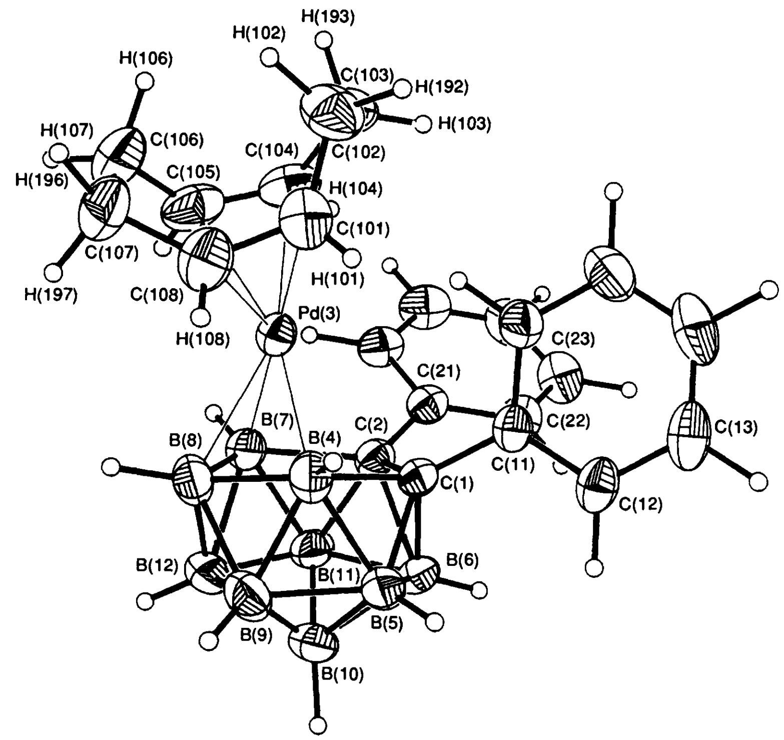

Fig. 1 Perspective view of a single molecule of compound **2a** (50% probability ellipsoids). Phenyl rings are numbered cyclically, C(*ij*), *j* = 1–6. Cage H and phenyl H atoms carry the same number as the B or C atom to which they are bound

and SHELXTL PC.[11] Atomic scattering factors for Pd were taken from ref. 12. Fractional coordinates of non-H atoms are given in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The reactions between [$PdCl_2$(cod)] and both Tl_2[7-Ph-7,8-$C_2B_9H_{10}$] and Tl_2[7,8-Ph_2-7,8-$C_2B_9H_9$], under the conditions described above, give rise to a number of products. In both cases the major species is the intended one, *viz.* 1-Ph-3-(cod)-3,1,2-$PdC_2B_9H_{10}$ **1a** and 1,2-Ph_2-3-(cod)-3,1,2-$PdC_2B_9H_9$ **2a** respectively, characterised by microanalysis and ^{11}B, ^{11}B-{^1H} and ^1H NMR spectroscopies plus, in the case of **2a**, a crystallographic study (see later). Note that in **2a** the cage carbon atoms remain adjacent, no spontaneous isomerisation having occurred.

