Synthesis and Characterisation of a Triple Cluster of Gold and Boron

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Reaction of $B_{10}H_{14}$ with Et_3PAuMe affords the triple cluster $[(H_{12}B_{10}Au)(AuPEt_3)_4(AuB_{10}H_{12})]$, and with Cy_3PAuMe (CY = cyclohexyl) the substituted complex $[Cy_3PAu(B_{10}H_{13})]$ is isolated; a mechanism for the formation of the triple cluster is proposed.

The replacement of μ-H atoms in transition-metal cluster complexes by isolobal $\{AuPR_3\}$ fragments frequently leads to derivatives which are more stable and more easily characterised,[1] and close analogies between clusters of boron and clusters of metals have been recognised for several years.[2] Since the readily available borane $B_{10}H_{14}$ has an open face containing four μ-H atoms we became interested in the possible replacement of one or more of these by $\{AuPR_3\}$ fragments, with the potential formation of products with gold–gold bonds.

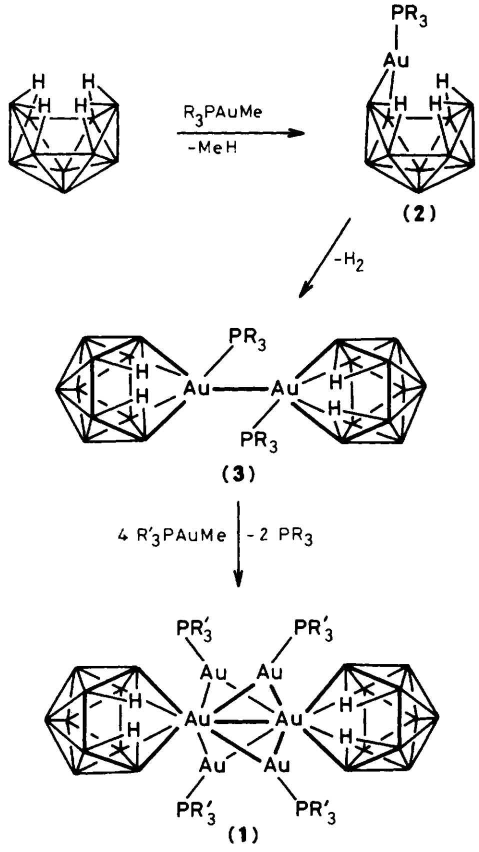
The addition of R_3PAuMe (R = Et or Ph) to an equimolar amount of $B_{10}H_{14}$ in CH_2Cl_2 at room temperature affords a yellow solution which rapidly becomes dark red. For R = Et the final product has been characterised by microanalysis and multinuclear n.m.r. spectroscopy† as $[(H_{12}B_{10}Au)(\mu\text{-}AuPEt_3)_4(AuB_{10}H_{12})]$ (**1a**). An *X*-ray diffraction study of (**1a**) as its 2MeCN solvate‡ revealed the structure shown in Figure 1.

In (**1a**) two *nido*-icosahedral $7\text{-}AuB_{10}H_{12}$ polyhedra are directly linked by an Au(7)–Au(7′) bond, 2.9188(16) Å. Although not located in the crystallographic study, two bridging hydrogen atoms per cage have been detected by $^1H\{^{11}B\}$ n.m.r., and these are assigned to B(8)–B(9) and B(10)–B(11) (and equivalent primed) connectivities. The two auraborane clusters are twisted with respect to each other by *ca.* 90° about the Au(7)–Au(7′) bond, which is bridged by four $\{Et_3PAu\}$ units in an asymmetric, but regular, manner; the open face of each cage lies below a phosphine ligand whose bound gold atom is somewhat closer to the polyhedral gold atom of the other cage. The arrangement of six gold atoms in (**1a**) is that of a radially compressed octahedron, and thus the species may be regarded overall as a 'triple cluster' with the inner Au_6 part fused to the outer AuB_{10} parts by common gold vertices. Such a system is without precedent.

In an attempt to understand the mechanism by which (**1a**) is formed, the reaction of $B_{10}H_{14}$ with the sterically demanding reagent Cy_3PAuMe (Cy = cyclohexyl) has been studied in the hope of isolating relatively stable reaction intermediates.

In CH_2Cl_2 at room temperature $B_{10}H_{14}$ and Cy_3PAuMe give initially a yellow solution from which a colourless product (**2c**), characterised spectroscopically† and crystallographically‡ as $[\textit{nido}\text{-}\mu\text{-}5,6\text{-}(AuPCy_3)\text{-}B_{10}H_{13}]$, is deposited. As shown (Figure 2) the structure of (**2c**) is simply that of $B_{10}H_{14}$ with one μ-H replaced by μ-$AuPCy_3$. Addition of Et_3PAuMe to (**2c**) in CH_2Cl_2 results in the successive production of yellow then red colourations. Free PCy_3 has been detected (as $OPCy_3$, by ^{31}P n.m.r.) in the final mixture.

