Reactions of Heteroboranes. Synthesis of $[2,2\text{-}(PPh_3)_2\text{-}1,2\text{-}SePtB_{10}H_{10}]\cdot CH_2Cl_2$, its Crystal and Molecular Structure and that of $SeB_{11}H_{11}$†

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The reaction (refluxing ethanol) of $[Pt(PPh_3)_4]$ with *closo*-$SeB_{11}H_{11}$ affords two products. One, characterised spectroscopically, is $[PtH(PPh_3)_3][SeB_{10}H_{11}]$. The second product, isolated after recrystallisation from dichloromethane–ethanol solution is $[2,2\text{-}(PPh_3)_2\text{-}1,2\text{-}SePtB_{10}H_{10}]\cdot CH_2Cl_2$ (**1**). An *X*-ray diffraction study shows crystals of (**1**) to be triclinic, space group $P\bar{1}$, with two formula units in a cell of dimensions a = 12.837(3), b = 14.534(2), c = 11.898(3) Å, α = 96.59(2), β = 107.31(2), γ = 81.89(1)°. Using 5 046 reflections, the structure was refined to R = 0.028. The dodecahedral $SePtB_{10}$ cage has Se and Pt atoms occupying adjacent sites. The principal dimensions include the bond lengths Pt–Se 2.676(1), Se–B 2.098(9)—2.210(6), Pt–P 2.326(1) and 2.350(2), and Pt–B 2.231(8)—2.311(6) Å and an interplanar angle of 80.0° between the plane containing the PtP_2 unit and that containing the Se and Pt atoms and passing through the mid-point of the B(2)–B(3) bond opposite the Se atom. The crystal and molecular structure of $SeB_{11}H_{11}$ was studied by *X*-ray diffraction methods in an attempt to provide more information on Se–B bonding. Crystals of $SeB_{11}H_{11}$ are cubic, space group $Pa3$, with four molecules in a cell, a = 9.847(3) Å. The structure was refined to R = 0.075 for 164 reflections. The molecule lies on a site with $\bar{3}$ crystallographic symmetry; the electron density and refinement are consistent with scrambling of the Se atom and eleven B–H groups over the twelve dodecahedral positions. This precluded any precise determination of Se–B bond distances.

Several routes are now established for the synthesis of cage substituted metalla-boranes, -carbaboranes, and -heteroboranes.[1,2] Perhaps the most common reactions are the 'direct' insertions, as exemplified by Stone and co-workers,[3] and salt elimination reactions which use metal halides and appropriate boron cluster anions. Most reactions are not simple and little is understood about the mechanisms. Many reactions are accompanied by loss of ligands (usually PR_3 or CO) from metal fragments or the elimination of hydrogen. In several reactions partial degradation of the boron cluster cage occurs to give unexpected products. An example of the complications which can occur in heteroborane chemistry is given by the reaction in ethanol of $[Pt(PPh_3)_4]$ and either *closo*-SB_9H_9 or *closo*-$SB_{11}H_{11}$.[4] It was expected that an oxidative addition would occur to give an *exo*-polyhedral platinum *closo* sulphur–borane species. Instead *nido*-$[9,9\text{-}(PPh_3)_2\text{-}6,9\text{-}SPtB_8H_{10}]$ was isolated from both reactions. It is noteworthy that $SB_{11}H_{11}$ had reacted quite differently to the previously reported isoelectronic system *closo*-$1,2\text{-}R_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ (R = H or Me). The carbaborane failed to react even with $[Pt(PEt_3)_3]$ which is much more reactive than $[Pt(PPh_3)_4]$.[5] Likewise the *closo*-$[B_{12}H_{12}]^{2-}$ anion is unreactive towards $[Pt(PR_3)_4]$ species.[6] To investigate further the effect of the heteroatom on the reactivity of the borane cage we decided to examine the reaction of $[Pt(PPh_3)_4]$ with *closo*-$1\text{-}SeB_{11}H_{11}$. The products were *closo*-$[2,2\text{-}(PPh_3)_2\text{-}1,2\text{-}SePtB_{10}H_{10}]$ and $[PtH(PPh_3)_3]$-$[SeB_{10}H_{11}]$.

