MACROPOLYHEDRAL BORON-CONTAINING CLUSTER CHEMISTRY. A METALLATHIABORANE FROM $S_2B_{17}H_{17}$: ISOLATION AND CHARACTERISATION OF $[(PMe_2Ph)_2PtS_2B_{16}H_{16}]$; A *neo-arachno* TEN-VERTEX CLUSTER SHAPE, AND THE CONSTITUTION OF THE $[$*arachno*-$B_{10}H_{15}]^-$ ANION+

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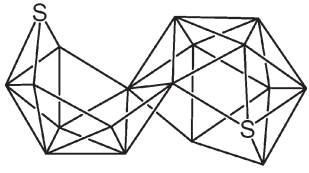
Received March 22, 2005
Accepted April 14, 2005

The deprotonation of $S_2B_{17}H_{17}$ with sodium hydride and subsequent reaction with $[PtCl_2(PMe_2Ph)_2]$ gives the new macropolyhedral metallathiaborane $[(PMe_2Ph)_2PtS_2B_{16}H_{16}]$, of which the cluster consists of a conventional eleven-vertex *nido* $\{SB_{10}\}$ unit, fused, with two boron atoms in common, with a $\{PtSB_8\}$ unit of unique ten-vertex *neo-arachno* constitution and geometry. The latter geometry suggests a configuration for the previously structurally uncharacterised $[B_{10}H_{15}]^-$ anion; starting from this configuration, DFT calculations of structure and thence of boron nuclear shieldings, which are found very closely to mimic those found experimentally, thence support a fluxional structure for $[B_{10}H_{15}]^-$ with three {BHB(bridging)} and two {BH(*endo*)} hydrogen atoms around a six-membered open face.

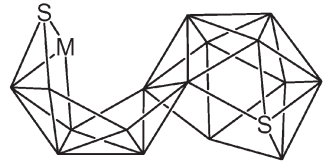
Keywords: Macropolyhedral; *neo-arachno* ten-vertex cluster; X-ray diffraction; Crystal structure; Platinum-sulfur-polyboron cluster; Sulfur-platinum-polyboron cluster; Metallaboranes; Boranes; Metallathiaborane; Thiametallaboranes; Borane anions; DFT calculations.

+ A IUPAC nomenclature for the title compound as illustrated in Fig. 1 would be 10,10-bis(dimethylphosphine)-*nido*-9′-thiaundecaborano-⟨7′,8′:5,6⟩-*neo-arachno*-9-thia-10-platinadecaborane. The compound is chiral: the other enantiomer would be named 8,8-bis(dimethylphosphine)-*nido*-11′-thiaundecaborano-⟨7′,8′:6,7⟩-*neo-arachno*-9-thia-8-platinadecaborane

Known macropolyhedral thiaboranes are the six neutral species [*n*-$S_2B_{16}H_{16}$], [*iso*-$S_2B_{16}H_{16}$], [*iso*-$S_2B_{16}H_{14}(PPh_3)$], [$S_2B_{17}H_{17}$], [$S_2B_{17}H_{17}(SMe_2)$] and [$S_2B_{18}H_{20}$] (lit.[1–6]), and the six monoanions [$S_2B_{16}H_{15}]^-$, [$SB_{17}H_{19}]^-$, [$S_2B_{17}H_{16}]^-$, [$S_2B_{17}H_{18}]^-$, [$S_2B_{18}H_{19}]^-$ and [*iso*-$S_2B_{18}H_{19}]^-$ (lit.[4–9]). It is apparent, from the limited chemistry of these macropolyhedral thiaborane skeletal systems that is so far known, that they are architecturally very flexible[1–10]. In the only one of these species so far investigated for macropolyhedral metallathiaborane creation, specifically the neutral [*n*-$S_2B_{16}H_{16}$] species, it is apparent that the capacity for cluster flexibility and rearrangement is carried through and often enhanced in reactions leading to observed metallathiaborane products[3,4,10–12]. In view of the macropolyhedral metallathiaborane structural novelty thus observed, it is of interest to examine reactions of the other macropolyhedral thiaborane species with metal centres, and in this context here we report preliminary results on metallathiaborane formation from the reaction between neutral [$S_2B_{17}H_{17}$] (compound **1**, schematic cluster structure **I**) and [$PtCl_2(PMe_2Ph)_2$].