In light of these results we suggest the mechanism outlined in Scheme 1 for formation of the triple cluster (**1**). Initial



a; R = Et, R′ = Et
b; R = Ph, R′ = Ph
c; R = Cy

Scheme 1

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† (**1a**) ($CDCl_3$, 298 K) $^{11}B\{^1H\}$: δ 11.93 (br., 4B), 0.70 (2B), −4.93 (2B), and −24.48 (2B) p.p.m. $^1H\{^{11}B\}$ includes: δ 4.12, 3.41, 2.60, 2.44, 2.39, 1.35 (all B–*H*), and −3.40 (B–*H*–B) p.p.m. (**2c**) ($CDCl_3$, 303 K) $^1B\{^1H\}$: δ 16.12 (1B), 9.32 (1B), 8.41 (1B), 2.82 (1B), 1.41 (1B), −0.57 (2B), −1.01 (1B), −29.53 (1B), and −35.63 (1B) p.p.m. $^1H\{^{11}B\}$ includes: δ 5.05, 3.72, 3.50, 3.29, 3.17, 2.94, 2.90, 2.62, 0.64, 0.60 (all B–*H*), and −0.13, −2.93, and −3.48 (all B–*H*–B) p.p.m.

‡ *Crystal Data:* (**1a**) $C_{24}H_{84}Au_6B_{20}P_4 \cdot 2C_2H_3N$, $M = 2061.0$, $a = 16.817(10)$, $b = 16.067(5)$, $c = 21.798(12)$ Å, $\beta = 92.02(4)°$, $U = 5886$ Å^3, space group $P2_1/c$, $D_c = 2.325$ g cm^{-3}, $Z = 4$, $F(000) = 3742$, $\mu(\text{Mo-}K_{\alpha^-}) = 155.2$ cm^{-1}. Using 4855 $[F \geqslant 5.0\sigma(F)]$ out of 10325 symmetry-independent data measured (185 K) to $\theta_{max.}$ 25° on an Enraf-Nonius CAD4, and corrected for *X*-ray absorption, the structure has been refined to a current *R* index of 0.0620. (**2c**) $C_{18}H_{46}AuB_{10}P$, $M = 598.6$, $a = 11.6583(20)$, $b = 22.663(6)$, $c = 11.418(3)$ Å, $\beta = 118.061(16)°$, $U = 2662$ Å^3, space group $P2_1/a$, $D_c = 1.493$, $Z = 4$, $F(000) = 1192$, $\mu(\text{Mo-}K_{\alpha^-} = 57.7$ cm^{-1}. Of 2473 symmetry-independent data measured at 291K to $\theta_{max.}$ 20°, 1830 $[F \geqslant 5.0\sigma(F)]$ have been used to refine the structure to a current *R* value of 0.0556. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