Compound **1a** exhibits seven resonances in the ^{11}B-{^1H} NMR spectrum (one triple coincidence) clearly demonstrating the asymmetry of the cage. All become doublets ($^1J_{BH}$ 135–160 Hz) in the proton-coupled spectrum. The observation of only two resonances assigned to cod CH protons and three resonances assigned to cod CH_2 protons in the ^1H NMR spectrum imples that the cod ligand is free to rotate about the metal–cage axis at ambient temperature. The ^{11}B-{^1H} NMR spectrum of **2a** consists of five peaks in the ratio (high to low frequency) 1:2:2:3:1 (all doublets, $^1J_{BH}$ 125–155 Hz, in the ^{11}B spectrum) consistent with at least time-averaged C_S molecular symmetry (one coincidence). A feature of the ^{11}B NMR spectra of both **1a** and **2a** is a peak (corresponding to one boron atom) at high frequency, δ 20.06 for **1a** and 25.21 for **2a**. Wallbridge and co-workers[13] have analysed spectra from a series of 3-L_2-3,1,2-$PdC_2B_9H_{11}$ carbametallaboranes and convincingly argued that this high-frequency resonance arises from B(8), the symmetry-unique boron atom in the C_2B_3 ligand face, and therefore the observation of such resonances in the spectra of **1a** and **2a** can be taken as evidence of a 3,1,2-PdC_2B_9 structure. They tentatively suggested that the low-field nature of the resonance could be correlated with the degree of slippage[14] (Δ) of the metal atom across the C_2B_3 face towards B(8), since for L_2 = $Me_2NCH_2CH_2NMe_2$ Δ_{Pd} = 0.52 Å and $\delta_{B(8)}$ 20.04 whilst for L_2 = $(PMe_3)_2$ Δ_{Pd} = 0.26 Å and $\delta_{B(8)}$ 6.68. However, this idea was called into doubt by the subsequent structural characterisation[15] of 3-(cod)-3,1,2-$PdC_2B_9H_{11}$ **5** revealing Δ_{Pd} = 0.24 Å for a compound for which $\delta_{B(8)}$ 17.67. Nevertheless, for the series **5** $\longrightarrow$ **1a** $\longrightarrow$ **2a** a clear trend in $\delta_{B(8)}$ is apparent (17.67, 20.06 and 25.21 respectively) and we will subsequently show that Δ_{Pd} for **2a** is 0.56 Å, substantially greater than that in **5**, as a consequence of steric congestion between the cod ligand and the cage Ph substituents. It may well be the case, therefore, that a correlation *does* exist between Δ_{Pd} and $\delta_{B(8)}$ in slipped carbametallaboranes, but only in cases where the exopolyhedral ligand bound to the metal atom is kept constant. If this is true, Δ_{Pd} for **1a** would be predicted to lie between 0.24 and 0.56 Å.

Compound **2a** represents the first species of the type 1,2-Ph_2-3,3-L_2-3,1,2-$MC_2B_9H_9$ to be isolated. We have previously reported[3] that the reaction between *cis*-[$PtCl_2(PMe_2Ph)_2$] and Tl_2[7,8-Ph_2-7,8-$C_2B_9H_9$] affords 1,11-Ph_2-3,3-$(PMe_2Ph)_2$-3,1,11-$PtC_2B_9H_9$ as the only isolable product. Presumably the reaction initially affords the 3,1,2-PtC_2B_9 species which spontaneously isomerises into the less crowded 3,1,11 isomer to relieve congestion between the phosphine ligands and cage Ph substituents. In view of this it was appropriate to confirm the structural novelty of compound **2a** by a diffraction study.

The compound is obtained as diffraction-quality single crystals by solvent diffusion (CH_2Cl_2–Et_2O). Intensity data were collected at room temperature and the structure was solved and refined without difficulty or ambiguity. Fig. 1 shows a perspective view of a single molecule and demonstrates the atomic numbering scheme. Table 2 lists selected interatomic distances and interbond angles determined.

The molecule is confirmed as 1,2-Ph_2-3-(cod)-3,1,2-$PdC_2B_9H_9$ and as noted is the first example of an ML_2 complex of $Ph_2C_2B_9H_9$ in which the cage carbon atoms have not mutually separated *via* skeletal isomerisation. As a consequence