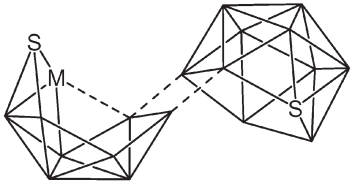
I



II

Thus, the deprotonation of [$S_2B_{17}H_{17}$] **1** (lit.[8]) (100 mg, 380 μmol) with NaH (9.1 mg, 380 μmol) in THF (20 ml) at –78 °C (solid CO_2/Me_2CO bath), followed by reaction with [$PtCl_2(PMe_2Ph)_2$] (205 mg, 380 μmol) at room temperature for twelve hours, yielded a mixture of coloured products. Separation by preparative TLC (silica gel G (Fluka, type GF_{254}); CH_2Cl_2/*n*-C_6H_{14} 80:20) revealed four principal coloured components, albeit only in low yield. After purification by repetitive preparative TLC, the first of these components was isolated and identified as yellow crystalline air-stable [$(PMe_2Ph)_2PtS_2B_{16}H_{16}$] (compound **2**; 9 mg, 12 μmol, 3.3%; R_F 0.81), a formulation established by single-crystal X-ray diffraction analysis[13] (Fig. 1) and multinuclear NMR spectroscopy[14]. Preliminary studies on the second component (orange, R_F 0.75) and the third component (yellow, R_F 0.67), also utilising NMR spectroscopy, indicated that these were also macropolyhedral metallathiaborane products. We hope to purify and unequivocally to characterise these in due course after attempts to optimise yields. The fourth

component (red, R_F ca. 0.6) was identified as a salt of the $[S_2B_{17}H_{18}]^-$ anion[8] by NMR spectroscopy. We here present a preliminary report on the structure of compound **2** because it has some interesting features and implications.



III A III B

The molecular structure of compound **2** (Fig. 1) is seen to be based on a nineteen-vertex $\{PtS_2B_{16}\}$ framework (schematic cluster structures **II** and **III**). Obviously the starting $\{S_2B_{17}\}$ cluster skeleton has lost a boron vertex during the course of the reaction; loss of boron vertices is not without prece-

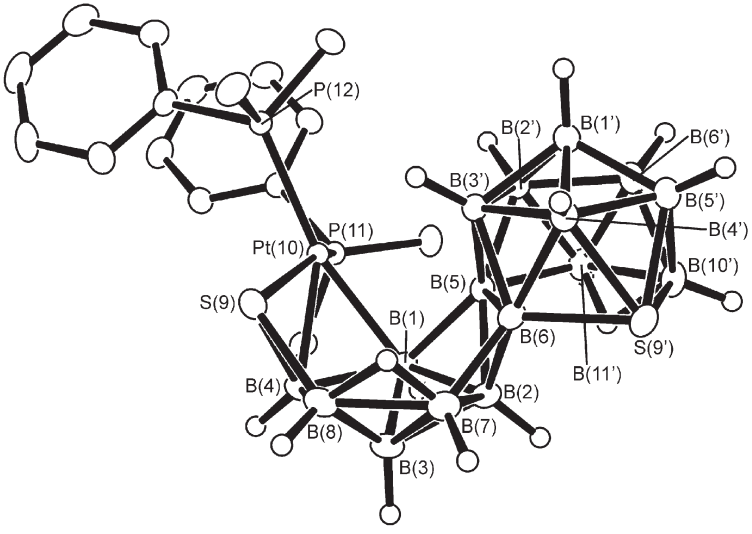
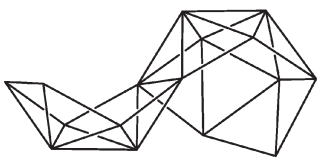


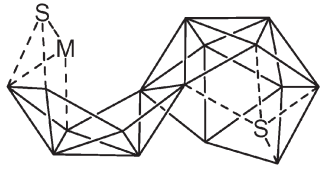
FIG. 1

ORTEP-3 (lit.[40]) plot of the molecular structure of $[(PMe_2Ph)_2PtS_2B_{16}H_{16}]$ (**2**), as determined crystallographically[13]; organyl hydrogen atoms are omitted for clarity. Selected interatomic distances (in Å) are as follows: from Pt(10) to P(11) 2.2633(6), to P(12) 2.3046(6), to S(9) 2.3500(6), to B(1) 2.243(3), to B(4) 2.279(3) and to B(5) non-bonding at 2.726(4); from S(9) to B(4) 1.940(3) and to B(8) 1.918(3); from S(9′) to B(6) 1.992(3), to B(4′) 2.018(3), to B(5′) 1.991(3′) and to B(10′) 1.973(3); B(5)–B(6) is 1.772(4). Angle B(5)–B(1)–Pt(10) is 84.17(12)° and angle P(11)–Pt(10)–P(12) is 98.05(2)°. Angles P(11)–Pt(10)–S(9), P(12)–Pt(10)–B(1) and P(12)–Pt(10)–B(4) are 153.27(4), 164.12(4) and 139.59(3)°, respectively

