The Synthesis and Molecular Structure of 9-H-9,9-$(Et_3P)_2$-$\mu_{10,11}$-H-7,8,9-$C_2PtB_8H_{10}$ and 9-H-9,10-$(Et_3P)_2$-7,8,9-$C_2PtB_8H_9$; Pt(9) → B(10) Migration of a Triethylphosphine Ligand, and Evidence for the Redox Sequence $Pt^0 \rightarrow Pt^{IV} \rightarrow Pt^{II}$

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Summary Reaction of $[Pt_2(\mu$-cyclo-octa-1,5-diene$)(PEt_3)_4]$ with 5,6-dicarba-*nido*-decaborane affords 9-H-9,9-$(Et_3P)_2$-$\mu_{10,11}$-H-7,8,9-$C_2PtB_8H_{10}$, which on pyrolysis (100 °C) loses H_2 and forms 9-H-9,10-$(Et_3P)_2$-7,8,9-$C_2PtB_8H_9$; the structures of these compounds have been determined by *X*-ray crystallography.

We have previously shown[1] that $[Pt_2(\mu$-cod$)(PEt_3)_4]$ (cod = cyclo-octa-1,5-diene) reacts with *nido*-2,3-$C_2B_4H_8$ to afford [*nido*-$\mu_{4,5}$-{*trans*-$(Et_3P)_2Pt(H)$}-$\mu_{5,6}$-H-2,3-$C_2B_4H_6$], which on pyrolysis loses a molecule of hydrogen and forms a *closo*-platinacarbaborane. In attempting to extend this synthetic strategy we have examined the corresponding reaction with 5,6-dicarba-*nido*-decaborane and have observed an unusual sequence of reactions.

A diethyl ether solution of $[Pt_2(\mu$-cod$)(PEt_3)_4]$ reacts at room temperature with *nido*-5,6-$C_2B_8H_{12}$ to form a tan crystalline complex (**1**) {70% yield, m.p. 104—106 °C, ν_{Pt-H} 2 010s and ν_{B-H} 2 555s, 2 520vs, and 2 494s cm^{-1}; n.m.r.: ^{31}P (rel. extn. H_3PO_4) ($CD_3C_6D_5$; −80 °C), δ, 3·9 [d, *J*(PtP) 2 435, *J*(PP) 22 Hz] and −7·2 p.p.m. [d, *J*(PtP) 2 349, *J*(PP) 22 Hz]; ^{11}B, (rel. extn. $BF_3{\cdot}Et_2O$) (C_6D_6; 25 °C), δ, 8·9(2), −11·9(2), −22·2, and −26·8(4) p.p.m.}. When complex (**1**) was heated (100 °C; 1 h) in toluene solution a molar equivalent of molecular hydrogen was evolved and a red crystalline species was formed in high yield (80%). Recrystallisation from diethyl ether afforded (**2**) {m.p. 116 °C, ν_{Pt-H} 2 115m and ν_{B-H} 2 560m, 2 514s, 2 480(sh), and 2 465m cm^{-1}; n.m.r.: ^1H (C_6D_6; 25 °C), τ, 17·5 [dd, Pt–H, *J*(PH) 24, *J*(P^1H) 16, *J*(PtH) 600 Hz]; ^{31}P ($CD_3C_6D_5$; −70 °C), δ, 17·2 [*J*(PtP) 2 775 Hz] and 9·6 p.p.m. [*J*(PtP) 95 Hz]; ^{11}B (C_6D_6; +100 °C), δ, 8·8(3), 0·6(1), −13·7(2), and −22·5(2) p.p.m.}.

The structural identities of (**1**) and (**2**) were established by single crystal *X*-ray diffraction studies.

