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# B-frame-supported bimetallics. Isoelectronic *arachno*-structured $[(PMe_2Ph)_4Pd_2B_8H_{10}]$ and *closo*-structured $[(PMe_3)_4(CO)_2Ir_2B_8H_8]$

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## Abstract

Reaction of $[IrCl(CO)(PMe_3)_2]$ with $[NEt_4][$*nido*-$B_9H_{12}]$ gives the ten-vertex eight-boron cluster species $[(PMe_3)_4(CO)_2Ir_2B_8H_8]$. This formally has a *closo* cluster electron count compatible with its *closo* structure. By contrast, ten-vertex eight-boron $[(PMe_2Ph)_4Pd_2B_8H_{10}]$, isolated from $[4\text{-}(NH_2Ph)$-*arachno*-$B_9H_{13}]$ and $[PdCl_2(PMe_2Ph)_2]$, has a *closo* electron count but an *arachno* structure. The origins of this apparent anomaly are briefly addressed and enunciated. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Crystal structures; Palladium complexes; Iridium complexes; Borane complexes

## 1. Introduction

In 1971 it was recognised that most of the then known polyhedral boron-containing cluster structures could be systematically described in terms of (a) closed deltahedral geometries, (b) such closed deltahedral geometries with one vertex missing, and (c) such closed geometries with two vertices missing [1,2]. These geometries are generally described as *closo*, *nido* and *arachno* respectively. It was then rapidly realised that, if the cluster bonding electrons are counted up according to simple empirical rules, then the *closo*, *nido* and *arachno* $n$-vertex structures are respectively associated with $2n + 2$, $2n + 4$ and $2n + 6$ cluster bonding electrons [3,4]. This useful combination of observations is now well recognized, and is commonly known as 'Wade's rules'. There is currently a developing interest in exceptions and apparent exceptions to these rules [5–12]. One aspect of this interest focuses on metallaborane and metallaborane cluster structures that also incorporate late transition-element square-planar centres [7–9]. Here some interest has involved the phenomenon of cluster structures that have similar symmetries, but that have differing formal electron counts [13–19]. There is also interest in the converse phenomenon, i.e. formally isoelectronic structures that exhibit quite different geometries. Frequently, structures are exhibited that are more open than the formal 'Wade's rules' electron count may imply. To assess this type of phenomenon, it is useful to have pairs of comparison species [20]. In this paper we report the isolation and structural characterisation of one such pair, consisting of ten-vertex *closo*-structured $[(PMe_3)_4(CO)_2Ir_2B_8H_8]$ (**1**), and ten-vertex *arachno*-structured $[(PMe_2Ph)_4Pd_2B_8H_{10}]$ (**2**), of which each has a formal *closo* ten-vertex electron count.

## 2. Experimental

### 2.1. General

Reactions were carried out in dry solvent (thf) under dry nitrogen, but subsequent manipulatory and separatory procedures were carried out in air. $[4\text{-}(NH_2Ph)$-*arachno*-$B_9H_{13}]$ [21], $[PdCl_2(PMe_2Ph)_2]$ [22], $[NEt_4][$*nido*-$B_9H_{12}]$ [23] and $[Ir(CO)Cl(PMe_3)_2]$ [24] were prepared as described elsewhere. Preparative thin-layer chromatography (TLC) was carried out using 1 mm layers of silica gel G (Fluka, type GF254) made from water slurries on glass plates of dimensions 20 × 20 $cm^2$, followed by drying in air at 80°C.

### 2.2. Nuclear magnetic resonance spectroscopy

NMR spectroscopy was performed at ca. 5.9 and 9.4 T (fields corresponding to 250 and 400 MHz $^1H$ NMR fre-

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quencies respectively) using commercially available instrumentation and using techniques and procedures as described and enunciated elsewhere [25–27]. Chemical shifts $\delta$ are given in ppm relative to $\Xi = 100$ MHz for $\delta(^1\text{H})$ ($\pm$0.05 ppm) (nominally TMS), $\Xi = 32.083972$ MHz for $\delta(^{11}\text{B})$ ($\pm$0.5 ppm) (nominally $[\text{F}_3\text{BOEt}_2]$ in $\text{CDCl}_3$) [28], and $\Xi = 40.480730$ MHz for $\delta\,(^{31}\text{P})$ ($\pm$0.5 ppm) (nominally 85% $\text{H}_3\text{PO}_4$). $\Xi$ is as defined by McFarlane [29].

