

Preliminary communication

The relationship between the molecular structure
of [3,3-(PMe₂Ph)₂-closo-3,1,2-PtC₂B₉H₁₁] and the mechanism
of the fluxional behaviour of M(PR₃)₂-units in closo-twelve-atom
metallaheteroboranes

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Abstract

The upper limit of the free energy of the barrier to rotation of the platinum bis-phosphine unit in [3,3-(PMe₂Ph)₂-closo-3,1,2-PtC₂B₉H₁₁] **1** is < 30 kJ mol⁻¹ in dichloromethane solution. This relatively low value is similar in magnitude to crystal-packing forces, and compound **1** crystallises from CH₂Cl₂-hexane solution as a 1:1 mixture of two different conformers with significantly different platinum-to-C₂B₃ bonding. These observations lead to the proposal of a general mechanism for the mutual rotation of {M(PR₃)₂} units above C₂B₉H₁₁.

Keywords: Platinum; Carborane; Metallocarborane; Fluxionality; Crystal structure; Mechanism

1. Introduction

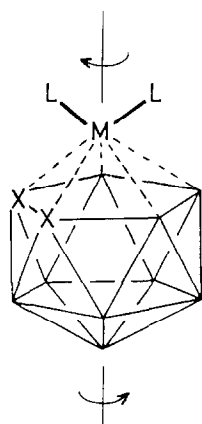
The rotation of ML₂ units such as {Pt(PMe₂Ph)₂} above the five-atom X₂B₃-faces of the heteroborane ligands C₂B₉H₁₁ and As₂B₉H₉ [1], Scheme 1, occurs in solution. The free energy of the barrier to rotation, ΔG[‡], has been measured for [3,3-(PMe₂Ph)₂-closo-3,1,2-PtC₂B₉H₁₁] **1**, vide infra, and is less than 30 kJ mol⁻¹. Extended Hückel molecular orbital calculations of metal–ligand interactions in {Pt(PH₃)₂}-containing twelve-vertex metal derivatives of carboranes have been taken to indicate that there are distinct preferences for the conformations of {Pt(PH₃)₂}-units above 7,8-C₂B₃-, 7-CB₄- and 7,9-C₂B₃-faced ligands. These are shown in Schemes 2(a), (c) and (b) respectively [2], and in many examples these preferences are manifest in the solid state [1–3]. However, it is apparent that this is not

always the case in metallaheteroborane chemistry; e.g. the crystal structure of [3,3-(PPh₃)₂-closo-3,1,2-PtAs₂B₉H₉] shows a mixture of conformers [1]. We now report the structure of **1** and suggest a mechanism for the rotation of ML₂ units above heteroborane ligands.

2. Results and discussion

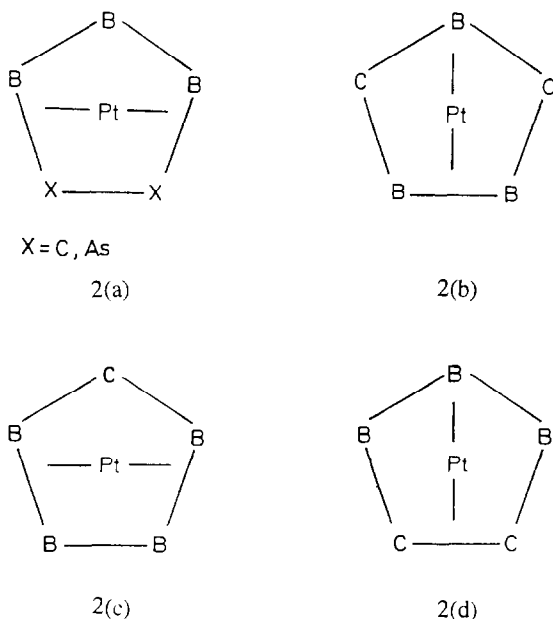
We found that the upper limit of the free energy of the barrier to rotation in [3,3-(PMe₂Ph)₂-closo-3,1,2-PtC₂B₉H₁₁] **1** is < 30 kJ mol⁻¹. This corresponds to the maximum energy difference between any two rotational conformers in solution and is of a similar magnitude to crystal-packing forces. We have also found that, in the solid-state, there are equal numbers of two quite different conformers in the asymmetric unit of **1** [5]. These molecules, **1A** and **1B**, clearly have different platinum-to-cage bonding, Fig. 1(a) and (b). The con-

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Scheme 1.

