ELSEVIER

Journal of Organometallic Chemistry 657 (2002) 262–266

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Macropolyhedral boron-containing cluster chemistry A novel triple-cluster structural motif. Isolation and characterisation of contiguous twenty-vertex $[(PPh_3)_4ClPd_4B_{16}H_{17}(PPh_3)_2]$[1]

Michael G.S. Londesborough, Colin A. Kilner, Mark Thornton-Pett, John D. Kennedy *

The Department of Chemistry of the University of Leeds, Leeds LS2 9JT, UK

Received 30 October 2001; accepted 23 April 2002

Abstract

Twenty-vertex $[(PPh_3)_4ClPd_4B_{16}H_{17}(PPh_3)]$ (**1**),[1] from the thermolysis of $[(PPh_3)_2PdB_8H_{12}]$ (**2**)[1] in refluxing toluene solution, followed by CH_2Cl_2 extraction, has a core *nido* five-vertex $\{Pd_2B_3\}$ unit that has opposing triangular faces in common with an *arachno* ten-vertex $\{Pd_2B_8\}$ unit and a *nido* eleven-vertex $\{Pd_3B_8\}$ unit. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Thermolysis; Cluster chemistry; Macropolyhedral; Fusion modes; Metallaborane; Palladium-boron cluster

Although several thirteen-vertex closed metallcarbaboranes have been known for some time [1], any truly extensive contiguous polyhedral boron-containing cluster chemistry that extends beyond the twelve-vertex barrier that is typified by the stable twelve-vertex icosahedron requires the intimate fusion of smaller clusters [2]. To develop this potentially extensive field, there is merit in the examination for: (a) new cluster fusion modes and the architectures that they engender [3,4]; (b) generation of larger contiguous clusters beyond the eighteen-vertex limit of the most readily accessible macropolyhedral skeletons of the *syn* and *anti* isomers of $B_{18}H_{22}$ [5–7], and of the *anti* and *iso* isomers of $S_2B_{16}H_{16}$ [8–10]; and (c) macropolyhedral assembly independent of these $B_{18}H_{22}$ and $S_2B_{16}H_{16}$ systems [11–19]. A problem here is that generic routes to cluster fusion are lacking. However, it is found empirically that several *arachno* nine-vertex species, specifically $[B_9H_{13}(SMe_2)]$ [20], $[SB_8H_{12}]$ [8–10], $[SB_8H_{10}(SMe_2)]$ [21], $[(CO)(PMe_3)_2HIrB_8H_{12}]$ [12] and $[(PMe_2Ph)_2PtB_8H_{12}]$ [15,16], will engender macropolyhedral species upon mild thermolysis in refluxing solvents such as toluene, benzene, cyclohexane, etc. Of these *arachno* nine-vertex species, $[(PMe_2Ph)_2PtB_8H_{12}]$ in particular gives a very interesting variety of structural types [15,16], including fourteen-vertex $[(PMe_2Ph)_2Pt_2B_{12}H_{18}]$ [15], seventeen-vertex $[(PMe_2Ph)PtB_{16}H_{18}(PMe_2Ph)]$ [22], seventeen-vertex $[(PMe_2Ph)_4Pt_3B_{14}H_{16}]$ [23] and eighteen-vertex $[(PMe_2Ph)_2Pt_2B_{16}H_{15}(C_6H_4Me)(PMe_2Ph)]$ [16]. This variety in complexity of product structure must arise from a subtle balance of mechanism. It is thence tempting to speculate that the course of this last reaction may be changed, and thence that the variety of products with new structural characteristics may be extended, by modifications of the $[(PMe_2Ph)_2PtB_8H_{12}]$ starting substrate. Such modifications may be accomplished, for example, by the use of the other elements in the platinum group, viz. palladium and nickel, and also by the use of different *exo*-cluster ligands on the metal centre. We now have preliminary results to show that this is indeed the case, and here we now report the

---

* Corresponding author

E-mail address: johnk@chem.leeds.ac.uk (J.D. Kennedy).

[1] A cursive IUPAC nomenclature for compound **1** is μ-8,9-chloro-9″,5,7,9 - tetrakis(triphenylphosphine) - *arachno*-6″,9″ - dipalladadecaborano-{5″,6″,2″: 4′,1′,5′}-*nido*-1′,2′-dipalladapentaborano-{1′,2′,3′: 8,7,3}-*nido*-7,8,9-tripalladaundecaborane, and, for compound **2**, 4,4-bis(triphenylphosphine)-*arachno*-4-palladanonaborane. This article was freely submitted for publication without royalty. By acceptance of this paper, the publisher and/or recipient acknowledges the right of the authors to retain non-exclusive, royalty-free license in and to any copyright covering this paper, along with the right to reproduce all or part of the copyrighted paper.

