Bridge-to-vertex Oxidative Slipping in an Auraborane: Synthesis and Characterisation of $[(B_{10}H_{12})Au(B_{10}H_{13})]^{2-}$ and $[(B_{10}H_{12})Au(B_{10}H_{12})]^{-}$

Andrew J. Wynd and Alan J. Welch*

Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ, U.K.

The new auraboranes $[(B_{10}H_{12})Au(B_{10}H_{13})]^{2-}$ and $[(B_{10}H_{12})Au(B_{10}H_{12})]^{-}$ have been synthesised by the addition of $B_{10}H_{14}$ to a solution of R_3PAuMe (R = cyclo-C_6H_{11} or C_6H_4Me-2), a crystallographic study showing that the geometry of the $\{AuB_{10}H_{13}\}$ fragment of the former is that of an *arachno* fragment of a 13-vertex docosahedron; a mechanism is proposed which involves formal oxidative slipping of a gold atom from a B–Au–B bridge to a polyhedral vertex.

We have previously shown[1] that addition of CH_2Cl_2 to a mixture of Cy_3PAuMe (Cy = cyclo-C_6H_{11}) and $B_{10}H_{14}$, the latter in slight excess, produces the colourless $Cy_3PAuB_{10}H_{13}$ (**1**), in which the $\{Cy_3PAu\}$ fragment simply replaces a μ-H atom in the decaborane framework. We now report that dropwise addition of a CH_2Cl_2 solution of $B_{10}H_{14}$ to a slight excess of R_3PAuMe [**a**; R = Cy, **b**; R = *o*-tol (C_6H_4Me-2),] affords, in addition to (**1**) or its *o*-tol analogue[2] as the major product, small amounts of the bright yellow anions $[(B_{10}H_{12})Au(B_{10}H_{13})]^{2-}$ (**2**) and $[(B_{10}H_{12})Au(B_{10}H_{12})]^{-}$ (**3**), as their $[(R_3P)_2Au]^+$ salts. Compounds (**2a**)·$4CH_2Cl_2$ and (**3b**) have been characterised by *X*-ray diffraction studies at 185 and 273 K respectively.†

The structure of (**3**) is shown in Figure 1. Compound (**3**) is isostructural with the known,[3,4] species $[(B_{10}H_{12})M(B_{10}H_{12})]^{2-}$ (M = Ni, Pd, Pt), having a pseudo-square-planar metal co-ordination geometry [in (**3**) the metal is located on a crystallographic inversion centre]. Although H atoms are not shown in Figure 1, all [including the B(8)–H–B(9) and B(10)–H–B(11) bridge H atoms] have been located and successfully refined. $[(B_{10}H_{12})Au(B_{10}H_{12})]^{-}$ has 96

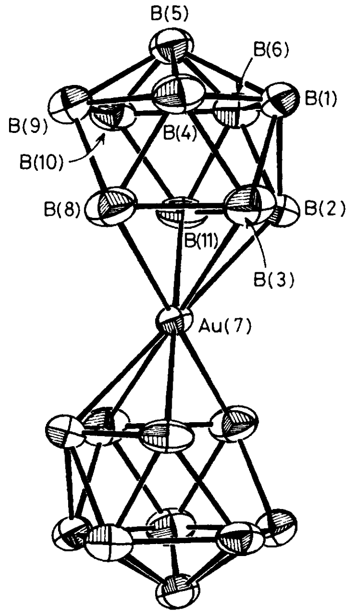

Figure 1. Perspective view of $[(B_{10}H_{12})Au(B_{10}H_{12})]^{-}$ (**3**). Important interatomic distances: Au(7)–B(2) 2.253(9), Au(7)–B(3) 2.275(10), Au(7)–B(8) 2.319(12), and Au(7)–B(11) 2.296(11) Å.

