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## Preliminary Communication

# Synthesis, molecular structure and NMR behaviour of $[9,9\text{-}(PMe_2Ph)_2\text{-}\mathit{arachno}\text{-}9,6,8\text{-}PtS_2B_7H_7]$: Direct evidence for the ten-vertex borane vertex-flip mechanism of isomerization *

Jane H. Jones [a], Xavier L.R. Fontaine [a], Norman N. Greenwood [a], John D. Kennedy [a], Mark Thornton-Pett [a], Bohumil Štíbr [b] and Harald Langhoff [c]

[a] *School of Chemistry, University of Leeds, Leeds LS2 9JT (UK)*
[b] *Institute of Inorganic Chemistry, Czech Academy of Sciences, 25068 Řež near Prague (Czech Republic)*
[c] *Stoe and Cie GmbH, Hilperstrasse 10, Postfach 4110, W-6100 Darmstadt (Germany)*

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### Abstract

The ten-vertex cluster compound $[9,9\text{-}(PMe_2Ph)_2\text{-}\mathit{arachno}\text{-}9,6,8\text{-}PtS_2B_7H_7]$ is fluxional between its two enantiomers *via* a vertex-flip of the $\{Pt(PMe_2Ph)_2\}$ group between the $\eta^3$-10,4,8 and $\eta^3$-10,5,6 positions of the formal nine-vertex *arachno*-shaped $\{S_2B_7H_7\}$ ligand moiety.

Reaction between $[\mathit{arachno}\text{-}4,6\text{-}S_2B_7H_9]$ [1] and *cis*-$[PtCl_2(PMe_2Ph)_2]$ in dichloromethane, followed by chromatographic separation in air, gave a 60% yield of a yellow crystalline product identified by single-crystal X-ray diffraction analysis as $[9,9\text{-}(PMe_2Ph)_2\text{-}\mathit{arachno}\text{-}9,6,8\text{-}PtS_2B_7H_7]$ (Fig. 1) [2], NMR spectroscopy at a variety of temperatures [5] showed that the compound is fluxional between its enantiomers in solution ($\Delta G$ *ca.* 44 kJ $mol^{-1}$ at 260 K), with the platinum vertex moving to and fro between the 10,4,8 and 10,5,6 $\eta^3$-$SB_2$ positions of the *arachno*-shaped nine-vertex $\{6,8\text{-}S_2B_7H_7\}$ fragment (structure I, numbered here for convenience as in the ten-vertex $\{PtS_2B_7\}$ cluster in Fig. 1): Retention of the two discrete $^{31}P$ resonances at higher temperatures indicates that this process is not associated with a general rotation of the $\{Pt(PMe_2Ph)_2\}$ group (contrast refs. [6] and [7], although the evidence does not distinguish between a 1,2 jump (as indicated in Structure I) and a 1,3 jump via an unstable $\eta^3$-6,7,8-SBS intermediate.

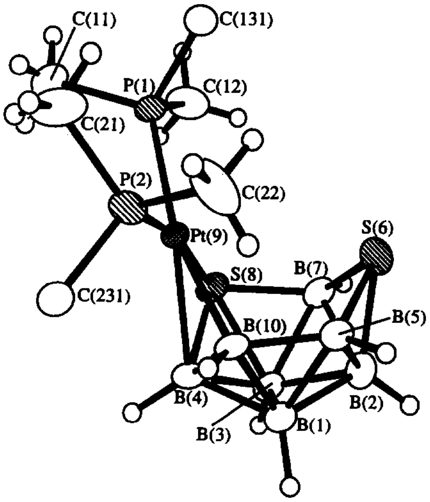
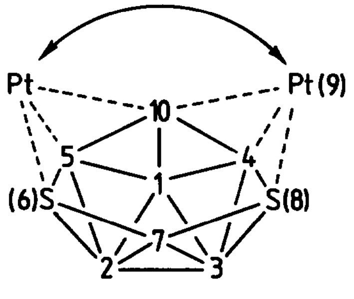


Fig. 1. ORTEP drawing of the molecular structure of $[9,9\text{-}(PMe_2Ph)_2\text{-}\mathit{arachno}\text{-}9,6,8\text{-}PtS_2B_7H_7]$. Salient interatomic dimensions are as follows: Pt(9)–P(1) 232.4(3), Pt(9)–P(2) 225.5(3), Pt(9)–S(8) 234.5(3), Pt(9)–B(4) 232.1(6), Pt(9)–B(10) 220.3(6), S(6)–B(5) 197.0(7), S(6)–B(7) 188.6(7), S(8)–B(7) 190.7(7), B(5)–B(10) 171.1(9) pm; P(1)–Pt(9)–P(2) 98.4(1) S(8)–Pt(9)–B(10) 89.2(2), B(10)–B(5)–S(6) 121.4(4), B(5)–S(6)–B(7) 98.9(3), S(6)–B(7)–S(8) 118.4(3), B(7)–S(8)–Pt(9) 105.5(2) and Pt(9)–B(10)–B(5) 107.9(4)°.