### 2.3. *Preparation of $[(\text{PMe}_3)_4(\text{CO})_2\text{Ir}_2\text{B}_8\text{H}_8]$ (1)*

The preparative procedure was essentially that described in the literature for the synthesis of *arachno*-$[(\text{CO})\text{H}(\text{PMe}_3)_2\text{IrB}_8\text{H}_{12}]$ [28], using $[\text{IrCl}(\text{CO})(\text{PMe}_3)_2]$ (350 mg, 860 µmol) and $[\text{NEt}_4]$[*nido*-$\text{B}_9\text{H}_{12}$] (0.25 g, 1000 µmol) dissolved in $\text{CH}_2\text{Cl}_2$ (25 ml), with the exception that, before separation of the products using thin-layer chromatography (TLC), the reaction mixture was washed through silica gel with $\text{CH}_2\text{Cl}_2$ (200 ml), leaving a trace of yellow–red material on the silica gel which was then removed by extraction with MeCN. The MeCN extract was applied to a TLC plate and developed using MeCN/$\text{CH}_2\text{Cl}_2$ (20:80) as the mobile phase, giving a red–yellow band ($R_\text{F} = 0.25$) identified as $[2,2,6,6\text{-}(\text{PMe}_3)_4\text{-}2,6\text{-}(\text{CO})_2$-*closo*-$2,6\text{-Ir}_2\text{B}_8\text{H}_8]$ (**1**) (3 mg, 0.4% yield). Crystals suitable for X-ray diffraction analysis were obtained by hexane diffusion into a solution of the compound in $\text{CH}_2\text{Cl}_2$. IR data (3 M teflon IR card): $\nu$(CO) 1950 and 1932 $\text{cm}^{-1}$, $\nu$(BH) 2465 $\text{cm}^{-1}$. Mass spectrum (70 eV EI): high-mass limit *m/z* 841 corresponding to $^{12}\text{C}_{14}\,^{1}\text{H}_{43}\,^{31}\text{P}_4\,^{16}\text{O}_2\,^{11}\text{B}_8\,^{193}\text{Ir}_2$ [$M^+$−H peak]. NMR data ($\text{CDCl}_3$, 294–300 K), ordered as $\delta(^{11}\text{B})$ [$\delta(^1\text{H})$ in square brackets], are as follows: +32.7 [+6.42, d, splitting 22.7 Hz, probably from $^3J(^{31}\text{P}–^1\text{H})$], −1.3 [+0.64], −3.4 [+2.97], −32.4 [−2.75, d, splitting 31.2 Hz, probably from $^3J(^1\text{P}–^1\text{H})$]; additionally, $\delta(^1\text{H})(\text{PMe}_3)$ +1.92 and +1.69, both d, both with $^2J(^{31}\text{P}–^1\text{H}) = 31$ Hz; $\delta(^{31}\text{P})$ −31.5 and −52.3, any coupling $^2J(^{31}\text{P}–^{31}\text{P})$ not resolved (< ca. 3 Hz).

### 2.4. *Preparation of $[(\text{PMe}_2\text{Ph})_4\text{Pd}_2\text{B}_8\text{H}_{10}]$ (2)*

A sample of $[4\text{-}(\text{NH}_2\text{Ph})$-*arachno*-$\text{B}_9\text{H}_{13}]$ (40 mg, 200 µmol) was dissolved in thf (10 ml), and then NaH (60% active, 17 mg, 410 µmol) was added at room temperature. The solution was stirred for 20 min at room temperature, and then $[\text{PdCl}_2(\text{PMe}_2\text{Ph})_2]$ (91 mg, 200 µmol) was added. After stirring for 4 h the more volatile components were removed, the solid residue redissolved in $\text{CH}_2\text{Cl}_2$ (ca. 10 ml) and the products separated and purified by repeated preparative TLC. Development with $\text{CH}_2\text{Cl}_2$ gave $[6,6,9,9\text{-}(\text{PMe}_2\text{Ph})_4$-*arachno*-$6,9\text{-Pd}_2\text{B}_8\text{H}_{10}]$ (**2**) (67 mg, 39%, $R_\text{F} = 0.4$) as a yellow TLC band, which was removed by extraction with $\text{CH}_2\text{Cl}_2$, and recrystallised from $\text{CH}_2\text{Cl}_2$/*n*-hexane. NMR data ($\text{CDCl}_3$, 294–300 K), ordered as assignment $\delta(^{11}\text{B})$ [$\delta(^1\text{H})$ in square brackets], are as follows: BH(2,4) +35.3 [+5.53], B(5,7,8,10) +11.0 [+3.26], B(1,3) −12.8 [+1.77]; additionally $\delta(^1\text{H})(\mu\text{-H})$ −0.63 (2H), $\delta(^1\text{H})(\text{PMe}_2)$ +1.43 with $^2J(^{31}\text{P}–^1\text{H}) =$ 31 Hz, $\delta(^1\text{H})$(PPh) 7.28–7.18; $\delta(^{31}\text{P})$ −12.1.