Table 1 Fractional coordinates of non-H atoms in compound **2a**

Atom	*x*	*y*	*z*
C(1)	0.505 68(25)	0.254 37(21)	0.207 81(14)
C(2)	0.565 89(25)	0.178 89(20)	0.150 69(15)
Pd(3)	0.330 36(2)	0.183 71(2)	0.108 55(1)
B(4)	0.358 1(3)	0.189 8(3)	0.230 75(19)
B(5)	0.495 3(4)	0.195 8(3)	0.291 63(19)
B(6)	0.629 2(4)	0.183 4(3)	0.242 46(19)
B(7)	0.473 4(3)	0.056 12(25)	0.132 30(18)
B(8)	0.347 7(4)	0.049 7(3)	0.194 86(20)
B(9)	0.408 2(4)	0.069 7(3)	0.285 63(21)
B(10)	0.569 0(4)	0.065 7(3)	0.286 12(22)
B(11)	0.612 7(3)	0.058 8(3)	0.188 34(20)
B(12)	0.484 2(4)	−0.016 4(3)	0.222 52(22)
C(11)	0.507 29(23)	0.377 09(21)	0.199 36(15)
C(12)	0.555 2(3)	0.445 50(24)	0.255 81(17)
C(13)	0.554 9(3)	0.560 3(3)	0.246 65(21)
C(14)	0.505 6(3)	0.608 2(3)	0.182 20(24)
C(15)	0.458 1(3)	0.541 0(3)	0.125 58(22)
C(16)	0.460 5(3)	0.426 74(24)	0.133 79(18)
C(21)	0.644 43(23)	0.224 64(21)	0.088 99(15)
C(22)	0.729 0(3)	0.309 09(23)	0.103 09(18)
C(23)	0.807 1(3)	0.344 0(3)	0.047 76(20)
C(24)	0.802 2(3)	0.296 2(3)	−0.023 38(21)
C(25)	0.719 1(3)	0.213 9(3)	−0.038 85(18)
C(26)	0.640 7(3)	0.177 23(23)	0.017 18(16)
C(101)	0.174 1(3)	0.310 9(3)	0.099 41(22)
C(102)	0.164 3(4)	0.365 1(3)	0.022 9(3)
C(103)	0.267 0(4)	0.338 7(4)	−0.030 19(22)
C(104)	0.327 3(3)	0.226 9(3)	−0.019 05(18)
C(105)	0.269 7(4)	0.128 5(3)	−0.010 66(19)
C(106)	0.132 8(4)	0.115 6(4)	−0.011 7(3)
C(107)	0.071 6(4)	0.126 8(3)	0.063 5(3)
C(108)	0.129 6(3)	0.209 7(3)	0.117 17(24)

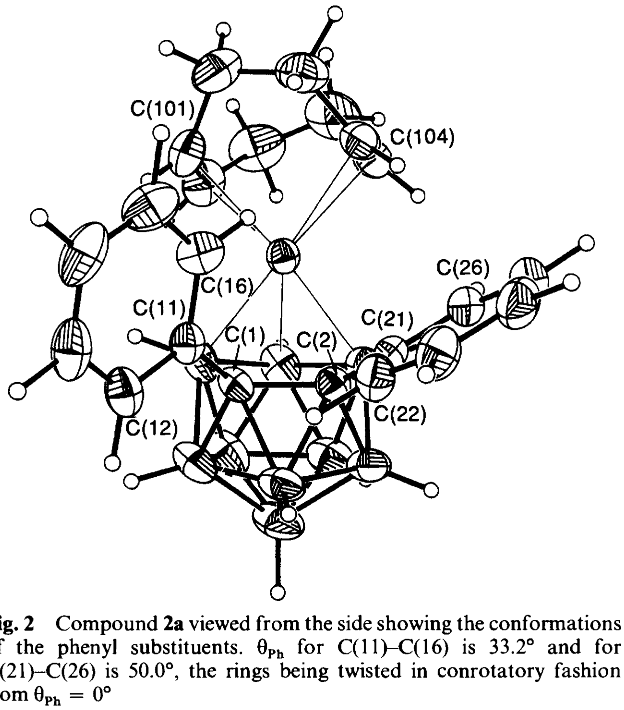

Fig. 2 Compound **2a** viewed from the side showing the conformations of the phenyl substituents. θ_{Ph} for C(11)–C(16) is 33.2° and for C(21)–C(26) is 50.0°, the rings being twisted in conrotatory fashion from $\theta_{Ph} = 0°$

of this non-isomerisation, however, the molecular structure of compound **2a** shows evidence of severe intramolecular overcrowding. First, the metal atom is substantially slipped (Δ_{Pd} = 0.56 Å) away from the cage Ph substituents towards B(8). Recall that in the non-cage-Ph analogue **5** Δ_{Pd} is only 0.24 Å.[15] Consistent with this greater slip in **2a** is a more severe buckling of the carbaborane C_2B_3 face, with the fold angles θ and φ, measured with respect to the lower B_5 belt,[14] being 8.3 and 5.2° respectively (*cf.* 5.9 and 4.9°, respectively, in **5**). Secondly, the cod ligand is substantially twisted away from the cage Ph substituents whilst still remaining η^2,η^2-bound to Pd(3). The twisting is uneven between the two η^2-ene functions: thus, the C(105)–C(104) vector makes an angle of 12.4° with the best plane through the B(5)B(6)B(11)B(12)B(9) belt, and Pd(3)–C(104) is greater than Pd(3)–C(105) by only 0.020(6) Å. In contrast, C(108)–C(101) is inclined at 21.6° to the B_5 belt with Pd(3)–C(101) longer than Pd(3)–C(108) by 0.073(6) Å. Overall, the average Pd–C(cod) distance in **2a** is 2.285(33) Å, longer than in **5**, 2.238(23) Å.