PII: S0022-328X(02)01552-8

structural characterisation of an interesting twenty-vertex species of formulation $[(PPh_3)_4Pd_4ClPdB_{16}H_{17}(PPh_3)_2]$ (compound **1**)[1]. This is isolated from the products of thermolysis of $[4,4\text{-}(PPh_3)_2\text{-}$*arachno*$\text{-}4\text{-}PdB_8H_{12}]$ (compound **2**)[1] in toluene solution.

Thus, initially, *cis*-$[PdCl_2(PPh_3)_2]$ (360 mg, 510 μmol) was quickly added to a stirred solution of $K[B_9H_{14}]$ (120 mg, 770 μmol) in dry MeOH (ca. 20 ml). The immediate yellow suspension was stirred at room temperature for 30 min, the yellow solid filtered off and washed with a small quantity of methanol to remove traces of excess $K[B_9H_{14}]$, and then dried to give yellow micro-crystals. These were readily identified by NMR spectroscopy,[2] and confirmed by a single-crystal X-ray diffraction analysis (Fig. 1),[3] as $[(PPh_3)_2PdB_8H_{12}]$ (compound **2**, 320 mg, 440 μmol, 86%). It is clearly of the nine-vertex *arachno*-4-metallanonaborane configuration that is well-recognised [24], for example in the platinum analogue $[(PMe_2Ph)_2PtB_8H_{12}]$ [25]. Thence, a suspension of compound **2** (300 mg, 410 μmol) in dry toluene (ca. 20 ml) was heated at reflux for 1 h, and the toluene was then removed in vacuo. The residue was dissolved in dichloromethane, with slight effervescence, and the mixture then subjected to preparative TLC in air (silica gel G, Fluka GF 254), revealing several coloured products. Purification of a predominant green component (R_F ca. 0.6, CH_2Cl_2–C_6H_{14} 4:1) by repeated TLC, followed by crystallisation by diffusion of hexane into a dichloromethane solution, gave an air-stable crystalline solid, of an apparent dichroic green–red appearance. This was characterised by a single-crystal X-ray diffraction analysis (Fig. 2)[3] as $[(PPh_3)_4ClPd_4B_{16}H_{17}(PPh_3)]$ (compound **1**, 40 mg, 20 μmol, 13.5%). Multinuclear NMR spectroscopy[2] was consistent with the crystallographically determined molecular structure, showing that the crystal used for the X-ray work was representative of the bulk sample.

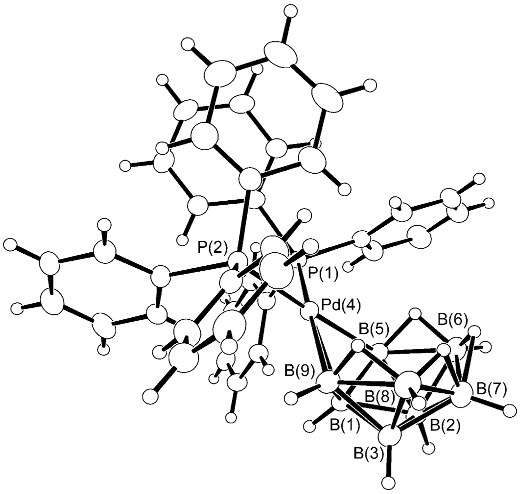


Fig. 1. Drawing of the crystallographically determined molecular structure of $[(PPh_3)_2PdB_8H_{12}]$ (compound **2**).[3] Note that, although H(6,7) and H(7,8) freely refined approximately to the bridging positions, it is probable that one atom is bridging and the other atom is in an *endo* position [43], and therefore that this structure is subject to some effective disorder in this regard. In solution, the *endo* and bridging hydrogen atoms associated with the B(6)–B(7)–B(8) notch will interchange character, giving, on time-average, an apparent mirror plane symmetry through Pd(4), B(1) and B(7) as manifested in the NMR properties.[2] Selected interatomic distances in Å are: from Pd(4) to P(1) 2.3635(6), to P(2) 2.3528(6), to B(1) 2.229(3), to B(5) 2.218(3), and to B(9) 2.230(3), with B(5)–B(6) 1.845(4), B(6)–B(7) 1.882(5), B(7)–B(8) 1.847(5) and B(8)–B(9) 1.837(4). Selected angles at Pd(4) are as follows: P(1)–P(2) 100.57(2)°, P(1)–B(5) 84.88(8)°, P(2)–B(9) 90.26(8)° and B(5)–B(9) 84.81(11)°.