formation in molecule **1B**, Fig. 1(b), approximates to the “minimum energy” conformer that is expected from the molecular orbital analysis [2]; this has been called the “parallel” conformer. In contrast, the Pt–P(1) vector in **1A** almost eclipses the Pt–C(2) vector when the molecule is viewed from above the platinum atom, Fig. 1(a). This conformation is rotated by ca. 50° from the “parallel” one, Scheme 2(a), and is approximately halfway between the “parallel” conformation and a “perpendicular” one, Scheme 2(d), which has not been observed. This is unexpected on the basis of the molecular orbital calculations. A comparison of the Pt–C₂B₃ distances in **1A** and **1B**, Fig. 1(a) and (b), confirms that the bonding to platinum is significantly different in these molecules. In **1A** the Pt–C(2) and Pt–B(4) distances are almost identical at 2.302(7) and 2.307(7) Å respectively, and the Pt–B(7) and Pt–B(8) distances are the same (within two σ) at 2.284(8) and 2.265(7) Å



Scheme 2.

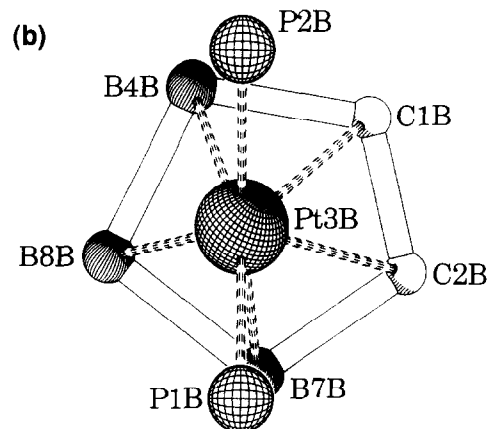
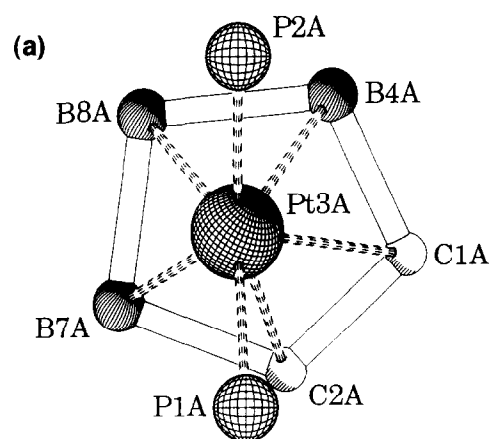


Fig. 1. (a) Molecule **1A** showing the conformation of the PtP₂ units above the C₂B₃-face with atoms represented as spheres. Interatomic distances (Å): Pt(3A)–C(1A) 2.515(6), Pt(3A)–C(2A) 2.302(7), Pt(3A)–B(4A) 2.307(7), Pt(3A)–B(7A) 2.284(8), Pt(3A)–B(8A) 2.265(7), Pt(3A)–P(1A) 2.2875(16), Pt(3A)–P(2A) 2.2353(16); angle P(1A)–Pt(3A)–P(2A) 93.11(6)°. (b) Molecule **1B** showing the conformation of the PtP₂ units above the C₂B₃-face with atoms represented as spheres. Interatomic distances (Å): Pt(3B)–C(1B) 2.529(6), Pt(3B)–C(2B) 2.574(6), Pt(3B)–B(4B) 2.264(7), Pt(3B)–B(7B) 2.266(7), Pt(3B)–B(8B) 2.260(7), Pt(3B)–P(1B) 2.2599(16), Pt(3B)–P(2B) 2.2705(15); angle P(1B)–Pt(3B)–P(2B) 92.33(6)°.

respectively. The Pt–C(1) distance of 2.515(6) is longer than Pt–C(2) by more than 0.2 Å. Hence the platinum-to-carborane distances in **1A** suggest an unusual η^5 -carborane-to-platinum bonding mode which is more like that expected for a CB₄-bonded cage than an η^5 -C₂B₃ one; i.e. in **1A**, the platinum could be described as essentially η^4 -bonded to CB₃ with a weaker fifth interaction to C(1). A comparable Pt–C(1) distance is observed in [2,2-(PMe₂Ph)₂-closo-2,1,8-PtC₂B₉H₁₁] **2** [5], 2.570(3) Å, in which the Pt–B distances are between 2.215(3) and 2.273(3) Å. In contrast, the Pt–C and Pt–B distances in **1B** are typical of “normal” η^5 -carborane-to-platinum bonding in 3,1,2-PtC₂B₃ platinadecarboranes [3], with Pt–C(1) and Pt–C(2) distances similar {2.529(6) and 2.574(6) Å in **1B**} and both about 10% longer than the three Pt–B distances {2.260(7), 2.264(7) and 2.266(7) Å in **1B**}. This conformer can be

described as exhibiting the expected “slippage” distortion towards η^3 bonding [2–4].