Results and Discussion

Reaction of $SeB_{11}H_{11}$ and $[Pt(PPh_3)_4]$ in refluxing ethanol for 18 h gave two products, one brown and the other orange. The brown compound was characterised spectroscopically as $[PtH(PPh_3)_3][SeB_{10}H_{11}]$. The presence of a terminal Pt–H bond is indicated by a strong i.r. stretching mode at 2 110 cm^{-1}. Absorptions for the PPh_3 and borane ligands are also seen in the i.r. spectrum. The ^1H spectrum of the $[PtH(PPh_3)_3]^+$ cation has previously been reported for a series of carboxylic acid derivatives. The present compound shows the unusual and complex splitting pattern in the Pt–H region of the ^1H and $^1H\text{-}\{^{11}B\}$ spectra which is exactly analogous to previously analysed spectra. In particular there are two double doublets at the centre of the Pt–H region (*ca.* 5.8 p.p.m.) which almost certainly arise from second-order effects and which have been explained satisfactorily previously.[7] The integrated ^1H resonances associated with the PPh_3 and borane ligands are in the ratio 45:11. The $^1H\text{-}\{^{11}B\}$ spectrum in the borane region shows broad singlets in the ratio 2:2:1:2:2:1:1. The undecoupled ^1H spectrum confirms that the resonance at highest field in this region (−4.10 p.p.m.), is due to the single bridging proton. The 115.5-MHz $^{11}B\text{-}\{^1H\}$ spectrum shows six resonances at positions very close to those previously reported in the 70.6-MHz spectrum of $[SeB_{10}H_{11}]^-$;[8] δ/p.p.m., present work (ref. 8): −5.6 (−6.0), 2 B; −9.2 (−9.5), 2 B; −14.6 (−15), 1 B; −16.3, 2 B, and −17.6, 2 B (−16.8, 4 B); −35.6 (−35.9), 1 B.

The i.r. and n.m.r. spectra of the orange product show no signs of Pt–H–B units. The $^1H\text{-}\{^{11}B\}$ spectrum indicates that the ratio of PPh_3 protons to borane protons is 3:1. The $^{11}B\text{-}\{^{11}H\}$ spectrum is consistent with the presence of ten B atoms in the ratio 1:3:2:2:2. Although the compounds $[Co(\eta^5\text{-}C_5H_5)SeB_{10}H_{10}]$ and $[M(SeB_{10}H_{10})]^{2-}$ (M = Co or Fe) have

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† *closo*-2,2-Bis(triphenylphosphine)-1-selena-2-platinadodecaborane-(10) and *closo*-selenadodecaborane(11) respectively.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

been characterised spectroscopically,[8] and some thia[9] and tellura[8] analogues have been obtained, no crystallographic studies have been reported. Hence an *X*-ray diffraction study of a single crystal of the orange product grown from dichloromethane–ethanol solution (**1**) was undertaken.

The crystals of (**1**)$\cdot CH_2Cl_2$ contain discrete, neutral monomeric molecules of $(PPh_3)_2PtB_{10}H_{10}Se$ and CH_2Cl_2 molecules of solvation. The structural analysis shows that there is no imposed symmetry on the molecule (**1**) and that Pt and Se occupy adjacent sites of a slightly distorted dodecahedron $PtSeB_{10}$. Figure 1 gives a perspective view of (**1**) with the atomic numbering scheme. Table 1 lists the polyhedral bond distances and interbond angles. The overall cluster structure is that of a *closo* dodecahedron as expected from Wade's rules where a BH unit in $SeB_{11}H_{11}$ has been replaced by $Pt(PPh_3)_2$.[10]

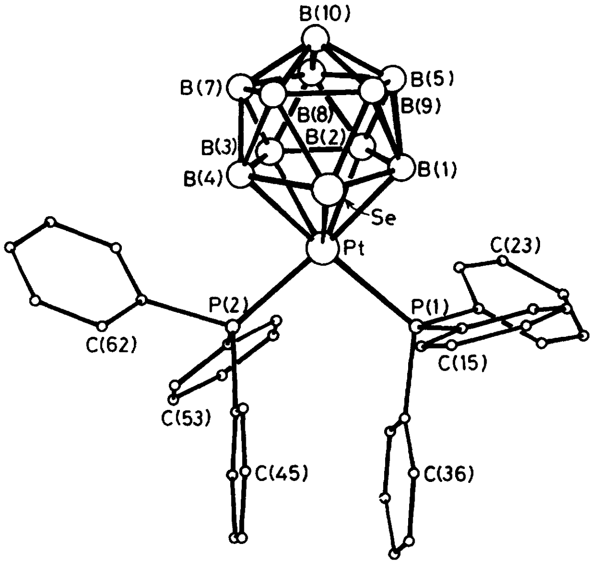

Figure 1. View of $[2,2\text{-}(PPh_3)_2\text{-}1,2\text{-}SePtB_{10}H_{10}]$ with the numbering scheme. For clarity, the heavy atoms are shown as spheres of arbitrary radius and hydrogen atoms are omitted

The Pt–B bonding distances fall within the range 2.231(8)—2.311(6) Å, and are typical of platinum-substituted borane clusters.[2,4] Likewise the Pt–P bond distances [2.326(1) and 2.350(2) Å] are typical of platinum phosphines. With respect to B–B bonds, the mean B–B distance in SeB_2 deltoid faces [1.919(10) Å] is longer than in PtB_2 faces [1.813(10) Å] and B_3 faces [1.768(10) Å]. The wide range of B–B distances (1.702—1.965 Å) is typical of metallaborane systems in general.[2,4] Although no *closo*-selenaborane structures have been reported previously, some comparisons may be made with *closo*-$[2,2'\text{-}(1\text{-}SB_9H_8)_2]$,[11] *closo*-$[Se_3B_{11}H_9]^{2-}$ which has an *exo*-polyhedral Se_3 chain,[12] and *nido*-$[7\text{-}(\eta^5\text{-}C_5H_5)\text{-}7,8,12\text{-}CoSe_2B_9H_9]$.[13] The B–B distances in *closo*-$[Se_3B_{11}H_9]^{2-}$ and the thiaborane dimer are in the ranges 1.738(20)—2.091(21) and 1.689(8)—1.940(4) Å respectively, whilst in the *nido* compound they are 1.708(7)—2.007(7) Å.