Crystal data: (**1**), $C_{14}H_{42}B_8P_2Pt$, *M* = 554·00, orthorhombic, *a* = 14·825(4), *b* = 10·1367(13), *c* = 16·1193(15) Å, *U* = 2 422·4 Å^3, *Z* = 4, D_c = 1·519 g cm^{-3}, μ(Mo-K_α) = 58·6 cm^{-1}, space group $P2_12_12_1$; 3 303 significant reflections, $F \geqslant 2{\cdot}0\sigma(F)$, to θ_{max} 30° (Mo-K_α) were measured on an

Enraf-Nonius CAD 4 diffractometer. (**2**), $C_{14}H_{40}B_8P_2Pt$, M = 551·98, monoclinic, a = 9·7813(16), b = 12·312(3), c = 20·519(3) Å, β = 99·053(16)°, U = 2 440·2 Å^3, Z = 4, D_c = 1·503, μ(Mo-K_α) = 56·4 cm^{-1}, space group $P2_1/c$; 3 192 reflections were measured (CAD 4) to θ_{max} 25°.

Both structures were solved by conventional Patterson and Fourier methods, and refined by least-squares to current R values of 0·058 and 0·060 respectively.‡ Cage carbon atoms were identified *via* internuclear separations and thermal parameters, having been refined as boron. Figures 1 and 2 show perspective molecular views, and list important molecular parameters.

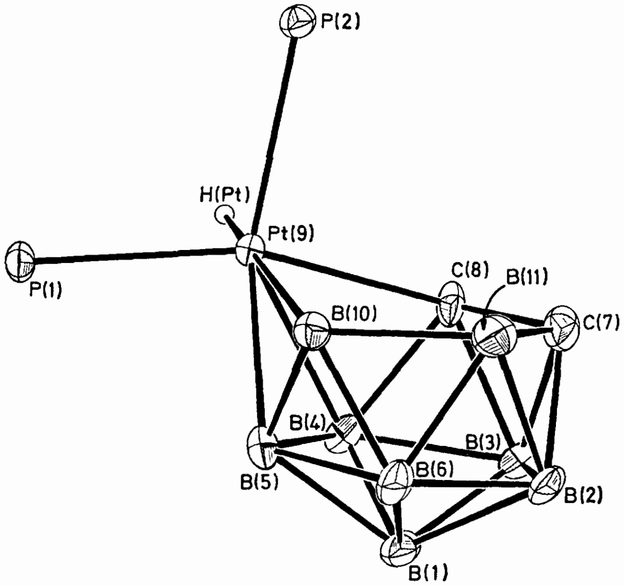


FIGURE 1. Molecular structure of 9-H-9,9-$(Et_3P)_2$-$\mu_{10,11}$-H-7,8,9-$C_2PtB_8H_{10}$, (**1**), with ethyl groups omitted for clarity: Pt(9)–P(1), 2·304(3); Pt(9)–P(2), 2·364(3); C(7)–C(8), 1·604(20); C(8)–Pt(9), 2·141(10); Pt(9)–B(10), 2·319(14); B(10)–B(11), 1·804(24); B(11)–C(7), 1·663(27); Pt(9) · · · · C(7), 3·233; Pt(9) · · · · B(11) 3·309 Å; ∠ P(1)–Pt(9)–P(2), 104·0(1)°.

Both polyhedra contain open $\overline{\mathrm{CCPtBB}}$ faces and may therefore be classified as *nido*. In neither case have we yet located the hydrogen atoms associated with the heteroborane face. Nevertheless, it is clear from the geometries about Pt(9) that a single terminal hydrido function is present in both molecules, and in the Figures H(Pt) is shown in idealised positions. In addition to the hydrogens terminally bound to all other polyhedral atoms, molecule (**1**) carries a μ-H function, whose probable location (based on comparative B-B distances) is bridging the B(10)–B(11) edge.

