Enhanced Slip Distortions in 1-Phenyl-2-methyldicarbaplatinaboranes. Conformational Destabilisation in the Isomerisation of 1-Phenyldicarbaplatinaboranes‡

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The compounds $Tl_2[7\text{-}Ph\text{-}8\text{-}Me\text{-}7,8\text{-}\textit{nido}\text{-}C_2B_9H_9]$, $[C_5H_{10}NH_2][7\text{-}Ph\text{-}8\text{-}Me\text{-}7,8\text{-}\textit{nido}\text{-}C_2B_9H_{10}]$, 1-Ph-2-Me-3,3-$L_2$-3,1,2-$PtC_2B_9H_9$ [L = PMe_2Ph, PEt_3, PPh_3 or $P(C_6H_4Me\text{-}p)_3$] have been prepared and characterised. The platinum complexes were obtained from the reactions between $Tl_2[7\text{-}Ph\text{-}8\text{-}Me\text{-}7,8\text{-}\textit{nido}\text{-}C_2B_9H_9]$ and the appropriate $[PtCl_2(PR_3)_2]$ species. Crystallographic studies upon the compounds where L = PEt_3 and two crystalline modifications of that where L = PPh_3 afforded evidence of a substantial influence of intramolecular crowding upon the observed structures, so that the lateral slippage (Δ) of the metal fragment is significantly enhanced: Δ = 0.74 and 0.94 and 0.91 Å respectively. These compounds do not isomerise under conditions which produce rearrangement in the corresponding (less-congested) derivatives of 1-phenylcarbaborane, consistent with the proposed conformational destabilisation in the latter system.

We have recently reported that novel molecular structures and unusually facile polyhedral rearrangements can result from the deliberate introduction of intramolecular crowding in carbametallaboranes. In particular, we have demonstrated that in 1,2-Ph_2-3-(η^5-C_5Me_5)-3,1,2-$RhC_2B_9H_9$ [2] and 1,2-Ph_2-3-(η^6-arene)-3,1,2-$RuC_2B_9H_9$ [3] the cage adopts an unusual *pseudo-closo* geometry to relieve congestion between the pendant phenyl groups which are themselves forced almost coplanar by the η^5-C_5Me_5 or η^6-arene ligands: in 1,2-Ph_2-3-(η^5-C_5H_5)-3,1,2-$CoC_2B_9H_9$ [4] a similar, although less severe, cluster deformation is found, whilst the related {(η^6-arene)Ru} complexes of the less-demanding $[7\text{-}Ph\text{-}8\text{-}Me\text{-}7,8\text{-}\textit{nido}\text{-}C_2B_9H_9]^{2-}$ ligand show [5] the onset of a similar deformation. Moreover, 1-Ph-3,3-$(PMe_2Ph)_2$-3,1,2-$PtC_2B_9H_{10}$ isomerises at only 55 °C to afford two C_{cage}-separated species, 1-Ph-3,3-$(PMe_2Ph)_2$-3,1,11-$PtC_2B_9H_{10}$ and 11-Ph-3,3-$(PMe_2Ph)_2$-3,1,11-$PtC_2B_9H_{10}$, whilst the analogous $(C_{cage}Ph)_2$ compound 1,2-Ph_2-3,3-$(PMe_2Ph)_2$-3,1,2-$PtC_2B_9H_9$ cannot be isolated but undergoes spontaneous sterically induced rearrangement to 1,11-Ph_2-3,3-$(PMe_2Ph)_2$-3,1,11-$PtC_2B_9H_9$.[6] In addition, the related ML_2 (M = Pt or Pd; L_2 = cycloocta-1,5-diene) derivatives of mono- and di-phenylcarbaborane[1] have been shown to possess enhanced metal-fragment slippage (Δ), and deformations of both the cage and the metal–ligand coordination relative to their non-C_{cage}Ph analogues.

In the present contribution we report the synthesis and characterisation of several bis(phosphine)platinum complexes of the moderately sterically demanding ligand $[7\text{-}Ph\text{-}8\text{-}Me\text{-}7,8\text{-}\textit{nido}\text{-}C_2B_9H_9]^{2-}$ and describe the highly distorted molecular structures of two of these compounds. This group of compounds is considered in relation to the analogous, but less crowded, derivatives of $[7\text{-}Ph\text{-}7,8\text{-}\textit{nido}\text{-}C_2B_9H_{10}]^{2-}$, in which a *ground-state destabilisation* effect has been proposed to account for the observed facile isomerisation.[6]

Experimental

Synthesis and Characterisation.—All syntheses were carried out under an atmosphere of dry, oxygen-free nitrogen using standard Schlenk-line techniques; some subsequent manipulations were performed in air. Solvents were freshly distilled and degassed prior to use. Infrared (difference) spectra were recorded from solutions (except where indicated) on a Perkin-Elmer 598 spectrophotometer. The NMR spectra were recorded from solutions at ambient temperatures on Bruker WH360 or WP200SY instruments. Chemical shifts are reported relative to external standards: $SiMe_4$ (^1H), 85% H_3PO_4 (^{31}P) and $BF_3{\cdot}OEt_2$ (^{11}B); positive shifts are to high frequency. Microanalyses were performed by the departmental service. Preparative thin-layer chromatography was performed using silica-coated (thickness 0.2 mm) 20 × 20 cm glass plates (Merck). The starting materials 1-Ph-2-Me-1,2-*closo*-$C_2B_{10}H_{10}$,[7] $[PtCl_2(PMe_2Ph)_2]$,[8] $[PtCl_2(PEt_3)_2]$,[9] $[PtCl_2(PPh_3)_2]$[10] and $[PtCl_2\{P(C_6H_4Me\text{-}p)_3\}_2]$[11] were prepared by literature methods (or slight variants thereof) and their purities confirmed by microanalysis.

Syntheses.—$Tl_2[7\text{-}Ph\text{-}8\text{-}Me\text{-}7,8\text{-}\textit{nido}\text{-}C_2B_9H_9]$. Typically, 1-Ph-2-Me-1,2-*closo*-$C_2B_{10}H_{10}$ (0.50 g, 2.13 mmol) was dissolved in EtOH (50 cm^3), and to this was added powdered KOH (0.72 g, 12.8 mmol). The mixture was heated to reflux and stirred for *ca.* 26 h, allowed to cool, and evaporated to dryness *in vacuo*. To the resulting waxy solid was added water (50 cm^3), and the aqueous solution of $K_2[7\text{-}Ph\text{-}8\text{-}Me\text{-}7,8\text{-}\textit{nido}\text{-}C_2B_9H_9]$ filtered [Celite®, 1 atm (*ca.* 10^5Pa)] to remove unreacted 1-Ph-2-Me-1,2-*closo*-$C_2B_{10}H_{10}$. Thallium(I) acetate (1.68 g, 6.38 mmol) was dissolved in water (5 cm^3) and this solution added to the above filtrate, instantly precipitating yellow, *solid* $Tl_2[7\text{-}Ph\text{-}8\text{-}Me\text{-}7,8\text{-}\textit{nido}\text{-}C_2B_9H_9]$. The precipitate was filtered off, washed with water (2 × 5 cm^3), and dried *in vacuo* in a foil-covered Schlenk tube. Yield 0.37 g, 0.59 mmol (27.4%) [Found: C, 19.30; H, 3.45. Calc. for $C_9H_{17}B_9Tl_2$: C, 17.10; H, 2.70% (incomplete combustion?)]. IR (KBr disc): ν_{BH} 2515 cm^{-1}.

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‡ Steric Effects in Heteroboranes. Part 10.[1] For consistency with previous contributions, the C_{cage} atom bearing the phenyl substituent is labelled as C(1) (*closo*-type structures) or C(7) (*nido*-type structures).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

$[C_5H_{10}NH_2]$[7-Ph-8-Me-7,8-*nido*-$C_2B_9H_{10}$]. 1-Ph-2-Me-1,2-*closo*-$C_2B_{10}H_{10}$ (0.50 g, 2.13 mmol) was dissolved in benzene (25 cm^3) and piperidine (0.80 g, 9.40 mmol) was added. The solution was heated to reflux for 20 h, cooled, evaporated *in vacuo*, and recrystallised from benzene. The product was dried *in vacuo* for several days, affording $[C_5H_{12}N]$[7-Ph-8-Me-7,8-*nido*-$C_2B_9H_{10}$] in good yield. Yield 0.53 g, 1.72 mmol (80.6%) (Found: C, 53.40; H, 10.10; N, 6.95. Calc. for $C_{14}H_{30}B_9N$: C, 54.30; H, 9.75; N, 4.50%). IR (Nujol mull): ν_{BH} 2520 cm^{-1}. NMR [298 K, $(CD_3)_2CO$]: $\delta(^1H)$ 7.29–7.01 (m, 5 H, C_6H_5), 3.04 (br m, 4 H, NCH_2), *ca.* 2.1 (CH_3, obscured by solvent) and 1.77 (br m, 6 H, NCH_2CH_2 and $N(CH_2)_2CH_2$); $\delta(^{11}B)$ (integral, $^1J_{BH}$/Hz) −6.48 (1 B, 138), −7.24 (1B, 138), −9.98 (1B, 152), −15.09 (1B, *ca.* 134), −16.12 (2B, 141), −17.39 (1B, 150), −30.05 (1B, $^1J_{BH(endo)}$ 55, $^1J_{BH(exo)}$ 137) and −34.47 (1B, 135).

The corresponding benzyltrimethylammonium salt may be prepared by analogy to the route to $[NMe_3(CH_2Ph)]$[7,8-Ph_2-7,8-*nido*-$C_2B_9H_{10}$][12] and shows similar ^{11}B NMR properties to those above.