### 2.5. *Single-crystal X-ray diffraction analysis*

Crystal data and refinement parameters for both structures are listed in Table 3. Orange irregular crystals of $[(\text{PMe}_3)_4(\text{CO})_2\text{Ir}_2\text{B}_8\text{H}_8]$ (**1**) and pale yellow rectangular prisms of $[(\text{PMe}_2\text{Ph})_4\text{Pd}_2\text{B}_8\text{H}_{10}]$ (**2**) that were suitable for the single-crystal X-ray work were both grown from chloroform/hexane. Crystallographic measurements for compound **1** were carried out at 218 K using a Siemens SMART CCD area-detector diffractometer with narrow $\omega$-rotation frames, and for compound **2** at 160 K using a Stoe STADI-4 four-circle diffractometer operating in the $\omega$–$\theta$ scan mode. In both cases, graphite-monochromated Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å) was used. An absorption correction was applied to both data sets after correction for Lorentz and polarisation effects, and was empirical (SADABS) [31] for compound **1**, and semi-empirical (based on *psi*-scans) for compound **2**.

Both structures were solved by heavy-atom methods SHELXS-86 [32] and were refined by full-matrix least-squares (against all the unique $F^2$ data) using SHELXL-93 [33] (Programs part of the SHELXTL-PLUS (5.03) program suite [34] for compound **1**). In both cases, half a molecule of the complex was located in the asymmetric unit. For compound **2**, the half molecule was near a $C_2$ axis running along the *b* axis at $x = 0$ and $z = 0.25$, passing through the midpoint of the plane defined by atoms B(5), B(5′), B(7) and B(7′), and the midpoint of the B(1)–B(3) vector, and for compound **1** it was near a two-fold axis along the *b* axis at $x = 0$, $z = 0.25$. Refinement was similar for both structures. All non-hydrogen atoms were refined with anisotropic displacement parameters. Phenyl rings were restrained to be flat and of overall $C_{2v}$ symmetry. All organophosphine hydrogen atoms were constrained to idealized positions with a riding model and were assigned isotropic displacement parameters. Cluster hydrogen atoms were located on Fourier-difference syntheses and were refined freely.

## 3. Results and discussion

The first compound that is the subject of this report, $[2,2,6,6\text{-}(\text{PMe}_3)_4\text{-}2,6\text{-}(\text{CO})_2$-*closo*-$2,6\text{-Ir}_2\text{B}_8\text{H}_8]$ (**1**), was obtained in a very small yield (0.4%) as a by-product from the reaction of the [*nido*-$\text{B}_9\text{H}_{12}]^-$ anion with $[\text{Ir}(\text{CO})\text{Cl}(\text{PMe}_3)_2]$ that has previously been described [30] to give *arachno*-$[(\text{CO})\text{H}(\text{PMe}_3)_2\text{IrB}_8\text{H}_{12}]$. The formulation of **1** readily follows from the results of single-crystal X-ray diffraction analysis (Fig. 1, Tables 1 and 3). These results reveal a classical *closo* ten-vertex bicapped square antiprismatic cluster structure [1,2], with the iridium atoms of the two $\{\text{Ir}(\text{CO})(\text{PMe}_3)_2\}$ centres in adjacent positions, one in each of the two different tropical belts (schematic **IA**). The