Thirdly, the carbaborane cage shows distortions which further serve to reduce cod–phenyl crowding. The distances C(1)–B(4) and C(2)–B(7), 1.846(4) and 1.821(4) Å, are the longest icosahedral C–B bonds of which we are aware [*cf.* 1.785(5) and 1.765(4) Å in **5**] and the former is actually longer than any measured B–B separation in compound **2a**. The C(1)–C(11) and C(2)–C(21) vectors are inclined with respect to the reference B_5 belt by 29.1 and only 23.8° respectively {*cf.* average of 30.5° in two salts of $[7,8\text{-}Ph_2\text{-}nido\text{-}7,8\text{-}C_2B_9H_{10}]^-$}.[16] The Ph rings in **2a** are conrotated from their positions in $1,2\text{-}Ph_2\text{-}1,2\text{-}C_2B_{10}H_{10}$[17] to define θ_{Ph} (modulus of the average C_{cage}–C_{cage}–C–C torsion angle)[18] values of 33.2 and 50.0° for C(11)–C(16) and C(21)–C(26) respectively; these conformations are readily appreciated in Fig. 2. Perhaps not surprisingly, the phenyl ring which is the less depressed towards the lower B_5 belt and which also is the more perpendicular to the C_2B_3 face [C(11)–C(16)] is on the same side of the molecule as is the more distorted η^2-ene function [C(101)–C(108)]. The C(1)–C(2) distance in **2a** is 1.521(4) Å, longer than that in **5** [1.495(4) Å] in spite of the greater Δ_{Pd} distortion in **2a** [usually, the greater the slip the shorter is C(1)–C(2)][14] which clearly reflects some mutual repulsion of the phenyl groups. Interestingly, however, C(1)–C(2) in **2a** is the shortest such distance yet recorded in a C-adjacent diphenylcarbaborane,[2,16,17,19] a fact which may be related to the average θ_{Ph} value of *ca.* 42°: extended-Hückel molecular-orbital calculations[17] on idealised models of $1,2\text{-}Ph_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ in which the phenyl substituents were synchronously conrotated from $\theta_{Ph} = 0°$ revealed steadily increasing C(1)/C(2) overlap and molecular stabilisation; however, beyond θ_{Ph} *ca.* 45° rapid and catastrophic <u>de</u>stabilisation occurred because of Ph···Ph crowding, suggesting that, in the absence of the cage carbon atoms being pushed apart (as occurs in *pseudocloso* species),[2,20] θ_{Ph} *ca.* 40–45° describes the optimum and limiting conformation of *closo* diphenylcarbaborane species.

Compound **1a** is recovered unchanged from refluxing toluene save for the appearance of two additional resonances in the ^{11}B NMR spectrum, possibly the results of slight decomposition. Crucially, however, the high-frequency resonance (δ 20.06) remains, confirming retention of a $3,1,2\text{-}PdC_2B_9$ architecture. In contrast, thermolysis of **2a** at toluene reflux results in the formation of a new yellow product **2a′**, the ^{11}B NMR spectrum of which *does not* contain a high-frequency signal, suggesting that cluster isomerisation has occurred. Although the $^{11}B\text{-}\{^1H\}$ NMR spectrum of **2a′** appears to indicate a symmetric structure (only three resonances, 1:4:4, all of which are doublets, $^1J_{BH}$ 140–155 Hz, in the proton-coupled spectrum), the ^1H spectrum (two signals, 2:2, for cod CH protons and three signals, 4:2:2, for cod CH_2 protons) reveals that this is not so. We tentatively identify **2a′** as the C-separated species $1,11\text{-}Ph_2\text{-}3\text{-}(cod)\text{-}3,1,11\text{-}PdC_2B_9H_9$ by analogy with $1,11\text{-}Ph_2\text{-}3,3\text{-}(PMe_2Ph)_2\text{-}3,1,11\text{-}PtC_2B_9H_9$.[3]

