Pentahapto-bonded gold heteroborane clusters $[3-(R_3P)-closo-2,1-AuTeB_{10}H_{10}]^-$ and $[3-(R_3P)-closo-3,1,2-AuAs_2B_9H_9]^-$

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Gold acetylide compounds $[(R_3P)AuC \equiv CC(Me)(OH)Et]$, where $R = Ph \mathbf{1}$ or cyclohexyl (Cy) $\mathbf{2}$, were synthesised and 2 was characterised using X-ray diffraction techniques. The solid-state structure of 2 contained a two-coordinate gold atom and a linear P-Au-C≡C-C bonding sequence. The reactions between 1 or 2 and $[NR_4][nido-7,8-As_2B_9H_{10}]$ or $[NR_4][nido-7-TeB_{10}H_{10}]$ in ethanol-acetone solvent afforded the twelve-vertex cluster species $[NMe_4][3-(R_3P)-closo-3,1,2-AuAs_2B_9H_9]$, where R = Ph 5 or Cy 6, or $[NEt_4][3-(R_3P)-closo-2,1-AuTeB_{10}H_{10}]$, where R = Ph 7 or Cy 8, in moderate or low yields (ca. 35% for 5, 6 and 8 and ca. 20% for 7). Compounds 5 and 7 were characterised with X-ray crystallographic techniques. Although there was crystallographic disorder in the $\{As_2B_3\}$ and $\{TeB_4\}$ rings to which the gold atoms were attached, the structures of 5 and 7 strongly suggested that the gold atoms were pentahapto bonded to all the atoms in the $\{As_2B_3\}$ or $\{TeB_4\}$ rings giving formally *closo* cluster geometries with closo cluster electron counts. The solution-phase NMR properties of 5, 6 and 7 were consistent with closo descriptions.

Introduction

The chemistry of metallaboranes^{2,3} and metallaheteroboranes^{4,5} is extensive and well documented and compounds of virtually all the transition elements have been studied including the Group 11 elements copper and gold. To date almost all the gold heteroborane compounds which have been reported were carbaborane derivatives and the gold reagent used was almost exclusively [(R₃P)AuCl]. We wished to investigate the potential use of gold acetylides of the general form $[(R_3P)AuC \equiv CR]$ as reagents for $\{(R_3P)Au\}$ complexes with heteroborane ligands. The compounds synthesised for this purpose were $[(R_3P)AuC \equiv CC(Me)(OH)Et]$ with R = Ph1 or cyclohexyl 2.

Additionally, we wished to investigate the bonding potential of $\{(R_3P)Au\}$ units to heteroborane ligands other than carbaboranes. Numerous authors have commented on the isolobal relationship between the proton and the phosphine gold(I) cation $\{(Ph_3P)Au\}^+$ and many have suggested that the ${(Ph_3P)Au}^+$ unit could replace a proton in cluster compounds.^{6,7} A detailed analysis based on extended-Hückel MO calculations of the energies and forms of the frontier orbitals of the $\{(H_3P)Au\}^+$ -unit has suggested that the energies of the gold hybrid $6s/6p_z$ valence orbital and that the $6p_x/6p_y$ orbital pair were well separated and that the empty hybrid $6s/6p_z$ orbital in a {(H₃P)Au}⁺ unit might be expected to behave in a similar manner to the s orbital of [H⁺].⁸ By extension, this would also apply to the $\{(R_3P)Au\}^+$ unit. This rationale has been used to explain certain structural similarities in carbaboranes and their gold derivatives: one example is the *endo*-positionings of

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the open-face twelfth hydrogen atom in the $[nido-7, 8-C_2B_9H_{12}]^$ dicarbaborane anion and the {(Ph₃P)Au} unit in the [10-endo- $\{(Ph_3P)Au\}$ -nido-7,8-C₂B₉H₁₁]⁻ anion 3 [diagram I, where X = H or $\{(Ph_3P)Au\}^{9}$ and a second is the μ_2 bridging position of a hydrogen atom in $[10,11-\mu$ -H-9-SMe₂-nido-7,8-C₂B₉H₁₀]¹⁰ and the $\{(Ph_3P)Au\}$ unit in $[10,11-\mu-(Ph_3PAu)-9-SMe_2-nido-7,8-C_2B_9H_{10}]$ 4 [diagram II, where X = H or {(Ph₃P)Au}].¹¹ However, a closer scrutiny of the bonding in [10-endo-(Ph₃PAu)-nido-7,8-C₂B₉H₁₁]⁻ **3** shows that the {(Ph₃P)Au} unit is not simply η^1 -bound since there are also significant interactions with the two flanking boron atoms, so that it is perhaps better described as η^3 -bonded with one short Au–B interaction of 2.222(9) Å and two longer interactions of 2.486(9) and 2.528(9) Å (diagram III).9