Two Se–B distances are observed in (**1**). For bonds to atoms B(1) and B(4), which are also attached to Pt, the Se–B distances are 2.210(6) and 2.198(7) Å whereas for bonds to B(8) and B(9) the Se–B distances are 2.098(9) and 2.101(7) Å respectively. In the *nido*-cobaltadiselenaborane the Se–B distances lie in the range 2.004(5)—2.160(5) Å. However comparison with (**1**) is difficult since the two selenium atoms in the *nido* compound are in an open face and interact with only two or three B atoms respectively. The *exo*-polyhedral Se–B bond distances in $[Se_3B_{11}H_9]^{2-}$ are 2.016(15) and 2.023(16) Å. Bearing in mind the difference in covalent radii of Se and S which is generally taken to be 0.11—0.13 Å, the Se–B distances in (**1**) are comparable with the S–B distance of 1.930(8) Å in *closo*-$[2,2'\text{-}(1\text{-}SB_9H_8)_2]$.

Table 1. Important molecular dimensions for $[(PPh_3)_2PtSeB_{10}H_{10}]$ (**1**), with estimated standard deviations in parentheses

(*a*) Bond lengths (Å)

Pt–P(1)	2.350(2)	Pt–B(1)	2.311(6)	Pt–B(4)	2.299(7)	Se–B(8)	2.098(9)
Pt–P(2)	2.326(1)	Pt–B(2)	2.267(6)	Se–B(1)	2.210(6)	Se–B(9)	2.101(7)
Pt–Se	2.676(1)	Pt–B(3)	2.231(8)	Se–B(4)	2.198(7)		

B–B in the $PtSeB_{10}$ cage

	Se–B–B triangles	Pt–B–B triangles	B–B–B triangles
Range	1.843—1.965(11)	1.767—1.840(10)	1.702—1.825(10)
Mean	1.919(10)	1.813(10)	1.768(10)

P–C Range	1.823—1.849(4)	B–H Range	1.00—1.24
Mean	1.833(4)	Mean	1.11
C–C Constrained to be	1.395	C–H Constrained to be	0.95

(*b*) Bond angles (°)

P(1)–Pt–P(2)	97.8(1)	Se–Pt–B(1)	52.0(2)	Pt–Se–B(4)	55.2(2)	Pt–P(1)–C(31)	122.7(2)
P(1)–Pt–Se	105.2(1)	Se–Pt–B(2)	88.0(2)	Pt–Se–B(8)	100.6(2)	C(11)–P(1)–C(21)	108.5(2)
P(1)–Pt–B(1)	86.2(2)	Se–Pt–B(3)	87.7(2)	Pt–Se–B(9)	101.3(2)	C(11)–P(1)–C(31)	104.0(2)
P(1)–Pt–B(2)	106.1(2)	Se–Pt–B(4)	51.8(2)	B(1)–Se–B(4)	87.4(2)	C(21)–P(1)–C(31)	96.2(2)
P(1)–Pt–B(3)	149.9(2)	B(1)–Pt–B(2)	47.4(2)	B(1)–Se–B(8)	90.7(3)	Pt–P(2)–C(41)	115.0(2)
P(1)–Pt–B(4)	156.2(2)	B(1)–Pt–B(3)	80.6(2)	B(1)–Se–B(9)	54.2(3)	Pt–P(2)–C(51)	113.8(2)
P(2)–Pt–Se	119.0(1)	B(1)–Pt–B(4)	82.7(2)	B(4)–Se–B(8)	53.9(3)	Pt–P(2)–C(61)	117.4(2)
P(2)–Pt–B(1)	171.0(2)	B(2)–Pt–B(3)	46.2(2)	B(4)–Se–B(9)	91.5(3)	C(41)–P(2)–C(51)	107.6(2)
P(2)–Pt–B(2)	137.6(2)	B(2)–Pt–B(4)	81.4(2)	B(8)–Se–B(9)	52.1(3)	C(41)–P(2)–C(61)	101.3(2)
P(2)–Pt–B(3)	99.3(2)	B(3)–Pt–B(4)	47.7(2)	Pt–P(1)–C(11)	108.5(2)	C(51)–P(2)–C(61)	100.1(2)
P(2)–Pt–B(4)	90.6(1)	Pt–Se–B(1)	55.5(2)	Pt–P(1)–C(21)	115.5(2)		

