$[\{(dppe)Pt\}_2B_7H_{11}]$: An *arachno*-bimetallanonaborane based on the uncommon *n*-B_9H_{15} cluster framework

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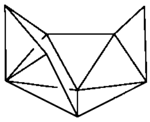
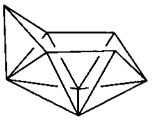
The first bimetallanonaborane, $[\{(dppe)Pt\}_2B_7B_{11}]$, based on the uncommon *n*-B_9H_{15} cluster framework, is prepared and characterized as a final product from the reaction of pentaborane (9) with $[PtCl_2(dppe)]$.

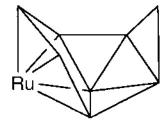
The coordination number pattern recognition theory for boranes and carbaboranes, as described by Williams in 1976,[1] requires that in order to generate *arachno*-clusters from *nido* systems, a highest connectivity vertex, adjacent to the open face, is removed. The predicted cluster framework for an *arachno* 9-vertex system is illustrated by structure **I** and recognized as *n-arachno* B_9H_{15}. In contrast, the more commonly encountered 9-vertex *arachno*-species are derived by removal of a low connectivity vertex from *nido*-$B_{10}H_{14}$ to generate derivatives of what are referred to as *i*-B_9H_{15} (structure **II**) and *i*-$C_2B_7H_{13}$.[2] With the exception of the ruthenanonaborane, $[2\text{-}(\eta^6\text{-}C_6Me_6)\text{-}2\text{-}RuB_8H_{14}]$, (structure **III**)[3] reported in trace yields in a preliminary communication in 1986, all the known nine-vertex *arachno*-metallaboranes have structures based on the *i*-B_9H_{15} framework.[4] This article describes the synthesis and complete characterization of a diplatinanonaborane whose structure is based on a polyhedral nine-vertex *n*-B_9H_{15} *arachno*-cluster type and for which the application of electron-counting rules suggest that the species is another example of the growing list of 'rule-breakers'.



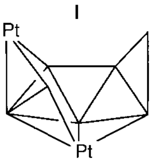
I



II



III



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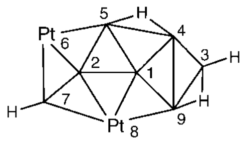
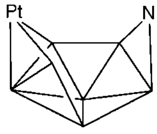


V



VI

Derivatives of B_5H_9, in which an electrophilic group has replaced a bridging H atom, are well known.[5] Group 10 derivatives, $[2,3\text{-}\mu\text{-}\{ML_n(X)\}B_5H_8]$, where M = Ni, Pd, Pt, L_n = $(PR_3)_2$, dppe [dppe = $(Ph_2PCH_2)_2$], X = Cl, Br, are isolated if the reaction between $[B_5H_8]^-$ and ML_nX_2 is carried out and worked up at low temperatures.[6] Such species are generally unstable at room temperature in solution, usually resulting in decomposition involving reduction of the metal moiety to elemental metal by the borane moiety. Herein, we describe the results when the reaction mixture, $Li[B_5H_8]$ and $PtCl_2(dppe)$, is allowed to warm to room temperature, dried *in vacuo* for 2 days, exposed to air and separated using TLC on silica gel following filtration through silica gel.[8] Thus $[\{(dppe)Pt\}_2B_7H_{11}]$ is prepared from $[2,3\text{-}\mu\text{-}\{(dppe)Pt(Cl)\}B_5H_8]$, in *ca.* 10% yield as a yellow air-stable crystalline solid, along with $[(dppe)PtB_3H_7]$,[8a] $[(dppe)(BH_3)_2]$,[8b] and what appear to be Pt chloride salts. NMR and mass spectral data identified the yellow solid as $[\{(dppe)Pt\}_2B_7H_{11}]$.[9] This was confirmed by a single crystal structure determination of the diethyl ether sequisolvate.[10]