From these considerations, it is evident that the gold-to-ligand hapticity of gold carbaborane complexes such as 3 and 4 can be regarded as between one and three. An η^3 -bonded gold atom also exists in gold cyclopentadienyl complexes, for example in $[{(Ph_3P)Au}C_5Ph_4H]$, where the gold atom is bonded to the cyclopentadienyl ring by one shorter connectivity of 2.15(1) Å and two longer ones of 2.67(1) and 2.76(1) Å.12 These observations contrast with the bonding in related copper compounds, for example as in [{ $(Ph_3P)Cu$ } C_5H_5], where the { $(Ph_3P)Cu$ } unit is symmetrically η^5 -bound,¹³ and as in cupracarbaborane compounds that have been described as belonging to the twelvevertex *closo* structural group with the copper atoms η^5 -bonded, for example in the $[3-(Ph_3P)-closo-3,1,2-CuC_2B_9H_{11}]^-$ anion¹⁴ and in

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the neutral compound [3-(Ph₃P)-4-SMe₂-*closo*-3,1,2-CuC₂B₉H₁₀].⁷ Pentahapto bonding is also seen in copper heteroboranes with arsenic or tellurium heteroatoms, for example as in [3-(Ph₃P)-8-{*iso*PrOEt}-*closo*-3,1,2-CuAs₂B₉H₈].¹⁵ In the present work we thought it of interest to explore the possibility of synthesising a *closo* gold heteroborane compound with a hapticity greater than three. Accordingly, we chose ligands with heteroatoms other than carbon which, on grounds of atomic orbital size and energy compatibility, may be more conducive to the formation of more than three interactions with a gold-based fragment and thus afford compounds with higher hapticity in the gold-to-heteroborane bonding. The "softer" ligands that we chose were derived from the [*nido*-7,8-As₂B₉H₁₀]⁻ and [*nido*-7-TeB₁₀H₁₀]⁻ anions.

Results and discussion

Synthesis and characterisation of phosphine gold acetylides 1 and 2

Both [(R₃P)AuC=CC(Me)(OH)Et] compounds, where R = Ph 1 or cyclohexyl (Cy) 2, were synthesised by the reaction between a suspension of [AuC=CC(Me)(OH)Et] in toluene and a toluene solution of R₃P.¹⁶ Yields of 1 and 2 from the gold acetylide were 79% and 75% respectively and the values of ν_{max} (C=C) for 1 and 2 were 2134 and 2120 cm⁻¹ respectively. The solid-state structure of 2 was confirmed by single-crystal X-ray analysis.

Molecular structure of $[(Cy_3P)AuC \equiv CC(Me)(OH)Et] 2$

The X-ray analysis showed that there is one molecule in the asymmetric unit. There is no bonding interaction between adjacent molecules and hence $[(Cy_3P)AuC \equiv CC(Me)(OH)Et]$ **2** is an example of a simple monomeric gold acetylide with the acetylide ligand end-on σ -bonded to the gold atom, Fig. 1. It became clear during the structural analysis that several atoms were disordered: one of the cyclohexyl rings was disordered unequally over two orientations [A and B with occupancies 0.356(13) and 0.644(13) respectively] and the five carbon atoms of the 3-hydroxy-3-methyl-1-pentyne moiety were also disordered over two sites with occupancies 0.36(2) and 0.64(2), essentially identical to those of the disordered cyclohexane ring. Important bond distances and angles for the predominant molecule are given in the legend to Fig. 1.

The P–Au–C≡C–C chain is essentially linear with P–Au–C 176.7(3)°, Au–C–C 173(5)° and C≡C–C 177(7)°, this is similar to $[(Ph_3P)AuC≡CPh]$ where P–Au–C 173.5(5)°, Au–C≡C 175.7(16)° and C≡C–C 176.5(18)° were reported.¹⁷ The Au–P distance is typical at 2.274(3) Å. It is identical to that reported for $[(Ph_3P)AuC≡CC_6F_5]$,¹⁸ and similar to the values of 2.276(5) and 2.282(4) Å reported for the two independent molecules in the unit cell of $[(Ph_3P)AuC≡CPh]$.¹⁷ The Au–C distance of 2.005(8) Å is close to the two Au–C distances of 1.994(6) and 2.006(6) Å reported for the anion $[Au(C≡CCH_2OH)_2]^{-19}$ The C(1)–C(2) acetylide bond distance is 1.199(5) Å, which is similar to the values of 1.197(16) Å reported for neutral $[(Ph_3P)AuC≡CC_6F_5]$ and 1.206(6) Å and 1.189(6) Å observed in the $[Au(C≡CCH_2OH)_2]^{-19}$



Fig. 1 ORTEP plot of $[(Cy_3P)AuC≡CC(Me)(OH)Et]$ **2**, showing the numbering scheme. Only one of the two orientations of the disordered groups are shown. Ellipsoids are at the 30% probability level. Selected interatomic distances (Å) and angles (°): Au(1)–P(1) 2.274(3), Au(1)–C(1) 2.005(8), C(1)–C(2) 1.199(5), C(2)–C(3) 1.467(12); P(1)–Au(1)–C(1) 176.7(3), Au(1)–P(1)–C(11A) 109.6(11), Au(1)–P(1)–C(21) 113.2(3), Au(1)–P(1)–C(31) 110.3(3), Au(1)–C(1)–C(2) 173(5), C(1)–C(2)–C(3) 177(7).