dent in reactions of metal centres with both single-cluster and macropolyhedral boron-containing cluster species[10,15–17]. The $\{PtS_2B_{16}\}$ framework of **2** consists of an open *nido*-type eleven-vertex $\{SB_{10}\}$ subcluster (schematic cluster structure **III B**) and a somewhat more open $\{PtSB_8\}$ subcluster (schematic cluster structure **III A**) fused with two boron atoms held in common.



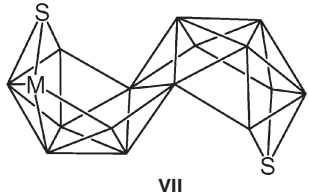
IV



V

The basic $\{B_{16}\}$ boron skeletal framework approximates to the configuration of the long-recognised binary borane $B_{16}H_{20}$ (schematic skeletal configuration **IV**)[18,19], and the overall cluster structure of **2** can be visualised as derived from $B_{16}H_{20}$ by the replacement of connectivites to open-face hydrogen atoms by connectivities to the three cluster heteroatoms S(9), S(9′) and Pt(10) (schematic cluster structure **V**). The *nido* eleven-vertex $\{SB_{10}\}$ subcluster is as also seen in other macropolyhedral thiaborane species[2–8], and closely mimics that in the *nido* eleven-vertex single-cluster model $[SB_{10}H_{12}]$ itself[20–24].

VI



VII

The $\{PtSB_8\}$ subcluster of **2** is of more interest. Its geometry has some resemblance to the classical open *nido*/*arachno* ten-vertex boat-geometry (schematic **VI**), but the "long" platinum–boron distance of 2.762(4) Å (hatched lines in schematic **III A** above) is essentially non-bonding, and gives the platinum-containing subcluster an interesting more open aspect. This is in contrast to the eighteen-vertex platinathiaborane $[(PMe_2Ph)_2PtS_2B_{15}H_{14}(NHCOMe)]$ (compound **3**, schematic **VII**)[15], which has a closely related configuration of *nido*-type ten-vertex $\{SB_9\}$ and $\{PtSB_8\}$ subclusters fused with two boron atoms in common. However, in this last compound **3** the $\{PtSB_8\}$ subcluster is now *nido* in character[15], as evidenced by the different positioning of the bridging hydrogen atom, and by the shorter Pt(10)–

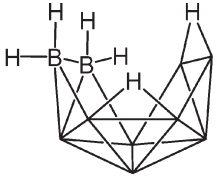
B(5) distance of 2.391(4) Å, now well within a recognised[17] platinum-to-boron cluster-bonding range. The geometry exhibited by the {$PtSB_8$} subcluster of compound **2** is more open than *nido*: this geometry can be termed "*neo-arachno*", because an "*iso-arachno*" nomenclature has previously been invoked for the so far unique shape of the ten-vertex {SB_9} subcluster in [$S_2B_{17}H_{17}(SMe_2)$] (lit.[2]). This new type of "*neo-arachno*" shape is also seen in [1-(C_6Me_6)RuB_9H_{13}] (compound **4**) (schematic cluster structure **VIII**)[25,26], but this species has a conventional *nido* ten-vertex cluster-electron count and has conventionally disposed *nido* ten-vertex hydrogen bridges and is therefore perhaps best regarded as a "stretched" *nido*. By contrast, the {$PtSB_8$} subcluster of compound **2** is in principle an [*arachno*-$B_{10}H_{14}$]$^{2-}$ analogue, but the basic cluster shape does not readily derive from the removal of two vertices from any reasonable closed deltahedral twelve-vertex cluster, nor does it relate to the "*iso-arachno*" shape of the ten-vertex {SB_9} subcluster in [$S_2B_{17}H_{17}(SMe_2)$] (lit.[2]), hence we would propose a "*neo-arachno*" descriptor. The single-cluster model would be of formulation [$(PMe_2Ph)_2$-$PtSB_8H_{10}$], with the {$Pt(PMe_2Ph)_2$} and {S} vertices both being isolobal and isoelectronic in cluster terms with anionic {BH_2}$^-$ units[27,28], which gives the cluster its overall ten-vertex conventional [$B_{10}H_{14}$]$^{2-}$ formulation-equivalence. The conventional isomer of this, [6,6-$(PMe_2Ph)_2$-*arachno*-6,9-$PtSB_8H_{10}$], with structure of conventional ten-vertex [*arachno*-$B_{10}H_{14}$]$^{2-}$ geometry **IX**, is well recognised, along with many other {PtB_8E} platinaheteroborane structural congeners, where E represents, for example the O, S, Se, {B(PMe_2Ph)}, {NH} or {CH_2} units[12,29–32].