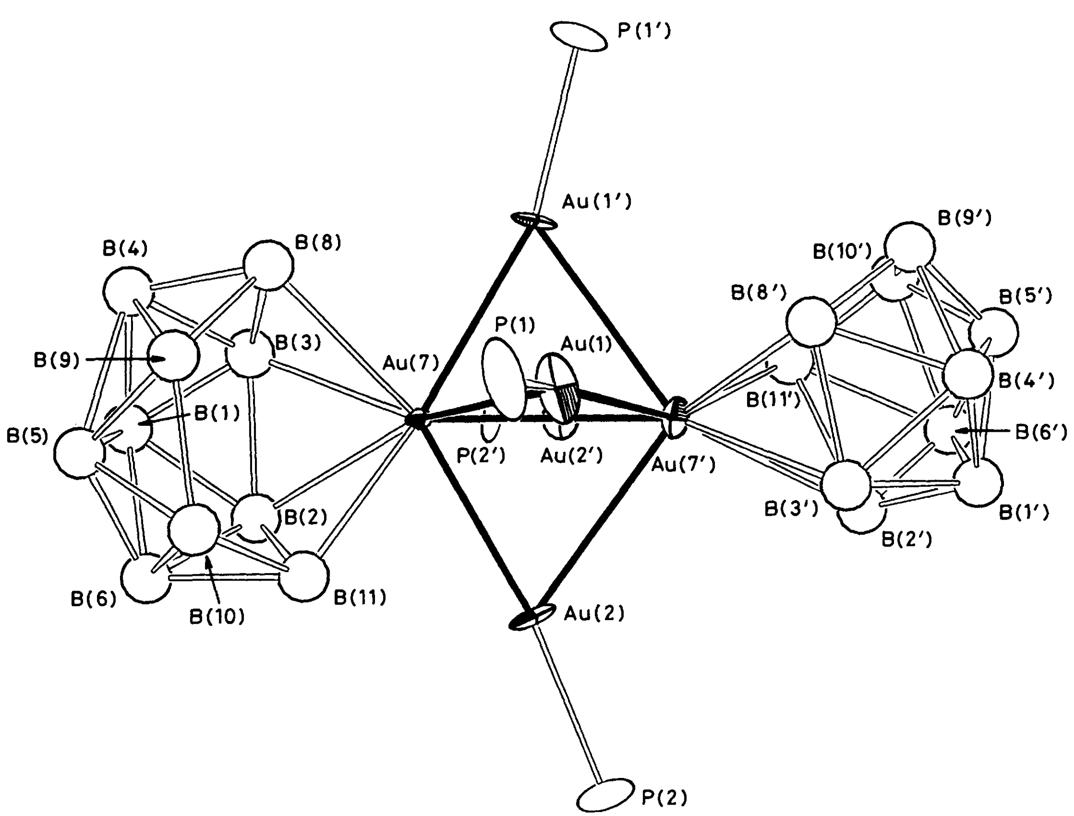

Figure 1. Perspective view of (**1a**). Ethyl groups are omitted for clarity. Each boron atom has one terminal H atom, and there are bridging H's on B(8)–B(9), B(10)–B(11), B(8')–B(9'), and B(10')–B(11') connectivities.

formation of the colourless Au^{I} complex (**2**) is followed by collapse of the Au atom from an η^2- to η^4-bonded cluster site, with concomitant dimerisation and hydrogen elimination, yielding the yellow Au^{III} species (**3**), for which the structure illustrated is proposed. It may be of relevance that species with Au atoms η^3-bonded to boranes and heteroboranes are known.[3,4] Detailed n.m.r. experiments show no evidence for the presence of a terminal or bridging hydride in (**3**). In the presence of unreacted R_3PAuMe (R = Et or Ph) (**3**) undergoes phosphine loss and is quadruply bridged by $\{AuPR_3\}$ units. We suggest that with Cy_3PAuMe alone the combination of the insolubility of (**2c**) and the large cone angle of the phosphine prevent ultimate formation of a triple cluster.

We thank the Chemistry Department of the University of Edinburgh for a vacation studentship (A. J. Wynd), and Dr. D. Reed for the $^{11}B\{^{1}H\}$ and $^{1}H\{^{11}B\}$ n.m.r. spectra.

Received, 28th February 1985; Com. 272

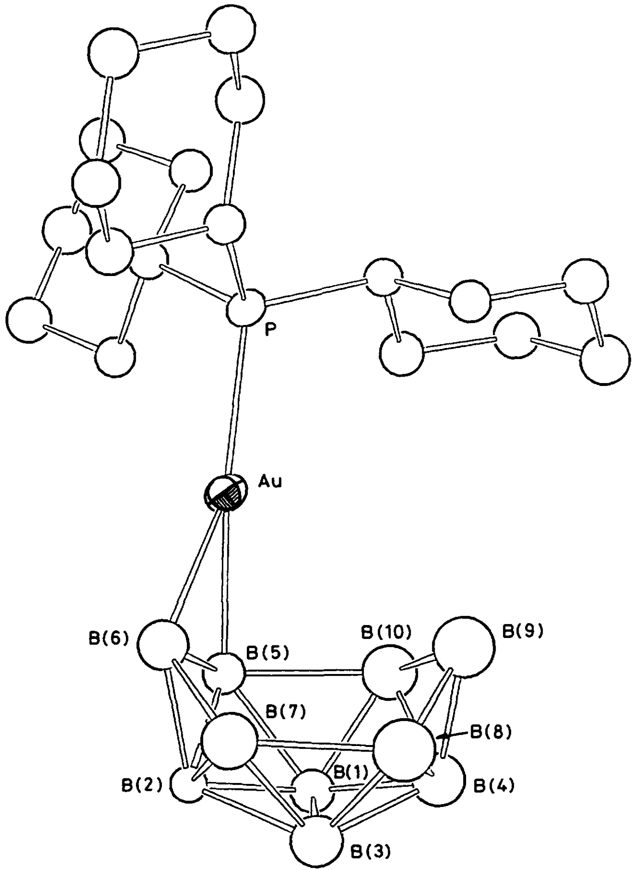

Figure 2. The non-hydrogen skeleton of (**2c**). In addition to 10 H atoms terminal to boron there are μ-H's on the B(6)–B(7), B(8)–B(9), and B(9)–B(10) connectivities.

References

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