C–C–C Constrained to be 120°

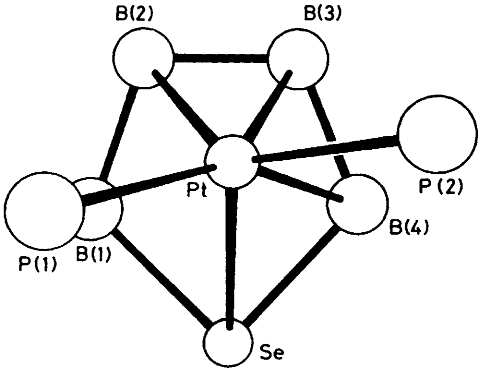

Figure 2. View of the Pt co-ordination in (**1**) observed normal to the B(1),B(2),B(3),B(4),Se plane

Although the Pt–Se distance reported here [2.676(1) Å] is unique since no analogous system has been studied previously, it may be compared with the Pt–S bond in *nido*-[2,2-$(PEt_3)_2$-2-H-1,2-$SPtB_9H_{10}$] which is 2.43 Å.[14]

The bonding between the PtP_2 unit and the $SeB_{10}H_{10}$ unit is of interest. A view normal to the SeB_4 plane is given in Figure 2. The interplanar angle between the plane containing PtP(1)P(2) and the plane through Pt, Se, and the mid-point of the B(2)–B(3) bond is 80.0°, *i.e.* approaches 90°. This orientation can be rationalised by consideration of the h.o.m.o.–l.u.m.o. (highest occupied and lowest unoccupied molecular orbitals) interactions of the PtP_2 and $SeB_{10}H_{10}$ or analogous $SB_{10}H_{10}$ units. The analysis is similar to that of Mingos *et al.*[15] who studied ML_2 [$Pd(CNBu^t)_2$ or $Pt(PEt_3)_2$] derivatives of 1-NMe_3-1-$CB_{10}H_{10}$ and 3,4-$C_2B_9H_{11}$. In the present case the energy level ordering and composition of the m.o.s of the $SB_{10}H_{10}$ unit were calculated using the MNDO program,[16] allowing free variation of all bond lengths. The form and composition of the h.o.m.o.s and l.u.m.o.s of the PtP_2 and $SB_{10}H_{10}$ units are shown schematically in Figure 3. The h.o.m.o. of $SB_{10}H_{10}$ has 52% of its composition contributed by the SB_4 face atoms while the l.u.m.o. has 56%. From the observed structure it is clear that the conformation of the isoelectronic $SeB_{10}H_{10}$ compound (**1**) is consistent with the major interaction occurring between the $XB_{10}H_{10}$ l.u.m.o. (X = Se) and ML_2 h.o.m.o. (M = Pt, L = PPh_3). Mingos *et al.*[15] reached similar conclusions in their more detailed analysis of metallacarbaboranes.

Several tentative comments may be made concerning the mode of formation of (**1**). It appears that solvent participation is important. The ethanol could act to degrade $SeB_{11}H_{11}$, to initiate the dissociation of [$Pt(PPh_3)_4$] into [$Pt(PPh_3)_3$] and PPh_3, and as a proton source for the formation of $[PtH(PPh_3)_3]^+$. Stereoselective degradation of SB_9H_9 or $SB_{11}H_{11}$ in alcoholic KOH to *nido* anions $[SB_8H_9]^-$ and $[SB_{10}H_{11}]^-$ respectively has been reported,[17] and protonations of [$Pt(PR_3)_n$] species by alcohol (R = Et),[18] or carboxylic acids (R = Ph)[7] are established in the literature. However, in the present case the highly nucleophilic nature of the zero-valent Pt complex may provide the driving force for the production of the ionic product $[PtH(PPh_3)_3]^+$ by direct attack on the selenaborane. If such an attack initiated the disruption of Se–B as well as B–H bonds, then degradation of the selenaborane cage by ethanol would be facilitated. The isolation of [8-OEt-9,9-$(PPh_3)_2$-6,9-$SPtB_8H_9$] from the reaction of [$Pt(C_2H_4)(PPh_3)_2$] and SB_9H_9 in ethanol further supports the view that solvent participation is important.[4] Previous experiments by Rudolph and co-workers[4] have established that reaction of SB_9H_9 and [$Pt(PMe_2Ph)_4$] in aprotic solvents (*e.g.* cyclohexane) was consistent with the formation of a product with Pt inserted into an *exo*-polyhedral B–H bond and no cage degradation.[4]

