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Preliminary Communication

Sterically-induced low temperature polyhedral rearrangements of carbaplatinaboranes: synthesis and crystal structures of 1-Ph-3,3-$(PMe_2Ph)_2$-3,1,2-$PtC_2B_9H_{10}$, 1-Ph-3,3-$(PMe_2Ph)_2$-3,1,11-$PtC_2B_9H_{10}$, 11-Ph-3,3-$(PMe_2Ph)_2$-3,1,11-$PtC_2B_9H_{10}$ and 1,11-Ph_2-3,3-$(PMe_2Ph)_2$-3,1,11-$PtC_2B_9H_9$

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Abstract

Reaction of *cis*-$Pt(PMe_2Ph)_2Cl_2$ with Tl_2[7-Ph-7,8-*nido*-$C_2B_9H_{10}$] affords 1-Ph-3,3-$(PMe_2Ph)_2$-3,1,2-$PtC_2B_9H_{10}$, mild thermolysis (55°C) of which yields 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-$PtC_2B_9H_{10}$. Both of the latter compounds are produced by the microwave irradiation of a mixture of *cis*-$Pt(PMe_2Ph)_2Cl_2$ and $[HNMe_3]$[7-Ph-7,8-*nido*-$C_2B_9H_{11}$]. When *cis*-$Pt(PMe_2Ph)_2Cl_2$ is allowed to react with Tl_2[7,8-Ph_2-7,8-*nido*-$C_2B_9H_9$] at room temperature the only isolable species is 1,11-Ph_2-3,3-$(PMe_2Ph)_2$-3,1,11-$PtC_2B_9H_9$. The generation of rearranged products with 3,1,11-PtC_2B_9 architectures is inconsistent with a diamond-square-diamond mechanism for the isomerisation of icosahedral heteroboranes.

The 1,2 → 1,7 → 1,12 isomerisation of *closo*-$C_2B_{10}H_{12}$ 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 phenylcarbaboranes might undergo relatively facile rearrangement processes.

Reaction of *cis*-$Pt(PMe_2Ph)_2Cl_2$ with Tl_2[7-Ph-7,8-*nido*-$C_2B_9H_{10}$] [6] in CH_2Cl_2 at room temperature affords the expected product 1-Ph-3,3-$(PMe_2Ph)_2$-3,1,2-$PtC_2B_9H_{10}$ (**1**), characterised by microanalysis and multinuclear (^1H, ^{11}B, $^{11}B\{^1H\}$, ^{31}P) NMR spectrosopy. 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 PtP_2 plane lies essentially orthogonal to the best plane through C(2)–B(4),

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* *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, $\lambda_{bar} = 0.71069$ Å.

Compound **1**, $C_{24}H_{37}B_9P_2Pt$, $M = 679.89$, monoclinic, space group $P2_1/c$, $a = 10.381(3)$, $b = 25.706(4)$, $c = 10.880(7)$ Å, $\beta = 104.57(4)°$, $V = 2810.0$ Å^3, $Z = 4$, $D_{calc} = 1.607$ g cm^{-3}, μ(Mo Kα) = 51.71 cm^{-1}, $F(000) = 1336$. $R = 0.048$ for 3310 reflections $[F \geq 2.0\sigma(F)]$ measured in the range $1 \leq \theta \leq 23°$.

Compound **2**, $C_{24}H_{37}B_9P_2Pt$, $M = 679.89$, monoclinic, space group $P2_1/c$, $a = 10.408(3)$, $b = 25.847(5)$, $c = 10.993(3)$ Å, $\beta = 105.95(2)°$, $V = 2843.4$ Å^3, $Z = 4$, $D_{calc} = 1.588$ g cm^{-3}, μ(Mo Kα) = 51.10 cm^{-1}, $F(000) = 1336$. $R = 0.045$ for 3772 reflections $[F \geq 6.0\sigma(F)]$ measured in the range $0 \leq \theta \leq 25°$.

Compound **3**, $C_{24}H_{37}B_9P_2Pt$, $M = 679.89$, triclinic, space group $P\bar{1}$, $a = 10.082(3)$, $b = 12.785(3)$, $c = 13.830(2)$ Å, $\alpha = 122.19(2)$, $\beta = 96.07(2)$, $\gamma = 94.23(2)°$, $V = 1479.0$ Å^3, $Z = 2$, $D_{calc} = 1.526$ g cm^{-3}, μ(Mo Kα) = 49.12 cm^{-1}, $F(000) = 668$. $R = 0.018$ for 4264 reflections $[F \geq 6.0\sigma(F)]$ measured in the range $0 \leq \theta \leq 24.5°$.