Both compounds **1a** and **2a** are formed in reactions which also afford a number of other products, **1b**–**1f** and **2b**–**2e** respectively, all isolated in only very small quantities. This fact, together with, in some cases, the instability of these minor products, resulted in their incomplete characterisation. All are coloured and contain carbaborane ligand (IR and ^{11}B NMR evidence). Compounds **1b**, **1c**, **2b** and **2d** clearly also contain cod ligands (^1H NMR). For four of the minor compounds (**1c**,

Table 2 Selected interatomic distances (Å) and interbond angles (°) in compound **2a**

C(1)–C(2)	1.521(4)	B(7)–B(12)	1.821(5)	Pd(3)–C(101)	2.302(4)	C(22)–C(23)	1.379(4)
C(1)–B(4)	1.846(4)	B(8)–B(9)	1.740(5)	Pd(3)–C(104)	2.315(4)	C(22)–C(21)	1.396(4)
C(1)–B(5)	1.648(4)	B(8)–B(12)	1.754(5)	Pd(3)–C(105)	2.295(4)	C(23)–C(24)	1.384(5)
C(1)–B(6)	1.704(4)	B(9)–B(10)	1.760(6)	Pd(3)–C(108)	2.229(4)	C(24)–C(25)	1.371(5)
C(1)–C(11)	1.490(4)	B(9)–B(12)	1.749(6)	B(4)–B(5)	1.830(5)	C(25)–C(26)	1.396(4)
C(2)–B(6)	1.752(4)	B(10)–B(11)	1.806(5)	B(4)–B(8)	1.810(5)	C(26)–C(21)	1.393(4)
C(2)–B(7)	1.821(4)	B(10)–B(12)	1.751(6)	B(4)–B(9)	1.823(5)	C(101)–C(102)	1.504(5)
C(2)–B(11)	1.671(4)	B(11)–B(12)	1.791(5)	B(5)–B(6)	1.727(5)	C(101)–C(108)	1.355(5)
C(2)–C(21)	1.508(4)	C(12)–C(13)	1.395(4)	B(5)–B(9)	1.798(6)	C(102)–C(103)	1.515(6)
Pd(3)–C(1)	2.710(3)	C(12)–C(11)	1.389(4)	B(5)–B(10)	1.770(6)	C(103)–C(104)	1.514(5)
Pd(3)–C(2)	2.699(3)	C(13)–C(14)	1.377(5)	B(6)–B(10)	1.753(5)	C(104)–C(105)	1.355(5)
Pd(3)–B(4)	2.177(4)	C(14)–C(15)	1.381(5)	B(6)–B(11)	1.790(5)	C(105)–C(106)	1.506(6)
Pd(3)–B(7)	2.230(3)	C(15)–C(16)	1.388(5)	B(7)–B(8)	1.786(5)	C(106)–C(107)	1.508(7)
Pd(3)–B(8)	2.229(4)	C(16)–C(11)	1.393(4)	B(7)–B(11)	1.801(5)	C(107)–C(108)	1.510(6)
C(2)–C(1)–B(6)	65.50(19)	B(8)–B(9)–B(12)	60.37(22)	C(1)–B(4)–B(5)	53.27(17)	C(23)–C(22)–C(21)	121.0(3)
C(2)–C(1)–C(11)	121.6(2)	B(10)–B(9)–B(12)	59.86(23)	C(1)–B(5)–B(4)	63.88(19)	C(22)–C(23)–C(24)	120.3(3)
B(4)–C(1)–B(5)	62.85(19)	B(5)–B(10)–B(6)	58.70(22)	C(1)–B(5)–B(6)	60.58(20)	C(23)–C(24)–C(25)	119.8(3)
B(4)–C(1)–C(11)	117.0(2)	B(5)–B(10)–B(9)	61.25(23)	B(4)–B(5)–B(9)	60.31(21)	C(24)–C(25)–C(26)	120.2(3)