3. Conclusions

Consideration of the structures of **1A** and **1B** leads us to conclude that, for compounds with low barriers to rotation, the preferred conformations which were deduced from extended Huckel molecular orbital studies may not always be observed in the solid-state. A more sophisticated form of molecular orbital calculation which allows for molecular relaxation is necessary if all conformational preferences are to be interpreted correctly. The experimental observations which we report here suggest a mechanism for the $\{\text{Pt}(\text{PMe}_2\text{Ph})_2\}$ unit rotation that occurs in solutions of **1**, **2** and related compounds [1]. The process is initiated by the ML_2 unit shifting from the η^5 -bonded system to an η^4 -bonded one. This is illustrated for the 7,8- X_2B_3 -faced ligands in Scheme 3(a) and (b). The shift requires that the ML_2 unit begins to twist about the face of the heteroborane ligand to maximise the ML_2 -to-face η^4 -bonding, Scheme 3(b) and (c). This new conformation may then be “stabilised” by proceeding to another η^5 -bonded species, 3(d), or it can reverse, i.e. 3(c) to 3(a). If further steps are realised, a succession of η^5 - η^4 - η^5 processes leads to complete rotation of the ML_2 unit by a “shift-twist” mechanism.

4. Experimental

Synthesis of [3,3-(PMe₂Ph)₂-closo-3,1,2-PtC₂B₉H₁₁] 1 and [2,2-(PMe₂Ph)₂-closo-2,1,8-PtC₂B₉H₁₁] 2

To a solution of Cs[7,8-C₂B₉H₁₂] (0.100 g, 0.376 mmol) in ethanol (20 cm³) was added triethylamine (0.38 g, 3.76 mmol) and *cis*-[Pt(PMe₂Ph)₂Cl₂] (0.204 g, 0.376 mmol). The mixture was heated under reflux for 6 d. The dark yellow solution was filtered and the solvent was removed under reduced pressure (rotatory evaporator, 35°C). The reaction mixture was dissolved in CH₂Cl₂ and subjected to preparative TLC with CH₂Cl₂-hexane (3:2) as eluant. Two major products were isolated. One, (*R_f* = 0.3), was recrystallised from

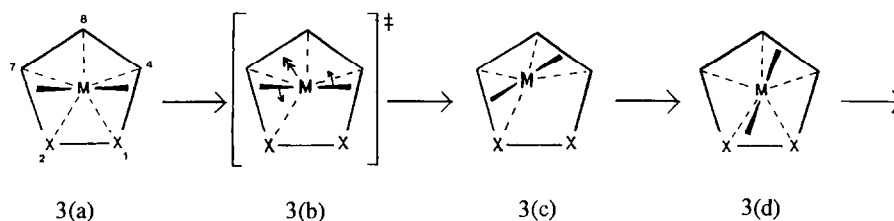
CH₂Cl₂-hexane (3:2) as orange crystals of [3,3-(PMe₂Ph)₂-closo-3,1,2-PtC₂B₉H₁₁] **1** (0.060 g, 26.4%). (Found: C, 35.90; H, 5.80. C₁₈H₃₃B₉P₂Pt requires C, 35.80; H 5.50%). ¹H NMR (CDCl₃, 21°C), δ (¹H) (PMe) +1.72, $N(^{31}\text{P}-^1\text{H})$ 10.5 Hz, $^3J(^{195}\text{Pt}-^1\text{H})$ +32.6 Hz. Low-temperature ¹H NMR of (PMe) groups {ordered as: temperature, δ , peak-width at half height in Hz} CD₂Cl₂ solution; -70°C, +1.63, 6.6; -90°C, +1.62, 8; -110°C, +1.62, 13; CD₃C₆H₅ solution; -82°C, +1.28, 7.5; -94°C, +1.30, 8.5. These data imply that ΔG^\ddagger has an upper limit of 30 kJ mol⁻¹ at -110°C. ³¹P NMR: (CDCl₃) δ -13.1, $^1J(^{195}\text{Pt}-^{31}\text{P})$ 3445 ± 5 Hz at -54°C; (CD₂Cl₂) δ -12.6 $^1J(^{195}\text{Pt}-^{31}\text{P})$ 3450 ± 5 Hz at -90°C. A second compound, (*R_f* = 0.65), was recrystallised from CH₂Cl₂-hexane (3:2), as colourless crystals of [2,2-(PMe₂Ph)₂-closo-2,1,8-PtC₂B₉H₁₁] **2** (0.008 g, 3.5%). (Found: C, 36.20; H, 5.90. C₁₈H₃₃B₉P₂Pt requires C, 35.80; H 5.50%). ¹H NMR (CDCl₃, 21°C): δ (¹H) (PMe) {ordered as: δ (N, $^3J(^{195}\text{Pt}-^1\text{H})/\text{Hz})$ +1.72^(a) (N 9.1, 22.4), +1.53^(a) (N 9.9, 33.2), +1.69^(b) (N 9.6, 23.5), +1.47^(b) (N 9.9, 33.0); signals coalesce in pairs ^(a) and ^(b) at -1°C (100 MHz spectrum; $\Delta G^\ddagger_{272} = 57.8 \pm 1.2$ kJ mol⁻¹) to give (at 21°C) δ +1.63 for ^(a) and +1.66 for ^(b).