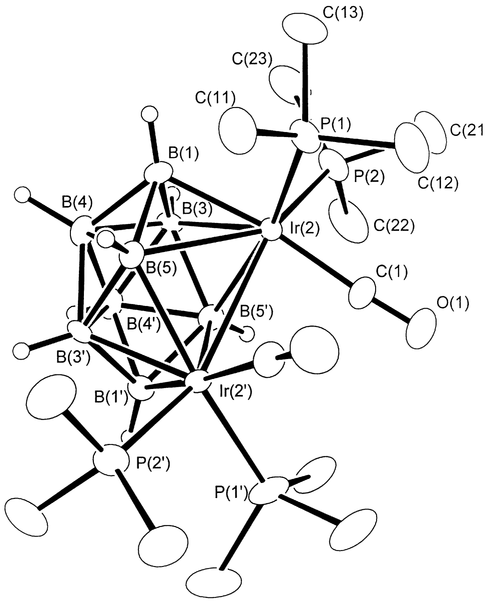


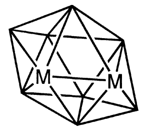
Fig. 1. ORTEP-type [35] drawing of the crystallographically determined molecular structure of $[(PMe_3)_4(CO)_2Ir_2B_8H_{10}]$ (**1**). The atomic numbering scheme shows the crystallographic two-fold symmetry of **1**. In the formal IUPAC numbering system (Table 1), Ir(2′), B(1′), B(3′), B(4′) and B(5′) become Ir(6), B(10), B(9), B(8) and B(7) respectively.

Table 1
Selected interatomic distances (pm) and angles (°) for $[2,2,6,6\text{-}(PMe_3)_4\text{-}2,6\text{-}(CO)_2\text{-}\mathit{closo}\text{-}2,6\text{-}Ir_2B_8H_8]$ (**1**)[a]

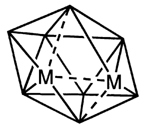
| | | | |
|---|---|---|---|
| Ir(2)–C(1) | 1.893(6) | Ir(2)–P(1) | 2.331(2) |
| Ir(2)–P(2) | 2.283(2) | Ir(2)–Ir(6) | 2.9408(4) |
| Ir(2)–B(1) | 2.144(6) | Ir(2)–B(5) | 2.578(6) |
| Ir(2)–B(3) | 2.304(7) | Ir(2)–B(7) | 2.331(6) |
| B(1)–B(3) | 1.731(9) | B(3)–B(4) | 1.798(10) |
| B(1)–B(4) | 1.692(9) | B(3)–B(7) | 1.840(9) |
| B(1)–B(5) | 1.770(9) | B(3)–B(8) | 1.787(9) |
| B(4)–B(8) | 1.773(14) | B(4)–B(5) | 1.803(9) |
| O(1)–C(1) | 1.146(6) | | |
| | | | |
| P(1)–Ir(2)–P(2) | 94.54(6) | C(1)–Ir(2)–P(1) | 95.6(2) |
| C(1)–Ir(2)–P(2) | 87.8(2) | C(1)–Ir(2)–B(1) | 168.4(3) |
| P(1)–Ir(2)–B(5) | 89.67(14) | P(2)–Ir(2)–B(3) | 84.9(2) |
| B(3)–Ir(2)–B(5) | 65.9(2) | B(4)–B(3)–Ir(2) | 103.9(4) |
| B(3)–B(4)–B(5) | 95.5(4) | B(4)–B(5)–Ir(2) | 93.9(3) |

[a] Estimated standard deviations are given in parentheses.

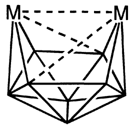
NMR properties were entirely consistent with the crystallographically determined molecular structure, indicating that the bulk material was represented by the crystal selected. The cluster structure of compound **1** is in accord with the Williams–Wade structure-geometry – electron-counting ‘Wade’s rules’ paradigm [1–4]. The two formally ‘octahedral’ iridium(III) units each contribute three electrons and three orbitals to the cluster bonding scheme, and each of the eight {BH} vertices two electrons and three orbitals. This generates a 22-electron count and thence demonstrates a clear classical $(2n+2)$-cluster-electron *closo*-$[B_{10}H_{10}]^{2-}$ analogy.