Synthesis and characterisation of the gold heteroborane compounds [Me₄N] [3-(PR₃)-*closo*-3,1,2-AuAs₂B₉H₉], where R = Ph 5 or Cy 6, and [Et₄N][3-(R₃P)-*closo*-2,1-AuTeB₁₀H₁₀], where R = Ph 7 or Cy 8

These compounds were synthesised from the reaction between the corresponding phosphine gold acetylide and heteroborane anion in an ethanol-acetone 1 : 1 mixture heated at reflux temperature. Yields of the pale yellow products were low, at *ca.* 20% for 7, or moderate, at *ca.* 35% for 5, 6 and 8. Initial characterisation by elemental analysis and FT-IR spectroscopy supported the compound formulations. Further characterisation was obtained from solution-phase NMR spectroscopy and, for compounds 5 and 7, from single-crystal X-ray crystallography.

Molecular structures of $[Me_4N][3-(Ph_3P)-closo-3,1,2-AuAs_2B_9H_9]$ 5 and $[Et_4N][2-(Ph_3P)-closo-2,1-AuTeB_{10}H_{10}]$ 7

The X-ray diffraction study of $[Me_4N][3-(Ph_3P)-3,1,2-closo-AuAs_2B_9H_9]$ **5** shows the gold-to-heteroborane ligand bonding mode as pentahapto, Fig. 2; see also diagram IV. Thus, the gold atom in **5** does not behave as an *endo*-bonded moiety as in the isoelectronic carbaborane cluster $[10-endo-\{(Ph_3P)Au\}-nido-7,8-C_2B_9H_{11}]^-$ **3**, see diagram I. The geometrical and bonding considerations leading to these conclusions are summarised in the following paragraphs, with relevant and other important structural data listed in the legend of Fig. 2.



Fig. 2 ORTEP plot of the anion in $[Me_4N][3-(Ph_3P)-closo-3,1,2-AuAs_2B_9H_9]$ 5 showing the numbering scheme. Ellipsoids are shown at the 30% probability level. Selected interatomic distances (Å) and angles (°): Au(3)–P(1) 2.2459(16), Au(3)–B/As(8) 2.378(5), Au(3)–B/As(7) 2.506(3), Au(3)–B/As(4) 2.537(2), Au(3)–As/B(2) 2.6975(12), Au(3)–As/B(1) 2.7094(12), As/B(1)–As/B(2) 2.4611(15), As/B(1)–B/As(4) 2.383(2), As/B(2)–B/As(7) 2.296(4), B/As(4)–B/As(8) 2.173(5), B/As(7)–B/As(8) 2.108(7), P(1)–Au(3)–B/As(8) 139.14(15), P(1)–Au(3)–B/As(7) 132.79(11), P(1)–Au(3)–B/As(4) 131.07(7), P(1)–Au(3)–As/B(2) 125.37(5), P(1)–Au(3)–As/B(1) 126.02(5).

The structural analysis showed that the two arsenic atoms of the {AuAs₂B₉H₉} cage were disordered unequally over all five sites of the $\{As_2B_3\}$ face bonded to the gold atom. There were two major arsenic sites and three minor ones. The discussion below is with reference to the major atom types. Atom disorder in metallaheteroborane structures is a common phenomenon. A similar but less significant disorder to that in 5 was observed in [3,3- $(PMe_2Ph)_2$ -closo-3,1,2-PtAs₂B₉H₉].²⁰ The Au–As(1) and Au–As(2) distances in 5 are slightly different at 2.7094(12) Å and 2.6975(12) Å respectively, but in view of the disorder this difference may not be significant. Previously reported two centre-two electron goldarsenic distances are 2.342(5) Å in [(Ph₃As)AuBr], 2.334(3) and 2.331(1) Å in two crystalline forms of [(Ph₃As)AuCl] and 2.386(1) Å in [2-NO₂C₆H₄AuAsPh₃].²¹⁻²³ The gold–arsenic distance for a two-centre two-electron bond can be estimated using Pauling's radii as 2.40 Å. However, comparison of second- and third-row transition-element-to-arsenic distances in non-cluster compounds versus cluster compounds shows that the distances in clusters are longer by 0.2 to 0.3 Å. Hence, gold-arsenic distances in 5 may be expected to be in the region of 2.6 to 2.7 Å. The derived average Au–As distance of 2.703 Å in 5 is at the high end of this range even though the occupancy of the As(1) or As(2) sites are 82.5% and 70.6% respectively which might be expected to lead to a shortening of the Au-As bonds due to the involvement of gold-to-boron contributions.

The gold-to-B/As distances in the predominantly boronoccupied sites 4,7 and 8, *i.e.* Au–B(4) 2.537(2), Au–B(7) 2.506(3) Å and Au–B(8) 2.378(5) Å, may be compared with the Au–B(10) 2.222(9), Au–B(9) 2.528(9) and Au–B(11) 2.486(9) Å distances in the η^3 -gold compound [10-*endo*-{(Ph₃P)Au}-*nido*-7,8-C₂B₉H₁₁]⁻ **3** (diagram III)⁹ and the distances Au–B(10) 2.233(6) and Au–B(11) 2.357(6) Å in the μ_2 -bridged [10,11- μ -{(Ph₃P)Au}-9-SMe₂-*nido*-7,8-C₂B₉H₁₀] species **4** (diagram II).¹¹ Thus the Au–B(8) distance in **5** lies between the shortest and longest distances in **3** and **4** as might be expected if the gold atom in **5** significantly interacts in a bonding manner with all the boron atoms on the {As₂B₃} face of the arsenaborane ligand and gold atom hapticity thereby increases above three.