1-Ph-2-Me-3,3-$(PMe_2Ph)_2$-3,1,2-$PtC_2B_9H_9$ **1**. To a frozen (77 K) solution of $[PtCl_2(PMe_2Ph)_2]$ (0.20 g, 0.37 mmol) in CH_2Cl_2 (20 cm^3) was added solid Tl_2[7-Ph-8-Me-7,8-*nido*-$C_2B_9H_9$] (0.23 g, 0.37 mmol); the mixture was allowed slowly to warm to room temperature and stirred for *ca.* 20 h. During this period the progress of the reaction was evidenced by the formation of a yellow-orange solution. The reaction mixture was filtered (Celite®, 1 atm) and concentrated by evaporation *in vacuo* to *ca.* 5 cm^3. Preparative thin-layer chromatography (CH_2Cl_2–hexane 4:1) of this reduced filtrate yielded only one mobile coloured band (R_f 0.8) which was collected and identified as compound **1**. Yield 0.13 g, 0.19 mmol (51.2%) (Found: C, 43.45; H, 5.35. Calc. for $C_{25}H_{39}B_9P_2Pt$: C, 43.25; H, 5.65%). IR (CH_2Cl_2): ν_{BH} 2520 cm^{-1}. NMR [298 K, $(CD_3)_2CO$]: $\delta(^1H)$ 8.33–8.28 (br m, 2 H, $C_{cage}Ph$), 7.74–7.36 (m, 13 H, $C_{cage}Ph$ and PPh), *ca.* 2.1 ($C_{cage}Me$, obscured by acetone solvent) and 1.80 (br, 12 H, PMe); $\delta(^{31}P)$ −7.74 ($^1J_{PtP}$ 3037 Hz); $\delta(^{11}B\text{-}\{^1H\})$ 21.10 [1B, B(8), $^1J_{PtB} \approx 280$], 2.37 (1B), 1.08 (1B), −3.19 (1B), −7.57 (1B), −8.24 (1B), −10.58 (1B), −18.89 [1B, B(4) or B(7)], $^1J_{PtB} \approx 190$ Hz] and −21.68 [1B, B(4) or B(7), apparent $^1J_{PtB}$ not resolved].

1-Ph-2-Me-3,3-$(PEt_3)_2$-3,1,2-$PtC_2B_9H_9$ **2**. Similarly, a solution of $[PtCl_2(PEt_3)_2]$ (0.25 g, 0.50 mmol) in CH_2Cl_2 (20 cm^3) was frozen to 77 K and to this was added solid Tl_2[7-Ph-8-Me-7,8-*nido*-$C_2B_9H_9$] (0.32g, 0.50 mmol). The mixture was allowed gradually to warm to ambient temperature and stirred for *ca.* 16 h. Filtration of the reaction mixture (Celite®, 1 atm) afforded an orange solution which was reduced by evaporation *in vacuo* to *ca.* 5 cm^3, and subjected to preparative thin-layer chromatography (CH_2Cl_2–hexane 3:1). A single mobile orange band (R_f 0.8) was obtained; this was collected and identified as compound **2**. Yield 0.24 g, 0.37 mmol (74.1%) (Found: C, 38.40; H, 7.75. Calc. for $C_{21}H_{47}B_9P_2Pt$: C, 38.50; H, 7.25%). IR (CH_2Cl_2): ν_{BH} 2548 (sh) and 2536 cm^{-1}. NMR (298 K, $CDCl_3$): $\delta(^1H)$ 8.24–8.20 (m, 2 H, Ph), 7.26–7.21 (m, 3 H, Ph), 2.06–1.62 (m, 12 H, CH_2), 1.95 (br, s, 3 H, $C_{cage}Me$) and 1.27–1.01 (m, 18 H, PCH_2CH_3); $\delta(^{31}P)$ 16.09 ($^1J_{PtP} \approx 2933$) and 13.72 ($^1J_{PtP} \approx 2947$ Hz); $^2J_{PP}$ not resolved; $\delta(^{11}B\text{-}\{^1H\})$ 22.17 [1B, B(8), $^1J_{PtB} \approx 270$ Hz], 3.42 (1B), 1.49 (1B), −4.31 (1B), −7.98 (2B), −10.34 (1B), −20.64 [1B, B(4) or B(7), apparent $^1J_{PtB}$ not resolved] and −23.38 [1B, B(4) or B(7), apparent $^1J_{PtB}$ not resolved].

Slow diffusion of hexane into a concentrated CH_2Cl_2 solution of compound **2** at −30 °C afforded well formed *blocks*. However, very slow evaporation of a CH_2Cl_2 solution of **2** under ambient conditions yielded superior-quality *blocks*, one of which was the subject of an X-ray diffraction analysis.

1-Ph-2-Me-3,3-$(PPh_3)_2$-3,1,2-$PtC_2B_9H_9$ **3**. The complex $[PtCl_2(PPh_3)_2]$ (0.25 g, 0.32 mmol) was dissolved in CH_2Cl_2 (20 cm^3) and the solution frozen to 77 K. To this was added solid Tl_2[7-Ph-8-Me-7,8-*nido*-$C_2B_9H_9$] (0.20 g, 0.32 mmol), the mixture was warmed to room temperature and stirred for *ca.* 24 h. The filtered (Celite®, 1 atm) reaction mixture was concentrated by evaporation *in vacuo*, and the resulting dark orange solution applied to a chromatographic column (20 × 2 cm, Florisil® prewashed with eluent; CH_2Cl_2-hexane 9:1). Upon elution, a single mobile orange band was obtained; this was collected and evaporated *in vacuo* to yield compound **3** as an orange solid. Yield 0.10 g, 0.11 mmol (35.7%) (Found: C, 56.30; H, 5.90. Calc. for $C_{45}H_{47}B_9P_2Pt$: C, 57.35; H, 5.05%). IR (CH_2Cl_2): ν_{BH} 2524 cm^{-1}. NMR [298 K, $CDCl_3$ (^1H), $(CD_3)_2CO$ (^{31}P, ^{11}B)]: $\delta(^1H)$ 7.94–7.00 (m, 35 H, Ph) and *ca.* 2.17 (3 H, $C_{cage}Me$); $\delta(^{31}P)$ 29.13 ($^1J_{PtP} \approx 3075$), 22.16 ($^1J_{PtP} \approx 3295$ Hz); $^2J_{PP}$ not resolved; $\delta(^{11}B\text{-}\{^1H\})$ 25.83 [1B, B(8); $^1J_{PtB}$ not resolved], 4.95 (br, 1B), 3.61 (2B), −6.62 (2B), −8.88 (1B), −20.80 [1B, B(4) or B(7), apparent $^1J_{PtB}$ not resolved] and −24.65 [1B, B(4) or B(7), apparent $^1J_{PtB}$ not resolved].

Diffraction-quality *crystals* of compound **3** were obtained by slow diffusion of hexane into a CH_2Cl_2 solution of **3** at −30 °C. A second crystalline modification was obtained by diffusion of hexane into an NMR sample [CH_2Cl_2–$(CD_3)_2CO$ solvents] of **3**. Both crystalline forms were studied by X-ray diffraction techniques.

1-Ph-2-Me-3,3-$[P(C_6H_4Me\text{-}p)_3]_2$-3,1,2-$PtC_2B_9H_9$ **4**. In a manner analogous to that which afforded the closely related compound **3** above, a frozen (77 K) CH_2Cl_2 (20 cm^3) solution of $[PtCl_2\{P(C_6H_4Me\text{-}p)_3\}_2]$ (0.25 g, 0.29 mmol) was allowed to react with solid Tl_2[7-Ph-8-Me-7,8-*nido*-$C_2B_9H_9$] (0.18 g, 0.29 mmol) while warming to room temperature. After being stirred for *ca.* 25 h the reaction mixture was filtered (Celite®, 1 atm) and the filtrate concentrated by evaporation *in vacuo*. The resulting orange solution was applied to a chromatographic column (20 × 2 cm, Florisil® prewashed with eluent; CH_2Cl_2–hexane 9:1), and the mixture eluted to afford a single mobile orange band. This was collected, evaporated *in vacuo* and identified as compound **4** by conventional means. Yield 0.09 g, 0.09 mmol (32.1%) (Found: C, 57.10; H, 5.60. Calc. for $C_{51}H_{59}B_9P_2Pt$: C, 59.70; H, 5.80%). IR (CH_2Cl_2): ν_{BH} 2525 cm^{-1}. NMR [298 K, $CDCl_3$ (^1H), $(CD_3)_2CO$ (^{31}P, ^{11}B)]: $\delta(^1H)$ 7.92 (m, 2 H, $C_{cage}Ph$), 7.33 (t, 12 H, PC_6H_4, $^3J_{HH} \approx 8.5$), 7.17–7.02 (m, 3 H, $C_{cage}Ph$), 6.89 (t, 12 H, PC_6H_4, $^3J_{HH} \approx 8.5$), 2.29 (s, 9 H, $PC_6H_4CH_3$), 2.27 (s, 9 H, $PC_6H_4CH_3$) and 2.16 (s, 3 H, $C_{cage}Me$); $\delta(^{31}P)$ 27.67 ($^1J_{PtP} \approx 2986$), 26.72 ($^1J_{PtP} \approx 3175$ Hz); $^2J_{PP} \approx 20$ Hz; $\delta(^{11}B\text{-}\{^1H\})$ 25.30 [1B, B(8); $^1J_{PtB}$ not resolved], 3.84 (br, 2B), −3.26 (2B), −6.97 (2B), −21.59 [br, 1B, B(4) or B(7)] and −24.44 [br, 1B, B(4) or B(7)].

Poor-quality orange *plates* of (solvated) compound **4**, which were somewhat unstable with respect to solvent loss, were obtained by slow diffusion of hexane into a CH_2Cl_2 solution of **4** at −30 °C.

Attempted Thermolysis of Compound **3**.—A sample of compound **3** (*ca.* 50 mg) was dissolved in $CHCl_3$ (10 cm^3) and warmed to reflux (61 °C) for several hours. Spectroscopic analysis (^{31}P, ^{11}B NMR) of the recovered material suggested that **3** had not been affected by the thermolysis.

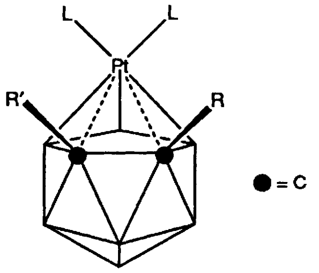
Crystallography.—All measurements were performed at room temperature on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα X-radiation ($\bar{\lambda}$ = 0.710 69 Å) operating in the ω–2θ mode.