IA

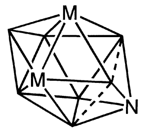


IB

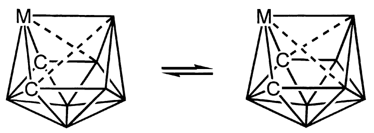


IC

Within the context of this *closo* structure, the detail of compound **1** does however indicate interesting features. Thus, within each tropical belt, the iridium–boron distance of ca. 260 pm that flanks the iridium atom in the other tropical belt is at the long end of iridium-to-boron distances typical for polyhedral iridaboranes [36], and the inter-iridium distance is also long at nearly 300 pm (hatched lines in schematic structure **IB**). Each of these two iridium–boron stretches is suggestive of ten-vertex ‘*isonido*’ stretching [10–12,37]. In **1**, the two iridium centres generate two such stretchings. This phenomenon, coupled with the long inter-iridium distance, demonstrates an incipient distortion towards ten-vertex *nido* character (schematic **IC**). There is a closely related double stretching in formally *closo* ten-vertex $[(C_5Me_5)_2Rh_2B_7H_7NEt]$ (schematic cluster structure **ID**) [38]. These stretchings are also similar to those involved in the initial stages of the double diamond-square-diamond process associated with the inter-enantiomeric fluxionalites of classically *closo* ten-vertex metalladicarbaboranes (schematic structures **IE** and **IF**) [39,40]. However, in spite of these deviations, the compound is reasonably in the classical *closo* ten-vertex category, both from the structural [1,2] and the electron-counting [3,4] points of view.



ID



IE IF

This, however, is not the case with the second compound, formulated as $[6,6,9,9\text{-}(PMe_2Ph)_4\text{-}\mathit{arachno}\text{-}6,9\text{-}Pd_2B_8H_{10}]$ (**2**), which was obtained in moderately good yield (39%) from the reaction of $[4\text{-}(NH_2Ph)\text{-}\mathit{arachno}\text{-}B_9H_{13}]$ with NaH

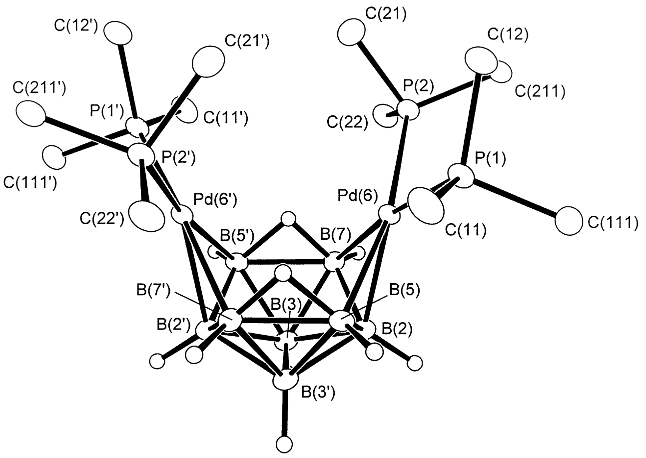


Fig. 2. ORTEP-type [35] drawing of the crystallographically determined molecular structure of $[(PMe_2Ph)_4Pd_2B_8H_{10}]$ (**2**). Hydrogen atoms have been assigned a small arbitrary radius for clarity. The atomic numbering scheme shows the crystallographic two-fold symmetry possessed by compound **2**. In the formal IUPAC numbering system (Table 2), Pd(6′), B(3′), B(2′), B(5′) and B(7′) become Pd(9), B(1), B(4), B(8) and B(10) respectively.

Table 3
Crystal data, together with data collection and refinement parameters, for the crystallographically determined structures of **1** and **2**

| | **1** | **2** |
|---|---|---|
| Formula | $C_{16}H_{46}B_8Cl_6Ir_2O_2P_4$ | $C_{32}H_{54}B_8P_4Pd_2$ |
| Temperature (K) | 218(2) | 160 |
| *M* | 1077.99 | 861.91 |
| Crystal dimensions | 0.30 × 0.15 × 0.10 | 0.56 × 0.27 × 0.11 |
| Crystal system | orthorhombic | monoclinic |
| Space group | *Pbcn* (No. 60) | *C2/c* (No. 15) |
| *a* (Å) | 12.7926(1) | 13.7909(9) |
| *b* (Å) | 15.0723(1) | 15.1212(8) |
| *c* (Å) | 19.4712(2) | 19.0736(11) |
| $\beta$ (°) | – | 92.672(5) |
| *U* (Å$^3$) | 3754.32(5) | 3973.2(4) |
| *Z* | 4 | 4 |
| *F* (000) | 2056 | 1752 |
| $D_c$ (mg m$^{-3}$) | 1.907 | 1.441 |
| $\mu$ (mm$^{-1}$) | 7.697 | 1.089 |
| Data collection range (°) | 2.09–28.99 | 2.0–25.0 |
| Decay (%) | 0 | 3.6 |
| Measured reflections | 32011 | 3519 |
| Unique data | 4777 | 3497 |
| Observed reflections $[I > 2\sigma(I)]$ | 4775 | 2959 |
| No. of independent parameters | 188 | 232 |
| $R_{int}$ | 0.0920 | 0.0422 |
| $T_{max}$, $T_{min}$ | 0.90, 0.46 | 0.394, 0.337 |
| $\omega R_2$ (all data) | 0.1016 | 0.0824 |
| $wR_2$ (observed data) | 0.0901 | 0.0577 |
| $R_1$ (all data) | 0.0776 | 0.0443 |
| $R_1$ (observed data) | 0.0388 | 0.0291 |
| Goodness of fit, *S* | 1.003 | 1.132 |
| Weighting parameters | 0.050 | 0.0218, 12.3937 |
| Max. residual electron density (e Å$^{-3}$) | +3.173(close to Ir2) | +0.447 |
| Min. residual electron density (e Å$^{-3}$) | −3.199 (close to Ir2) | −0.483 |