The structure of $[\{(dppe)Pt\}_2B_7H_{11}]$, given in Fig. 1, consists of a nine-vertex *n-arachno* framework, obtained by removal of two adjacent vertices of connectivity six and four respectively, from an 11-vertex *closo*-octadecahedron. The {(dppe)Pt} moieties are located at the 6 and 8 positions in the *n-arachno* B_9H_{15} framework, each replacing a BH group and a bridging H atom. There are bridging H atoms at the B(4)–B(5) and B(3)–B(9) edges and *endo*-H atoms on B(3) and B(7). Only the latter *endo*-H atom is observed from the X-ray structure determination but the presence is clearly confirmed from NMR spectral data. $[\{(dppe)Pt\}_2B_7H_{11}]$ is shown as structure **IV** and a topological representation, showing the numbering scheme and the *endo*-hydrogens, is given as structure **V**. Bond distances are within the normal ranges for Pt–B, Pt–P and B–B bonding connections. The B(4)–B(9) edge bridged by a BH_2 group, at 1.739(13) Å, is similar to that observed for the same cluster interboron connection in *n*-B_9H_{15}[2,11] and in the ruthenaborane,[3] but it is much shorter than the corresponding B–B interaction in the recently discovered azaplatinaborane, $[3,3\text{-}(PMe_2Ph)_2\text{-}3\text{-}PtB_7H_{10}\text{-}\mu\text{-}5,6\text{-}(NHR)]$, 1.92(2) Å,[12] in which the B–B edge is bridged by a NHEt group (structure **VI**). NMR data conform to the observed molecular structure for this new biplatinaborane. The ^{11}B spectrum exhibits four resonances of relative

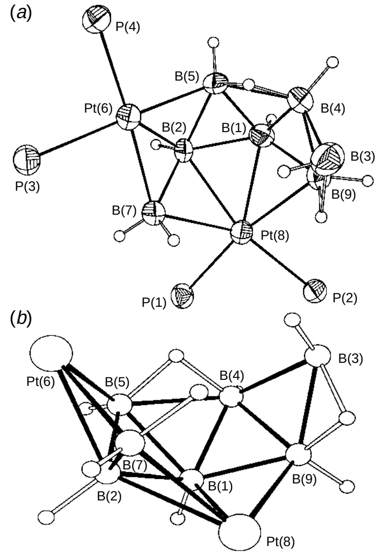


Fig. 1 (*a*) Projection of $[\{(dppe)Pt\}_2B_7H_{11}]]$, showing only the P atoms of the chelating ligand on Pt. Ellipsoids are drawn at the 50% probability level. In addition to a terminal H atom on each B there is an *exo*-terminal H at position 3, indicated by ^1H NMR spectra. (*b*) Alternative representation with the ligands omitted for clarity. Selected interatomic distances (Å): from Pt(6) to P(3) 2.285(2), to P(4) 2.278(2), to B(2) 2.190(9), to B(5) 2.192(0), to B(7) 2.208(9); from Pt(8) to P(1) 2.289(2), to P(2) 2.295(2), to B(1) 2.227(9), to B(2) 2.267(9), to B(7) 2.328(9), to B(9) 2.302(9); interboron values: B(4)–B(9) 1.739(13), B(3)–B(9) 1.80(2), B(3)–B(4) 1.82(2), the other B–B distances are in the range 1.765(13)–1.883(13). Selected angles (°) P(3)–Pt(6)–P(4) 85.83(8), P(1)–Pt(8)–P(2) 84.97(7), P(3)–Pt(6)–B(5) 174.5(2), P(4)–Pt(6)–B(7) 167.6(3), P(1)–Pt(8)–B(9) 170.3(2), P(2)–Pt(8)–B(7) 152.1(2), B(4)–B(3)–B(9) 57.5(5).

intensity 1 : 4 : 1 : 1 and ^{1}H-{^{11}B(selective)} experiments reveal eleven different cage H atoms of which two are bridging and two are *endo*-hydrogen atoms. In addition, ^{31}P NMR spectra exhibit four different resonances of equal intensity; two doublets, an overlapped doublet of doublets that is seen as an apparent triplet, and a singlet. Each signal shows additional coupling to ^{195}Pt. Since P atoms in the same chelating dppe ligand effectively do not couple, we must be observing four-bond $^{4}J(^{31}\mathrm{P}–^{31}\mathrm{P})$ coupling constants. From Fig. 1(*a*), it appears that P(3) and P(4) are effectively *trans* to P(2) whereas P(1) is directed towards the cluster B(1)–B(9) connection. This conformation suggests that the P atoms involved in ^{31}P–^{31}P coupling are P(3), P(4) and P(2). Thus we assign P(2) to the observed apparent triplet, P(3) and P(4) to the doublets and P(1) to the singlet. The cage connectivities of the Pt atoms are different; that for Pt(6) is three whereas that for Pt(8) is four and this appears to be reflected in the differences in ^{195}Pt–^{31}P coupling constants listed in ref. 9. Characterization of $[\{(\mathrm{dppe})\mathrm{Pt}\}_2\mathrm{B}_7\mathrm{H}_{11}]$ is completed by mass spectral data. The most intense envelope is that for the $[\mathrm{M} - \mathrm{BH}_3]^+$ ion, suggesting that the connection of the μ-H-BH$_2$ group is quite fragile, perhaps accounting for the preference of *i*-$\mathrm{B}_9\mathrm{H}_{15}$ isomers for nonaboranes and their derivatives.