Compound **4**, $C_{30}H_{41}B_9P_2Pt$, $M = 755.99$, triclinic, space group $P\bar{1}$, $a = 11.060(4)$, $b = 12.997(4)$, $c = 13.293(3)$ Å, $\alpha = 79.703(24)$, $\beta = 80.314(24)$, $\gamma = 65.14(3)°$, $V = 1696.5$ Å^3, $Z = 2$, $D_{calc} = 1.480$ g cm^{-3}, μ(Mo Kα) = 42.90 cm^{-1}, $F(000) = 748$. $R = 0.030$ for 5482 reflections $[F \geq 2.0\sigma(F)]$ measured in the range $1 \leq \theta \leq 25°$.

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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 $3,3\text{-}(PEt_3)_2\text{-}3,1,2\text{-}PtC_2B_9H_{11}$ [7].

The ^{31}P NMR spectrum of **1** in $CDCl_3$ at room temperature (singlet at -12.08 ppm with double satellites, $J(PtP)$ 3227 Hz) is consistent with essentially free rotation of the $\{Pt(PMe_2Ph)_2\}$ 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 concommitant disappearance of the signal due to **1** and the growth of two new signals (-15.37 ppm $J(PtP)$ 3258 Hz, compound **2**; -14.53 ppm, $J(PtP)$ 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*-$Pt(PMe_2Ph)_2Cl_2$ and $[HNMe_3][7\text{-}Ph\text{-}7,8\text{-}\textit{nido}\text{-}C_2B_9H_{11}]$ in EtOH at 10 atm. Following separation by TLC each compound was characterized by ^{11}B, $^{11}B\{^1H\}$ and ^{31}P NMR spectroscopies, mass spectrometry, and by X-ray crystallographic studies *. Compound **1** was not observed in the product mixture.

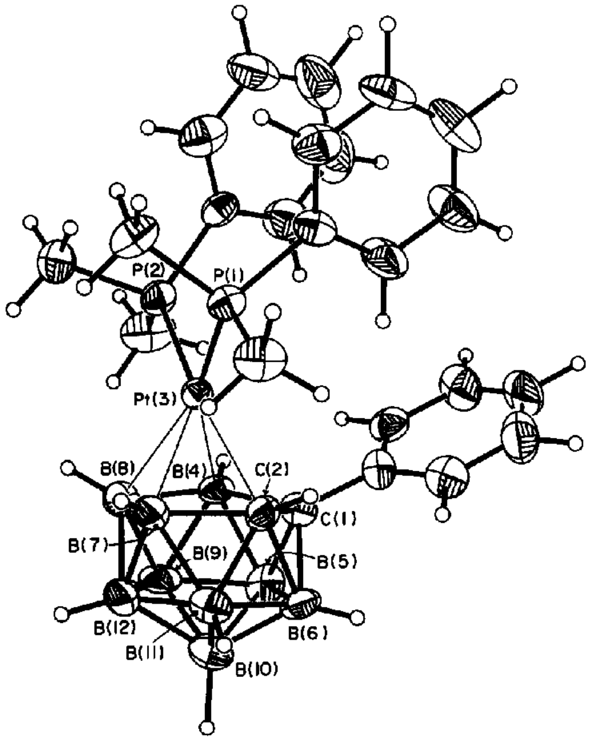

Fig. 1. Molecular structure of $1\text{-}Ph\text{-}3,3\text{-}(PMe_2Ph)_2\text{-}3,1,2\text{-}PtC_2B_9H_{10}$ (**1**). Important molecular parameters (Å and °) Pt(3)–C(1) 2.596(10), Pt(3)–C(2) 2.326(10), Pt(3)–B(7) 2.257(12), Pt(3)–B(8) 2.239(12), Pt(3)–B(4) 2.313(12), Pt(3)–P(1) 2.288(3), Pt(3)–P(2) 2.250(3), C(1)–C(2) 1.594(14), P(1)–Pt(3)–P(2) 95.05(9).