B(5)–C(1)–B(6)	62.01(20)	B(6)–B(10)–B(11)	60.38(21)	B(6)–B(5)–B(10)	60.17(22)	C(25)–C(26)–C(21)	120.7(3)
B(5)–C(1)–C(11)	121.2(2)	B(9)–B(10)–B(12)	59.76(23)	B(9)–B(5)–B(10)	59.10(22)	C(2)–C(21)–C(22)	121.6(2)
B(6)–C(1)–C(11)	121.7(2)	B(11)–B(10)–B(12)	60.45(22)	C(1)–B(6)–C(2)	52.22(16)	C(2)–C(21)–C(26)	120.2(2)
C(1)–C(2)–B(6)	62.28(18)	C(2)–B(11)–B(6)	60.67(19)	C(1)–B(6)–B(5)	57.41(19)	C(22)–C(21)–C(26)	118.0(2)
C(1)–C(2)–C(21)	121.5(2)	C(2)–B(11)–B(7)	63.12(18)	C(2)–B(6)–B(11)	56.30(18)	Pd(3)–C(101)–C(102)	113.1(2)
B(6)–C(2)–B(11)	63.02(19)	B(6)–B(11)–B(10)	58.36(21)	B(5)–B(6)–B(10)	61.13(22)	Pd(3)–C(101)–C(108)	69.67(21)
B(6)–C(2)–C(21)	116.0(2)	B(7)–B(11)–B(12)	60.95(20)	B(10)–B(6)–B(11)	61.25(21)	C(102)–C(101)–C(108)	125.6(3)
B(7)–C(2)–B(11)	61.90(18)	B(10)–B(11)–B(12)	58.25(22)	C(2)–B(7)–Pd(3)	81.75(15)	C(101)–C(102)–C(103)	115.2(3)
B(7)–C(2)–C(21)	119.5(2)	B(7)–B(12)–B(8)	59.89(20)	C(2)–B(7)–B(11)	54.97(17)	C(102)–C(103)–C(104)	115.7(3)
B(11)–C(2)–C(21)	115.6(2)	B(7)–B(12)–B(11)	59.79(20)	Pd(3)–B(7)–B(8)	66.37(16)	Pd(3)–C(104)–C(103)	109.0(2)
B(4)–Pd(3)–B(8)	48.48(13)	B(8)–B(12)–B(9)	59.56(22)	B(8)–B(7)–B(12)	58.18(20)	Pd(3)–C(104)–C(105)	72.10(22)
B(7)–Pd(3)–B(8)	47.21(12)	B(9)–B(12)–B(10)	60.39(23)	B(11)–B(7)–B(12)	59.26(20)	C(103)–C(104)–C(105)	126.5(3)
C(101)–Pd(3)–C(104)	77.64(12)	B(10)–B(12)–B(11)	61.30(22)	Pd(3)–B(8)–B(4)	64.23(16)	Pd(3)–C(105)–C(104)	73.72(22)
C(101)–Pd(3)–C(108)	34.75(13)	C(13)–C(12)–C(11)	120.5(3)	Pd(3)–B(8)–B(7)	66.42(16)	Pd(3)–C(105)–C(106)	108.0(3)
C(104)–Pd(3)–C(105)	34.19(13)	C(12)–C(13)–C(14)	120.9(3)	B(4)–B(8)–B(9)	61.76(21)	C(104)–C(105)–C(106)	123.6(4)
C(105)–Pd(3)–C(108)	80.65(14)	C(13)–C(14)–C(15)	119.2(3)	B(7)–B(8)–B(12)	61.93(20)	C(105)–C(106)–C(107)	116.2(4)
Pd(3)–B(4)–B(8)	67.29(16)	C(14)–C(15)–C(16)	120.1(3)	B(9)–B(8)–B(12)	60.07(22)	C(106)–C(107)–C(108)	115.1(4)
Pd(3)–B(4)–C(1)	84.28(16)	C(15)–C(16)–C(11)	121.4(3)	B(4)–B(9)–B(5)	60.70(21)	Pd(3)–C(108)–C(101)	75.58(22)
B(5)–B(4)–B(9)	58.99(21)	C(1)–C(11)–C(12)	121.6(2)	B(4)–B(9)–B(8)	61.01(21)	Pd(3)–C(108)–C(107)	105.4(3)
B(8)–B(4)–B(9)	57.24(20)	C(1)–C(11)–C(16)	120.5(2)	B(5)–B(9)–B(10)	59.65(23)	C(101)–C(108)–C(107)	126.9(3)
		C(12)–C(11)–C(16)	117.9(3)				