The new macropolyhedral compound $[(PPh_3)_3ClPd_3B_{16}H_{17}Pd(PPh_3)]$ (compound **1**, Fig. 2) has a most interesting condensed twenty-vertex macropolyhedral cluster structure (schematics **I**). It is somewhat more condensed than the several species [15,16] from the platinum system mentioned above, and therefore of somewhat different character. The molecule contains several unusual and unique features. Although, in architectural terms, the twenty-vertex $\{Pd_4B_{16}\}$ skeletal

---

[2] Measured NMR data for $[(PPh_3)_4ClPd_4B_{16}H_{17}(PPh_3)_2]$ (compound **1**) and $[(PPh_3)_2PdB_8H_{12}]$ (compound **2**) are as follows, $CDCl_3$ at 295–300 K: compound **2**, ordered as assignment $\delta(^{11}B)$/ppm [$\delta(^{1}H)$/ppm of attached *exo*-H atom in square brackets] BH(1) +22.1 [+4.60], BH(7) +16.0 [+3.88], BH(5,9) +08.8 [+2.86], BH(6,8) −24.1 [+1.62], and BH(2,3) −28.7 [+0.72]; additionally $\delta(^{1}H)$ for H(Ph) at +7.5 to +7.0 ppm (unresolved multiplets), for H(μ-5,6;μ-8,9) at −2.54 ppm, and for H(*endo*/μ-6,7;7,8) ca. +0.4 ppm, with $\delta(^{31}P)(PPh_3)$ at +24.7 ppm; compound **1** is as yet unassigned in this preliminary work, but has tentative ^{11}B and ^{1}H resonance positions as follows, listed as $\delta(^{11}B)$/ppm [$\delta(^{1}H)$/ppm of an attached H atom (either *exo* or μ) in square brackets] +31.8 [+5.72], ca. +16.5 [+2.96], +14.7 [+0.02], ca. +14.4 (broad) [+1.88 μ?], +14.0 [+4.41], +13.1 [+4.51], ca. +11.0 (broad) [+3.00], ca. +8.0 (broad) [no apparent directly-bound H], ca. +6.50 (broad) [+1.97], ca. +4.4 [+3.49], ca. +4.0 (broad) [+2.04, +1.47 μ?], ca. +2.2 (broad) [+2.05], −13.5 [+1.59], −16.7 [+1.26], −18.1 [+0.67] and −18.3 [+0.88]; additionally $\delta(^{1}H)$(Ph) at +7.5 to +7.0 ppm (unresolved multiplets) and $\delta(^{1}H)$(μ-H) at +0.27 ppm associated with $\delta(^{11}B)$ +16.5 to +11.0 ppm, with $\delta(^{31}P)(PdPh_3)$ P(1) and P(2) both at ca. +33.8 ppm, P(6) and P(9) at +29.2, and +24.1 ppm with $^{3}J(^{31}P–^{31}P)$ ca. 15 Hz, and P(4) at ca. +9.5 ppm (broad quartet, $^{1}J(^{31}P–^{11}B)$ ca. 110 Hz).

[3] Crystal data for $[(PPh_3)_4ClPd_4B_{16}H_{17}(PPh_3)_2]$ (compound **1**), as the $CHCl_3$ sesqui-solvate $C_{91.5}H_{93.5}B_{16}Cl_{5.5}P_5Pd_4\cdot(CHCL_3)_{1.5}$: $M = 2141.55$, triclinic (deep red–green prism from C_6H_{14}–$CHCl_3$), 0.65 × 0.49 × 0.42 mm, space group $P\bar{1}$, $a = 14.98470(10)$, $b = 18.6685(2)$, $c = 1.4763(2)$ Å, $\alpha = 105.7950(4)$, $\beta = 106.8560(5)$, $\gamma = 100.6430(4)°$, $U = 5301.07(8)$ Å^3, $D_{calc} = 1.342$ Mg m^{-3}, $Z = 2$, Mo–K$_\alpha$, $\lambda = 0.71073$ Å, $\mu = 0.922$ mm^{-1}, $T = 150(2)$ K, $R_1 = 0.0498$ for 17 115 reflections with $I > 2\sigma(I)$, and $wR_2 = 0.1539$ for all 20 595 unique reflections; CCDC reference number 172802. Crystal data for $[(PPh_3)_2PdB_8H_{12}]$ (compound **2**), as the C_6H_6 hemi-solvate $C_{36}H_{42}B_8P_2Pd\cdot\frac{1}{2}C_6H_6$: $M = 768.57$, triclinic (yellow rod from C_6H_6–C_6H_{14}–$CHCl_3$), 0.48 × 0.42 × 0.1 mm, space group $P\bar{1}$, $\alpha = 11.0840(2)$, $b = 11.7122(2)$, $c = 17.0127(3)$ Å, $\alpha = 78.8610(11)$, $\beta = 87.0810(9)$, $\gamma = 63.3610(9)°$, $U = 1935.32(6)$ Å^3, $D_{calc} = 1.319$ Mg m^{-3}, $Z = 2$, Mo–K$_\alpha$, $\lambda = 0.71073$ Å, $\mu = 0.590$ mm^{-1}, $T = 150(2)$ K, $R_1 = 0.0356$ for 7159 reflections with $I > 2\sigma(I)$, and $wR_2 = 0.0969$ for all 7576 unique reflections; CCDC reference number 172803. Methods and programs were standard [44,45].