VIII

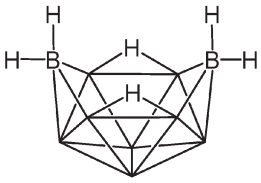
IX

Subrogation by isolobal {BH_2}$^-$ units of the {$Pt(PMe_2Ph)_2$} and {S} vertices of [$(PMe_2Ph)_2PtSB_8H_{10}$] of configuration **III A** would result in a [$B_{10}H_{14}$]$^{2-}$ anion of *neo-arachno* type configuration **X** (note that, in structures **X** to **XIII**, unlabelled vertices are {BH(*exo*)} units). We surmise that a species with this latter structure **X** would be kinetically and thermodynamically unstable compared to the conventional [*arachno*-$B_{10}H_{14}$]$^{2-}$ configuration **XI**, but the structure nevertheless prompts the idea that notional monoprotonation would result in a [$B_{10}H_{15}$]$^-$ anion **5** of a structure with connectivities closely related to those shown in schematic **XII**, which would have mirror-plane

symmetry. Although the $[B_{10}H_{15}]^-$ anion **5** has long been known, and is characterised by NMR spectroscopy (Table I), which also indicates fluxionality[30,31], the static disposition of the hydrogen atoms on the open face of the cluster, and, indeed, the shape of the $\{B_{10}\}$ cluster matrix itself, are not established.



X



XI

Starting from the approximate geometry of **XII**, we have thence conducted density-functional theory (DFT) calculations to ascertain whether such a molecular structure, or one closely related, represents a reasonable thermodynamic minimum, and have carried out gauge-independent atomic orbital (GIAO) boron nuclear-shielding calculations on the minimised structure so obtained and minimised[33]. These calculations resulted in energy minimisation at a structure as given in Fig. 2 (schematic structure as in **XIII**), and the results of the nuclear-shielding calculations for this structure, presented as $\delta(^{11}B)$ values, are summarised in Table I.

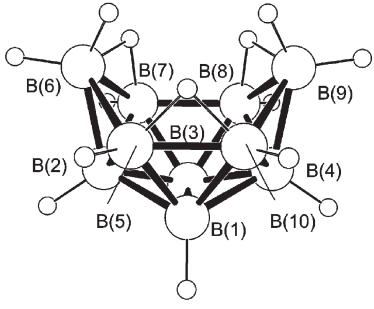
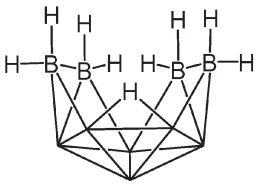
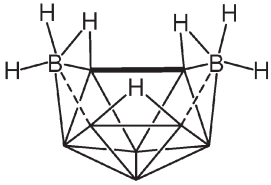


FIG. 2

ORTEP-3 (lit.[40]) plot of the molecular structure of the $[B_{10}H_{15}]^-$ monoanion **5**, as calculated by DFT techniques[33] (B3LYP/6-31G*). This minimum-energy molecule has mirror-plane symmetry through B(1), B(3) and H(5,10). Selected interatomic distances (in Å) are as follows: B(5)–B(6) 2.045, B(6)–B(7) 1.921, B(7)–B(8) 1.866, B(5)–B(10) 1.805 and B(3)–B(7) 1.752, B(5)–H(6)(*endo*) 2.281, B(6)–H(6)(*endo*) 1.209, B(6)–H(6)(*exo*) 1.201, B(6)–H(6,7) 1.385, B(7)–H(6,7) 1.280 and B(5)–H(5,10) 1.312