1d, **2c** and **2d**) there are resonances in the ^{11}B-{^{1}H} NMR spectrum which do not show $^1J_{BH}$ coupling in the ^{11}B spectrum, possibly suggesting systems in which two cages are linked *via* a B–B bond or in which an organic group is directly bonded to a carbaborane cage through a C–B link, for which precedents have been established.[21] To some extent the multiplicity of products of these reactions could be due to the fact that they were deliberately non-stoichiometric (an excess of thallium carbaborate, the insoluble reactant, being used to ensure complete reaction of the metal substrate) but it is likely that other factors are also important, since (*i*) stoichiometric reaction of $Tl_2[C_2B_9H_{11}]$ and $[PdCl_2(cod)]$ also gives rise to a number of products[15] and (*ii*) similar non-stoichiometric reactions involving $[PtCl_2(cod)]$ are considerably cleaner.

Thus, the reaction between $Tl_2[7\text{-}Ph\text{-}7,8\text{-}C_2B_9H_{10}]$ and $[PtCl_2(cod)]$ (*ca.* 4:3 molar ratio) affords one major species **3a** and one very minor one **3b** (not fully characterised) after chromatographic separation. Compound **3a** was identified as $1\text{-}Ph\text{-}3\text{-}(cod)\text{-}3,1,2\text{-}PtC_2B_9H_{10}$ (*i.e.* the platinum analogue of **1a**) on the basis of ^{11}B, ^{11}B-{^{1}H} and ^{1}H NMR spectroscopies. In the ^{11}B-{^{1}H} spectrum there are eight resonances, all of which couple ($^1J_{BH}$ 140–175 Hz) in the ^{11}B spectrum. Importantly, these spectra feature one relatively high-frequency resonance (δ 10.26) which additionally shows ^{195}Pt satellites, J_{PtB} *ca.* 280 Hz. This resonance is readily assigned to B(8), the central boron atom of the C_2B_3 ligand face. Similar high-frequency resonances, with attendant satellites, have previously been observed for $1\text{-}(CH_2OCH_3)\text{-}3,3\text{-}(PMe_2Ph)_2\text{-}3,1,2\text{-}PtC_2B_9H_{10}$[22] (δ 6.52, $^1J_{PtB}$ 254 Hz) and $1\text{-}Ph\text{-}3,3\text{-}(PMe_2Ph)_2\text{-}3,1,2\text{-}PtC_2B_9H_{10}$[3,23] (δ 11.01, $^1J_{PtB}$ 225 Hz) both of which have been characterised crystallographically; they are absent, however, in the spectra of compounds $1\text{-}Ph\text{-}3,3\text{-}(PMe_2Ph)_2\text{-}3,1,11\text{-}PtC_2B_9H_{10}$ and $11\text{-}Ph\text{-}3,3\text{-}(PMe_2Ph)_2\text{-}3,1,11\text{-}PtC_2B_9H_{10}$[3,23] (again, both crystallographically characterised) in which the ML_2 fragment binds a CB_4 ligand face. We may conclude, therefore, that the observation of a ^{195}Pt-coupled high-frequency ^{11}B resonance is *diagnostic* of a $3,1,2\text{-}PtC_2B_9$ structure, using ^{11}B NMR spectroscopy in a similar way to that employed for compounds **1a** and **2a**.

Compound **4** is the only isolable product (*ca.* 60% yield) of the reaction between $Tl_2[7,8\text{-}Ph_2\text{-}7,8\text{-}C_2B_9H_9]$ and $[PtCl_2(cod)]$ in 3:2 molar ratio. The ^{11}B-{^{1}H} NMR spectrum reveals nine resonances (all doublets, $^1J_{BH}$ 135–160 Hz, in the proton-coupled spectrum) of equal integral, suggesting that the molecule is asymmetric. Moreover, the highest-frequency ^{11}B NMR signal is only δ −1.72 with no resonance showing evidence of platinum satellites, suggesting that **4** does not contain Pt bonded to a C_2B_3 ligand face, as discussed above. All attempts to grow diffraction-quality single crystals of **4** have so far failed, but the available evidence is fully consistent with the formulation $1,11\text{-}Ph_2\text{-}3\text{-}(cod)\text{-}3,1,11\text{-}PtC_2B_9H_9$, *i.e.* analogous to **2a**′, but in which the C_{cage} atoms have *spontaneously* separated as in $1,11\text{-}Ph_2\text{-}3,3\text{-}(PMe_2Ph)_2\text{-}3,1,11\text{-}PtC_2B_9H_9$.[3]