A final point of note concerning $[\{(\mathrm{dppe})\mathrm{Pt}\}_2\mathrm{B}_7\mathrm{H}_{11}]$ is that it appears not to conform to the polyhedral skeletal electron pair theory (PSEPT) counting rules.[13] An *arachno* nine-vertex cluster requires $n + 3$ skeletal electron pairs, which for this cluster would be 12 electron pairs. Using the conventional electron-counting methods devised by Wade,[14] $[\{(\mathrm{dppe})\mathrm{Pt}\}_2\mathrm{B}_7\mathrm{H}_{11}]$ possesses 11 skeletal electron pairs. Such ambiguity has been observed for essentially all clusters containing three-connectivity group 10 metal moieties.[15] Some examples of such systems include $[(\mathrm{PPh}_3)_2(\mathrm{CO})\mathrm{Os}(\mathrm{PPhMe}_2)\mathrm{Cl}(\mu\text{-H})\mathrm{PtB}_5\mathrm{H}_7]$,[15a] $[(\mathrm{PEt}_3)_2\mathrm{Pt}(\mathrm{CMe})_2\mathrm{B}_4\mathrm{H}_4]$[15b] and $[(\mathrm{PPhMe}_2)_2\mathrm{PtB}_8\mathrm{H}_{12}]$.[15c] In these systems, the organometallic Pt fragment is best regarded as a square planar 16-electron center that contributes two orbitals and two electrons to the cluster framework. Under this scenario, the metal moiety is not isolobal with a conventional three orbital, two electron conical vertex and the skeletal electron count is two electrons short of the number required for compliance with the PSEPT. In $[\{(\mathrm{dppe})\mathrm{Pt}\}_2\mathrm{B}_7\mathrm{H}_{11}]$ this feature may be ascribed to the vertex unit [(dppe)Pt] at the 6-position. Apparently in $[\{(\mathrm{dppe})\mathrm{Pt}\}_2\mathrm{B}_7\mathrm{H}_{11}]$, the two Pt vertices, with different connectivity, contribute differently to the total skeletal electron count for the cluster. The vertex Pt(8), which has connectivity 4 may be considered to be a 'normal' conical vertex conforming to the PSEPT, although in a formal sense each [(dppe)Pt] vertex subrogates a BH(μ-H) moiety. This appears to represent a new example of the so-called rule breakers, and such phenomena warrant further investigation.

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8 (*a*) NMR data for $[(\mathrm{dppe})\mathrm{PtB}_3\mathrm{H}_7]$, ($\mathrm{CDCl}_3$, 294–297 K) {ordered as: relative intensity $\delta(^{11}\mathrm{B})$ (rel. to $\mathrm{BF}_3\cdot\mathrm{OEt}_2$) $[\delta(^{1}\mathrm{H})]$} 1BH 19.8 [3.28]; 2BH$_2$ 4.1 [4.20 (2 H); 2.80 (2 H), $^{1}J(^{195}\mathrm{Pt}–^{1}\mathrm{H})$ *ca.* 63 Hz]; additional cage $\delta(^{1}\mathrm{H})$ −2.64 (2μ-H). δ(H)(dppe) 7.69–7.41 ($4\mathrm{C}_6\mathrm{H}_5$), 2.37 (m 2CH$_2$). $\delta(^{31}\mathrm{P})$ (CDCl_3, 294–297 K, rel. 85% $\mathrm{H}_3\mathrm{PO}_4$) 55.4, $^{1}J(^{195}\mathrm{Pt}–^{31}\mathrm{P})$ 2541 Hz. Data compare very well with those for $[(\mathrm{PPh}_3)_2\mathrm{PtB}_3\mathrm{H}_7]$, in J. Bould, J. D. Kennedy and W. S. McDonald, *Inorg. Chim. Acta.*, 1992, **196**, 201; (*b*) $[(\mathrm{dppe})(\mathrm{BH}_3)_2]$, ($\mathrm{CDCl}_3$, 294–297 K): 2BH$_3$ −39.9 [1.02; AA′XX′ spin system, N = 15.77 Hz]; $^{1}J(^{11}\mathrm{B}–^{1}\mathrm{H})$ coupling constants not resolved due to the broadness of the boron resonances. $\delta(^{31}\mathrm{P})$ (CDCl_3, 294–297 K, rel. 85% $\mathrm{H}_3\mathrm{PO}_4$) 18.9 (br).