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† *Crystal data:* (**2a**)·$4CH_2Cl_2$, $2[C_{36}H_{66}AuP_2][H_{25}AuB_{20}]\cdot 4CH_2Cl_2$, $M = 2293.8$, triclinic, space group $P\bar{1}$, $a = 12.628(6)$, $b = 15.141(7)$, $c = 15.182(6)$ Å, $\alpha = 70.60(4)$, $\beta = 69.86(3)$, $\gamma = 80.86(4)°$, $U = 2567.3$ Å^3, $Z = 1$, $D_c = 1.483$ g cm^{-3}, $\mu(Mo\text{-}K_\alpha) = 45.8$ cm^{-1}. $R = 0.0480$ for 7874 data measured to $\theta_{max.} = 25°$ on an Enraf-Nonius CAD4 diffractometer. (**3b**) $[C_{44}H_{42}AuP_2][H_{24}AuB_{20}]$, $M = 1243.1$, triclinic, space group $P\bar{1}$, $a = 10.572(3)$, $b = 11.665(3)$, $c = 11.711(3)$ Å, $\alpha = 73.658(20)$, $\beta = 70.360(24)$, $\gamma = 86.680(22)°$, $U = 1304.1$ Å^3, $Z = 1$, $D_c = 1.583$ g cm^{-3}, $\mu(Mo\text{-}K_\alpha) = 57.0$ cm^{-1}. $R = 0.0265$ for 2973 data to $\theta_{max.} = 25°$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

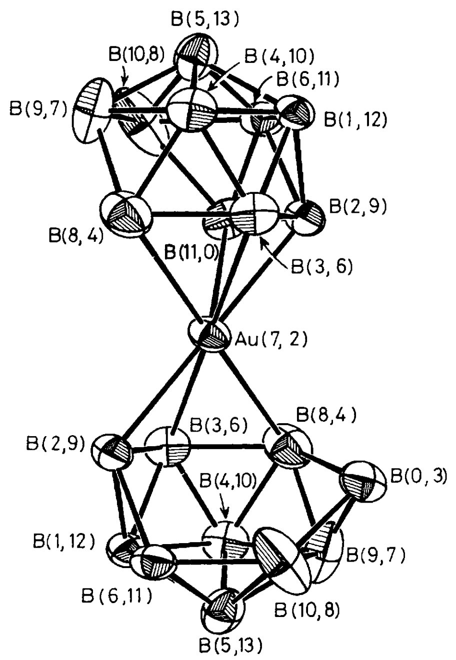
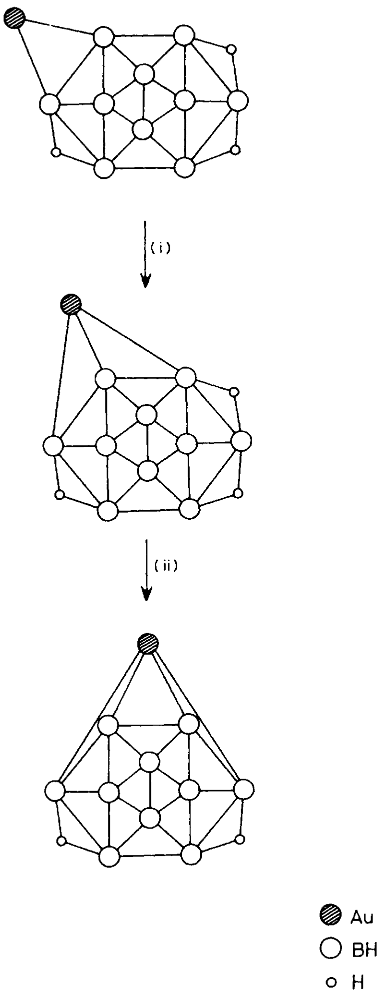


Figure 2. The anion $[(B_{10}H_{12})Au(B_{10}H_{13})]^{2-}$ (**2**). Au(7,2)–B(3,6) 2.231(10), Au(7,2)–B(8,4) 2.447(12), Au(7,2)–B(11,0) 2.499(21), and Au(7,2)–B(2,9) 2.262(10) Å.

valence electrons. This is the correct[5] number for two $\{MB_{10}H_{12}\}$ fragments fused about a common 16 valence electron vertex {compare, for example, $(Me_2PhP)_2Pt(B_{10}H_{12})$ (ref. 6) and $[(B_{10}H_{12})Pt(B_{10}H_{12})]^{2-}$ (refs. 3,4)}, thus implying an effective Au oxidation state in (**3**) of +3.