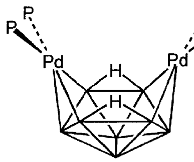
followed by $[PdCl_2(PMe_2Ph)_2]$. This reaction was investigated as part of a program of exploratory investigation into the reactions of amine-substituted boranes with metallic reagents, in which either nitrogen incorporation in the cluster to generate azametallaboranes, or loss of the nitrogen-substituted boron vertex to generate cluster compounds with lower boron-atom counts, may be expected [38,41–43]. This reaction is clearly in the latter category. As with the diiridium compound **1**, the constitution of the dipalladium compound **2** was confirmed by single-crystal X-ray work (Fig. 2, Tables 2 and 3). The NMR properties are entirely consistent with the crystallographically determined molecular structure, indicating that the bulk material was represented by the crystal selected. The NMR data also exhibit clear similarities with the previously reported diplatinum and palladium–platinum mixed-metal analogues [44,45].

Compound **2** is clearly not of *closo* geometrical aspect. It has an open classical ten-vertex *arachno* boat shape (schematic **IIA**), as typified by the *arachno*-$[B_{10}H_{14}]^{2-}$ anion itself (schematic **IIB**), and has two bridging hydrogen atoms in the 5,10 and 7,8 ‘gunwale’ positions, typical for *arachno* ten-vertex species. Further, its cluster $^{11}B$ and $^1H$ NMR properties show clear parallels with the *arachno*-$[B_{10}H_{14}]^{2-}$ anion [12,44,45]. However, this *arachno* structure, together with the other *arachno* ten-vertex characteristics, apparently belies its cluster electron count. Eight cluster {BH} units each contribute two electrons to the cluster bonding scheme, two bridging hydrogen atoms one electron each, and each $\{Pd(PMe_2Ph)_2\}$ unit two electrons, generating a 22-electron count. This would correspond to a $(2n + 2)$-electron *closo* total for a ten-vertex cluster.

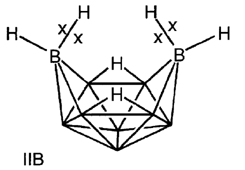
Table 2
Selected interatomic distances (pm) and angles (°) for [6,6,9,9-$(PMe_2Ph)_4$-*arachno*-6,9-$Pd_2B_8H_{10}$] (**2**)[a]

| | | | |
|---|---|---|---|
| Pd(6)–P(1) | 2.3379(9) | | 2.3411(9) |
| Pd(6)–B(2) | 2.251(4) | Pd(6)–B(5) | 2.251(4) |
| Pd(6)–B(7) | 2.245(4) | | |
| B(1)–B(2) | 1.768(6) | B(2)–B(3) | 1.769(6) |
| B(1)–B(3) | 1.739(8) | B(2)–B(5) | 1.762(5) |
| B(1)–B(5) | 1.792(5) | B(2)–B(7) | 1.773(5) |
| B(3)–B(4) | 1.768(6) | B(3)–B(8) | 1.792(5) |
| B(3)–B(7) | 1.786(6) | B(7)–B(8) | 1.875(6) |
| B(5)–B(10) | 1.875(6) | | |
| P(1)–Pd(6)–P(2) | 98.43(3) | | |
| P(1)–Pd(6)–B(2) | 124.93(10) | P(2)–Pd(6)–B(2) | 132.45(10) |
| P(1)–Pd(6)–B(5) | 88.71(10) | P(2)–Pd(6)–B(5) | 167.88(10) |
| P(1)–Pd(6)–B(7) | 171.36(10) | P(2)–Pd(6)–B(7) | 89.74(10) |
| B(2)–Pd(6)–B(7) | 46.44(14) | B(2)–Pd(6)–B(5) | 46.09(14) |
| B(5)–Pd(6)–B(7) | 83.74(14) | | |

[a] Estimated standard deviations are given in parentheses.