Overall, the cage of 5 may be best described as a twelvevertex *closo*-type structure of $\{AuAs_2B_9\}$ atoms (diagram IV) and not as either an η^1 -bonded gold, diagram V, or η^3 -bonded gold cluster, diagram VI. Using Wade's rules,²⁴ the structure of 5 can be interpreted in terms of a formally anionic $\{(Ph_3P)Au\}^-$ unit acting as two-electron three-orbital cluster vertex affording an electron count of 26 cluster electrons which is expected for a twelve-vertex closo cage. An alternative description of 5 with a formally cationic {(Ph₃P)Au}⁺ unit as a zero-electrons one-orbital unit "bridging" the open face of an anionic ${nido-As_2B_9H_9}^{2-}$ cluster is not as satisfactory, bearing in mind the interatomic dimensions discussed above in comparison to the structures of compounds 3 and 4 (diagrams I and II). Thus, it appears that in 5 the gold atom uses not only one of its $6s/6p_z$ hybrid orbital, but also both its $6p_x$ and $6p_v$ orbitals, in cluster bonding to the "soft" heteroborane $\{As_2B_9\}$ ligand. Compound 5 is, on this basis, the first gold heteroborane reported to contain a pentahapto gold atom.

The As(1)–As(2) distance in **5** is 2.4611(15) Å. This is similar to the As–As distances reported in the structure of $[As_2B_{10}H_8I_2]^{25}$ of 2.435(2) and 2.421(2) Å and in $[3,3-(PMe_2Ph)_2-closo-3,1,2-PtAs_2B_9H_9]$ of 2.497(3) Å.²⁰ Other interatomic distances in the cage and in the {(Ph₃P)Au} unit are not unusual. The P–Au–B angles in **5** are P(1)–Au(3)–B(4) 131.07(7)°, P(1)–Au(3)–B(8) 139.14(15)° and P(1)–Au(3)–B(7) 132.79(11)°. These are similar to the P–Cu–B angles in the η^5 -bonded compound $[3-(Ph_3P)-8-\{iso-PrOEt\}-closo-3,1,2-CuAs_2B_9H_8]$,¹⁵ which range from 134.0(2)° to 131.9(2)°, but they are significantly smaller than the B–Au–P angles of 166.80(15)° and 144.99(15)° reported for the η^3 -bonded anionic compound $[10-endo-\{(R_3P)Au\}-nido-7,8-C_2B_9H_{11}]^-$ **3**.⁹ A decrease in the P–Au–B angle in **5** is expected if the {(R₃P)Au} unit has become η^5 -bonded.

The analysis of the single-crystal X-ray diffraction data from the gold telluraborane compound $[Et_4N][2-Ph_3P-closo-2,1-AuTeB_{10}H_{10}]$ 7, revealed that it had a *closo* twelve-vertex {AuTeB_{10}} geometry (Fig. 3 and diagram VII). There are two independent anion/cation pairs in the asymmetric unit and it was apparent from electron-density maps that in each anion the tellurium atom was disordered over different sites in the {TeB_4} ring adjacent to gold. In one anion the refinement showed that the tellurium atom was disordered over three sites [Te(1), Te(3), Te(7), with



Fig. 3 ORTEP plot of the one of the anions in $[Et_4N][2-(Ph_3P)-closo-2,1-AuTeB_{10}H_{10}]$ 7 showing the numbering scheme. The crystallographic analysis shows that the tellurium atom is disordered over three sites Te(1) Te(3)/B(3) and Te(7)/(B7). Ellipsoids are shown at the 30% probability level. Selected interatomic distances (Å) and angles (°): Au(2)–Te(1) 2.839(3), Au(2)–P(1) 2.237(6) Å. The corresponding values in the other anion are 2.853(3) and 2.263(6) Å. The Au–(minor-Te)/B distance in both anions is 2.294(12)–2.825(13) Å. For the major Te components the Te–B range is 2.28(5)–2.36(3) Å.

occupancies 0.911, 0.028, 0.061 respectively], while in the other only two sites were affected [Te(21) and Te(27), with occupancies 0.956(3) and 0.044(2) respectively]. The two anions showed only small differences in the orientation of the gold phosphine unit over the {TeB₄} face to which it is bonded. A view of the anion with the tellurium atom disordered over three sites is shown in Fig. 3.

The tellurium disorder affects the various tellurium–boron and Te/B–boron distances; ranges are given in the legend to Fig. 3. There have been no reported structural characterisations of gold telluraboranes but the gold–tellurium distances of 2.839(3) and 2.853(3) Å in the major anion components of **7** are very long when compared with the reported gold–tellurium distance of 2.566(1) Å in [(Ph₃P)AuTeC(SiMe₃)₃].²⁶ The gold–phosphorus distances of 2.237(6) and 2.263(6) Å for the two major components of **7** are similar to reported values for such distances in other cluster compounds in which gold is bound to the open face of a *nido*-shaped eleven-vertex residue, for example 2.249(2) Å in the [10-*endo*-{(Ph₃P)Au}*-nido*-7,8-C₂B₉H₁₁]⁻ anion **3** and 2.2461(19) Å in the [3-(PPh₃)-*closo*-3,1,2-AuAs₂B₉H₉]⁻ anion of **5**.