These studies therefore establish that direct insertion of a $[Pt(PEt_3)_2]$ fragment into the *nido*-carbaborane 5,6-$C_2B_8H_{12}$ involves incorporation of the metal into an expanded polyhedral framework to give (**1**) (see Scheme). This is in contrast with the reaction between $[Pt_2(\mu\text{-cod})(PEt_3)_4]$ and *nido*-2,3-$C_2B_4H_4R_2$ (R = H, Me), where the metal, having inserted into a μ-B–H–B function, simply occupies an

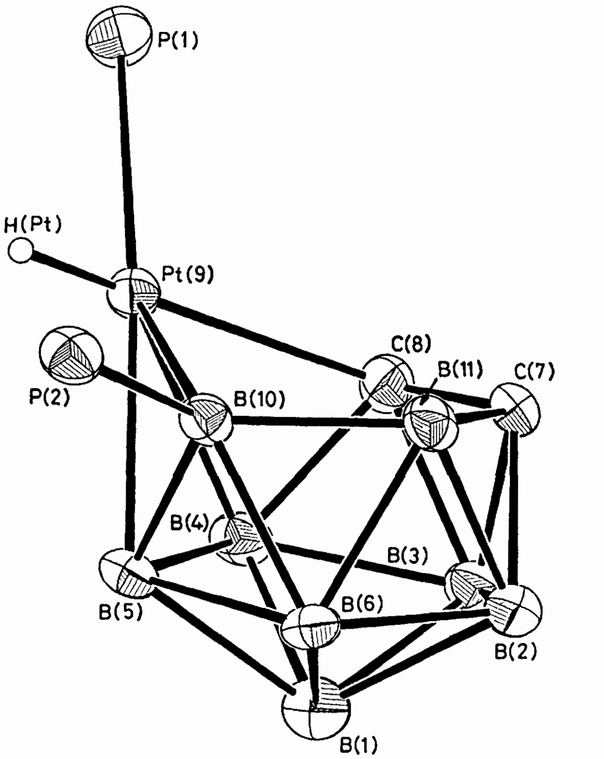
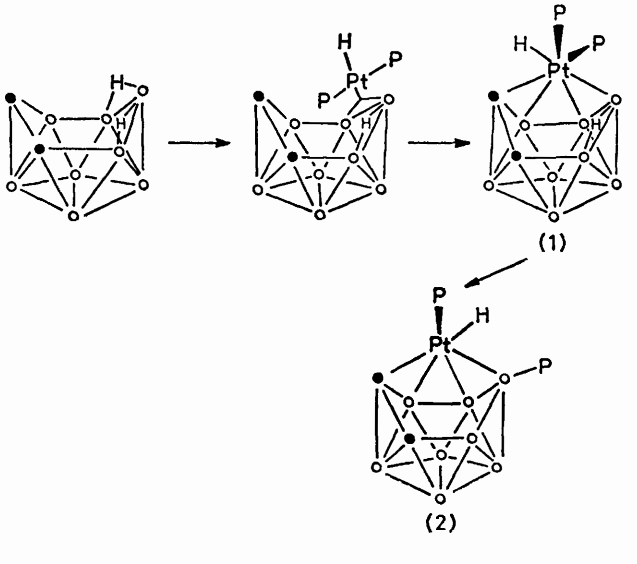


FIGURE 2. Molecular structure of 9-H-9,10-$(Et_3P)_2$-7,8,9-$C_2PtB_8H_9$, (**2**), with ethyl groups omitted for clarity: Pt(9)–P(1), 2·293(3); B(10)–P(2), 1·917(12); C(7)–C(8), 1·477(15); C(8)–Pt(9), 2·179(10); Pt(9)–B(10), 2·171(11); B(10)–B(11), 1·684(17); B(11)–C(7), 1·723(15); Pt(9) · · · · C(7), 2·999; Pt(9) · · · · B(11), 3·071 Å.



SCHEME. P = PEt_3; ○ = BH; ● = CH.

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‡ Atomic co-ordinates for complexes (**1**) and (**2**) may be obtained on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

edge-bridging site in a non-expanded *nido*-cage.[1] Moreover, on thermolysis of (**1**) loss of 1 mol. equiv. of molecular hydrogen is accompanied by migration of one PEt_3 function from Pt(9) to B(10).§ It is likely that the hydrogen atoms 'lost' are those attached to B(10) and bridging B(10)–B(11) in (**1**), although with the present data it is not possible to comment on the identity of the migrating phosphine. The crystallographic labelling of P(1) and P(2) has no implied significance in this respect.