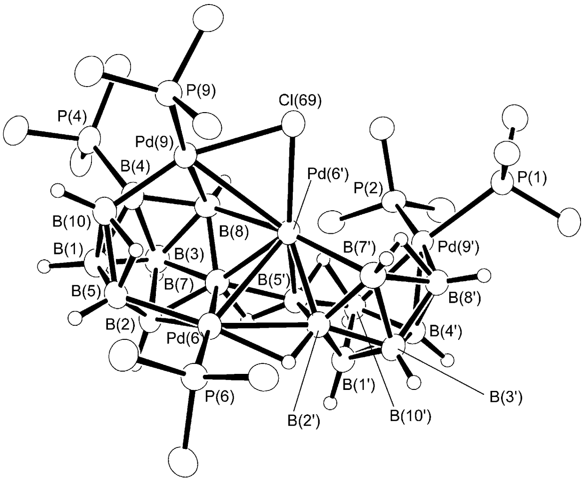
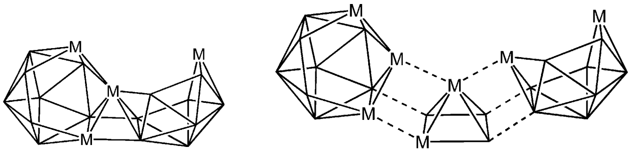
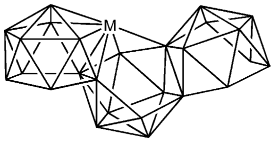


Fig. 2. Drawing of the crystallographically determined molecular structure of $[(PPh_3)_4ClPd_4B_{16}H_{17}(PPh_3)_2]$ (compound **1**),[3] with P-phenyl atoms, except the *ipso* carbon ones, omitted for clarity. Selected interatomic distances in Å are: from Pd(6) to Pd(6′) 2.9017(4), to P(6) 2.3309(11), to H(6,2′) 1.91(6), to B(2) 2.235(5), to B(2′) 2.515(4), to B(5) 2.181(5), and to B(7) 2.226(5); from Pd(6′) to Pd(9) 2.9221(4), to Cl(6,9) 2.4618(10), to H(5,1′) 2.17(6), to B(2′) 2.184(5), to B(5′) 2.070(4), to B(7) 2.211(5), to B(7′) 2.294(5), and to B(8) 2.359(5); from Pd(9) to P(9) 2.3394(10), to Cl(6,9) 2.4930(10) to B(4) 2.205(4), to B(8) 2.225(4), and to B(10) 2.175(5); and from Pd(9′) to P(1) 2.3674(11), to P(2) 2.3297(11), to B(4′) 2.228(5), to B(8′) 2.249(5), and to B(10′) 2.230(5); with B(2′)–B(5′) 1.805(6), B(5′)–B(7) 1.890(6), and B(4)–P(4) 1.946(5). Selected angles are: at Pd(6), Pd(6′)–B(5) 108.98(13)° and P(6)–H(6,2′) 88.8(19)°; at Pd(6′), B(5′)–B(7′) 84.12(17)°, Pd(9)–Pd(6) 82.030(11)°, Cl(6,9)–B(2′) 150.89(12)°, and B(7′)–B(8) 168.93(16)°; at Pd(9), P(9)–Cl(6,9) 89.39(4)°, Cl(6,9)–B(10) 161.66(14)°, and Pd(6′)–B(10) 109.00(13)°; and at Pd(9′), P(1)–P(2) 99.70(4)° and B(8′)–B(10′) 84.08(17)°; with Pd(9)–Cl(6,9)–Pd(6′) 72.27(3)°. Note the bridging hydrogen atoms at B(5′)–B(10′) and B(7′)–B(8′) on the right-hand sub-cluster, which are consistent with *arachno* ten-vertex character [35], and the bridging hydrogen atoms at B(2′)–Pd(6) and B(5′)–B(7) on the open face of the central five-vertex {Pd(6)–B(2′)B(5′)–B(7)–Pd(6′)} square pyramid, which, together with the geometry, is consistent with *nido* five-vertex character. The disposition of the bridging atoms around the open face of the left-hand eleven-vertex sub-cluster, together with the overall geometry, is consistent with *nido* eleven-vertex character.