This vertex-flip mechanism (see Scheme 1) in the open ten-vertex *nido-arachno* cluster shape has long been postulated as being an important mechanism for rearrangement or selective scrambling of cluster vertices both in heteroborane [8] and metallaborane [9]



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Correspondence to: Dr. J.D. Kennedy.

* Contribution No. 23 from the Řež-Leeds Anglo-Czech Polyhedral Collaboration (A.C.P.C.).

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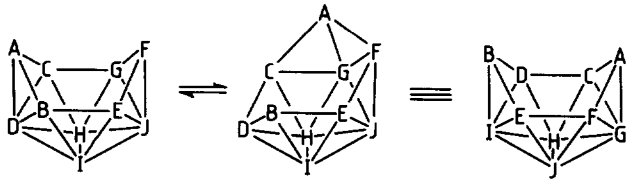

Scheme 1

chemistry but, as far as we are aware, evidence for this has been based only on product analysis and is thus largely circumstantial. The present results now directly demonstrate the occurrence of the process.

## Acknowledgements

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## References and notes

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2 *Crystal data.* $C_{16}H_{29}B_7P_2PtS_2$, $M = 618.24$, orthorhombic, space group $P2_12_12_1$, $a = 893.5(1)$, $b = 1502.5(1)$, $c = 1822.6(1)$ pm, $U = 2.4468(4)$ nm$^{-3}$, $D_c = 1.67$ Mg m$^{-3}$, $Z = 4$, $F(000) = 1199.94$, $\mu$ (Mo $K_\alpha$) = 57.85 cm$^{-1}$, $4.0 < 2\theta < 50.0°$. $R(R_w) = 0.0142(0.0200)$ for all 2448 reflections collected.
Crystallographic data were collected on a Stoe STADI4 diffractometer using an $\omega/\theta$ scan mode with an on-line profile method [3] and graphite-monochromated Mo K$\alpha$ radiation. A semi-empirical absorption correction, based on azimuthal $\psi$-scans, was applied. The structure was solved using Patterson and Fourier method and refined by full-matrix least-squares [4]. All non-hydrogen atoms were assigned anisotropic thermal parameters. Phosphine-associated hydrogen atoms were included in calculated positions and were refined with an overall isotropic thermal parameter, while the borane hydrogen-atoms were located on a Fourier difference synthesis and were refined with individual isotropic thermal parameters. The weighting scheme $w = [\sigma^2(F_o) + 0.0005(F_o)^2]^{-1}$ was applied. Atomic co-ordinates, interatomic distances and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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5 Cluster BH parameters at 213 K in $CD_2Cl_2$ solution, ordered as assignment $\delta(^{11}B)$/ppm [$\delta(^1H)$/ppm in square brackets]: BH(4) + 20.0 [+3.11], BH(5) *ca.* −1.0 [+2.75], BH(10 and 7) *ca.* −6.5 {+3.21 and +2.10], BH(1) −23.0 [+1.26], BH(2) *ca.* −27.0 [+2.06] and (BH)3 −34.7 [+1.19]; at 303 K, values were BH(4,5) + 8.6 [+3.10], BH(7) −6.3 [+3.32], BH(10) −7.1 [+2.33], BH(1) −21.8 [+1.47] and BH(2,3) −29.5 [+1.75]. The observed coalescence temperatures for the $^{11}B(4)(5)$ and $^{11}B(2)(3)$ pairs were within the range 260 ± 5 K for the 128 MHz (9.4 T) spectrum, giving a value for $\Delta G^{\ddagger}_{260}$ of 44 kJ mol$^{-1}$. $^{31}P$ parameters ($CD_2Cl_2$, 223 K) were $\delta(^{31}P)$ (relative to 85%$H_3PO_4$) + 0.3 [$^1J(^{195}Pt-^{31}P)$ 3939 Hz] and −10.5 ppm [$^1J(^{195}Pt-^{31}P)$ 2651 H], $^2J(^{31}P-^{31}P)$ 22 Hz. At 183 K in $CDCl_2$ there were four P-methyl $^1H$ resonance patterns, centered at $\delta(^1H)$ = (a) +2.10 (b) +1.76 (c) +1.66 and (d) +1.55, all with *ca.* 9 Hz splittings arising from $^2J(^{31}P-^1H)$; at higher temperatures (a) and (c), and (b) and (d) coalesced to give patterns centered at (293 K) +2.01 and +1.67 ppm respectively.

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