In Table 4 are listed crystal data, as well as details of data collection and structure refinement, for crystals of compounds **2**, **3**·0.5CH_2Cl_2 and **3**·unknown solvent. For each crystal, unit cell parameters and the orientation matrix for data collection were obtained from a least-squares refinement of the accurately measured setting angles of 25 strong, high-angle reflections. Two standard reflections were remeasured every 8 X-ray hours and revealed negligible crystal decay in every case. Only data for which $F \geqslant 2.0\sigma(F)$ were retained for use in structure solution and refinement.

Each structure was solved[13] by Patterson methods for the Pt atom and by Fourier-difference syntheses for B, C and P atoms; in the case of compound **2**, several of the cage H atoms were located in the difference maps, but their positions did not refine satisfactorily. The structures were refined by iterative full-matrix least squares on F; H atoms in hydrocarbon functions, and those bound to the cage, were set in idealised positions (C–H 1.08, B–H 1.10 Å), whilst the C atoms of phenyl rings were constrained to be rigid, planar hexagons (C–C 1.395 Å). [An unidentified solvent molecule was located in the crystal lattice of **3**·unknown solvent, and was modelled as five carbon atoms with fixed isotropic thermal parameters of 0.06 Å^2. The positions and occupancies of these were allowed some refinement before these, too, were fixed. (The ultimate values of these are listed in the supplementary data.) It is thought that a mixture of dichloromethane, hexane and $(CD_3)_2CO$ may occupy this rather unrestricted cavity.] An empirical absorption correction[14] was applied to each data set following isotropic convergence. Thereafter, with the exception of the solvates, all non-H atoms were allowed anisotropic refinement; H atoms in each structure were assigned a single (variable) group thermal parameter, U_H. In the final stages of refinement, reflection data were weighted according to $w^{-1} = [\sigma^2(F) + gF^2]$.

Atomic scattering factors for Cl, P, C, B and H atoms were those inlaid in SHELX 76,[13] whilst those for Pt were taken from ref. 15. In addition to the programs referenced above, the following were used: CADABS,[16] CALC[17] and SHELXTL.[18] Tables of final (non-H) fractional coordinates appear in Tables 5–7.

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



	R	R'	L
1	Ph	Me	PMe_2Ph
2	Ph	Me	PEt_3
3	Ph	Me	PPh_3
4	Ph	Me	$P(C_6H_4Me\text{-}p)_3$
5	Ph	H	PMe_2Ph
6	R = R' = Ph		PMe_2Ph
7	R = R' = H		PEt_3
8	R = R' = H		$\frac{1}{2}$dppe
9	CH_2OMe	H	PMe_2Ph

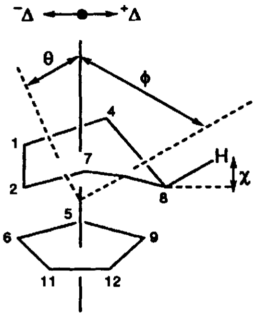


Fig. 1 Definitions of 'slipping' (Δ) and 'folding' parameters (θ and φ) and substituent elevation angle (χ) in 12-vertex carbametallaboranes, numbered as for a 3,1,2-MC_2B_9 species (● = M)

Results and Discussion

Synthesis and Characterisation.—The carbaborane 1-Ph-2-Me-1,2-*closo*-$C_2B_{10}H_{10}$ constitutes the precursor to a moderately sterically demanding *nido*-carbaborane from which has been prepared a homologous series of bis(phosphine)platinum complexes. It may be decapitated with 6 equivalents of KOH in refluxing ethanol, to afford [7-Ph-8-Me-7,8-*nido*-$C_2B_9H_9]^{2-}$ in reasonable yield. This species is conveniently isolated as the dithallium salt, a useful reagent in the formation of metal complexes of the dianion. Microanalysis and infrared spectroscopy confirmed the identity of Tl_2[7-Ph-8-Me-7,8-*nido*-$C_2B_9H_9$]. The protonated form of the dianion may be obtained by deboronation under similar, milder conditions (ethanolic KOH, 3 equivalents), and precipitated from aqueous solution as the benzyltrimethylammonium salt.

This protonated species may be more conveniently formed as the piperidinium salt by treatment of the parent carbaborane with an excess of piperidine in refluxing benzene.[19] Thus [$C_5H_{10}NH_2$][7-Ph-8-Me-7,8-*nido*-$C_2B_9H_{10}$] was identified and characterised by microanalysis, and both infrared and NMR (^{1}H, ^{11}B) spectroscopies. The ^{11}B-{^{1}H} NMR spectrum shows nine resonances (two are coincident), fully consistent with the absence of molecular symmetry. Upon retention of proton coupling, the ^{11}B spectrum contains eight doublets arising from coupling to terminal H_{cage} atoms ($^1J_{BH}$ 135–152 Hz), and one doublet of doublets corresponding to the boron atom {B(10) by analogy to the situation in the unsubstituted $[C_2B_9H_{12}]^-$ parent[20]} bearing both *exo*- and *endo*-H atoms; the proton couplings to this unique boron atom are typical, being 137 [$^1J_{BH(exo)}$] and 55 Hz [$^1J_{BH(endo)}$].

Reactions between $[PtCl_2(PR_3)_2]$ and Tl_2[7-Ph-8-Me-7,8-*nido*-$C_2B_9H_9$] in CH_2Cl_2 and appropriate work-up (as described in the Experimental section) afford the new dicarbaplatinaboranes 1-Ph-2-Me-3,3-$(PR_3)_2$-3,1,2-$PtC_2B_9H_9$ [R_3 = Me_2Ph **1**, Et_3 **2**, Ph_3 **3**, or $(C_6H_4Me\text{-}p)_3$ **4**] in good yields as the only isolatable heteroborane products. These compounds have been extensively characterised by microanalysis and by ^{1}H, ^{31}P, ^{11}B-{^{1}H} and ^{11}B NMR spectroscopies, and in the cases of **2** and **3** (two crystalline forms) by crystallographic studies (see later). The ^{31}P NMR spectra reveal preliminary evidence of steric congestion in these compounds. Thus, the spectrum of **1** consists of a single resonance with ^{195}Pt satellites, consistent with unhindered rotation (at room temperature) of the {$(PhMe_2P)_2Pt$} moiety about the platinum-cage vector (**1** contains the phosphine with lowest cone angle[21] in the complexes **1**–**4**), whereas the spectra of **2**–**4** indicate that rotation of the respective metal fragments is restricted, shown by the presence of two separate, platinum-coupled phosphorus resonances. The ^{11}B-{^{1}H} NMR spectra of all four complexes are rather similar in form, having nine boron resonances (some are coincident) which, upon retention of proton coupling, show characteristic $^1J_{BH}$ in the range 120–170 Hz. Crucially, a common feature of these spectra is a single, high-frequency resonance, well separated from the others (in the spectra of **1** and **2** this resonance shows distinct platinum satellites); this characteristic has been proposed[1] to be *diagnostic* of a 3,1,2-PtC_2B_9 cluster architecture, confirmed in the following X-ray crystallographic studies.

Structural Studies.—In Fig. 1 are illustrated deviations from regular icosahedral geometry which may be observed in 12-vertex carbametallaboranes.[22] Lateral slippage of the metal atom across the ligating C_2B_3 face gives rise to the parameter Δ, measured relative to the centroid of the reference B(5, 6, 11, 12, 9) plane; Δ > 0 corresponds to movement towards a position above B(8). The upper and lower pentagonal girdles may, in addition, slip with respect to each other (measured as the lateral

Table 1 Selected interatomic distances (Å) and interbond angles (°) in compound **2**

Pt(3)–P(1)	2.2952(13)	B(4)–B(8)	1.806(8)	P(2)–C(231)	1.822(7)	B(9)–B(10)	1.753(10)
Pt(3)–P(2)	2.2972(14)	B(4)–B(9)	1.832(9)	C(1)–C(2)	1.532(7)	B(9)–B(12)	1.753(10)
Pt(3) ··· C(1)	2.834(5)	B(5)–B(6)	1.749(9)	C(1)–B(4)	1.786(7)	B(10)–B(11)	1.764(10)
Pt(3) ··· C(2)	2.835(5)	B(5)–B(9)	1.770(9)	C(1)–B(5)	1.673(8)	B(10)–B(12)	1.755(10)
Pt(3)–B(4)	2.276(6)	B(5)–B(10)	1.796(9)	C(1)–B(6)	1.727(8)	B(11)–B(12)	1.736(10)
Pt(3)–B(7)	2.272(6)	B(6)–B(10)	1.757(10)	C(1)–C(101)	1.507(6)	C(111)–C(112)	1.531(8)
Pt(3)–B(8)	2.182(6)	B(6)–B(11)	1.766(9)	C(2)–B(6)	1.724(8)	C(121)–C(122)	1.492(9)
P(1)–C(111)	1.834(6)	B(7)–B(8)	1.792(9)	C(2)–B(7)	1.783(8)	C(131)–C(132)	1.538(10)
P(1)–C(121)	1.855(6)	B(7)–B(11)	1.811(9)	C(2)–B(11)	1.666(9)	C(211)–C(212)	1.540(9)
P(1)–C(131)	1.824(6)	B(7)–B(12)	1.826(9)	C(2)–C(201)	1.515(8)	C(221)–C(222)	1.527(10)
P(2)–C(211)	1.836(6)	B(8)–B(9)	1.757(9)	B(4)–B(5)	1.838(9)	C(231)–C(232)	1.520(10)
P(2)–C(221)	1.819(6)	B(8)–B(12)	1.761(9)				