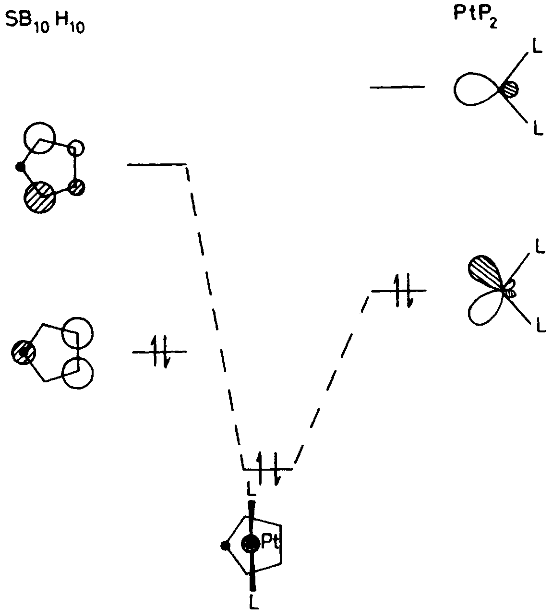

Figure 3. Conformation of the PtL_2 (L = PPh_3) unit on $SB_{10}H_{10}$: interaction of l.u.m.o.s and h.o.m.o.s

The isolation of two products from the reaction of $SeB_{11}H_{11}$ is of interest. In an attempt to discover if the ionic product [$PtH(PPh_3)_3$][$SeB_{10}H_{11}$] is an intermediate in the formation of [2,2-$(PPh_3)_2$-1,2-$SePtB_{10}H_{10}$], the ionic material was isolated and an ethanol solution was refluxed for 18 h. Thin-layer chromatography of the reaction solution showed unreacted starting material (*ca.* 90%) and some (**1**) (*ca.* 5%). Hence only a small fraction of (**1**) is formed *via* the ionic material. Such a reaction would be unusual. Whereas the elimination of H_2 or a ligand such as PR_3 is well known during reactions producing metallaboranes or carbaboranes and often leads to cage closure, such eliminations usually occur when the metal unit is already attached as part of the cluster cage.[2] In the present case it appears that H_2 and PPh_3 are both lost from the ionic intermediate either prior to or accompanying the insertion of the metal into the cage.

Previously some spectroscopic evidence for an intermediate species [$PtH(PMe_2Ph)_3$][$SB_{10}H_{11}$] has been mentioned in the work on the reaction of $SB_{11}H_{11}$ with [$Pt(PMe_2Ph)_4$] (see ref. 38 in ref. 4). Prolonged reaction afforded *nido*-[9,9-$(PMe_2Ph)_2$-6,9-$SPtB_8H_{10}$] in 30% yield. The platinaselenaborane produced in the present reaction is more stable to further degradation than the corresponding thiaborane derivative. The reasons for this are unclear at present and require further investigation.

Because of the absence of any structural data on selenaboranes in the literature it was decided to study the crystal and molecular structure of $SeB_{11}H_{11}$ by single-crystal *X*-ray diffraction methods. A suitable crystal was grown from dichloromethane–ethanol solution. The crystal has a cubic space group ($Pa\bar{3}$) and the molecule lies on a site with $\bar{3}$ crystallographic symmetry. The electron density and refinement are consistent with complete scrambling of the Se atom and eleven B–H groups over the 12 dodecahedral positions, see Figure 4. While no meaningful discussions of the Se–B or B–B bond distance are possible, the values found on refinement are in the anticipated ranges: Se–B 2.07—2.12(3), B–B 1.87—1.91(3) Å. The latter may be compared with values of 1.787 and 1.777(2) Å for B–B bonds in $[B_{12}H_{12}]^{2-}$ (which has $\bar{3}$ crystallographic symmetry).[19]