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- [3] See for example; E.A. Carroll, M. Green, F.G.A. Stone and A.J. Welch, *J. Chem. Soc., Dalton Trans.*, (1975) 2263; A.J. Welch, *J. Chem. Soc., Dalton Trans.*, (1975) 743.
- [4] H.M. Colquhoun, T.J. Greenhough and M.G.H. Wallbridge, *J.*



Scheme 3.

Chem. Soc., Dalton Trans., (1979) 629, and references cited therein.

[5] Crystal Data for **1**: $C_{18}H_{33}B_9P_2Pt$, $M = 1207.56$, monoclinic, $P2_1/c$, $a = 12.7387(5)$, $b = 21.7062(12)$, $c = 17.9793(11)$ Å, $\beta = 99.105(4)^\circ$, $U = 4908.8(4)$ Å³, $Z = 8$, $D_c = 1.634$ gcm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7093$ Å, $\mu(\text{Mo } K\alpha) = 5.91$ mm⁻¹, $F(000) = 2352$, $T = 294$ K, $R = 0.030$, $R_w = 0.029$ for 6762 observed reflections.

Crystal Data for **2**: $C_{18}H_{33}B_9P_2Pt$, $M = 603.78$, triclinic, $P\bar{1}$, $a = 9.3892(5)$, $b = 10.0918(5)$, $c = 14.1517(6)$ Å, $\alpha = 81.045(4)$, $\beta = 72.233(4)$, $\gamma = 76.766(4)^\circ$, $U = 1237.7(1)$ Å³, $Z = 2$, $D_c = 1.62$ gcm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7093$ Å, $\mu(\text{Mo } K\alpha) = 5.9$ mm⁻¹, $F(000) = 584$, $T = 294$ K, $R = 0.018$, $R_w = 0.023$ for 6431 observed reflections.

Structure Solution of **1** and **2**: – For both structures, data were collected using an Enraf-Nonius CAD4 diffractometer to a maximum θ of 27° for **1** and 30° for **2**, using graphite monochromatized Mo $K\alpha$ radiation. Data were corrected for Lorentz, polarization and absorption effects. The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares calculations using the NRCVAX system of programs [6] on a Silicon Graphics 4D-35 work station. The assignment of

chemical types to the B and C atoms in the $PtC_2B_9H_{11}$ cages of the two independent molecules of **1** was done from an initial inspection of bond length data and peak heights in both F_0 and difference maps. All non-Pt cage atoms were then refined as ‘‘B’’ atoms allowing the occupancies to refine. In each cage the two atoms which we had tentatively assigned as ‘‘C’’ atoms refined to the largest occupancies consistent with the initial assignment. The structure was then fully refined to convergence with this assignment. To check the assignment, at the conclusion of the refinement, atoms C(2A) were treated as ‘‘boron’’, and B(4A) as ‘‘carbon’’ in further refinement cycles; atom C(2A) as ‘‘boron’’ refined to much smaller U_{ii} values and atom B(4A) as a ‘‘carbon’’ refined to much larger U_{ii} values in a manner which indicated that the initial tentative chemical assignment was correct. Figs. 1(a) and 1(b) were prepared with the aid of PLUTON [7] Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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