P(1)–Pt(3)–P(2)	97.81(5)	Pt(3)–B(4)–B(8)	63.4(3)	Pt(3)–P(2)–C(221)	116.45(20)	B(4)–B(9)–B(8)	60.4(3)
P(1)–Pt(3)–C(1)	108.65(10)	C(1)–B(4)–B(5)	55.0(3)	Pt(3)–P(2)–C(231)	107.29(21)	B(5)–B(9)–B(10)	61.3(4)
P(1)–Pt(3)–C(2)	134.91(11)	C(1)–B(4)–B(8)	109.7(4)	C(211)–P(2)–C(221)	102.6(3)	B(8)–B(9)–B(12)	60.2(4)
P(1)–Pt(3)–B(4)	97.54(15)	B(5)–B(4)–B(9)	57.7(3)	C(211)–P(2)–C(231)	104.0(3)	B(10)–B(9)–B(12)	60.1(4)
P(1)–Pt(3)–B(7)	171.03(16)	B(8)–B(4)–B(9)	57.8(3)	C(221)–P(2)–C(231)	101.6(3)	B(5)–B(10)–B(6)	59.0(4)
P(1)–Pt(3)–B(8)	128.12(17)	C(1)–B(5)–B(4)	60.9(3)	Pt(3)–C(1)–C(2)	74.3(3)	B(5)–B(10)–B(9)	59.8(4)
P(2)–Pt(3)–C(1)	137.66(10)	C(1)–B(5)–B(6)	60.5(3)	Pt(3)–C(1)–B(4)	53.34(22)	B(6)–B(10)–B(11)	60.2(4)
P(2)–Pt(3)–C(2)	108.39(11)	B(4)–B(5)–B(9)	61.0(3)	Pt(3)–C(1)–C(101)	107.2(3)	B(9)–B(10)–B(12)	60.0(4)
P(2)–Pt(3)–B(4)	163.86(15)	B(6)–B(5)–B(10)	59.4(4)	C(2)–C(1)–B(4)	109.5(4)	B(11)–B(10)–B(12)	59.1(4)
P(2)–Pt(3)–B(7)	91.00(16)	B(9)–B(5)–B(10)	58.9(4)	C(2)–C(1)–B(6)	63.6(3)	C(2)–B(11)–B(6)	60.3(4)
P(2)–Pt(3)–B(8)	117.42(17)	C(1)–B(6)–C(2)	52.7(3)	C(2)–C(1)–C(101)	120.0(4)	C(2)–B(11)–B(7)	61.5(3)
C(1)–Pt(3)–C(2)	31.35(14)	C(1)–B(6)–B(5)	57.5(3)	B(4)–C(1)–B(5)	64.1(3)	B(6)–B(11)–B(10)	59.7(4)
C(1)–Pt(3)–B(4)	39.02(17)	C(2)–B(6)–B(11)	57.0(3)	B(4)–C(1)–C(101)	118.4(4)	B(7)–B(11)–B(12)	61.9(4)
C(1)–Pt(3)–B(7)	63.11(18)	B(5)–B(6)–B(10)	61.6(4)	B(5)–C(1)–B(6)	61.9(3)	B(10)–B(11)–B(12)	60.2(4)
C(1)–Pt(3)–B(8)	70.32(19)	B(10)–B(6)–B(11)	60.1(4)	B(5)–C(1)–C(101)	120.1(4)	B(7)–B(12)–B(8)	59.9(4)
C(2)–Pt(3)–B(4)	63.04(18)	Pt(3)–B(7)–C(2)	87.9(3)	B(6)–C(1)–C(101)	118.5(4)	B(7)–B(12)–B(11)	61.1(4)
C(2)–Pt(3)–B(7)	38.93(18)	Pt(3)–B(7)–B(8)	63.7(3)	Pt(3)–C(2)–C(1)	74.3(3)	B(8)–B(12)–B(9)	60.0(4)
C(2)–Pt(3)–B(8)	70.07(19)	C(2)–B(7)–B(8)	110.1(4)	Pt(3)–C(2)–B(7)	53.21(23)	B(9)–B(12)–B(10)	60.0(4)
B(4)–Pt(3)–B(7)	73.85(21)	C(2)–B(7)–B(11)	55.2(3)	Pt(3)–C(2)–C(201)	110.3(3)	B(10)–B(12)–B(11)	60.7(4)
B(4)–Pt(3)–B(8)	47.76(22)	B(8)–B(7)–B(12)	58.3(4)	C(1)–C(2)–B(6)	63.7(3)	C(1)–C(101)–C(102)	119.9(3)
B(7)–Pt(3)–B(8)	47.39(22)	B(11)–B(7)–B(12)	57.0(4)	C(1)–C(2)–B(7)	109.8(4)	C(1)–C(101)–C(106)	120.0(3)
Pt(3)–P(1)–C(111)	115.07(18)	Pt(3)–B(8)–B(4)	68.8(3)	C(1)–C(2)–C(201)	120.1(4)	P(1)–C(111)–C(112)	115.4(4)
Pt(3)–P(1)–C(121)	115.88(19)	Pt(3)–B(8)–B(7)	69.0(3)	B(6)–C(2)–B(11)	62.8(4)	P(1)–C(121)–C(122)	120.2(4)
Pt(3)–P(1)–C(131)	112.10(20)	B(4)–B(8)–B(7)	98.8(4)	B(6)–C(2)–C(201)	115.6(4)	P(1)–C(131)–C(132)	112.1(5)
C(111)–P(1)–C(121)	102.2(3)	B(4)–B(8)–B(9)	61.8(4)	B(7)–C(2)–B(11)	63.3(4)	P(2)–C(211)–C(212)	116.0(4)
C(111)–P(1)–C(131)	102.0(3)	B(7)–B(8)–B(12)	61.8(4)	B(7)–C(2)–C(201)	119.9(4)	P(2)–C(221)–C(222)	114.9(5)
C(121)–P(1)–C(131)	108.2(3)	B(9)–B(8)–B(12)	59.8(4)	B(11)–C(2)–C(201)	118.5(5)	P(2)–C(231)–C(232)	114.6(5)
Pt(3)–P(2)–C(211)	122.41(19)	B(4)–B(9)–B(5)	61.3(3)	Pt(3)–B(4)–C(1)	87.6(3)		

displacement of their respective centroids). Relative to the above (essentially planar) reference plane, the ligating C(1, 2)B(7, 8, 4) face may suffer some folding, quantified by dihedral angles θ and φ. The substituent elevation parameter χ describes the angle between the reference plane and the cage atom–substituent bond: in a regular icosahedron $\chi \approx 26°$.

We have previously observed[6] that compound **5** undergoes a facile thermal rearrangement, and that **6** isomerises spontaneously. In the former system we believe that the presence of the C_{cage}-bound phenyl group forces the platinum fragment to adopt an electronically unfavourable conformation and thereby facilitates rearrangement, whereas relief of intramolecular crowding between the pendant cage and phosphine (phenyl) groups is thought to produce the spontaneous reorganisation in the latter species. Accordingly, the structures of **1**–**4** are of interest as potential examples of congested structures intermediate between the two above extremes.

Crystallographic studies of compound **2** and two crystalline forms of **3** have confirmed the above 3,1,2-PtC_2B_9 formulation of the cage geometry. Figs. 2 and 3 present comparable views of each compound. In Tables 1–3 are listed selected interatomic distances and interbond angles. To our knowledge these represent the first species of the type 1-Ph-2-Me-3,3-L_2-3,1,2-$MC_2B_9H_9$ to be so characterised. (Note that molecules of **3** in **3**·0.5CH_2Cl_2 have been termed **3a** and those in **3**·unknown solvent **3b**.)

The structure of compound **2** was determined to establish the detailed geometry of a species of type 1-Ph-2-Me-3,3-$(PR_3)_2$-3,1,2-$PtC_2B_9H_9$ in which exists a (relatively) modest degree of intramolecular crowding. The cluster moiety comprises a rather distorted icosahedron in which the three heteroatoms (Pt, 2C) occupy mutually adjacent vertices of a triangular face, similar to that observed in the analogous compounds **5** and 1-R-3,3-L_2-3,1,2-$PtC_2B_9H_{10}$ [R = H, L = PEt_3 **7**,[22] L_2 = dppe **8**,[23] R = $MeOCH_2$, L = PMe_2Ph **9** (two crystallographically independent molecules)[24]]. The geometry of the metal fragment is comparable to that in **7**, save that the largest Pt–P–C angles are those for the ethyl groups closest to the C_{cage}-bound substituents, further evidencing the crowded nature of this molecule.

The cage-bound phenyl group is oriented to afford a value of θ_{Ph}[7] of 33.2°, larger than in the parent *closo*-carbaborane 1-Ph-2-Me-1,2-*closo*-$C_2B_{10}H_{10}$[7] (where θ_{Ph} = 16.7°), despite the unfavourable $\{C_{cage}Me\} \cdots \{C_{cage}Ph\}$ approach that this produces. This conformation appears to allow this phenyl substituent to 'insert' between the two triethylphosphine ligands. A further consequence of this behaviour is a close Pt ··· H approach: Pt(3) ··· H(102) is only 2.76 Å. (There is no evidence for any such interaction in the room-temperature solution ^1H NMR spectrum.) The phenyl and methyl groups bound to the carbaborane moiety at C(1) and C(2) have χ = 28.2 and 24.8° respectively, despite this (unfavourably) bringing the phenyl substituent closer to the area occupied by the two phosphines.