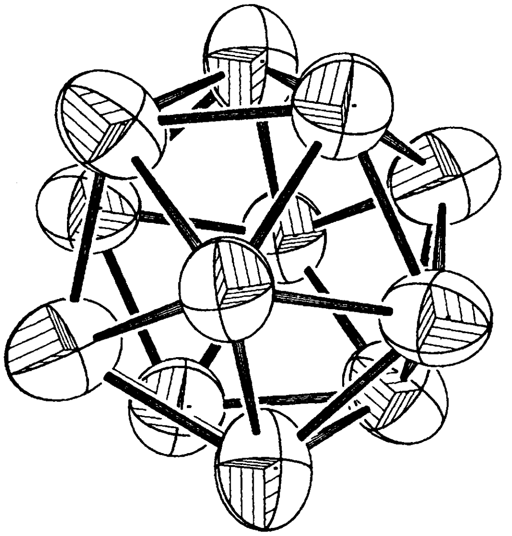

Figure 4. ORTEP plot of $SeB_{11}H_{11}$ showing scrambled Se and B–H groups

Experimental

Infrared spectra were recorded as KBr discs on Perkin-Elmer 257 and 457 spectrometers. The n.m.r. spectra were recorded on a Bruker WH360 spectrometer. Chemical shifts (δ) are relative to $SiMe_4$ (^1H) and external $BF_3{\cdot}OEt_2$ (^{11}B); positive values represent shifts to high frequency (low field) of the standards. Mass spectra were recorded on a AEI-Kratos MS3074 double-beam spectrometer. All experiments were carried out under dry, oxygen-free nitrogen. Solvents were dried and distilled under nitrogen before use. The compound $[Pt(PPh_3)_4]$ was obtained from Fluorochem Ltd. (England), and used as supplied. The compound *closo*-$SeB_{11}H_{11}$ was prepared by the literature method[20] with the slight modification of reacting the $[B_{11}H_{14}]^-$ ion as $Na[B_{11}H_{14}]{\cdot}xO(CH_2CH_2OMe)_2$ in a slurry in $O(CH_2CH_2OMe)_2$, and extracting the product using the Soxhlet procedure (yield 25%; lit.,[20] 18%). The compound $SeB_{11}H_{11}$ was identified from its i.r. spectrum, $\nu_{max.}$ at 2 585 (sh) (BH), 2 567s (BH), 2 530s (BH), 2 512s (BH), 1 014s, 910s, 853m, 770m, and 722s cm^{-1}; ^{11}B-{^1H} n.m.r. ($CDCl_3$, 115.5 MHz, 25 °C), δ 24.1(1), −2.6(5), −3.5(5); and mass spectrum, cut-off at *m*/*z* 214 (P^+) (calc. for $^{82}Se^{11}B_{11}{}^1H_{11}$, 214).

Reaction of closo-$SeB_{11}H_{11}$ *with* $[Pt(PPh_3)_4]$.—A solution of *closo*-$SeB_{11}H_{11}$ (0.10 g, 0.5 mmol) and $[Pt(PPh_3)_4]$ (0.60 g, 0.48 mmol) in ethanol (40 cm^3) was refluxed for 18 h. On cooling, a mixture of brown and orange products was observed. These were filtered under nitrogen and separated manually to give *ca.* 0.05 g (*ca.* 10%) of the brown material. The orange material was recrystallised (25 °C) from ethanol–dichloromethane (1:1) to give orange *crystals* of $[2,2\text{-}(PPh_3)_2\text{-}1,2\text{-}SePtB_{10}H_{10}]{\cdot}CH_2Cl_2$ (**1**) (0.019 g, 43%). Attempted recrystallisation of the brown material from ethanol–dichloromethane gave a mixture of the brown and orange products.

The brown material was characterised spectroscopically as $[PtH(PPh_3)_3][SeB_{10}H_{11}]$: $\nu_{max.}$ at 3 055m, 2 960m, 2 520vs (BH), 2 440w (BH), 2 110s (PtH), 1 480vs, 1 435vs, 1 312m, 1 263m, 1 184w, 1 163w, 1 100vs, 1 095s, 1 059w, 1 029m, 1 017w, 1 000m, 810m, 749s, 743s, 707s, and 696vs cm^{-1}. N.m.r. spectra: ^1H-{^{11}B(broad band)} (CD_2Cl_2, 25 °C), δ 7.55—7.05 (complex m, 45 H, P-C_6H_5), 2.39 (br s, 2 H, BH), 2.06 (br s, 2 H, BH), 1.84 (br s, 1 H, BH), 1.68 (br s, 2 H, BH), 1.27 (br s, 2 H, BH), 1.06 (br s, 1 H, BH), −4.10 (br s, 1 H, BHB), −5.77 [1 H PtH, *J*(Pt-H) 773, *J*(P-H_{trans}) 160, *J*(P-H_{cis}) 12.7 Hz];[7] ^{11}B-{^1H} (CD_2Cl_2, 115.5 MHz, 25 °C), δ −5.6 (s, 2 B), −9.2 (s, 2 B), −14.6 (s, 1 B), −16.3 (s, 2 B), −17.6 (s, 2 B), −35.6 (s, 1 B).[8]

The orange *crystals* of (**1**) were characterised by analysis (Found: C, 43.8; H, 4.1. Calc. for $C_{37}H_{42}B_{10}Cl_2P_2PtSe$: C, 44.4; H, 4.2%) and spectroscopy: $\nu_{max.}$ at 3 055m, 2 582 (sh) (BH), 2 565s (BH), 2 535 (sh) (BH), 2 527vs (BH), 1 480s, 1 437vs, 1 431vs, 1 427m, 1 310w, 1 265w, 1 186w, 1 157w, 1 095s, 1 015s, 1 000m, 810m, 750s, 740s, 710 (sh), 700vs, and 691vs cm^{-1}. N.m.r. spectra: ^1H-{^{11}B(broad band)} (CD_2Cl_2, 25 °C), δ 7.65—7.20 (complex m, 30 H, P–C_6H_5), 5.27 (br s, 1 H, BH), 4.08 (br s, 1 H, BH), 3.47 (br s, 2 H, BH), 2.33 (br s, 2 H, BH), 1.37 (br s, 2 H, BH), 1.20 (br s, 2 H, BH); ^{11}B-{^1H} (CD_2Cl_2, 115.5 MHz, 25 °C), δ 18.5 (s, 1 B), 6.7 [m, 3 B, *J*(Pt–B) 226 Hz], −2.1 (s, 2 B), −12.2 (s, 2 B), −20.9 (s, 2 B).

