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Preliminary Communication

Sterically-induced low temperature polyhedral rearrangements of carbaplatinaboranes: synthesis and crystal structures of 1-Ph-3,3-(PMe₂Ph)₂-3,1,2-PtC₂B₉H₁₀, 1-Ph-3,3-(PMe₂Ph)₂-3,1,11-PtC₂B₉H₁₀, 11-Ph-3,3-(PMe₂Ph)₂-3,1,11-PtC₂B₉H₁₀ and 1,11-Ph₂-3,3-(PMe₂Ph)₂-3,1,11-PtC₂B₉H₉

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Abstract

Reaction of *cis*-Pt(PMe₂Ph)₂Cl₂ with Ti₂[7-Ph-7,8-*nido*-C₂B₉H₁₀] affords 1-Ph-3,3-(PMe₂Ph)₂-3,1,2-PtC₂B₉H₁₀. mild thermolysis (55°C) of which yields 1-Ph-3,3-(PMe₂Ph)₂-3,1,11-PtC₂B₉H₁₀ and 11-Ph-3,3-(PMe₂Ph)₂-3,1,11-PtC₂B₉H₁₀. Both of the latter compounds are produced by the microwave irradiation of a mixture of *cis*-Pt(PMe₂Ph)₂Cl₂ and [HNMe₃][7-Ph-7,8-*nido*-C₂B₉H₁₁]. When *cis*-Pt(PMe₂Ph)₂Cl₂ is allowed to react with Ti₂[7,8-Ph₂-7,8-*nido*-C₂B₉H₉] at room temperature the only isolable species is 1,11-Ph₂-3,3-(PMe₂Ph)₂-3,1,11-PtC₂B₉H₉. The generation of rearranged products with 3,1,11-PtC₂B₉ architectures is inconsistent with a diamond-square-diamond mechanism for the isomerisation of icosahedral heteroboranes.

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The 1,2 → 1,7 → 1,12 isomerisation of *closo*-C₂B₁₀H₁₂ and its C-substituted analogues at elevated temperatures (*ca.* 470°C and 700°C, respectively, for the parent compound) has been known for many years [1], but the precise mechanism(s) of such rearrangement processes continue to be the subject of speculation [2]. With very few exceptions, [3], polyhedral rearrangements in carbametallaboranes also involve a high activation barrier [4]. Recently [5], we have found that severe molecular deformation in essentially icosahedral carbametallaboranes can be induced by the presence of bulky (phenyl) substituents at the cage carbon atoms, implying that transition metal derivatives of phenyl-carboranes might undergo relatively facile rearrangement processes.

Reaction of *cis*-Pt(PMe₂Ph)₂Cl₂ with Ti₂[7-Ph-7,8-*nido*-C₂B₉H₁₀] [6] in CH₂Cl₂ at room temperature affords the expected product 1-Ph-3,3-(PMe₂Ph)₂-3,1,2-PtC₂B₉H₁₀ (1), characterised by microanalysis and multinuclear (¹H, ¹¹B, ¹¹B{¹H}, ³¹P) NMR spectroscopy. An X-ray diffraction study* reveals the molecular structure shown in Fig. 1. Pt(3) is between 2.24 and 2.33 Å from atoms C(2), B(7), B(8) and B(4), but 2.596(10) Å from C(1). The PtP₂ plane lies essentially orthogonal to the best plane through C(2)–B(4),

* *Crystal data:* All measurements were made at room temperature on CAD4 diffractometers (Edinburgh, compounds 1 and 4; Oxford, compounds 2 and 3) operating with graphite-monochromated Mo Kα X-radiation, λ_{bar} = 0.71069 Å.

Compound 1, C₂₄H₃₇B₉P₂Pt, *M* = 679.89, monoclinic, space group *P*2₁/c, *a* = 10.381(3), *b* = 25.706(4), *c* = 10.880(7) Å, β = 104.57(4)°, *V* = 2810.0 Å³, *Z* = 4, *D*_{calc} = 1.607 g cm⁻³, μ(Mo Kα) = 51.71 cm⁻¹, *F*(000) = 1336. *R* = 0.048 for 3310 reflections [*F* ≥ 2.0σ(*F*)] measured in the range 1 ≤ θ ≤ 23°.