XII



XIII

As can be seen from Fig. 2, the structural calculations do in fact result in a configuration with mirror-plane symmetry, of basic classical *nido*/*arachno* ten-vertex boat shape. In contrast to the equivalent linkage Pt(10)–B(5) in the {$PtSB_8$} subcluster of **2** (hatched lines in schematic cluster structure **III A**), however, the (calculated) B(7)–B(8) distance in **5** is not overly long at 1.866 Å (bold connectivity in structure **XIII**). On the other hand, the B(5)–B(6) distance (and its mirror-equivalent B(9)–B(10) distance) at 2.045 Å (hatched lines in **XIII**) is now outside the arbitrary interboron cluster-bonding cut-off distance of 2.00 Å. There are three {BHB(bridging)} and two {BH(*endo*)} hydrogen atoms around the six-membered open face. This type of open-face hydrogen-atom configuration is very similar to the configuration now established for the nine-vertex analogue, the [*arachno*-B_9H_{14}]$^-$ anion[34]. The calculated structure of mirror-plane symmetry represented in Fig. 2, together with the calculated boron nuclear-shielding values (Table I), would predict an ^{11}B NMR spectrum with a 1:2:1:2:2:2 relative-intensity pattern, well spread over a large range of some 50 ppm. This is in contrast to the compact spectrum observed[35,36] (Table I). However, a rapid exchange of the five *endo* and bridging hydrogen atoms around the open face, which

TABLE I
Results of 6-31G*/GIAO calculations for the ^{11}B nuclear shieldings in the [$B_{10}H_{15}$]$^-$ monoanion **5**

Position	δ(^{11}B) (calc)	Position	δ(^{11}B) (mean)	δ(^{11}B) (exp)[a]	Δδ(^{11}B)
B(1)	–47.82	B(1,3)	–20.03	–19.8	–0.2
B(2,4)	–20.13	B(2,4)	–20.13	–19.8	–0.3
B(3)	+7.75				
B(5,10)	+2.83	B(5,7,8,10)	–13.87	–14.2	+0.3
B(6,9)	–20.07	B(6,9)	–20.07	–21.8	+1.7
B(7,8)	–30.57				

[a] Data from lit.[36]; Na^+ salt; monoglyme solution.

would involve the equivalent structure with hydrogen bridges at B(7)B(8) rather than B(5)B(10), at B(5)B(6) rather than B(6)B(7), and at B(9)B(10) rather than B(8)B(9), again with parallels to the behaviour of the [*arachno*-$B_9H_{14}]^-$ anion[34], would render the B(1) and B(3) positions on time-average mutually equivalent, and also the B(5,10) and B(7,8) positions would similarly be on time-average mutually equivalent. The averaging of the calculated boron nuclear shieldings for each of these two sets of positions gives values that agree excellently with the measured values (Table I), thereby strongly matching (i) the molecular structure in Fig. 2 to experimental observation, as well as (ii) matching the proposed fluxionality. It is encouraging that the averaged values so closely mimic those determined experimentally, particularly in view of the large differences between the individual calculated values in each of the {B(1)B(3)} and {B(5,10)B(7,8)} sets.

In sum, the ready formation and isolation of the novel macropolyhedral metallathiaborane $[(PMe_2Ph)_2PtS_2B_{16}H_{16}]$ **2**, with interesting structural features that have structural implications that can be extended to other systems such as, here, the reasonably definitive establishment of the structure of the [*arachno*-$B_{10}H_{15}]^-$ anion **5**, augur well for the continued generation of other interesting and useful novel species in metallathiaborane syntheses of this type, and we currently experiment to extend the work to other metal centres and to thiaborane substrates other than the $S_2B_{16}H_{16}$ isomers and $S_2B_{17}H_{17}$.

Supplementary Data

Crystallographic data for the previously unreported $[(PMe_2Ph)_2PtS_2B_{16}H_{16}]$ species **2** are deposited at the Cambridge Crystallographic Data Centre, CCDC, deposition number CCDC 254726; these data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk]. The DFT-calculated coordinates for the $[B_{10}H_{15}]^-$ dianion **5** are appended as supplementary data to this submission and are available on http://cccc/uochb.cas.cz/Vol/70/No04/20050430.html.

Contribution No. 99 from the Řež–Leeds Anglo–Czech Polyhedral Collaboration (ACPC). We thank the Grant Agency of the Czech Republic (grant No. 203/05/2646), the Academy of Sciences of the Czech Republic, the Royal Society, the British Council and the UK EPSRC (grants Nos J/56929, K/05818, L/49505, M/83360 and R/61949) for support, and also the UK EPSRC for contributions to a DTA studentship to M. J. Carr. Some aspects of the work have been supported by personal financial contributions from J. Bould.