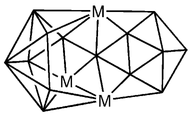
framework **IA** essentially consists of a *nido* eleven-vertex $\{Pd_3B_8\}$ skeletal unit **IB** conjoined with an *arachno* ten-vertex unit **ID**, their intimacy of conjunction is such that they are effectively conjoined by and fused to a linking *nido* five-vertex $\{Pd_2B_3\}$ unit **IC**. The overall metallaborane skeleton therefore can be described in terms of a core *nido* five-vertex $\{Pd_2B_3\}$ unit that has opposing triangular faces fused in common with an *arachno* ten-vertex $\{Pd_2B_8\}$ unit and a *nido* eleven-vertex $\{Pd_3B_8\}$ unit. The phenomenon of the intervening *nido* five-vertex unit shows an interesting intermediacy between the very condensed tetrahedral borons-only core in globular species such as $[(PPh_3)_3(PPh_2)_2Pd_3B_{20}H_{16}Pd(PPh_3)]$ [11], $[(PMe_3)_2IrB_{26}H_{24}Ir(CO)(PMe_3)_2]$ [14] and $[(C_5Me_5)_3Ir_3B_{18}H_{15}(OH)]$ [26], and the much more open type of inter-cluster linkage in species such as neutral $[C_4B_{18}H_{22}]$ and the $[B_{20}H_{18}]^{2-}$ anion [27–29], which can in principle be regarded in terms of sub-cluster units fused to a central, more open, *arachno*-type four-vertex unit. The *nido* $\{1,2\text{-}M_2B_3\}$ geometry of the five-vertex sub-cluster **IC** is long-recognised in single-cluster chemistry, as in Fehlner's $[(CO)_6Fe_2B_3H_7]$ species [30], although its incidence in a fused-cluster species is unprecedented. Because of the overall novelty of compound **1**, there is no close parallel with any known cluster species. The overall cluster structure perhaps has its closest architectural relationship in those of double-cluster $[(PMe_2Ph)_4Pt_3B_{14}H_{16}]$ (compound **3**, schematic **II**) [15,23], with its *nido* eleven-vertex $\{Pt_2B_9\}$ sub-cluster, and $[(PMe_2Ph)_2PtB_{26}H_{24}]$ (compound **4**, schematic **III**) [3,31], with its fused triple-cluster architecture. However, neither of these has a central structural feature such as this unique square-pyramidal five-vertex core. Although compound **4** does have a central *nido* cluster, this is of conventional eleven-vertex *nido* character, and is based on overlapping pentagonal pyramidal motifs, quite different from the quadrilateral pyramidal *nido* five-vertex shape, and it also exhibits the more usual edge-fusions with its conjoined clusters, rather than face-fusion (schematic **III**).