Compound 2, C₂₄H₃₇B₉P₂Pt, *M* = 679.89, monoclinic, space group *P*2₁/c, *a* = 10.408(3), *b* = 25.847(5), *c* = 10.993(3) Å, β = 105.95(2)°, *V* = 2843.4 Å³, *Z* = 4, *D*_{calc} = 1.588 g cm⁻³, μ(Mo Kα) = 51.10 cm⁻¹, *F*(000) = 1336. *R* = 0.045 for 3772 reflections [*F* ≥ 6.0σ(*F*)] measured in the range 0 ≤ θ ≤ 25°.

Compound 3, C₂₄H₃₇B₉P₂Pt, *M* = 679.89, triclinic, space group *P* $\bar{1}$, *a* = 10.082(3), *b* = 12.785(3), *c* = 13.830(2) Å, α = 122.19(2), β = 96.07(2), γ = 94.23(2)°, *V* = 1479.0 Å³, *Z* = 2, *D*_{calc} = 1.526 g cm⁻³, μ(Mo Kα) = 49.12 cm⁻¹, *F*(000) = 668. *R* = 0.018 for 4264 reflections [*F* ≥ 6.0σ(*F*)] measured in the range 0 ≤ θ ≤ 24.5°.

Compound 4, C₃₀H₄₁B₉P₂Pt, *M* = 755.99, triclinic, space group *P* $\bar{1}$, *a* = 11.060(4), *b* = 12.997(4), *c* = 13.293(3) Å, α = 79.703(24), β = 80.314(24), γ = 65.14(3)°, *V* = 1696.5 Å³, *Z* = 2, *D*_{calc} = 1.480 g cm⁻³, μ(Mo Kα) = 42.90 cm⁻¹, *F*(000) = 748. *R* = 0.030 for 5482 reflections [*F* ≥ 2.0σ(*F*)] measured in the range 1 ≤ θ ≤ 25°.

but is orientated in such a way that it is almost perpendicular to a plane through C(1), B(10) and B(12), *i.e.* is twisted through *ca.* 36° from its idealised position in the analogous compound 3,3-(PEt₃)₂-3,1,2-PtC₂B₉H₁₁ [7].

The ³¹P NMR spectrum of **1** in CDCl₃ at room temperature (singlet at -12.08 ppm with double satellites, $J(\text{PtP})$ 3227 Hz) is consistent with essentially free rotation of the {Pt(PMe₂Ph)₂} fragment about the metal-cage axis. Increasing the temperature to 55°C (sealed tube) causes the colour of the solution to change slowly from orange to yellow, with the concomitant disappearance of the signal due to **1** and the growth of two new signals (-15.37 ppm $J(\text{PtP})$ 3258 Hz, compound **2**; -14.53 ppm, $J(\text{PtP})$ 3327 Hz, compound **3**), in the approximate ratio 1:4, respectively.

Compounds **2** and **3** are also formed, this time in approximately equal amounts, by the microwave irradiation (2450 MHz, 500w) [8] for 30 min of a mixture of *cis*-Pt(PMe₂Ph)₂Cl₂ and [HNMe₃][7-Ph-7,8-*nido*-C₂B₉H₁₁] in EtOH at 10 atm. Following separation by TLC each compound was characterized by ¹¹B, ¹¹B{¹H} and ³¹P NMR spectroscopies, mass spectrometry, and