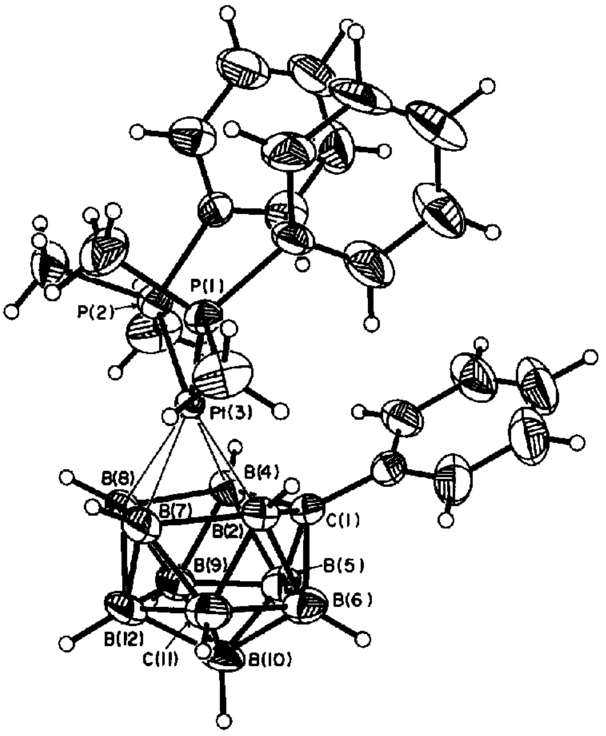

Fig. 2. Molecular structure of $1\text{-}Ph\text{-}3,3\text{-}(PMe_2Ph)_2\text{-}3,1,11\text{-}PtC_2B_9H_{10}$ (**2**). Important molecular parameters (Å and °) Pt(3)–C(1) 2.622(8), Pt(3)–B(2) 2.237(8), Pt(3)–B(7) 2.211(9), Pt(3)–B(8) 2.212(9), Pt(3)–B(4) 2.275(8), Pt(3)–P(1) 2.2988(21), Pt(3)–P(2) 2.2963(22), P(1)–Pt(3)–P(2) 95.82(8).

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 $1\text{-}Ph\text{-}3,3\text{-}(PMe_2Ph)_2\text{-}3,1,11\text{-}PtC_2B_9H_{10}$, *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 PMe_2Ph 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**, $11\text{-}Ph\text{-}3,3\text{-}(PMe_2Ph)_2\text{-}3,1,11\text{-}PtC_2B_9H_{10}$, 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 PtP_2 plane adopts an essentially perpendicular orientation to the C(1)B(10)B(12) plane, as is observed in the related species 1-NMe_3-3,3-$(^tBuNC)_2$-3,1-$PdCB_{10}H_{10}$ [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*-$C_2B_{10}H_{12}$, with the proviso that the ultimate metallabonded polyhedral face is B_4C and Pt is antipodal to boron.

As previously noted, the conformation of the PtP_2 plane in **1** is significantly distorted from that predicted to be of minimum energy for an $\{ML_2\}$ fragment above a B_3C_2(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-MC_2B_9 polyhedron. In both isomerised products the observed conformation of the $\{ML_2\}$ fragment is the predicted minimum energy one.

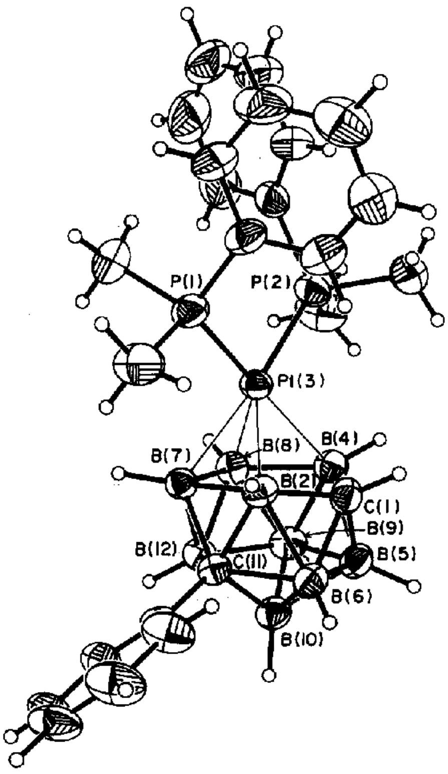

Fig. 3. Molecular structure of 11-Ph-3,3-$(PMe_2Ph)_2$-3,1,11-$PtC_2B_9H_{10}$ (**3**). Important molecular parameters (Å and °) Pt(3)–C(1) 2.581(4), Pt(3)–B(2) 2.233(5), Pt(3)–B(7) 2.211(4), Pt(3)–B(8) 2.246(5), Pt(3)–B(4) 2.281(5), Pt(3)–P(1) 2.2901(11), Pt(3)–P(2) 2.3037(11), P(1)–Pt(3)–P(2) 97.70(4).