IIA



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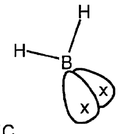
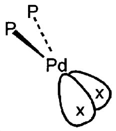


IIC

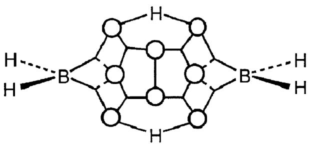


IID

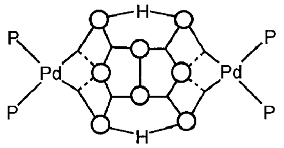
This *arachno*-structure–*closo*-count anomaly arises as follows. For the classically *arachno* $[B_{10}H_{14}]^{2-}$ anion, a formal anionic $\{BH_2\}^-$ unit (schematic **IIC**) contributes two electrons and two orbitals to the ten-boron cluster bonding proper. Application of Wade's rules [3,4] requires that the electron pairs in each of the two *endo* B–H bonds (xx in schematic **IIB**) be *counted* in the cluster-electron count. In the dipalladium compound **2**, the neutral square-planar $\{Pd(PMe_2Ph)_2\}$ palladium(II) unit (schematic **IID**) has a two-orbital two-electron contribution to the cluster bonding, analogous to that of a $\{BH_2\}^-$ unit. However, it has no electron pair in the *endo* position for electron *counting*, even though the basic *bonding* within the cluster (e.g. schematics **IIE** and **IIF**) will be the same in each case. This type of phenomenon will be quite general for square-planar 16-electron transition-element centres, and will lead to cluster electron-counts that are two fewer than the classical Wadian for each such centre in the cluster [8,9,12,46]. In **2**, there are two such centres, and so the electron count is four less than that otherwise expected for the ten-vertex *arachno* cluster shape.

Although the reasons for this apparent anomaly are long recognised [46–51], a comparison of this pair of compounds nicely illustrates its origins, which can still lead to confusion (a) when clusters may, for example, be categorically described as *closo* purely on the basis of perceived electron count [54], even though the observed geometry is patently much more open [49,50], as with the *arachno*-structured compound **2** in this present work, and (b) when attempts are unnecessarily made to locate extra electron pairs to redress the presumed electron deficiency.

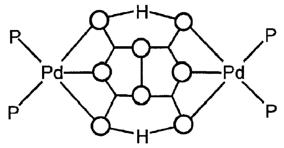
Some attempts to find 'extra' electrons have involved the postulation of interactions between the metal centre and hydrogen atoms bound to other groups when these are adjacent in crystal structures [5,6,52,53]. However, such positionings can generally derive from efficient packing [8,9,12,55], and it is uncertain whether any interaction is otherwise thermodynamically significant. Bonding comparisons as in **IIE** and **IIF**, and the known independent stability of square-planar transition-element centres, mitigate any need generally to invoke such processes to find extra electron pairs. Alternatively, a cluster bonding involvement of the electron-pair that is in the otherwise non-bonding *pd*-hybrid of the formal square-planar system has sometimes been invoked (schematic structure **IIG**) [30,44,45,56]. This could be regarded, depending on semantics, as either metal-to-cluster back-donation or as a contribution from a higher metal valence state. Comparison of representations **IIE, IIF** and **IIG** show that again it is not generally essential to invoke this in terms of the basic inter-boron bonding topology electronics of the cluster, or of its basic *arachno* character. Nevertheless, molecular orbital calculations suggest that it may have some validity in some species [57], and here the flexibility of transition-element fragments to be isolobal with more than one main-group element fragment should be recognised [58]



IIE



IIF



IIG

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## 4. Supplementary material

Atomic coordinates, displacement parameters, interatomic distances and angles between interatomic vectors for **1** and **2** are deposited with the Cambridge Crystallographic Data Centre (CCDC), deposition number 102286 for **1** and 102287 for **2**. Any request to the CCDC for this material should quote the full literature citation.

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