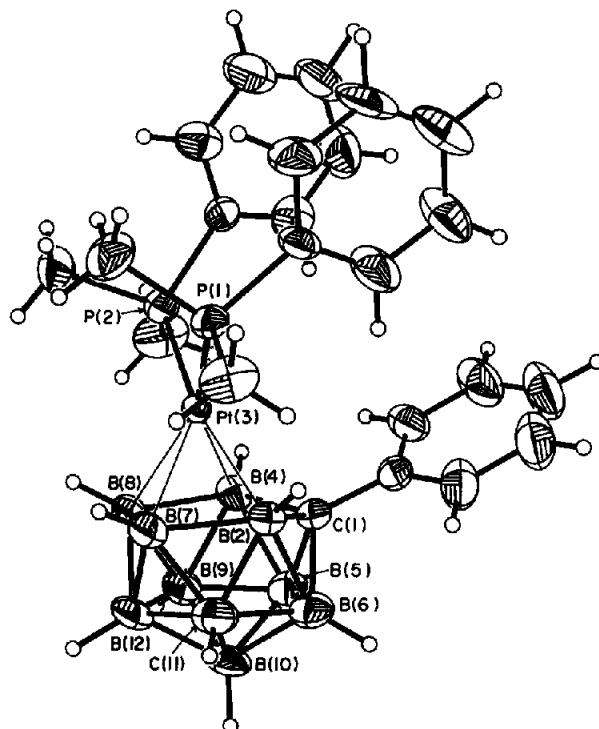


Fig. 2. Molecular structure of 1-Ph-3,3-(PMe₂Ph)₂-3,1,11-PtC₂B₉H₁₀ (**2**). Important molecular parameters (Å and °) Pt(3)–C(1) 2.622(8), Pt(3)–B(2) 2.237(8), Pt(3)–B(7) 2.211(9), Pt(3)–B(8) 2.212(9), Pt(3)–B(4) 2.275(8), Pt(3)–P(1) 2.2988(21), Pt(3)–P(2) 2.2963(22), P(1)–Pt(3)–P(2) 95.82(8).

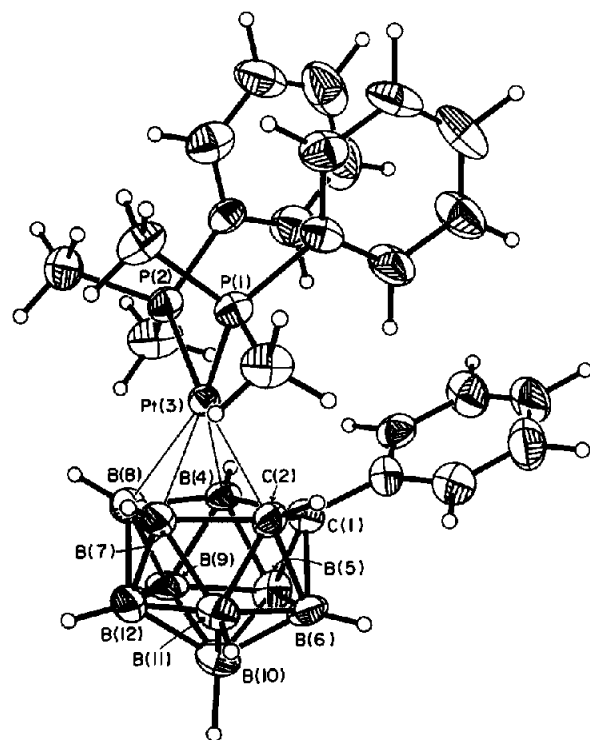


Fig. 1. Molecular structure of 1-Ph-3,3-(PMe₂Ph)₂-3,1,2-PtC₂B₉H₁₀ (**1**). Important molecular parameters (Å and °) Pt(3)–C(1) 2.596(10), Pt(3)–C(2) 2.326(10), Pt(3)–B(7) 2.257(12), Pt(3)–B(8) 2.239(12), Pt(3)–B(4) 2.313(12), Pt(3)–P(1) 2.288(3), Pt(3)–P(2) 2.250(3), C(1)–C(2) 1.594(14), P(1)–Pt(3)–P(2) 95.05(9).

by X-ray crystallographic studies *. Compound **1** was not observed in the product mixture.