IA **IB** **IC** **ID**



II



III

The *nido* eleven-vertex $\{Pd_3B_8\}$ unit of compound **2** has some parallels in the *nido* eleven-vertex $\{Pt_3B_8\}$ sub-cluster in $[(PMe_2Ph)_4Pt_3B_{14}H_{16}]$ (compound **3**, schematic **II**), although the relative dispositions of the three metal centres differ between these two sub-clusters. As far as we are aware, isolated three-metal *nido* eleven-vertex $\{M_3B_8\}$ single-cluster compounds have not been reported, although examples of two-metal *nido* eleven-vertex $\{M_2B_9\}$ species are known [32(a),32(b)], and a *nido*-shaped eleven-vertex $\{M_2B_9\}$ feature a distinguishable in species such as in $[(PPh_3)_2Cl_2(Ph_2PC_6H_4)Rh_2SB_9H_8]$ [32c]. This last compound also exhibits a four-electron chlorine bridge between its adjacent metal atoms, similar to the {Pd(9)–Cl–Pd(6′)} bridge in compound **2** reported here. This is also very unusual in boron-containing cluster chemistry, and, as far as we are aware, these are the only two examples. This four-electron bridge is, however, related to the four-electron {M(Ph_2P)M} bridges seen in [(CO)(PPh_3)Os(PPh_2)Pt-(PPh_3)B_5H_7Ph] [33] and in the [$(PPh_3)_3(PPh_2)_2Pd_3$-$B_{20}H_{16}Pd(PPh_3)$] species mentioned above [11], and we have also recently observed other new {Pd(PPh_2)Pd}-bridging examples in our laboratories, in species tentatively identified as eleven-vertex *nido*-type [$(PPh_3)_2$-$(PPh_2)Pd_2B_9H_8(OEt)_2$] and eight-vertex *arachno*-type [$(PPh_3)_2(PPh_2)Pd_2B_6H_9$], which we hope to be able to describe fully in due course [34]. The incidence of the chlorine bridge in an ostensibly chlorine-free initial reaction merits comment. It presumably arises from subsequent halocarbon solvent interaction with an initially formed reactive macropolyhedral palladaborane, perhaps involving an inter-metal hydrogen bridge—an effervescence was observed upon treatment of the reaction product mixture with CH_2Cl_2.

In the {Pd_3B_8} unit, the grouping of the three palladium atoms into a string is also noteworthy. Such metal-atom grouping also rare in larger metallaborane cluster chemistry [24] and is reminiscent of 'composite cluster' phenomena in species such as [$(C_5Me_5)_2$-$Ir_2CSB_6H_8$] [35], in which boron atoms on one hand, and heteroatoms on the other, group together in separate domains within a single-cluster. This palladium-atom grouping, together with the {Pd_3} string in globular [$(PPh_3)_3(PPh_2)_2Pd_3B_{20}H_{16}Pd(PPh_3)$] [11] and the {$Pd_2$} units in the more open *nido*-type [$(PPh_3)_2$-$(PPh_2)Pd_2B_9H_9(OEt)_2$] and *arachno*-type [$(PPh_3)_2$-$(PPh_2)Pd_2B_6H_{12}$] species just mentioned, may indicate a tendency for palladium atoms in particular to group together, which may presage interesting future composite-cluster species.

The *arachno* ten-vertex {Pd_2B_8} sub-cluster of compound **2** (schematic **ID**) has clearer precedent, being long known for the single-cluster species [$(PMe_2Ph)_4$-$Pt_2B_8H_{10}$] [25], and more recently established also for the palladium system in the direct analogue [$(PMe_2Ph)_4Pd_2B_8H_{10}$] [36], as well as being recognised for other {M_2B_8} systems [24], such as [(Et_2NC-$S_2)_2Au_2B_8H_{10}$] [37]. Its incidence here in compound **2** may have some relevance to mechanism, as the [$(PMe_2Ph)_4Pt_2B_8H_{12}$] molecular unit is known to be formed from [$(PMe_2Ph)_2PtB_8H_{12}$] under basic conditions [24]. In general terms, however, the mechanisms of formation of these highly condensed products from the [$(PMe_2Ph)_2PtB_8H_{12}$] system [15,16] and, now, from the corresponding [$(PPh_3)_2PdB_8H_{12}$] system, remain obscure. Although there may be some significance in the retention in compound **1** of two basic *arachno*-shaped {B_8} units that mimic the {B_8} geometry in the [$(PPh_3)_2PdB_8H_{10}$] starting compound **2**, the incorporation of the two extra Pd centres in the product **2** remains unexplained.

The identification of other products from this and related systems involving further metal and ligand variation may thence offer valuable 'snapshots' of structural intermediates. In this context, we currently devise experiments with this in mind, and we hope to be able to report on some such intermediate condensation products in due course. In sum, it is clear that even relatively subtle variations of metal and ligand in these *arachno* metallaborane species, as well as less subtle ones [9,12], will yield an increased variety of new macropolyhedral skeletal architectures, and well portends much interesting mechanistic and structural development in this contemporaneously burgeoning field [2–4,38–42].

1. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 172803 and 172802 for compounds [$(PPh_3)_4ClPd_4B_{16}H_{17}(PPh_3)_2$] (**1**) and [$(PPh_3)_2PdB_8H_{12}$] (**2**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the UK EPSRC for support (grants J56929, L49505 and M83360) and for a studentship to MGSL, and Dr Jonathan Bould for stimulating discussions.