NMR spectroscopy

The ¹¹B, ¹¹B-{¹H} and ³¹P NMR spectra of compounds $[Me_4N][3-(PPh_3)-closo-3,1,2-AuAs_2B_9H_9]$ **5**, $[Me_4N][3-(Cy_3P)-closo-3,1,2-AuAs_2B_9H_9]$ **6** and $[Et_4N][2-(Ph_3P)-closo-2,1-AuTeB_{10}H_{10}]$ **7** were recorded. The ¹¹B and ¹H resonances in the spectra of **5** and **6** were tentatively assigned on the basis of relative intensities and comparisons with linewidth and general shielding behaviour with

those of the related and previously reported *closo*-type species $[3,3-(R_3P)_2-closo-3,1,2-MAs_2B_9H_9]$, where $R_3 = Ph_3$ or $PhMe_2$ and M = Pd or Pt.²⁰ The relative intensity patterns in the ¹¹B spectra were 2:2:1:1:1:2. Whereas most of the ¹¹B resonances are in the region $\delta(^{11}B)$ 0–20 ppm, characteristic of *closo*-type twelve-vertex species, the B(8) and B(10) positions in 5, which are those respectively in adjacent and antipodal positions relative to the metal site, are significantly less deshielded than in the corresponding positions in the equivalent palladium and platinum species [3,3-(R₃P)₂-closo-3,1,2-MAs₂B₉H₉].^{20,27} Other differences in ¹¹B data between the analogous gold and platinum compounds are minor in terms of overall 11B shielding ranges. The adjacent and antipodal positions are known to be most affected by a change in character of the metal centre at the 3 position in closo-3,1,2 metalladiheteroboranes.²⁸ The overall ¹¹B-{¹H} spectrum of 5 is quite similar to that of the $[nido-7, 8-As_2B_9H_{10}]^-$ anion which might be taken to indicate that the structure of 5 in solution is nido, *i.e.* with the gold phosphine unit in an η^3 -bonding mode as in diagram III above. However, the use of the polar solvent, CD₃CN which was necessary for adequate solubility, may have caused the dislocation of the solid-state η^5 -bonding mode of 5 to give a lesscoordinated bonding mode in solution. Therefore, based on the current NMR data it is not possible to say with any certainty that, in solution, the gold atom is part of a closo twelve-vertex cluster or that the connectivity between the $\{As_2B_9\}$ cluster fragment and the gold centre can be better described as either monohapto to B(8)(diagram V) or trihapto to B(8), B(4) and B(7) (diagram VI). The NMR spectra of the PCy₃ gold arsenaborane, 6, are very similar to those of the PPh₃ species 5, indicating that the overall solution behaviour and geometry of these complexes are essentially the same.

In Part 9 of this series of papers the discussion of the NMR properties of the closely related palladium and platinum analogues $[3,3-(PhMe_2P)_2-closo-3,1,2-MAs_2B_9H_9]$, where M = Pd or Pt, noted that the compounds showed fluxional behaviour in solution.²⁰ The isoelectronic platinacarbaborane [3,3-(PhMe₂P)₂closo-3,1,2-PtC₂B₉H₁₁] was likewise fluxional: based on evidence from an X-ray analysis, in which two different rotamer "snapshot" structures were observed, it was concluded that the fluxionality involved a process of rotation of the $\{(PhMe_2P)_2Pt\}$ unit above the $\{C_2B_3\}$ face of the *nido*-shaped eleven-vertex $\{C_2B_9H_{11}\}$ unit, involving in turn a sequence of changing coordination modes between the Pt atom and the $\{C_2B_3\}$ face from pentahapto to tetrahapto, and then back to pentahapto, and so on.27 While it is possible that the $\{(R_3P)Au\}$ units in 5 and 6 are similarly fluxional above the As₂B₉-cage in solution in the same sense as the platinum-based units were above both $\{As_2B_9H_9\}$ and $\{C_2B_9H_{11}\}$ ligands, this could not be probed in the present study because the single R₃P phosphine ligands used did not provide a distinguishing spectroscopic "tag", whereas, in the platinum species, the incidence of two non-radially bound PMe₂Ph ligands engendered the necessary prochiral features in the ¹H spectrum.^{21,28}

The proton and boron NMR spectra of $[Et_4N][2-(Ph_3P)-closo-2,1-AuTeB_{10}H_{10}]$ 7 are not inconsistent with the *closo* molecular structure as determined by single-crystal X-ray analysis (Fig. 3 and diagram VII). The compound shows a 1:2:2:2:2:1 relative intensity pattern in the ¹¹B NMR spectrum. The ¹H resonances were assigned to their directly bound boron atoms by ¹H-{¹¹B selective} decoupling experiments and the assignment of the

boron resonances to the corresponding boron positions was made by comparison with previously assigned spectra of *closo* cupratelluraboranes.¹⁵ The resonance (broad) at δ (¹¹B) -11.2 ppm is assigned to the boron atoms directly adjacent to the tellurium atom, *i.e.* B(3) and B(6). Similar comments can be made about the spectrum of **7** to those made above for the related arsenaborane compounds **5** and **6**. Therefore it is not possible to conclude definitively that the structure of the gold telluraborane persists as *closo* with essentially pentahapto coordination in solution.