closo-octadecahedral, 26 and 24 electrons, respectively, are required for cage bonding, according to empirical electron-counting rules.[3] This, in turn, leads to assigned metal oxidation states of +4 and +2 in (**1**) and (**2**), respectively. Hence we conclude that the overall sequence of reactions involves for a boron system the most unusual formal redox sequence $Pt^0 \rightarrow Pt^{IV} \rightarrow Pt^{II}$. Secondary evidence for the higher metal oxidation state in (**1**) is indicated by the Pt–B distances not involved in the changing open face. Thus Pt(9)–B(4) [2·207(15) Å] and Pt(9)–B(5) [2·190(18) Å] are appreciably lengthened, to 2·240(12) and 2·255(10) Å, respectively, as (**1**) is transformed into (**2**).

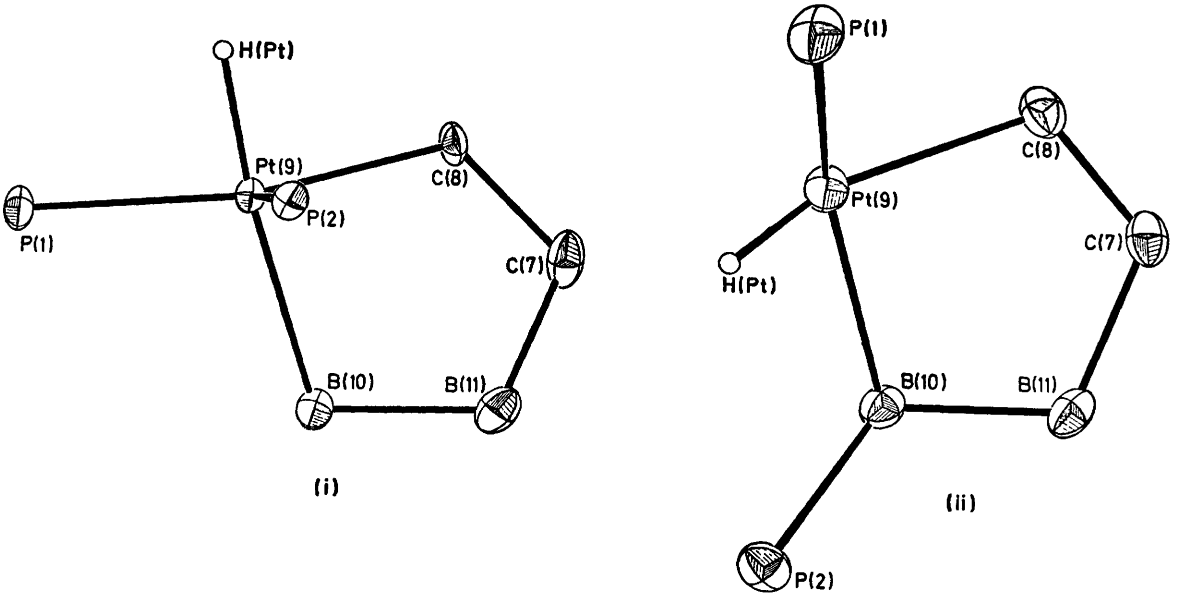

FIGURE 3. The open polyhedral faces of (i) (**1**), and (ii) (**2**).

Figures 3(i) and 3(ii) are projections normal to the open faces of (**1**) and (**2**), respectively. Strictly speaking neither face is planar, although that of (**1**) is substantially the flatter. This suggests[2] that, whilst the cage of (**1**) may adequately be described as *nido*-icosahedral, that of (**2**) might be better considered as a highly distorted formally *closo*-octadecahedron in which the Pt(9)–C(7) and Pt(9)–B(11) connectivities have extended to non-bonding distances Thus, if complex (**1**) is *nido*-icosahedral and (**2**) formally

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§ Migration of a triphenylphosphine ligand from nickel to a boron atom has been observed on thermolysis of *closo*-[3,3-$(PPh_3)_2$-3,1,2-$NiC_2B_9H_{11}$ (S. B. Miller and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 1976, 786).

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