X-*Ray Analysis of* $[2,2\text{-}(PPh_3)_2\text{-}1,2\text{-}SePtB_{10}H_{10}]{\cdot}CH_2Cl_2$ (**1**). *Crystal data.* $C_{37}H_{42}B_{10}Cl_2P_2PtSe$, M = 1 001(8), triclinic, a = 12.837(3), b = 14.534(2), c = 11.898(3) Å, α = 96.59(2), β = 107.31(2), γ = 81.89(1)°, U = 2 092.0 Å^3, Z = 2, D_c = 1.59 g cm^{-3}, $F(000)$ = 980, λ(Mo-K_α) = 0.710 69 Å, μ(Mo-K_α) = 45.8 cm^{-1}, space group $P\bar{1}$.

An orange crystal measuring 0.42 × 0.40 × 0.35 mm was used for data collection with an Enraf-Nonius CAD4 diffractometer. Following machine location and centring of 25 reflections in the range $10 < \theta < 15°$, accurate cell constants and the orientation matrix were determined by a least-squares refinement. Intensity data were collected in the range $2 \leqslant \theta \leqslant 22.5°$ by the ω–2θ scan method using monochromatic Mo-K_α radiation. The intensities of three standard reflections monitored at regular intervals did not change significantly over the period of data collection. A total of 5 455 unique reflections were measured of which 5 046 had $I \geqslant 3\sigma(I)$ and were used in structure solution and refinement. Data were corrected for Lorentz and polarisation factors and for absorption. Maximum and minimum values of transmission coefficients were 0.3365 and 0.1566 respectively.

The structure was solved by the heavy-atom method. Initial refinement using the SHELX system of programs[21] by full-matrix least-squares calculations with isotropic thermal parameters lowered R to 0.0885; this was followed by six cycles of refinement with anisotropic thermal parameters for the non-hydrogen atoms and the phenyl rings constrained as regular hexagons. A difference map calculated at this stage revealed maxima corresponding to the 42 hydrogen atoms; protons attached to C atoms were included in the subsequent refinement in geometrically idealised positions (C–H 0.95 Å) while co-ordinates for those on B atoms were taken from the difference map, only overall isotropic thermal parameters were refined for the two types of hydrogen atoms. B–H distances were in the range 0.99—1.24 Å. Refinement converged with R = 0.028 and $R' = w\Delta^2/wF_o^2$ = 0.034. In the final stages of refinement, a weighting scheme of the form $w = 1/(\sigma^2F + pF^2)$ was employed where the final p parameter was 0.000 92. A difference map calculated at the conclusion of the refinement showed electron density in the vicinity of the solvent molecule and was of no chemical significance. Scattering factors used in the calculations were taken from ref. 22, and allowance was made for anomalous dispersion. The final fractional co-ordinates and their standard deviations are shown in Table 2 and important molecular dimensions are summarised in Table 1.

X-*Ray Analysis of* $SeB_{11}H_{11}$.—*Crystal data.* $H_{11}B_{11}Se$, M = 209.0, cubic, a = 9.847(3) Å, U = 954.8 Å^3, Z = 4, D_c = 1.45 g cm^{-3}, $F(000)$ = 400, λ(Mo-K_α) = 0.71069 Å, μ(Mo−K_α) = 38.1 cm^{-1}. Space group $Pa3$, uniquely from systematic absences (0*kl* absent if $k = 2n + 1$) and the Laue symmetry.