References

[1] See, for example, R.N. Grimes, in: G. Wilkinson, F.G.A. Stone, E. Abel (Eds.), Comprehensive Organometallic Chemistry I (Chapter 5.5, and references cited therein), Pergamon, Elmsford, New York, 1982, pp. 459–542.

[2] J.D. Kennedy, in: W. Siebert (Ed.), Advances in Boron Chemistry, Royal Society of Chemistry, Cambridge, 1997, pp. 451–462.

[3] J. Bould, W. Clegg, S.J. Teat, L. Barton, N.P. Rath, M. Thornton-Pett, J.D. Kennedy, Boron Chemistry at the Millennium, special edition of Inorg. Chim. Acta 289 (1999) 95.

[4] J. Bould, D.L. Ormsby, H.-J. Yao, C.-H. Hu, J. Sun, R.-S. Jin, S.L. Shea, W. Clegg, T. Jelínek, N.P. Rath, M. Thornton-Pett, R. Greatrex, P.-J. Zheng, L. Barton, B. Štíbr, J.D. Kennedy, in: M. Davidson, A.K. Hughes, T.B. Marder, K. Wade (Eds.), Contemporary Boron Chemistry, Royal Society of Chemistry, Cambridge, England, 2000, pp. 171–174.

[5] A.R. Pitochelli, M.F. Hawthorne, J. Am. Chem. Soc. 84 (1962) 3218.

[6] P.G. Simpson, W.N. Lipscomb, J. Chem. Phys. 39 (1963) 26.

[7] P.G. Simpson, K. Folting, R.D. Dobrott, W.N. Lipscomb, J. Chem. Phys. 39 (1963) 2339.

[8] T. Jelínek, J.D. Kennedy, B. Štíbr, J. Chem. Soc. Chem. Commun. (1994) 1415.

[9] P. Kaur, Approaches to macropolyhedral boron-containing cluster chemistry (Thesis), University of Leeds, 1997.

[10] P.K. Dosanjh, J. Bould, T. Jelínek, M. Thornton-Pett, J.D. Kennedy, (to be) submitted.

[11] H.-J. Yao, C.-H. Hu, J. Sun, R.-S. Jin, P.-J. Zheng, J. Bould, R. Greatrex, J.D. Kennedy, D. Ormsby, M. Thornton-Pett, Collect. Czech. Chem. Commun. 64 (1999) 927.

[12] L. Barton, J. Bould, J.D. Kennedy, N.P. Rath, J. Chem. Soc. Dalton Trans. (1996) 3145.

[13] J. Bould, W. Clegg, J.D. Kennedy, S.J. Teat, M. Thornton-Pett, J. Chem. Soc. Dalton Trans. (1997) 2005.

[14] J. Bould, J.D. Kennedy, L. Barton, N.P. Rath, J. Chem. Soc. Chem. Commun. (1997) 2405.

[15] M.A. Beckett, J.E. Crook, N.N. Greenwood, J.D. Kennedy, J. Chem. Soc. Dalton Trans. (1986) 1879.

[16] M.A. Beckett, N.N. Greenwood, J.D. Kennedy, P.A. Salter, M. Thornton-Pett, J. Chem. Soc. Chem. Commun. (1986) 556.

[17] J. Bould, W. Clegg, J.D. Kennedy, S.J. Teat, J. Chem. Soc. Dalton Trans. (1998) 2777.

[18] J. Bould, U. Doerfler, W. Clegg, S.J. Teat, M. Thornton-Pett, J.D. Kennedy, J. Chem. Soc. Chem. Commun. (2001) 1788.

[19] J. Bould, M.G.S. Londesborough, J.A.H. MacBride, D.L. Ormsby, K. Wade, C.A. Kilner, W. Clegg, S.J. Teat, M. Thornton-Pett, R. Greatrex, J.D. Kennedy, J. Organomet. Chem. (2002) this volume, X_{ref} S0022-328X(02)01551-6.

[20] J. Plešek, S. Heřmánek, B. Štíbr, F. Hanousek, Collect. Czech. Chem. Commun. 32 (1967) 1095.

[21] P. Kaur, J. Holub, N.P. Rath, J. Bould, L. Barton, B. Štíbr, J.D. Kennedy, J. Chem. Soc. Chem. Commun. (1996) 273.

[22] M.A. Beckett, J.E. Crook, N.N. Greenwood, J.D. Kennedy, W.S. McDonald, J. Chem. Soc. Chem. Commun. (1982) 552.

[23] M.A. Beckett, J.E. Crook, N.N. Greenwood, J.D. Kennedy, J. Chem. Soc. Chem. Commun. (1983) 1228.