The formation (under identical conditions) of the diphenylcarbaborane complexes **2a** as the $3,1,2\text{-}PdC_2B_9$ isomer and **4** as the $3,1,11\text{-}PtC_2B_9$ isomer suggests that the nature of the metal atom is important in the ability of carbametallaboranes to undergo polyhedral rearrangement. We[3] and others[24] have already shown that isomerisation temperatures can be lowered by deliberately introducing steric crowding into carbametallaboranes (recall also the fact that the crowded molecule **2a** can be transformed into **2a′**, a compound apparently analogous to **4**, under conditions in which the less crowded **1a** is inert to isomerisation), but there is clearly another factor operating in the formation of **4** as a C-separated species, since Pd^{II} and Pt^{II} are generally regarded as very similar in size.[25] Stone and co-workers[26,27] have previously demonstrated the greater tendency of third-row transition-metal (W) carbametallaboranes to undergo rearrangement compared to their second-row (Mo) analogues *in chemical reactions* (*e.g.* with CO and aqueous HX). As far as we are aware, the actual *synthesis* of formally analogous second- and third-row transition-metal carbametallaboranes as different isomers, as demonstrated by **2a** and **4**, is novel. We are currently investigating the possible origins of this unexpected behaviour.

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References

1 Part 8, K. J. Adams, J. Cowie, S. G. D. Henderson, G. J. McCormick and A. J. Welch, *J. Organomet. Chem.*, 1994, **481**, C9.

2 Z. G. Lewis and A. J. Welch, *J. Organomet. Chem.*, 1992, **430**, C45.

3 D. R. Baghurst, R. C. B. Copley, H. Fleischer, D. M. P. Mingos, G. O. Kyd, L. J. Yellowlees, A. J. Welch, T. R. Spalding and D. O'Connell, *J. Organomet. Chem.*, 1993, **447**, C14.

4 J. Cowie, B. D. Reid, J. M. S. Watmough and A. J. Welch, *J. Organomet. Chem.*, 1994, **481**, 283.

5 D. Drew and J. R. Doyle, *Inorg. Synth.*, 1972, **13**, 52.

6 H. C. Clark and L. E. Manzer, *J. Organomet. Chem.*, 1973, **59**, 411.

7 CADABS, Program for Data Reduction, R. O. Gould and D. E. Smith, University of Edinburgh, 1986.

8 SHELX 76, Program for Crystal Structure Refinement, G. M. Sheldrick, University of Cambridge, 1976.

9 DIFABS, Program for Empirical Absorption Correction, N. G. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

10 CALC, Program for Molecular Geometry Calculations, R. O. Gould and P. Taylor, University of Edinburgh, 1986.

11 SHELXTL, PC version 4.2, G. M. Sheldrick, University of Göttingen, 1990.

12 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, p. 99.

13 H. M. Colquhoun, T. J. Greenhough and M. G. H. Wallbridge, *J. Chem. Soc., Dalton Trans.*, 1985, 761.

14 D. M. P. Mingos, M. I. Forsyth and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1978, 1363.

15 D. E. Smith and A. J. Welch, *Acta Crystallogr., Sect. C*, 1986, **42**, 1717.

16 J. Cowie, D. J. Donohoe, N. L. Douek and A. J. Welch, *Acta Crystallogr., Sect. C*, 1993, **49**, 710.

17 Z. G. Lewis and A. J. Welch, *Acta Crystallogr., Sect. C*, 1993, **49**, 705.

18 T. D. McGrath and A. J. Welch, *Acta Crystallogr.*, in the press.

19 Z. G. Lewis and A. J. Welch, *Acta Crystallogr., Sect. C*, 1993, **49**, 715.

20 P. T. Brain, M. Bühl, J. Cowie, Z. G. Lewis and A. J. Welch, unpublished work.

21 Z. G. Lewis and A. J. Welch, *J. Organomet. Chem.*, 1992, **438**, 353.

22 K. F. Shaw, B. D. Reid and A. J. Welch, *J. Organomet. Chem.*, in press.

23 G. O. Kyd, Ph.D. Thesis, University of Edinburgh, 1993.

24 See, for example, L. F. Warren, jun., and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1970, **92**, 1157.

25 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon, Oxford, 1982.

26 S. A. Brew, N. Carr, J. C. Jeffrey, M. U. Pilotti and F. G. A. Stone, *J. Am. Chem. Soc.*, 1992, **114**, 2203.

27 S. Li and F. G. A. Stone, *Polyhedron*, 1993, **12**, 1689.

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