The C(1)–C(2) distance in compound **2** is 1.532(7) Å, essentially the same as in the analogues **7**–**9**. Likewise, the

Table 2 Selected interatomic distances (Å) and interbond angles (°) in compound **3a** and the solvate molecule in **3**·0.5CH_2Cl_2

C(1)–C(2)	1.525(9)	B(5)–B(10)	1.772(12)	Pt(3)–B(4)	2.324(8)	B(10)–B(12)	1.734(12)
C(1) ··· Pt(3)	3.003(6)	B(6)–B(10)	1.748(12)	Pt(3)–B(7)	2.291(7)	B(11)–B(12)	1.756(11)
C(1)–B(4)	1.765(10)	B(6)–B(11)	1.767(11)	Pt(3)–B(8)	2.143(7)	P(1)–C(101)	1.843(4)
C(1)–B(5)	1.658(10)	B(7)–B(8)	1.850(10)	Pt(3)–P(1)	2.3140(15)	P(1)–C(201)	1.818(4)
C(1)–B(6)	1.713(10)	B(7)–B(11)	1.801(10)	Pt(3)–P(2)	2.2940(16)	P(1)–C(301)	1.830(4)
C(1)–C(11)	1.502(8)	B(7)–B(12)	1.861(11)	B(4)–B(5)	1.797(11)	P(2)–C(401)	1.830(5)
C(2) ··· Pt(3)	2.980(6)	B(8)–B(9)	1.742(11)	B(4)–B(8)	1.826(11)	P(2)–C(501)	1.837(5)
C(2)–B(6)	1.730(10)	B(8)–B(12)	1.762(11)	B(4)–B(9)	1.849(11)	P(2)–C(601)	1.831(5)
C(2)–B(7)	1.728(9)	B(9)–B(10)	1.762(12)	B(5)–B(6)	1.751(12)	C(1S)–Cl(1S)	1.31(4)
C(2)–B(11)	1.643(9)	B(9)–B(12)	1.759(12)	B(5)–B(9)	1.766(12)	C(1S)–Cl(2S)	1.47(3)
C(2)–C(21)	1.513(9)	B(10)–B(11)	1.778(11)				
C(2)–C(1)–Pt(3)	74.4(3)	C(2)–B(7)–Pt(3)	94.7(4)	C(2)–Pt(3)–B(8)	68.20(23)	B(9)–B(12)–B(10)	60.6(5)
C(2)–C(1)–B(4)	109.0(5)	C(2)–B(7)–B(8)	111.3(5)	C(2)–Pt(3)–P(1)	105.15(12)	B(10)–B(12)–B(11)	61.2(5)
C(2)–C(1)–B(6)	64.3(4)	C(2)–B(7)–B(11)	55.4(4)	C(2)–Pt(3)–P(2)	142.83(12)	C(1)–C(11)–C(12)	120.1(4)
C(2)–C(1)–C(11)	118.9(5)	Pt(3)–B(7)–B(8)	61.2(3)	B(4)–Pt(3)–B(7)	71.9(3)	C(1)–C(11)–C(16)	119.9(4)
Pt(3)–C(1)–B(4)	50.6(3)	B(8)–B(7)–B(12)	56.7(4)	B(4)–Pt(3)–B(8)	48.1(3)	Pt(3)–P(1)–C(101)	123.97(14)
Pt(3)–C(1)–C(11)	108.4(3)	B(11)–B(7)–B(12)	57.3(4)	B(4)–Pt(3)–P(1)	163.35(19)	Pt(3)–P(1)–C(201)	108.02(14)
B(4)–C(1)–B(5)	63.2(4)	Pt(3)–B(8)–B(4)	71.2(3)	B(4)–Pt(3)–P(2)	97.91(19)	Pt(3)–P(1)–C(301)	113.67(14)
B(4)–C(1)–C(11)	118.6(5)	Pt(3)–B(8)–B(7)	69.6(3)	B(7)–Pt(3)–B(8)	49.2(3)	C(101)–P(1)–C(201)	104.70(19)
B(5)–C(1)–B(6)	62.6(4)	B(4)–B(8)–B(7)	94.9(5)	B(7)–Pt(3)–P(1)	91.96(18)	C(101)–P(1)–C(301)	98.31(19)
B(5)–C(1)–C(11)	122.3(5)	B(4)–B(8)–B(9)	62.3(4)	B(7)–Pt(3)–P(2)	168.69(18)	C(201)–P(1)–C(301)	106.71(19)
B(6)–C(1)–C(11)	118.8(5)	B(7)–B(8)–B(12)	62.0(4)	B(8)–Pt(3)–P(1)	123.50(20)	Pt(3)–P(2)–C(401)	112.03(15)
C(1)–C(2)–Pt(3)	76.1(3)	B(9)–B(8)–B(12)	60.3(5)	B(8)–Pt(3)–P(2)	120.32(20)	Pt(3)–P(2)–C(501)	116.03(16)
C(1)–C(2)–B(6)	63.1(4)	B(4)–B(9)–B(5)	59.6(4)	P(1)–Pt(3)–P(2)	98.50(5)	Pt(3)–P(2)–C(601)	117.91(17)
C(1)–C(2)–B(7)	110.6(5)	B(4)–B(9)–B(8)	61.1(4)	C(1)–B(4)–Pt(3)	93.5(4)	C(401)–P(2)–C(501)	97.54(21)
C(1)–C(2)–C(21)	120.3(5)	B(5)–B(9)–B(10)	60.3(5)	C(1)–B(4)–B(5)	55.5(4)	C(401)–P(2)–C(601)	105.74(21)
Pt(3)–C(2)–B(7)	50.0(3)	B(8)–B(9)–B(12)	60.4(5)	C(1)–B(4)–B(8)	111.4(5)	C(501)–P(2)–C(601)	105.23(22)
Pt(3)–C(2)–C(21)	110.3(4)	B(10)–B(9)–B(12)	59.0(5)	Pt(3)–B(4)–B(8)	60.8(3)	P(1)–C(101)–C(102)	123.3(3)
B(6)–C(2)–B(11)	63.1(4)	B(5)–B(10)–B(6)	59.7(5)	B(5)–B(4)–B(9)	57.9(4)	P(1)–C(101)–C(106)	116.7(3)
B(6)–C(2)–C(21)	117.2(5)	B(5)–B(10)–B(9)	60.0(5)	B(8)–B(4)–B(9)	56.6(4)	P(1)–C(201)–C(202)	117.7(3)
B(7)–C(2)–B(11)	64.5(4)	B(6)–B(10)–B(11)	60.1(4)	C(1)–B(5)–B(4)	61.3(4)	P(1)–C(201)–C(206)	122.3(3)
B(7)–C(2)–C(21)	117.6(5)	B(9)–B(10)–B(12)	60.4(5)	C(1)–B(5)–B(6)	60.2(4)	P(1)–C(301)–C(302)	121.7(3)
B(11)–C(2)–C(21)	118.2(5)	B(11)–B(10)–B(12)	60.0(5)	B(4)–B(5)–B(9)	62.5(5)	P(1)–C(301)–C(306)	118.3(3)
C(1)–Pt(3)–C(2)	29.53(16)	C(2)–B(11)–B(6)	60.8(4)	B(6)–B(5)–B(10)	59.5(5)	P(2)–C(401)–C(402)	119.9(3)
C(1)–Pt(3)–B(4)	35.93(22)	C(2)–B(11)–B(7)	60.0(4)	B(9)–B(5)–B(10)	59.7(5)	P(2)–C(401)–C(406)	119.9(3)
C(1)–Pt(3)–B(7)	58.93(21)	B(6)–B(11)–B(10)	59.1(4)	C(1)–B(6)–C(2)	52.6(4)	P(2)–C(501)–C(502)	117.0(3)
C(1)–Pt(3)–B(8)	68.07(23)	B(7)–B(11)–B(12)	63.1(4)	C(1)–B(6)–B(5)	57.2(4)	P(2)–C(501)–C(506)	123.0(3)
C(1)–Pt(3)–P(1)	131.41(12)	B(10)–B(11)–B(12)	58.8(5)	C(2)–B(6)–B(11)	56.0(4)	P(2)–C(601)–C(602)	122.1(4)
C(1)–Pt(3)–P(2)	115.52(12)	B(7)–B(12)–B(8)	61.4(4)	B(5)–B(6)–B(10)	60.8(5)	P(2)–C(601)–C(606)	117.9(4)
C(2)–Pt(3)–B(4)	59.25(22)	B(7)–B(12)–B(11)	59.6(4)	B(10)–B(6)–B(11)	60.8(4)	Cl(1S)–C(1S)–Cl(2S)	134.7(24)
C(2)–Pt(3)–B(7)	35.31(21)	B(8)–B(12)–B(9)	59.3(5)				

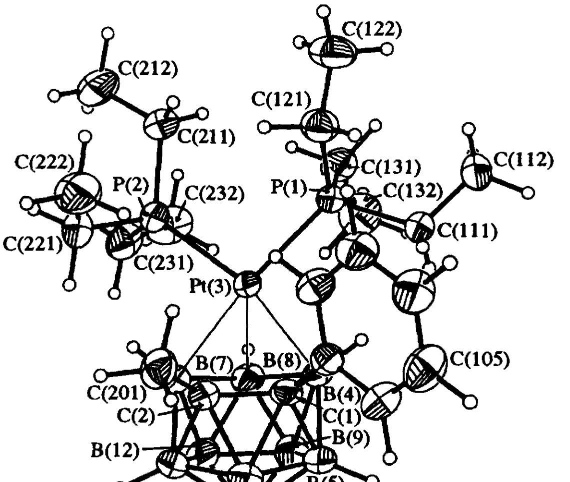


Fig. 2 Perspective view of a single molecule of compound 2 (50% thermal ellipsoids). The phenyl ring is numbered cyclically; cage and aromatic H atoms carry the same number as the B or C atom to which they are bound

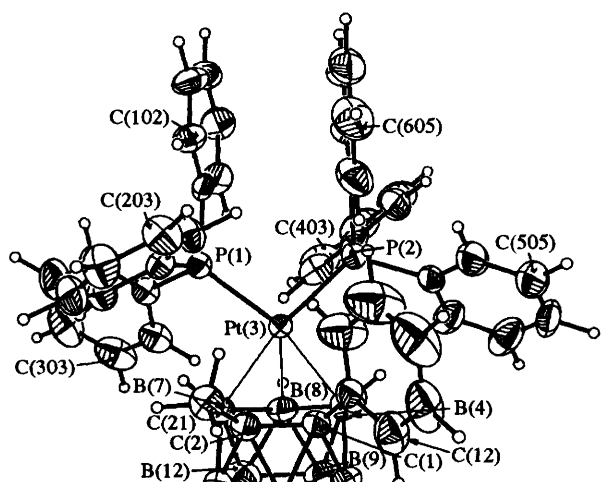


Fig. 3 Perspective view of a single molecule of compound 3 (50% thermal ellipsoids) in **3**·0.5CH_2Cl_2. Cage H atoms and those in the phenyl group are numbered following the conventions in Fig. 2

ligating carbaborane face in **2** is folded about the B(4) ··· B(7) vector, resulting in fold angles $\theta = 5.53°$ and $\varphi = 8.11°$; these are comparable to, but slightly larger than, those found in **5** and **7**–**9**. However, in contrast to these previous analogues, the value of the slip parameter Δ is substantially greater, being 0.74 Å (*cf.*