The structure of the anion of (**2**) (Figure 2) is unprecedented in a metallaborane. It too, is located on a crystallographic inversion centre [at Au(7,2)],‡ a consequence of which is that although the two halves of one ion are chemically different they appear superimposed in the crystallographic study. The mapping of nine B atoms onto their inversion-related equivalents is acceptably good, as evidenced by the refined anisotropic thermal parameters. B(11,0) and B(0,3), however, refine successfully with occupancy factors of 0.5, and their different locations distinguish the two polyhedra present in the ion.

Thus (**2**) consists of $\{AuB_{10}H_{12}\}$ and $\{AuB_{10}H_{13}\}$ fragments fused about a common Au vertex. The former (upper half of Figure 2) has a *nido*-icosahedral geometry with an AuB_4 open face. This sub-unit has previously been found in the 'triple cluster' $(B_{10}H_{12}Au)(AuPEt_3)_4(AuB_{10}H_{12})$[1] and in (**3**), and appears to be a thermodynamically stable entity. The $\{AuB_{10}H_{13}\}$ fragment in (**2**) is, in contrast, structurally based on (and is numbered in accordance with) an *arachno*-fragment derived from a closed 13-vertex C_{2v} polyhedron[7] by removal of vertices 1 and 5. This is the first time such a metallaborane fragment has been structurally characterised, although the geometry of the cage in $(Ph_3P)Ag(C_2B_8H_{11})$ has previously been interpreted in this way.[8] Evidence for the three μ-H atoms associated with the lower cage of (**2**) derives from (i) the fact that the lower cages of (**2**) and (**3**) differ by two skeletal electrons, only one of which is attributable to the change in anionic charge, (ii) the $^1H\{^{11}B\}$ n.m.r. spectrum of (**2**) (CD_2Cl_2, 298 K) which includes resonances at −1.85 (1H), −3.75 (1H), −4.12 (2H), and −4.78 (1H) p.p.m., and (iii) the proposed formulation of (**2**) arises straightforwardly from the mechanism outlined below.



Scheme 1. Schlegel diagrams of the proposed mechanism by which (i) the *nido*-octadecahedral $\{AuB_{10}H_{13}\}$ fragment transforms into the *arachno*-docosahedral $\{AuB_{10}H_{13}\}$ fragment, and (ii) the *arachno*-docosahedral $\{AuB_{10}H_{13}\}$ fragment transforms into the *nido*-icosahedral $\{AuB_{10}H_{12}\}$ fragment.

Compounds (**2**) and (**3**) are nominally related by the loss/addition of a hydride ion, and, since the starting borane in their syntheses is $B_{10}H_{14}$, it is reasonable to suggest that (**3**) is formed from (**2**). The known structure of (**1**) demonstrates the existence of the fragment $\{AuB_{10}H_{13}\}$ in which the metal is simply a one-electron donor bridge. We suggest that this fragment yields the structurally different $\{AuB_{10}H_{13}\}$ fragment in (**2**) by oxidative slippage of the metal from bridge to vertex [this implies that in (**2**) the B(2,9)–B(6,11), B(10,8)–B(0,3), and B(8,4)–B(0,3) connectivities are H-bridged]. Continuation of this lateral movement of the gold atom, with concomitant hydride ion loss, transforms (**2**) into (**3**). This overall sequence is sketched in Schlegel form in Scheme 1.

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‡ A consequence of the crystallographic superimposition of the two different polyhedra is that it is necessary to number the atoms (*i,j*) where *i* refers to the *nido*-icosahedron and *j* to the *arachno*-docosahedron.

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