9 Selected NMR data for $[\{(\mathrm{dppe})\mathrm{Pt}\}_2\mathrm{B}_7\mathrm{H}_{11}]$, ($\mathrm{CDCl}_3$, 294–297 K) {ordered as: relative intensity $\delta(^{11}\mathrm{B})$ (rel. to $\mathrm{BF}_3\cdot\mathrm{OEt}_2$) $[\delta(^{1}\mathrm{H})]$} 1BH 39.2 [3.98], 4B 15.2 [4.98, 4.80, 4.22, 4.12, 2.82 (*endo*) [$^{2}J(^{195}\mathrm{Pt}–^{1}\mathrm{H})$ *ca.* 67 Hz], 1BH$_2$ −4.7 [2.07 (m, J 5.1 Hz; *endo*/*exo*)], 1BH −24.6 [1.34]; additional cage $\delta(^{1}\mathrm{H})$ −0.23 (bridging), −1.74 (bridging). $\delta(^{1}\mathrm{H})$(dppe) 8.0–6.9 ($4\mathrm{C}_6\mathrm{H}_5$), 2.31 (m, CH$_2$), 1.87 (m, CH$_2$). The ^{11}B spectra were too broad to observe coupling constants. $\delta(^{31}\mathrm{P})$ (CDCl_3, 228 K, rel. 85% $\mathrm{H}_3\mathrm{PO}_4$) 55.7 [d, P(3 or 4)], 53.1 [d of d, P(2)], 49.4 [s, P(1) and 45.3 d, P(4 or 3)]; $^{4}J[^{31}\mathrm{P}(4\text{ or }3)–^{31}\mathrm{P}(2)]$ 12.2 Hz, $^{1}J[^{195}\mathrm{Pt}–^{31}\mathrm{P}(4\text{ or }3)]$ 2658 Hz; $^{4}J[^{31}\mathrm{P}(4\text{ or }3)–^{31}\mathrm{P}(2)] + {}^{4}J[^{31}\mathrm{P}(3\text{ or }4)–^{31}\mathrm{P}(2)]$ 19.0 Hz, $^{1}J[^{195}\mathrm{Pt}–^{31}\mathrm{P}(2)]$ 2534 Hz; $^{1}J[^{195}\mathrm{Pt}–^{31}\mathrm{P}(1)]$ 2419 Hz; $^{4}J[^{31}\mathrm{P}(2)–^{31}\mathrm{P}(3\text{ or }4)]$ 22.6 Hz, $^{1}J[^{195}\mathrm{Pt}–^{31}\mathrm{P}(3\text{ or }4)]$ 2609 Hz. Low resolution MS (VG, ZAB-E: FAB in $\mathrm{CH}_2\mathrm{Cl}_2$, 3-nitrobenzyl alcohol matrix) overlapped with the $\mathrm{M} - \mathrm{H}_2$ ion, gave an apparent cutoff at m/z 1280 (calc. for $^{12}\mathrm{C}_{52}{}^{1}\mathrm{H}_{59}{}^{11}\mathrm{B}_7{}^{31}\mathrm{P}_4{}^{198}\mathrm{Pt}_2$ 1280). Observed and calculated mass spectral parent profiles showing isotopic distribution for the $[\mathrm{M} - \mathrm{BH}_3]$ ion, with m/z (max.) = 1259, compare very well.

10 *Crystal data* for $\mathrm{C}_{58}\mathrm{H}_{74}\mathrm{B}_7\mathrm{O}_{1.5}\mathrm{P}_4\mathrm{Pt}_2$, $[(\mathrm{dppe})_2\mathrm{Pt}_2\mathrm{B}_7\mathrm{H}_{11}]$, M = 1384.90 (includes 1.5 molecules of $\mathrm{Et}_2\mathrm{O}$), triclinic, space group $P\bar{1}$, a = 12.8918(1), b = 13.7153(1), c = 17.8679(2) Å, α = 97.118(1), β = 94.409(2), γ = 108.92(1)°, U = 2942.44(5) Å^3, D_c = 1.563 Mg m^{-3}, Z = 2, $F(000)$ = 1370, $\mu(\text{Mo-K}\alpha)$ = 4.897 mm^{-1}, T = 223(2) K. A total of 11 509 (R_{int} = 0.07) independent reflections, $2\theta_{\max}$ = 52.0° on a Siemens CCD single-crystal X-ray diffractometer using ω scans. The final $wR(F^2)$ for all unique reflections was 0.119 with a conventional $R(F)$ of 0.049 [for 8526 reflections with $I > 2\sigma(I)$] for 677 parameters. CCDC 182/824.

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