Table 3 Selected internuclear distances (Å) and interbond angles (°) in compound **3b** in **3**·unknown solvent

C(1)–C(2)	1.554(19)	B(5)–B(9)	1.78(3)	C(2)–C(21)	1.514(21)	B(9)–B(12)	1.73(3)
C(1) · · · Pt(3)	2.933(14)	B(5)–B(10)	1.79(3)	Pt(3)–B(4)	2.294(18)	B(10)–B(11)	1.78(3)
C(1)–B(4)	1.809(22)	B(6)–B(10)	1.75(3)	Pt(3)–B(7)	2.320(18)	B(10)–B(12)	1.81(3)
C(1)–B(5)	1.691(22)	B(6)–B(11)	1.76(3)	Pt(3)–B(8)	2.171(17)	B(11)–B(12)	1.80(3)
C(1)–B(6)	1.747(23)	B(7)–B(8)	1.844(25)	Pt(3)–P(1)	2.301(4)	P(1)–C(111)	1.854(10)
C(1)–C(11)	1.504(17)	B(7)–B(11)	1.82(3)	Pt(3)–P(2)	2.309(4)	P(1)–C(121)	1.822(11)
C(2) · · · Pt(3)	2.952(14)	B(7)–B(12)	1.832(25)	B(4)–B(5)	1.844(25)	P(1)–C(131)	1.824(11)
C(2)–B(6)	1.767(23)	B(8)–B(9)	1.72(3)	B(4)–B(8)	1.754(25)	P(2)–C(211)	1.815(10)
C(2)–B(7)	1.756(22)	B(8)–B(12)	1.700(24)	B(4)–B(9)	1.83(3)	P(2)–C(221)	1.842(12)
C(2)–B(11)	1.638(23)	B(9)–B(10)	1.78(3)	B(5)–B(6)	1.76(3)	P(2)–C(231)	1.811(10)
C(2)–C(1)–Pt(3)	75.4(7)	C(2)–B(7)–Pt(3)	91.8(9)	C(2)–Pt(3)–B(8)	68.0(5)	B(9)–B(12)–B(10)	60.4(10)
C(2)–C(1)–B(4)	109.1(11)	C(2)–B(7)–B(8)	109.3(12)	C(2)–Pt(3)–P(1)	105.4(3)	B(10)–B(12)–B(11)	59.2(10)
C(2)–C(1)–B(6)	64.4(9)	C(2)–B(7)–B(11)	54.5(9)	C(2)–Pt(3)–P(2)	139.5(3)	C(1)–C(11)–C(12)	118.8(9)
C(2)–C(1)–C(11)	121.2(11)	Pt(3)–B(7)–B(8)	61.6(7)	B(4)–Pt(3)–B(7)	72.8(6)	C(1)–C(11)–C(16)	121.2(10)
Pt(3)–C(1)–B(4)	51.5(7)	B(8)–B(7)–B(12)	55.1(9)	B(4)–Pt(3)–B(8)	46.2(6)	Pt(3)–P(1)–C(111)	123.2(3)
Pt(3)–C(1)–C(11)	105.6(7)	B(11)–B(7)–B(12)	58.9(10)	B(4)–Pt(3)–P(1)	164.1(5)	Pt(3)–P(1)–C(121)	113.4(4)
B(4)–C(1)–B(5)	63.5(9)	Pt(3)–B(8)–B(4)	70.6(8)	B(4)–Pt(3)–P(2)	96.5(5)	Pt(3)–P(1)–C(131)	110.7(4)
B(4)–C(1)–C(11)	116.2(11)	Pt(3)–B(8)–B(7)	70.0(8)	B(7)–Pt(3)–B(8)	48.4(6)	C(111)–P(1)–C(121)	97.0(5)
B(5)–C(1)–B(6)	61.5(10)	B(4)–B(8)–B(7)	99.1(12)	B(7)–Pt(3)–P(1)	91.2(4)	C(111)–P(1)–C(131)	104.0(5)
B(5)–C(1)–C(11)	120.8(11)	B(4)–B(8)–B(9)	63.8(10)	B(7)–Pt(3)–P(2)	169.2(4)	C(121)–P(1)–C(1	106.8(5)
B(6)–C(1)–C(11)	121.1(11)	B(7)–B(8)–B(12)	62.1(10)	B(8)–Pt(3)–P(1)	122.4(5)	Pt(3)–P(2)–C(211)	117.3(4)
C(1)–C(2)–Pt(3)	74.0(7)	B(9)–B(8)–B(12)	60.8(10)	B(8)–Pt(3)–P(2)	122.7(5)	Pt(3)–P(2)–C(221)	114.7(4)
C(1)–C(2)–B(6)	63.1(9)	B(4)–B(9)–B(5)	61.4(10)	P(1)–Pt(3)–P(2)	99.42(14)	Pt(3)–P(2)–C(231)	112.3(3)
C(1)–C(2)–B(7)	109.7(11)	B(4)–B(9)–B(8)	59.1(10)	C(1)–B(4)–Pt(3)	90.5(8)	C(211)–P(2)–C(221)	103.1(5)
C(1)–C(2)–C(21)	121.0(12)	B(5)–B(9)–B(10)	60.6(10)	C(1)–B(4)–B(5)	55.1(9)	C(211)–P(2)–C(231)	105.6(5)
Pt(3)–C(2)–B(7)	51.8(7)	B(8)–B(9)–B(12)	59.1(10)	C(1)–B(4)–B(8)	110.1(12)	C(221)–P(2)–C(231)	102.1(5)
Pt(3)–C(2)–C(21)	113.1(9)	B(10)–B(9)–B(12)	62.1(10)	Pt(3)–B(4)–B(8)	63.2(8)	P(1)–C(111)–C(112)	116.2(7)
B(6)–C(2)–B(11)	62.3(10)	B(5)–B(10)–B(6)	59.5(10)	B(5)–B(4)–B(9)	57.8(10)	P(1)–C(111)–C(116)	123.7(7)
B(6)–C(2)–C(21)	114.9(12)	B(5)–B(10)–B(9)	59.6(10)	B(8)–B(4)–B(9)	57.1(10)	P(1)–C(121)–C(122)	120.9(7)
B(7)–C(2)–B(11)	64.7(10)	B(6)–B(10)–B(11)	59.9(10)	C(1)–B(5)–B(4)	61.4(9)	P(1)–C(121)–C(126)	119.1(7)
B(7)–C(2)–C(21)	119.6(12)	B(9)–B(10)–B(12)	57.5(10)	C(1)–B(5)–B(6)	60.8(10)	P(1)–C(131)–C(132)	115.5(8)
B(11)–C(2)–C(21)	117.1(12)	B(11)–B(10)–B(12)	59.9(10)	B(4)–B(5)–B(9)	60.8(10)	P(1)–C(131)–C(136)	124.5(8)
C(1)–Pt(3)–C(2)	30.6(4)	C(2)–B(11)–B(6)	62.5(10)	B(6)–B(5)–B(10)	59.0(10)	P(2)–C(211)–C(212)	115.7(7)
C(1)–Pt(3)–B(4)	38.1(5)	C(2)–B(11)–B(7)	60.8(10)	B(9)–B(5)–B(10)	59.9(10)	P(2)–C(211)–C(216)	124.3(7)
C(1)–Pt(3)–B(7)	60.8(5)	B(6)–B(11)–B(10)	59.1(10)	C(1)–B(6)–C(2)	52.5(8)	P(2)–C(221)–C(222)	122.8(9)
C(1)–Pt(3)–B(8)	67.9(5)	B(7)–B(11)–B(12)	60.9(10)	C(1)–B(6)–B(5)	57.7(9)	P(2)–C(221)–C(226)	117.2(8)
C(1)–Pt(3)–P(1)	132.9(3)	B(10)–B(11)–B(12)	60.8(10)	C(2)–B(6)–B(11)	55.3(9)	P(2)–C(231)–C(232)	120.1(7)
C(1)–Pt(3)–P(2)	111.9(3)	B(7)–B(12)–B(8)	62.8(10)	B(5)–B(6)–B(10)	61.5(10)	P(2)–C(231)–C(236)	119.9(7)
C(2)–Pt(3)–B(4)	61.6(5)	B(7)–B(12)–B(11)	60.2(10)	B(10)–B(6)–B(11)	61.0(10)		
C(2)–Pt(3)–B(7)	36.5(5)	B(8)–B(12)–B(9)	60.1(10)				

0.35–0.44 Å in **5** and **7**–**9**). This is reflected in distances to the C_{cage} atoms in **2** [Pt(3) · · · C(1) is 2.834(5), and Pt(3) · · · C(2) is 2.835(5) Å] which are much longer than previously (average 2.51 Å), and indeed are almost non-bonding, and a correspondingly much shorter Pt(3)–B(8) distance of 2.182(6) Å (*cf.* previous average 2.25 Å); the Pt(3)–B(4) and Pt(3)–B(7) distances [2.276(6) and 2.272(6) Å respectively] are similar to those observed formerly (average 2.27 Å). The upper C_2B_3 belt is also slightly slipped with respect to the lower B_5 belt by some 0.08 Å [towards the midpoint of the B(9)–B(12) vector]: this slightly enhances Δ, but this parameter is, even so, still very much greater than in the above-mentioned relatives which suffer similar interplanar slippages.

The substantial enhancement of the slip parameter Δ in compound **2** vastly exceeds any experimental uncertainty in its value (e.s.d. $\leqslant$ 0.01 Å), and must be directly attributed to the highly congested nature of **2**. [For example, the close proximity of H(102) to the platinum atom is a possible contributor to the large value of Δ: a filled d_{z^2} orbital points towards this H atom, a probable consequence of which is a repulsive Pt · · · H interaction.] This prompted the structural characterisation of a more crowded analogue such as **3**. The heteroborane polyhedron in both crystalline forms of **3** appears similar to that in **2**; again the metal fragment reveals some deviations from ideal geometry effected, at least in part, by intersubstituent interactions.