Conclusions

The successful solution and refinement of the molecular structures of [Me₄N][3-(PPh₃)-closo-3,1,2-AuAs₂B₉H₉] 5 and [Et₄N][2- (Ph_3P) -closo-2,1-AuTeB₁₀H₁₀] 7 showed that both compounds have *closo* twelve-vertex geometries based on the icosahedron, distorted from the regular as exhibited by the $[B_{12}H_{12}]^{2-}$ anion by the accommodation of the disparately sized heteroatoms. Both compounds appear to exhibit pentahapto gold-to-heteroborane coordination and therefore they are the first gold pentahaptoheteroborane species to be reported. Previously reported gold carbaborane compounds had gold-to-heteroborane dihapto or trihapto bonding interactions. Therefore, by the selection of "softer" ligands, namely the $\{As_2B_9H_9\}$ and $\{TeB_{10}H_{10}\}$ fragments, the possibility of synthesising gold heteroborane compounds with gold hapticity greater than three has been realised. It could perhaps be argued that the disorder in the crystals of 5 and 7 makes the evidence for the confirmation pentahapto coordination of the gold atom somewhat ambiguous. In this context, however, it is noteworthy that, in the crystals of the unambiguously pentahaptoconfigured closo platinacarbaborane, [3,3-(PhMe₂P)₂-closo-3,1,2- $PtC_2B_9H_{11}$, there were two distinctly different conformers in the asymmetric unit, and also that, in the diarsenic analogue [3,3-(Ph₃P)₂-closo-3,1,2-PtAs₂B₉H₉], which is also described unambiguously as pentahapto, one of the arsenic atoms was disordered over two sites.

Experimental

General

The compounds $[Me_4N]$ [nido-7,8-As₂B₉H₁₀] 9 and $[Et_4N]$ [nido-7,8-TeB₁₀H₁₁] 10 were prepared according to literature methods.^{29,30} The acetylene, $HC \equiv CC(Me)(OH)Et$, and phosphines, Ph_3P and Cy₃P, were used as purchased from the Aldrich Chemical Co. Ltd. The gold reagent H[AuCl₄]·2H₂O was generously supplied by Johnson Matthey Plc. The phosphine gold acetylides were prepared as described previously.16 NMR spectroscopy was performed at ca. 5.9 T and 9.4 T (fields corresponding to nominal 250 and 400 MHz ¹H frequencies respectively) using commercially available instrumentation and using techniques and procedures as adequately described and enunciated elsewhere.³¹⁻³³ Spectra were recorded for solutions in CD₃CN, and at 294–297 K unless otherwise indicated. Chemical shifts δ are given in ppm relative to $\Xi = 100$ MHz for $\delta({}^{1}\text{H})$ (± 0.05 ppm) (nominally TMS), $\Xi = 32.083972$ MHz for $\delta(^{11}B)$ (±0.5 ppm) (nominally Et₂OBF₃) in CDCl₃)³¹ and $\Xi = 40.480730$ MHz for $\delta v({}^{31}P)$ (±0.5 ppm) (nominally 85% aqueous H₃PO₄). Ξ is as defined by McFarlane.³⁴

Synthesis of [Me₄N][3-(PPh₃)-closo-3,1,2-AuAs₂B₉H₉] 5. To a suspension of [Me₄N][nido-7,8-As₂B₉H₁₀] 9 (0.0957 g, 0.289 mmol) in a 1 : 1 EtOH-acetone mixture (70 ml) was added $[(Ph_3P)AuC \equiv CC(Me)(OH)Et]$ 1, (0.161 g, 0.289 mmol). The mixture was heated at reflux for 2.5 h during which time a pale yellow colour developed. The reaction solution was filtered and the solvent removed from the filtrate under reduced pressure (50 °C). Crystallisation from CH₂Cl₂-hexane afforded pale yellow microcrystals of [Me₄N][3-(Ph₃P)-closo-3,1,2-AuAs₂B₉H₉] 5 (0.085 g, 37.3%). C₂₂H₃₆As₂AuB₉NP requires C, 33.5; H, 4.6; N, 1.8; found: C, 33.4; H, 4.6; N, 1.6%. IR: v_{max} (KBr) 2563(w), 2531(sh), 2505(s), 2488(vs), 2474(s), 2440(sh) (BH) cm⁻¹. Cluster NMR data, ordered as $\delta({}^{11}\text{B})/\text{assignment}/[\delta({}^{1}\text{H}) \text{ of directly attached H(exo) atom}]$: -3.6, B(9,12) [+2.80]; -3.6, B(4,7) [+1.65]; -7.2, B(6) [+2.20]; -12.1, B(8) [+3.45]; -16.1, B(10) [+4.27]; -18.7, B(5,11) [+2.32]. ³¹P NMR (CD₃CN, 243 K): δ +39.1.