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13. X-ray diffraction analysis: Crystallographic data for the previously unreported species $[(PMe_2Ph)_2PtS_2B_{16}H_{16}]$ (**2**) are as follows: $C_{16}H_{38}B_{16}P_2PtS_2$: M = 724.57, triclinic (yellow prisms from CH_2Cl_2/hexane), space group $P\bar{1}$, a = 10.3890(1) Å, b = 10.6560(1) Å, c = 14.3730(2) Å, α = 108.7010(7)°, β = 100.9300(7)°, γ = 94.8330(8)°, U = 1461.71(3) Å^3, D_{calc} = 1.646 Mg m^{-3}, Z = 2, λ = 0.71073 Å (MoKα), μ = 5.062 mm^{-1}, T = 150(2) K, R_1 = 0.018 for 6478 reflections with $I > 2\sigma(I)$, and wR_2 = 0.0439 for all 6729 unique reflections; CCDC 254726. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk).
14. NMR spectroscopy: NMR data for $[(PMe_2Ph)_2PtS_2B_{16}H_{16}]$ (**2**), CD_2Cl_2, 298 K, δ in ppm, δ(^{11}B) rel. Ξ 32.083972 MHz (nominally $BF_3(OEt_2)$ in $CDCl_3$), δ(^{31}P) rel. Ξ 40.480730 MHz (nominally 85% aqueous H_3PO_4) and δ(^{1}H) rel. Ξ 100 MHz (nominally internal $SiMe_4$). ^{11}B spectrum: sixteen resonance positions have been identified with chemical shifts δ(^{11}B) as follows (with δ(^{1}H) of directly attached *exo* hydrogen atom in square brackets): +11.2 [+3.85], +10.0 [+4.57], +6.3 [no H(*exo*)], +5.6 [+2.97], –0.5 [+2.79], –3.6 [no H(*exo*)], –4.9 [+3.20], –7.5 [+2.76], –11.1 [+3.68], –11.6 [+2.16], –15.4 [+2.34], –22.0 [+0.07], –27.9 [+0.91], 2 × –29.2 [2 × +1.08] (resonances in both ^{11}B and ^{1}H spectra accidentally coincident), and –36.4 [+0.87] ppm. The ^{1}H spectrum also shows δ(^{1}H)(PMe_2): +2.00 (3 H, d, $^2J(^{31}P\text{-}^1H)$ = 11 Hz), +1.90 (3 H, d, $^2J(^{31}P\text{-}^1H)$ = 11 Hz), +1.79 (3 H, d, $^2J(^{31}P\text{-}^1H)$ = 10 Hz), +1.67 (3 H, d, $^2J(^{31}P\text{-}^1H)$ = 10 Hz), with all exhibiting partially resolved ^{195}Pt satellite lines, $^3J(^{195}Pt\text{-}^1H)$ ≈ 25–30 Hz; additionally δ(^{1}H)(PPh) +7.15 to +7.55 (10 H, complex multiplets). ^{31}P spectrum shows: δ(^{31}P) –9.1 (P(12), broader, $^1J(^{195}Pt\text{-}^{31}P)$ ≈

3100 Hz) and –9.6 (P(11), sharper, $^{1}J(^{195}Pt\text{-}^{31}P)$ = 3818 Hz, $^{2}J(^{31}P\text{-}^{31}P)$ = 29 Hz): a similarly marked differential in magnitudes of coupling constants is general for Pt–P linkages *trans* to S (larger value) versus Pt–P linkages *trans* to cage boron atoms (smaller value) in platinathiaboranes[12,37,38].

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33. Calculational work: For the density-functional theory (DFT) calculations, the structure of the $[B_{10}H_{15}]^-$ monoanion **5** was initially optimised with the STO-3G* basis set, without symmetry constraints, using standard ab initio methods, and starting from an approximate geometry as represented in schematic **XII**. The final optimisations, including a frequency analysis to confirm a true minimum, followed by GIAO NMR nuclear shielding predictions, were performed using B3LYP methodology as incorporated in the Gaussian 98 package[39], and using the 6-31G* basis set. The minimum is represented in Fig. 2 as a molecular structure, and is represented schematically in structure **XIII**.
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