In compound **3a**, as in **2**, the C_{cage}-bound phenyl group has a conformation which is not very far from orthogonal to the C(1)–C(2) connectivity, with θ_{Ph} = 28.2°, whereas in **3b** this substituent is somewhat more twisted (about the C_{cage}–C_{Ph} bond), having θ_{Ph} = 44.6°. The elevations (χ) of the pendant phenyl and methyl groups in **3a** are 29.0 and 26.2° respectively, mirroring the situation in **2**; whilst in **3b** the greater twist of the phenyl substituent is reflected in a larger asymmetry in χ, the phenyl and methyl substituents having, respectively, χ = 31.5 and 23.5°. The orientation of the C-bound phenyl group in both **3a** and **3b** again appears to afford this substituent a niche between the two triphenylphosphine ligands. Furthermore, there is again, in both crystalline modifications of **3**, a γ-H atom which is close to Pt(3) [in **3a** Pt(3) · · · H(16) is only 2.84 Å; in **3b** the corresponding distance, Pt(3) · · · H(102), is 2.94 Å].

The C(1)–C(2) separation in compound **3a** is 1.525(9) Å, essentially the same as that in **2**, and in the analogues **7**–**9**; this distance in **3b**, 1.554(19) Å, is (numerically) slightly longer. Similarly, the upper C_2B_3 face of the carbaborane ligand in both structures of **3** is folded, about B(4) · · · B(7), giving rise to folding angles θ and φ of 6.4 and 8.9° in **3a**, and 4.9 and 10.5° in **3b**, respectively. However, molecules of **3** differ significantly from **2** and **7**–**9** in that the metal atom is now *very substantially slipped*: the parameter Δ is 0.94 Å in **3a** and 0.91 Å in **3b**. Thus, although Δ is again slightly increased by additional 'interplane slippages' (0.06 and 0.10 Å respectively), the platinum fragment is perhaps more appropriately described as pseudo-σ-bonded to B(8). [In σ-bound complexes of linear metal fragments such as

Table 4 Crystallographic data and details of data collection and structure refinement for compounds **2**, **3**·0.5CH$_2$Cl$_2$ and **3**·unknown solvent

	2	**3**·0.5CH$_2$Cl$_2$	**3**·unknown solvent
Crystal size/mm	0.5 × 0.5 × 0.25	0.4 × 0.3 × 0.3	0.4 × 0.25 × 0.2
Formula	$C_{21}H_{47}B_9P_2Pt$	$C_{45}H_{47}B_9P_2Pt·0.5CH_2Cl_2$	$C_{45}H_{47}B_9P_2Pt$·unknown solvent*
M_r	653.92	984.65	1002.25
System	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a/Å	11.038(6)	10.264(5)	10.316(13)
b/Å	16.1922(20)	12.206(3)	22.227(6)
c/Å	16.381(5)	19.340(3)	19.996(6)
α/°		78.301(16)	
β/°	100.95(4)	81.149(21)	89.86(6)
γ/°		74.82(3)	
U/Å^3	2874.4	2276.8	4584.0
Z	4	2	4
D_c/Mg m^{-3}	1.511	1.436	1.452
μ(Mo-Kα)/cm^{-1}	50.52	32.72	31.94
F(000)	1304	982	2000
$\theta_{\text{orientation}}$/°	10–10.5	10–12	8–9
$\theta_{\text{data collection}}$/°	1–26	1–25	1–22
hkl ranges	−13 to 13, 0–20, 0–20	0–12, −14 to 14, −23 to 23	−10 to 10, 0–23, 0–21
Data measured	6064	8494	5895
Unique data	5636	8007	5602
Data observed	4943	6834	4208
Period/h	131	202	132
T_{min}, T_{max}	0.732, 1.405	0.881, 1.136	0.858, 1.119
R_{int}	0.0812	0.0137	0.0162
U_H/Å^2	0.096(4)	0.100(4)	0.087(8)
g	0.000 393	0.000 221	0.000 669
R	0.0344	0.0420	0.0613
R'	0.0384	0.0377	0.0652
S	0.973	1.100	1.244
Variables	326	446	434
Maximum, minimum residues/e Å^{-3}	0.80, −0.75	0.74, −1.13	1.08 (near solvates), −1.32

* M_r, D_c, μ and F(000) calculated on the basis of 'unknown solvent' being five carbon atoms of unit occupancy per asymmetric unit.

Table 5 Fractional coordinates of non-H atoms in compound **2**

Atom	x	y	z
Pt(3)	0.250 81(2)	0.057 95(1)	0.217 72(1)
P(1)	0.455 20(11)	0.075 63(9)	0.276 20(7)
P(2)	0.256 21(12)	0.115 35(10)	0.090 22(7)
C(1)	0.108 8(4)	0.074 2(3)	0.344 0(3)
C(2)	0.024 0(4)	0.101 6(4)	0.263 4(3)
B(4)	0.195 2(5)	−0.014 3(4)	0.324 0(3)
B(5)	0.064 5(5)	−0.015 9(4)	0.378 7(4)
B(6)	−0.047 1(5)	0.057 2(5)	0.337 6(4)
B(7)	0.044 6(5)	0.035 3(4)	0.180 2(3)
B(8)	0.137 1(6)	−0.051 9(4)	0.220 1(4)
B(9)	0.072 3(6)	−0.091 7(5)	0.302 0(4)
B(10)	−0.070 6(6)	−0.046 0(5)	0.305 3(4)
B(11)	−0.088 0(5)	0.033 7(5)	0.230 6(4)
B(12)	−0.024 2(7)	−0.060 1(5)	0.209 6(4)
C(101)	0.171 6(3)	0.137 95(21)	0.404 65(15)
C(102)	0.248 4(3)	0.196 98(21)	0.378 85(15)
C(103)	0.309 1(3)	0.254 69(21)	0.435 47(15)
C(104)	0.293 0(3)	0.253 38(21)	0.517 89(15)
C(105)	0.216 2(3)	0.194 35(21)	0.543 69(15)
C(106)	0.155 5(3)	0.136 63(21)	0.487 06(15)
C(201)	−0.002 6(5)	0.192 6(4)	0.246 9(3)
C(111)	0.497 8(5)	0.045 1(4)	0.385 7(3)
C(112)	0.635 3(5)	0.052 0(5)	0.423 8(3)
C(121)	0.513 9(5)	0.183 1(4)	0.278 1(3)
C(122)	0.638 0(5)	0.200 2(4)	0.258 3(4)
C(131)	0.555 7(5)	0.010 2(4)	0.227 5(3)
C(132)	0.529 4(7)	−0.082 2(4)	0.237 2(5)
C(211)	0.396 1(5)	0.162 9(4)	0.065 8(3)
C(212)	0.389 4(7)	0.188 8(5)	−0.025 4(4)
C(221)	0.137 9(5)	0.191 6(4)	0.052 1(3)
C(222)	0.162 5(7)	0.277 8(4)	0.089 4(5)
C(231)	0.218 9(6)	0.033 8(4)	0.012 9(3)
C(232)	0.316 0(8)	−0.033 5(5)	0.018 0(5)

[10-*endo*-{M(PPh$_3$)}-7,8-C$_2$B$_9$H$_{11}$]$^{n-}$ (n = 0, M = Hg;[25] n = 1, M = Au[26]) values of Δ are 0.92 and 0.87 Å and the interplane slips are *ca.* 0.15 and 0.12 Å respectively.] Indeed, these large Δ values are reflected in the now considerable range of Pt(3) · · · cage distances: the Pt(3) · · · C$_{\text{cage}}$ contacts in **3** are essentially non-bonding [Pt(3) · · · C(1) is 3.003(6) Å and Pt(3) · · · C(2) is 2.980(6) Å in **3a**; in **3b** these are 2.933(14) and 2.952(14) Å respectively; all are much larger than previously observed.] The Pt(3)–B(4,7) distances are also somewhat increased [Pt(3)–B(4) is 2.324(8) and 2.294(18) and Pt(3)–B(7) is 2.291(7) and 2.320(18) Å, in **3a** and **3b** respectively], whilst the Pt(3)–B(8) bond [2.143(7) (**3a**), 2.171(17) Å (**3b**)] is very short.

In spite of the enhanced Pt-atom slippages noted in molecules of **2** and **3** the anticipated[22] shortening in the C(1)–C(2) connectivity is not observed, clearly manifesting some mutual repulsion between the cage-bound methyl and phenyl groups. (A similar scenario has been identified previously.[1]) The effect of the basicity of the metal-bound ligands upon slippage in systems of this type has been discussed elsewhere,[27] and it has been demonstrated that, in the absence of other influences such as steric factors, ligands of higher basicity (which increase the electron density at the metal centre) lead to increased slippage. This is confirmed in systems of the present type by comparison of **7** and **8**: in **7** the presence of the more basic PEt$_3$ ligands leads to a Δ value of 0.42 Å; in **8** the less basic phosphine dppe causes a reduction in Δ to 0.35 Å. Thus, in the ostensibly parallel cases **2** and **3**, intramolecular crowding has effected a three-fold perturbation of previously observed cluster behaviour. First, both species show remarkable enhancement in the slip distortion Δ (relative to the analogous compounds **7** and **8**) and, secondly, this larger slippage does not shorten the C$_{\text{cage}}$–C$_{\text{cage}}$ connectivity. Thirdly, and crucially, the electronic preference of **3** to adopt a smaller Δ than that of **2** has been overturned by the steric effects in the former.