The structure of **2** is shown in Fig. 2. It is isomorphous with **1** but it does not have the same structure. In fact, the compound is 1-Ph-3,3-(PMe₂Ph)₂-3,1,11-PtC₂B₉H₁₀, *i.e.* an isomer of **1** in which C(2) and B(11) of **1** are interchanged. This apart, the molecular geometries of **1** and **2** are practically superimposable, even down to fine details such as the slight twist of the phenyl ring attached to C(1) and the disposition of the PMe₂Ph ligands; indeed, an idealization calculation [9] on the entire molecules of **1** and **2** (excluding H atoms) yields an "r.m.s. misfit" of only 0.09 Å. In **2** Pt(3) to cage atom distances span 2.21–2.28 Å [B(2)–B(7)], with Pt(3)–C(1) again long at 2.622(8) Å. Thus compounds **1** and **2** represent a rare example of geometrical isomers of a compound that are isomorphous. Presumably this reflects the fact that the crystal packing of **1** and **2** is dictated by hydrocarbon contacts and is independent of the change in molecular dipole.

The molecular structure of compound **3**, 11-Ph-3,3-(PMe₂Ph)₂-3,1,11-PtC₂B₉H₁₀, is shown in Fig. 3. Thus **3** is yet another isomer of **1**, but now the {CPh} fragment is located in the lower pentagonal belt (cage

atoms 5, 6, 11, 12 and 9) with {CH} in the upper belt. Pt(3)–B distances again span the range 2.21–2.28 Å, and Pt(3)–C(1) is 2.581(4) Å. In both **2** and **3** the PtP₂ plane adopts an essentially perpendicular orientation to the C(1)B(10)B(12) plane, as is observed in the related species 1-NMe₃-3,3-(^tBuNC)₂-3,1-PdCB₁₀H₁₀ [10].

The isomerisations of **1** to **2** and **3** represent the two possible ways in which the cage carbon atoms can separate as they do in the 1,2 → 1,7 isomerization of *closo*-C₂B₁₀H₁₂, with the proviso that the ultimate metallabonded polyhedral face is B₄C and Pt is antipodal to boron.

As previously noted, the conformation of the PtP₂ plane in **1** is significantly distorted from that predicted to be of minimum energy for an {ML₂} fragment above a B₃C₂(C-adjacent) face [7], presumably because of the steric influence of the phenyl substituent bound to C(1). The relatively low temperature at which **1** undergoes isomerisation is fully consistent with such *ground state destabilisation* of the 3,1,2-MC₂B₉ polyhedron. In both isomerised products the observed conformation of the {ML₂} fragment is the predicted minimum energy one.

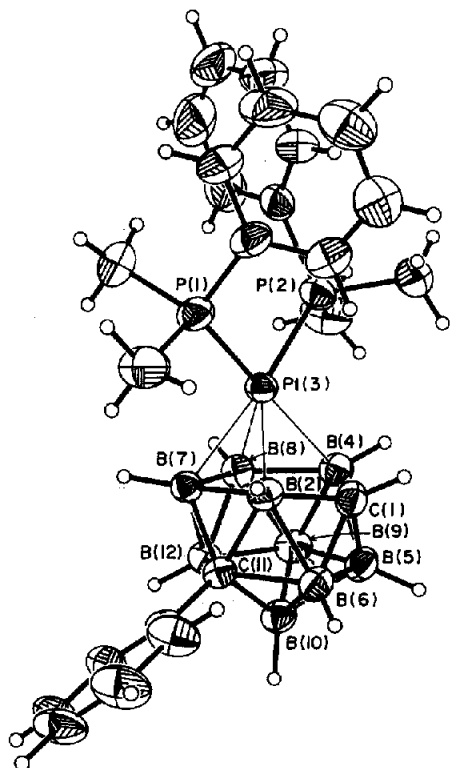


Fig. 3. Molecular structure of 11-Ph-3,3-(PMe₂Ph)₂-3,1,11-PtC₂B₉H₁₀ (**3**). Important molecular parameters (Å and °) Pt(3)–C(1) 2.581(4), Pt(3)–B(2) 2.233(5), Pt(3)–B(7) 2.211(4), Pt(3)–B(8) 2.246(5), Pt(3)–B(4) 2.281(5), Pt(3)–P(1) 2.2901(11), Pt(3)–P(2) 2.3037(11), P(1)–Pt(3)–P(2) 97.70(4).