Synthesis of [Me₄N][3-(Cy₃P)-closo-3,1,2-AuAs₂B₉H₉] 6. To a suspension of $[Me_4N][nido-7,8-As_2B_9H_{10}]$ 9, (0.11 g, 0.332 mmol) in a 1 : 1 EtOH-acetone mixture (70 ml) was added $[(Cy_3P)AuC \equiv CC(Me)(OH)Et]$ 2, (0.191 g, 0.332 mmol). The mixture was heated at reflux for 2.5 h during which time a pale yellow colour developed. The reaction solution was filtered and the solvent removed from the filtrate under reduced pressure (50 $^{\circ}$ C). Crystallisation from CH2Cl2-hexane afforded pale yellow microcrystals of [Me₄N][3-(Cy₃P)-closo-3,1,2-AuAs₂B₉H₉] 6 (0.094 g, 35.2%). C₂₂H₅₄As₂AuB₉NP requires C, 32.7; H, 6.7; N, 1.7; found: C, 33.4; H, 4.6; N, 1.6%. IR: v_{max} (KBr) 2561(w), 2547(sh), 2521(vs), 2513(vs), 2487(s), 2434(sh) (BH) cm⁻¹. Cluster NMR data, ordered as $\delta(^{11}B)/assignment/[\delta(^{1}H)]$ of directly attached H(exo) atom]: -4.1(9,12)[+1.51]; -4.1, B(4,7)[+2.64]; -8.0, B(6)[+1.88]; -11.2, B(8) [+3.38]; -17.9, B(10) [+4.04]; -18.7, B(5,11) [+2.19]. ³¹P NMR (CD₃CN, 243 K): δ +58.6.

Synthesis of $[Et_4N][2-(Ph_3P)-closo-2,1-AuTeB_{10}H_{10}]$ 7. To a suspension of [Et₄N][nido-7,8-TeB₁₀H₁₁] 10 (0.094 g, 0.25 mmol) in a 1 : 1 EtOH-acetone mixture (70 ml) was added [(Ph₃P)AuC=CC(Me)(OH)Et] 1 (0.139 g, 0.25 mmol). The mixture was heated at reflux for 4 h during which time a pale yellow colour developed. The reaction solution was cooled to room temperature, filtered and the solvent removed from the filtrate (rotary evaporator, 50 °C). The residue was crystallised from CH₂Cl₂ to yield yellow-green crystals of [Et₄N][2-(Ph₃P)closo-2,1-AuTeB₁₀H₁₀] 7 (0.042 g, 20%). Found: C, 37.7; H, 5.5; N, 2.15; C₂₆H₄₄TeAuB₁₀PN requires C, 37.4; H, 5.4; N, 1.7%. IR: v_{max} (KBr) 2549(s), 2541(s), 2526(s), 2501(vs), 2488(vs), 2478(vs), 2413(s) (BH) cm⁻¹. Cluster NMR data, ordered as δ ⁽¹¹B)/assignment/[δ ⁽¹H) of directly attached H(exo) atom]: +2.2, B(12) [+4.10]; -7.7, B(4,5) [+2.24]; -11.2, B(3,6) [+1.25]; -17.9, B(7,11) [+2.82]; -18.2, B(8,10) [+1.69]; -18.7, B(9) [+3.76]. ³¹P NMR (CD₃CN, 243 K): δ +38.7.

Synthesis of $[Et_4N][2-(Cy_3P)-closo-2,1-AuTeB_{10}H_{10}]$ 8. To a suspension of $[Et_4N][nido-7,8-TeB_{10}H_{11}]$ 10 (0.106 g, 0.28 mmol) in a 1 : 1 EtOH–acetone mixture (70 ml) was added $[(Cy_3P)AuC \equiv CC(Me)(OH)Et]$ 2 (0.1535 g, 0.27 mmol). The mixture was heated at reflux for 4 h during which time a pale yellow colour developed. The reaction solution was cooled to room temperature, filtered and the solvent removed from the filtrate (rotary evaporator, 50 °C). The residue was crystallised from

 $\begin{array}{l} CH_2Cl_2-hexane \ to \ yield \ yellow-green \ crystals \ of \ [Et_4N][2-(Cy_3P)-closo-2,1-AuTeB_{10}H_{10}] \ \textbf{8}, \ (0.037 \ g, \ 37.3\%). \ C_{26}H_{62}TeAuB_{10}PN \ requires \ C, \ 36.55; \ H, \ 7.55; \ N, \ 1.6; \ found: \ C, \ 36.4; \ H, \ 7.6; \ N, \ 1.6\%. \ IR: \ \nu_{max} \ (KBr) \ 2559(s), \ 2519(s), \ 2503(vs), \ 2497(vs) \ (BH) \ cm^{-1}. \end{array}$

X-Ray crystallographic studies

X-Ray analysis of $[(Cy_3P)AuC \equiv CC(Me)(OH)Et] 2$.