A colourless crystal (0.40 × 0.25 × 0.20 mm) was used for

Table 2. Final fractional co-ordinates (Pt and Se × 10^5, others × 10^4) of $[(PPh_3)_2PtSeB_{10}H_{10}]$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt	11 041(1)	24 539(1)	26 616(1)	C(32)	3 374(3)	1 603(2)	676(4)
Se	6 196(5)	39 806(4)	39 799(6)	C(33)	4 372(3)	1 211(2)	494(4)
P(1)	1 926(1)	2 974(1)	1 370(1)	C(34)	5 286(3)	1 704(2)	891(4)
P(2)	2 533(1)	1 351(1)	3 521(1)	C(35)	5 203(3)	2 590(2)	1 470(4)
B(1)	−264(5)	3 669(5)	2 107(6)	C(36)	4 204(3)	2 983(2)	1 652(4)
B(2)	−716(5)	2 498(5)	1 698(6)	C(41)	3 902(3)	1 743(2)	3 945(3)
B(3)	−289(5)	1 856(4)	2 961(6)	C(42)	4 804(3)	1 241(2)	3 646(3)
B(4)	444(5)	2 551(4)	4 274(6)	C(43)	5 824(3)	1 586(2)	4 030(3)
B(5)	−1 648(5)	3 496(5)	1 983(6)	C(44)	5 940(3)	2 433(2)	4 714(3)
B(6)	−1 639(6)	2 373(5)	2 500(7)	C(45)	5 038(3)	2 935(2)	5 013(3)
B(7)	−958(6)	2 422(5)	4 010(6)	C(46)	4 020(3)	2 588(3)	4 628(3)
B(8)	−656(6)	3 566(5)	4 501(6)	C(51)	2 586(3)	255(3)	2 615(3)
B(9)	−1 080(6)	4 262(5)	3 207(6)	C(52)	3 338(3)	−503(3)	3 047(3)
B(10)	−1 830(6)	3 405(5)	3 400(7)	C(53)	3 389(3)	−1 329(3)	2 332(3)
C(11)	2 034(3)	4 228(3)	1 724(3)	C(54)	2 688(3)	−1 397(3)	1 186(3)
C(12)	1 527(3)	4 898(3)	924(3)	C(55)	1 934(3)	−641(3)	753(3)
C(13)	1 591(3)	5 843(3)	1 281(3)	C(56)	1 883(3)	186(3)	1 469(3)
C(14)	2 161(3)	6 116(3)	2 437(3)	C(61)	2 508(3)	916(3)	4 910(3)
C(15)	2 670(3)	5 444(3)	3 238(3)	C(62)	3 205(3)	1 191(3)	6 004(3)
C(16)	2 605(3)	4 501(3)	2 881(3)	C(63)	3 094(3)	899(3)	7 035(3)
C(21)	1 215(3)	2 785(3)	−203(3)	C(64)	2 288(3)	328(3)	6 971(3)
C(22)	476(3)	2 117(3)	−571(3)	C(65)	1 591(3)	52(3)	5 877(3)
C(23)	37(3)	1 875(3)	−1 772(3)	C(66)	1 700(3)	346(3)	4 846(3)
C(24)	336(3)	2 300(3)	−2 605(3)	C(s)	4 267(22)	4 300(16)	8 433(24)
C(25)	1 075(3)	2 968(3)	−2 237(3)	Cl(1)	3 778(7)	3 440(7)	7 673(8)
C(26)	1 514(3)	3 211(3)	−1 036(3)	Cl(2)	5 437(8)	4 363(7)	8 572(11)
C(31)	3 290(3)	2 490(2)	1 255(4)				

Table 3. Final fractional co-ordinates and occupancy factors, *k* (× 10^4), with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	*k*
Se(1)	1 029(29)	1 528(23)	3 828(30)	792(20)
Se(2)	416(26)	−513(30)	2 919(9)	875(20)
B(1)	852(18)	1 257(16)	3 983(22)	9 622(225)
B(2)	359(12)	−430(14)	3 260(4)	8 710(255)
H(1)	1 402(0)	2 050(0)	3 454(0)	9 622(225)
H(2)	595(0)	−690(0)	2 221(0)	8 710(225)

Table 4. Bond distances (Å) in the disordered $SeB_{11}H_{11}$ cage (e.s.d. is 0.010 for all bonds)

Se(1)–Se(1)	2.250	Se(2)–B(1)	2.078
Se(1)–Se(2)	2.281	Se(2)–B(1)	2.111
Se(1)–Se(2)	2.271	Se(2)–B(1)	2.104
Se(1)–Se(2)	2.247	Se(2)–B(2)	2.089
Se(1)–B(1)	2.123	Se(2)–B(2)	2.082
Se(1)–B(1)	2.068	B(1)–B(1)	1.898
Se(1)–B(1)	2.113	B(1)–B(2)	1.871
Se(1)–B(2)	2.116	B(1)–B(2)	1.905
Se(1)–B(2)	2.093	B(1)–B(2)	1.912
Se(2)–Se(2)	2.254	B(2)–B(2)	1.876

data collection in a manner similar to that for (**1**). The intensities of 2 348 reflections were measured, corresponding to the set with indices *h* 0 to 10, *k* −10 to +10, *l* −10 to +10 (*i.e.* a 'triclinic' data set). These were then corrected for Lorentz polarisation and absorption factors (maximum and minimum transmission coefficients 0.616 and 0.236 respectively); after merging equivalent reflections 199 unique reflections were left of which 164 had $I > 3\sigma(I)$ and were labelled 'observed'.

The structure was solved by a detailed analysis of the three-dimensional Patterson function. In space group *Pa*3 with $Z = 4$, the molecule is required to lie on a site with $\bar{3}$ crystallographic symmetry. Consequently the selenium–boron cage is defined by two sites and the Se atom and 11 B atoms are scrambled over the 12 dodecahedral sites. Initially we refined the structure by placing two Se atoms with appropriate occupancy (0.218) to approximate the SeB_{11} system. Electron-density maps showed that the two unique atom maxima were not exactly equal in height and in the final round of calculations we used constrained refinement of both B and Se atoms with tied occupancies and with anisotropic thermal parameters in the SHELX system.[21] Final co-ordinates, and occupancy factors are in Table 3. The bond lengths for the disordered cage are given in Table 4. The final *R* and *R'* values were 0.075 and 0.088 respectively and a final difference map showed no significant features.

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