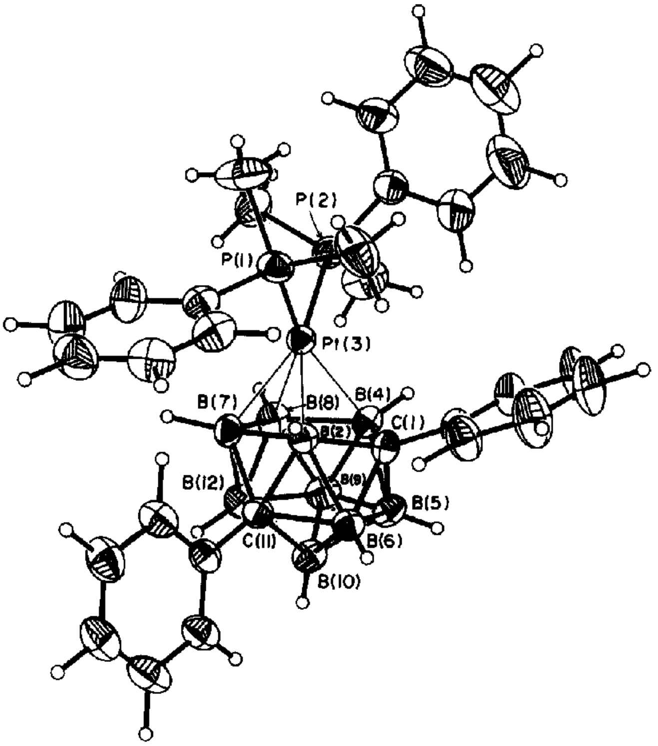

Fig. 4. Molecular structure of 1,11-Ph_2-3,3-$(PMe_2Ph)_2$-3,1,11-$PtC_2B_9H_9$ (**4**). Important molecular parameters (Å and °) Pt(3)–C(1) 2.610(5), Pt(3)–B(2) 2.222(6), Pt(3)–B(7) 2.199(6), Pt(3)–B(8) 2.231(6), Pt(3)–B(4) 2.293(6), Pt(3)–P(1) 2.2864(14), Pt(3)–P(2) 2.2909(14), P(1)–Pt(3)–P(2) 96.23(5).

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*-$Pt(PMe_2Ph)_2Cl_2$ and the diphenylcarbaborane ligand $[7,8\text{-}Ph_2\text{-}7,8\text{-}\textit{nido}\text{-}C_2B_9H_9]^{2-}$ [5] is the C-separated species 1,11-Ph_2-3,3-$(PMe_2Ph)_2$-3,1,11-$PtC_2B_9H_9$ (**4**), the structure of which * is shown in Fig. 4. In this case we assume that intramolecular crowding in the intermediate compound 1,2-Ph_2-3,3-$(PMe_2Ph)_2$-3,1,2-$PtC_2B_9H_9$ 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-MC_2B_9 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-MC_2B_9 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.

Acknowledgments

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References

1 *e.g.* R. N. Grimes, *Carboranes*, Academic Press, New York, 1970.
2 *e.g.* G. M. Edvenson and D. F. Gaines, *Inorg. Chem.*, *29* (1990) 1210; B. M. Gimarc, D. S. Warren, J. J. Ott and C. Brown, *Inorg. Chem.*, *30* (1991) 1598; B. F. G. Johnson, Y. V. Roberts and E. Parisini, *J. Chem. Soc., Chem. Commun.*, (1992) in press.
3 *e.g.* L. F. Warren, Jr. and M. F. Hawthorne, *J. Am. Chem. Soc.*, *92* (1970) 1157; C. B. Knobler, T. B. Marder, E. A. Mizusawa, R. G. Teller, J. A. Long, P. E. Behnker and M. F. Hawthorne, *J. Am. Chem. Soc.*, *106* (1984) 2990; S. A. Brew, N. Carr, J. C. Jeffrey, M. U. Pilotti and F. G. A. Stone, *J. Am. Chem. Soc.*, *114* (1992) 2203.
4 *e.g.* M. K. Kaloustian, R. J. Wiersema and M. F. Hawthorne, *J. Am. Chem. Soc.*, *94* (1972) 6679.
5 Z. G. Lewis and A. J. Welch, *J. Organomet. Chem.*, *430* (1992) C45.
6 B. D. Reid and A. J. Welch, unpublished results.
7 D. M. P. Mingos, M. I. Forsyth and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, (1978) 1363.
8 For experimental details see D. R. Baghurst and D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, (1992) 1151.
9 S. A. Macgregor, A. J. Wynd, R. O. Gould, N. Moulden, P. Taylor, L. J. Yellowlees and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, (1991) 3317.
10 W. E. Carroll, M. Green, F. G. A. Stone and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, (1975) 2265.
11 M. Green, J. L. Spencer, F. G. A. Stone and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, (1975) 179.