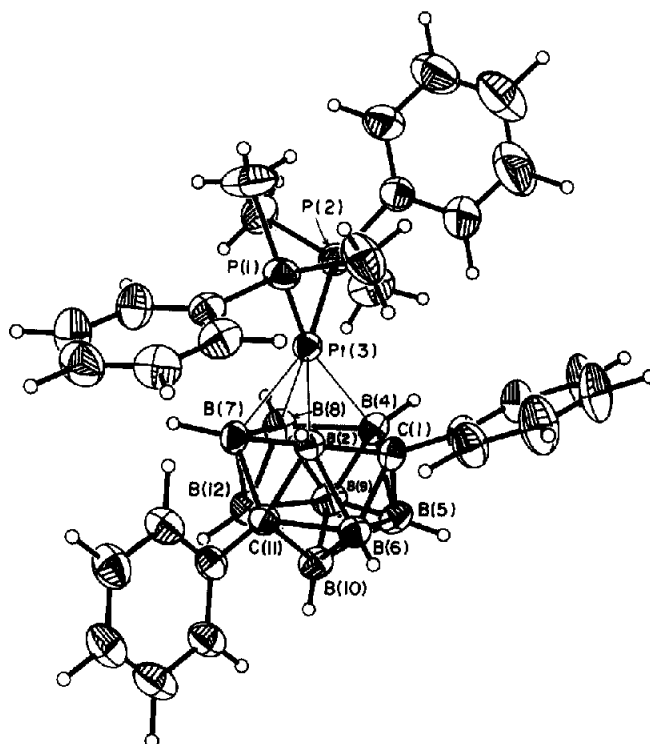


Fig. 4. Molecular structure of 1,11-Ph₂-3,3-(PMe₂Ph)₂-3,1,11-PtC₂B₉H₉ (**4**). Important molecular parameters (Å and °) Pt(3)–C(1) 2.610(5), Pt(3)–B(2) 2.222(6), Pt(3)–B(7) 2.199(6), Pt(3)–B(8) 2.231(6), Pt(3)–B(4) 2.293(6), Pt(3)–P(1) 2.2864(14), Pt(3)–P(2) 2.2909(14), P(1)–Pt(3)–P(2) 96.23(5).

A striking further example of sterically-induced low temperature polyhedral rearrangement is afforded by the fact that the only isolable product of the room temperature reaction between *cis*-Pt(PMe₂Ph)₂Cl₂ and the diphenylcarbaborane ligand [7,8-Ph₂-7,8-*nido*-C₂B₉H₉]²⁻ [5] is the C-separated species 1,11-Ph₂-3,3-(PMe₂Ph)₂-3,1,11-PtC₂B₉H₉ (**4**), the structure of which * is shown in Fig. 4. In this case we assume that intramolecular crowding in the intermediate compound 1,2-Ph₂-3,3-(PMe₂Ph)₂-3,1,2-PtC₂B₉H₉ is so severe that it isomerizes to **4** without the need for even mild heating.

The isomerization of icosahedral heteroboranes with an initial 3,1,2-MC₂B₉ architecture by a diamond-square-diamond mechanism in which the C(1)–C(2) connectivity is broken in the transition state would initially afford a species with a 1,2,4-MC₂B₉ heteroatom pattern. Although it remains to be tested by experimentation, it is likely that the predicted conformation [7,11] of such species, in which one or even two phenyl groups are bound to cage carbon atoms, would be such that intramolecular crowding would not be critical, and therefore the non-observation of products of this type in the thermolysis reactions described

above argues against a diamond-square-diamond mechanism. Studies designed to probe further the precise mechanisms of these important reactions are being undertaken.

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