Crystal Data. C₂₄H₄₂AuPO, M = 574.51, triclinic, $P\overline{1}$, a = 9.8012(11), b = 11.2980(18), c = 12.587(2) Å, a = 110.808(16), $\beta = 106.498(15)$, $\gamma = 92.064(15)^{\circ}$, Z = 2, $D_x = 1.546$ g cm⁻³, V = 1234.6(4) Å³, F(000) = 576, $\mu = 6.033$ mm⁻¹, λ (Mo-K_a) = 0.71073 Å. Total number of reflections = 4371, $R_F = 0.0524$ based on 2805 data with $[F^2 > 2\sigma(F^2)]$, $R_w = R[wR(F^2)] = 0.1293$ for 4371 data.

Crystals suitable for investigation were grown by slow evaporation of an acetone solution of $[(Cy_3P)AuC \equiv CC(Me)(OH)Et]$ 2. It became clear during the structural analysis that several atoms were disordered with one of the cyclohexyl rings disordered over two unequal sites and the five C atoms of the 3-hydroxy-3-methyl-1pentyne moiety disordered over two sites. However, it was possible to model the disorder successfully using DFIX restraints with SHELXL97.³⁵

X-Ray analysis of [Me₄N][3-(Ph₃P)-closo-3,1,2-AuAs₂B₉H₉] 5.

Crystal Data. C₂₃H₃₈As₂AuB₉C₁₂NP, M = 874.58, triclinic, $P\overline{1}$, a = 9.564(3), b = 9.882(3), c = 18.937(3) Å, a = 102.84(2), $\beta = 93.69(2)$, $\gamma = 101.08(2)^{\circ}$, Z = 2, $D_x 1.707$ g cm⁻³, V = 1701.8(7)Å³, F(000) = 844.1, $\mu = 6.474$ mm⁻¹, λ (Mo-K_a) = 0.71073 Å. Total number of reflections = 7389, $R_{\rm F} = 0.0464$ based on 4502 data with $[F^2 > 2\sigma(F^2)]$, $R_w = R[wR(F^2)] = 0.1037$ for 7389 data.

Crystals suitable for study were grown by diffusion of hexane into CH_2Cl_2 solutions of 5. The structure analysis showed that the two arsenic atoms of the $\{AuAs_2B_9H_9\}$ cage were disordered unequally over all five sites of the $\{As_2B_3\}$ face bonded to the gold atom. There were two major arsenic sites and three minor ones. For the final refinement with the SHELXL97 programme,³⁵ each disordered site was allowed for as an As/B mixture with the occupancies restrained so that the sum of the arsenic occupancies added to 2 and the boron atoms to 3. At each site the boron occupancy was arranged to have a value $\{1 - (\text{occupancy of As})\}$. The final arsenic occupancies (with labels according to position in Fig. 2) are: (1) 0.825(3), (2) 0.706(3), (4) 0.263(3), (7) 0.135(3), (8) 0.072(3). In Fig. 2 the atom labels of these disordered atoms are given as As(1), As(2), B(4), B(7) and B(8) but in the figure legend the atoms are given as As/B labels with the predominant atom type first.

X-Ray analysis of [Et₄N][2-(Ph₃P)-closo-2,1-AuTeB₁₀H₁₀] 7.

Crystal Data. C₂₆H₄₅TeAuB₁₀NP, M = 835.27, orthorhombic, *Pna2*₁, a = 20.705(3), b = 8.6844(9), c = 37.396(3) Å, $a = \beta = \gamma = 90^{\circ}$, Z = 8, $D_x = 1.650$ g cm⁻³, V = 6724.2(13) Å³, F(000) = 3232, $\mu = 5.292$ mm⁻¹, $\lambda = (Mo-Ka) = 0$. 71073 Å. Total number of reflections = 7421, $R_F = 0.0499$ based on 3744 data with $[F^2 > 2\sigma(F^2)]$, $R_w = R[wR(F^2)] = 0.1128$ for 7421 data.

Crystals suitable for study were grown by diffusion of hexane into CH_2Cl_2 solutions of 7. The compound crystallised in the orthorhombic system; space groups $Pna2_1$ or Pnam allowed from the systematic absences. Structure solution was only possible in $Pna2_1$ with two independent anions and two independent [Et₄N]⁺ cations in the asymmetric unit. It soon became apparent from electron-density peak heights and numerous subsequent refinement trials that in each case there was some B/Te interchange at the {TeB₄} face bonded to the gold atom. In one anion the tellurium atom was disordered unequally over three sites; in the other it was disordered unequally over two sites. For the final refinement with the SHELXL97 programme,³⁵ each disordered site was allowed for as a Te/B mixture with the occupancies restrained so that the sum of the tellurium occupancies added to 1. At each disordered site the boron occupancy was set at {1 – (occupancy of Te)}. Because of the disorder, all the B atoms were only refined isotropically with an overall Uiso value. The disorder may very well affect the crystal packing and several phenyl C atoms have prolate ellipsoids. H-atom coordinates were generated geometrically and treated as riding atoms (C–H 0.93 to 0.97, B–H 1.10 Å).

CCDC reference numbers 270401, 270402 and 270403 for compounds **2**, **5** and **7** respectively.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b515165a

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