[24] See, for example, J.D. Kennedy, Progress Inorg. Chem. 34 (1986) 211–434 (and references cited therein).

[25] S.K. Boocock, N.N. Greenwood, M.J. Hails, J.D. Kennedy, W.S. McDonald, J. Chem. Soc. Dalton Trans. (1981) 1415.

[26] S.L. Shea, T. Jelínek, B. Štíbr, M. Thornton-Pett, J.D. Kennedy, Inorg. Chem. Commun. 3 (2000) 169.

[27] Z. Janoušek, B. Štíbr, X.L.R. Fontaine, J.D. Kennedy, M. Thornton-Pett, J. Chem. Soc. Dalton Trans. (1996) 3813.

[28] R.L. Pilling, M.F. Hawthorne, E.A. Pier, J. Am. Chem. Soc. 86 (1964) 3568.

[29] C.H. Schwalbe, W.N. Lipscomb, J. Am. Chem. Soc. 91 (1969) 194.

[30] (a) K.J. Haller, E.L. Anderson, T.P. Fehlner, J. Am. Chem. Soc. 101 (1979) 4390;
(b) K.J. Haller, E.L. Anderson, T.P. Fehlner, Inorg. Chem. 20 (1981) 309.

[31] J. Bould, S.A. Barrett, L. Barton, N.P. Rath, J.D. Kennedy, Inorg. Chem. Commun. 1 (1998) 365.

[32] (a) J. Bould, J.E. Crook, J.D. Kennedy, M Thornton-Pett, Inorg. Chim. Acta 203 (1993) 193;
(b) Y.-H. Kim, P.A. Cooke, R Greatrex, J.D. Kennedy, M. Thornton-Pett, J. Organomet. Chem. 550 (1998) 341;
(c) G. Ferguson, M.C. Jennings, A.J. Lough, S. Coughlan, T.R. Spalding, J.D. Kennedy, X.L.R. Fontaine, B. Štíbr, J. Chem. Soc. Chem. Commun. (1990) 891.

[33] J. Bould, J.E. Crook, N.N. Greenwood, J.D. Kennedy, J. Chem. Soc. Dalton Trans. (1991) 185.

[34] M.G.S. Londesborough, J. Bould, P.-J. Zheng, S.J. Teat, W. Clegg, M. Thornton-Pett, J.D. Kennedy, (to be) submitted.

[35] P.A. Cooke, C. Price, M.G.S. Londsborough, J. Holub, B. Štíbr, M. Thornton-Pett, W. Clegg, S.J. Teat, J.D. Kennedy, J. Organomet. Chem. 614–615 (2000) 57.

[36] J. Bould, P.A. Cooke, U. Dörfler, J.D. Kennedy, L. Barton, N.P. Rath, M. Thornton-Pett, Inorg. Chim. Acta 285 (1999) 290.

[37] M.A. Beckett, J.E. Crook, N.N. Greenwood, J.D. Kennedy, J. Chem. Soc. Dalton Trans. (1984) 1427.

[38] O. Volkov, W. Dirk, U. Englert, P. Paetzold, Z. Anorg. Allgem. Chem. 625 (1999) 1193.

[39] N.S. Hosmane, A. Franken, G. Zhang, R.R. Srivastava, R.Y. Smith, B.F. Spielvogel, Main Group Metal Chem. 21 (1981) 319.

[40] J.A. Dopke, D.R. Powell, D.F. Gaines, Inorg. Chem. 39 (2000) 463.

[41] J. Bould, T. Jelínek, C.A. Kilner, M.G.S. Londesborough, M. Thornton-Pett, J.D. Kennedy, Abstracts Second European Symposium on Boron Chemistry, EUROBORON 2, Dinard, France, 2–6 September, 2001, Abstract no. O21.

[42] D.G. Allis, J.T. Spencer, Inorg. Chem. 40 (2001) 3373.

[43] J. Bould, R. Greatrex, J.D. Kennedy, D.L. Ormsby, M.G.S. Londesborough, K.L.F. Callaghan, M. Thornton-Pett, S.J. Teat, W. Clegg, H. Fang, N.P. Rath, L. Barton, T.R. Spalding, J. Am. Chem. Soc. 124 (2002) 7429.

[44] Z. Otwinowski, W. Minor, DENZO-SMN, processing of X-ray diffraction data collected in oscillation mode, in: C.W Carter, R.M. Sweet (Eds.), Methods Enzymology, vol. 276, Academic Press, 1997, p. 307.

[45] COLLECT, Data Collection Strategy Program, Nonius, 1999.