Table 6 Fractional coordinates of non-H atoms in compound **3**·$0.5CH_2Cl_2$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
C(1)	−0.255 5(6)	0.099 2(5)	−0.240 9(3)	C(204)	0.308 7(4)	−0.086 6(3)	−0.379 46(14)
C(2)	−0.187 8(6)	0.094 7(5)	−0.316 6(3)	C(205)	0.236 2(4)	−0.087 9(3)	−0.434 57(14)
Pt(3)	−0.217 42(3)	−0.144 88(2)	−0.261 79(1)	C(206)	0.128 4(4)	−0.141 8(3)	−0.420 76(14)
B(4)	−0.372 7(8)	0.011 1(7)	−0.221 6(4)	C(301)	−0.104 7(4)	−0.270 3(3)	−0.413 20(21)
B(5)	−0.418 7(9)	0.165 9(7)	−0.239 0(4)	C(302)	−0.237 1(4)	−0.221 5(3)	−0.430 38(21)
B(6)	−0.300 0(8)	0.222 6(6)	−0.301 3(4)	C(303)	−0.273 8(4)	−0.232 4(3)	−0.494 76(21)
B(7)	−0.248 4(7)	0.004 9(6)	−0.355 3(3)	C(304)	−0.178 0(4)	−0.291 9(3)	−0.541 95(21)
B(8)	−0.399 5(7)	−0.034 9(6)	−0.301 3(4)	C(305)	−0.045 6(4)	−0.340 7(3)	−0.524 76(21)
B(9)	−0.505 9(8)	0.092 8(7)	−0.279 4(4)	C(306)	−0.009 0(4)	−0.329 8(3)	−0.460 38(21)
B(10)	−0.450 4(8)	0.213 2(7)	−0.329 1(4)	C(401)	−0.326 2(4)	−0.379 8(3)	−0.166 70(20)
B(11)	−0.291 7(8)	0.159 9(6)	−0.377 0(4)	C(402)	−0.383 2(4)	−0.370 6(3)	−0.229 26(20)
B(12)	−0.425 2(8)	0.090 5(7)	−0.366 3(4)	C(403)	−0.466 0(4)	−0.443 0(3)	−0.232 93(20)
C(11)	−0.170 8(5)	0.099 0(3)	−0.184 1(3)	C(404)	−0.491 8(4)	−0.524 6(3)	−0.174 06(20)
C(12)	−0.198 3(5)	0.193 5(3)	−0.149 4(3)	C(405)	−0.434 8(4)	−0.533 9(3)	−0.111 50(20)
C(13)	−0.115 8(5)	0.195 3(3)	−0.098 8(3)	C(406)	−0.352 0(4)	−0.461 5(3)	−0.107 83(20)
C(14)	−0.005 8(5)	0.102 5(3)	−0.083 0(3)	C(501)	−0.331 0(4)	−0.221 9(4)	−0.081 99(23)
C(15)	0.021 7(5)	0.008 0(3)	−0.117 7(3)	C(502)	−0.471 8(4)	−0.194 0(4)	−0.082 11(23)
C(16)	−0.060 8(5)	0.006 2(3)	−0.168 2(3)	C(503)	−0.555 5(4)	−0.152 3(4)	−0.024 50(23)
C(21)	−0.039 3(6)	0.095 8(5)	−0.334 5(3)	C(504)	−0.498 6(4)	−0.138 5(4)	0.033 23(23)
P(1)	−0.051 74(15)	−0.259 20(13)	−0.329 27(7)	C(505)	−0.357 8(4)	−0.166 4(4)	0.033 34(23)
P(2)	−0.228 68(16)	−0.277 44(13)	−0.159 69(8)	C(506)	−0.274 1(4)	−0.208 1(4)	−0.024 27(23)
C(101)	0.022 2(3)	−0.413 4(3)	−0.299 48(22)	C(601)	−0.068 8(5)	−0.365 0(4)	−0.127 33(23)
C(102)	0.157 4(3)	−0.457 1(3)	−0.285 80(22)	C(602)	−0.036 5(5)	−0.485 1(4)	−0.117 64(23)
C(103)	0.207 9(3)	−0.575 5(3)	−0.266 63(22)	C(603)	0.086 5(5)	−0.548 1(4)	−0.092 63(23)
C(104)	0.123 3(3)	−0.650 3(3)	−0.261 14(22)	C(604)	0.177 1(5)	−0.491 0(4)	−0.077 32(23)
C(105)	−0.011 9(3)	−0.606 6(3)	−0.274 81(22)	C(605)	0.144 7(5)	−0.370 9(4)	−0.087 01(23)
C(106)	−0.062 4(3)	−0.488 2(3)	−0.293 98(22)	C(606)	0.021 8(5)	−0.307 9(4)	−0.112 02(23)
C(201)	0.093 1(4)	−0.194 2(3)	−0.351 83(14)	C(1S)	−0.369 7(23)	−0.527 7(19)	−0.503 3(12)
C(202)	0.165 5(4)	−0.192 9(3)	−0.296 72(14)	Cl(1S)	−0.398(3)	−0.486 7(24)	−0.443 6(14)
C(203)	0.273 3(4)	−0.139 1(3)	−0.310 53(14)	Cl(2S)	−0.442(3)	−0.580 3(17)	−0.542 7(11)

Table 7 Fractional coordinates of non-H atoms in compound **3**·unknown solvent

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
C(1)	0.541 1(13)	0.308 4(6)	0.129 4(7)	C(123)	0.221 4(10)	0.349 3(5)	0.435 6(4)
C(2)	0.514 5(13)	0.261 7(6)	0.185 7(7)	C(124)	0.241 4(10)	0.334 9(5)	0.502 7(4)
Pt(3)	0.537 99(5)	0.379 38(3)	0.253 10(3)	C(125)	0.367 0(10)	0.327 1(5)	0.526 8(4)
B(4)	0.452 1(15)	0.376 6(9)	0.147 4(9)	C(126)	0.472 8(10)	0.333 7(5)	0.483 8(4)
B(5)	0.408 0(17)	0.321 4(8)	0.082 5(9)	C(131)	0.685 5(10)	0.287 8(4)	0.366 2(5)
B(6)	0.444 2(17)	0.247 3(9)	0.106 8(9)	C(132)	0.810 5(10)	0.290 5(4)	0.339 6(5)
B(7)	0.411 4(17)	0.293 4(8)	0.246 2(9)	C(133)	0.891 2(10)	0.240 2(4)	0.342 7(5)
B(8)	0.344 4(17)	0.364 6(8)	0.214 1(9)	C(134)	0.846 9(10)	0.187 2(4)	0.372 4(5)
B(9)	0.284 8(17)	0.351 0(9)	0.135 5(10)	C(135)	0.722 0(10)	0.184 6(4)	0.399 0(5)
B(10)	0.284 6(16)	0.272 8(9)	0.115 6(9)	C(136)	0.641 2(10)	0.234 8(4)	0.395 9(5)
B(11)	0.364 5(17)	0.237 7(9)	0.184 2(10)	C(211)	0.808 3(10)	0.474 5(4)	0.276 1(5)
B(12)	0.259 2(17)	0.300 4(8)	0.199 8(9)	C(212)	0.893 1(10)	0.428 1(4)	0.258 9(5)
C(11)	0.674 8(10)	0.316 4(5)	0.100 5(4)	C(213)	1.019 9(10)	0.428 3(4)	0.283 0(5)
C(12)	0.780 2(10)	0.319 6(5)	0.144 0(4)	C(214)	1.061 9(10)	0.474 9(4)	0.324 3(5)
C(13)	0.905 3(10)	0.326 5(5)	0.118 6(4)	C(215)	0.977 1(10)	0.521 4(4)	0.341 5(5)
C(14)	0.925 1(10)	0.330 2(5)	0.049 7(4)	C(216)	0.850 4(10)	0.521 2(4)	0.317 3(5)
C(15)	0.819 8(10)	0.327 1(5)	0.006 2(4)	C(221)	0.671 1(10)	0.493 6(5)	0.153 5(6)
C(16)	0.694 6(10)	0.320 2(5)	0.031 6(4)	C(222)	0.786 2(10)	0.483 3(5)	0.118 6(6)
C(21)	0.617 6(16)	0.217 2(7)	0.206 9(8)	C(223)	0.798 9(10)	0.502 9(5)	0.052 6(6)
P(1)	0.592 7(4)	0.357 53(18)	0.361 94(20)	C(224)	0.696 5(10)	0.532 8(5)	0.021 6(6)
P(2)	0.646 7(4)	0.469 49(17)	0.240 80(19)	C(225)	0.581 4(10)	0.543 0(5)	0.056 5(6)
C(111)	0.683 9(8)	0.410 1(4)	0.416 3(5)	C(226)	0.568 7(10)	0.523 4(5)	0.122 5(6)
C(112)	0.622 6(8)	0.464 4(4)	0.431 4(5)	C(231)	0.557 4(9)	0.532 2(3)	0.275 8(5)
C(113)	0.681 1(8)	0.505 0(4)	0.475 1(5)	C(232)	0.443 4(9)	0.522 1(3)	0.311 7(5)
C(114)	0.800 8(8)	0.491 4(4)	0.503 7(5)	C(233)	0.375 1(9)	0.570 4(3)	0.338 9(5)
C(115)	0.862 0(8)	0.437 2(4)	0.488 6(5)	C(234)	0.420 8(9)	0.629 0(3)	0.330 2(5)
C(116)	0.803 6(8)	0.396 5(4)	0.444 9(5)	C(235)	0.534 8(9)	0.639 2(3)	0.294 3(5)
C(121)	0.452 8(10)	0.348 1(5)	0.416 7(4)	C(236)	0.603 1(9)	0.590 8(3)	0.267 0(5)
C(122)	0.327 1(10)	0.355 9(5)	0.392 6(4)				

Relation of these Compounds to the Isomerisations of Platinum Complexes of Aryl Carbaboranes.—Given that molecules such as **3** and **4** are (arguably) more congested than **5**, it is perhaps surprising that **2** fails to rearrange under thermolysis conditions which induce a skeletal reorganisation in **5**. This observation lends support to the proposed[6] influence of ground-state destabilisation in **5**: it appears that in complexes such as **3** the enhanced lateral slippage Δ of the metal fragment can adequately accommodate the increased intramolecular crowding without facilitating an isomerisation at moderate temperature. It may also be of significance that the C_{cage}–C_{cage} connectivity in **5** [1.594(14) Å] is rather longer (and therefore presumably weaker) than in any of **2**, **3** and **7**–**9** [range 1.525(9)–1.554(19) Å]. The sterically induced rotation of the platinum fragment in **5** from its electronically preferred conformation[22] may produce partial population of a previously unoccupied carbaborane molecular orbital which is strongly antibonding between the two C_{cage} atoms, and hence lead to lengthening of the C–C connectivity. Indeed, it may be the case that such bond lengthening in **5** represents the beginning of the isomerisation process, a possibility that is under current investigation.

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