A Novel Fused Metallaborane Cluster formed *via* Gold–Phosphorus Bond Cleavage: The Crystal Structure of $[\{HFe_4(CO)_{12}BH\}_2Au][Au(PPh_2Me)_2]$

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A product of the reaction of $[HFe_4(CO)_{12}BH][(Ph_3P)_2N]$ with $Me_2PhPAuCl$ or $MePh_2PAuCl$ is the cluster $[\{HFe_4(CO)_{12}BH\}_2Au][AuL_2]$ (L = PPh_2Me or $PPhMe_2$), the anion of which contains two tetrairon butterfly, boron containing, fragments linked by a naked gold atom; the formation of the linked product rather than a simple monogold(I) derivative of type $[HFe_4(CO)_{12}\{Au(PR_3)\}BH]$ is shown to depend upon the phosphine substituent.

Over the past decade, the literature has witnessed an increasing number of transition metal cluster compounds which incorporate gold(I) phosphine fragments as cluster building blocks.[1—5] The gold(I) phosphine generally adopts either an edge-bridging or face-capping environment. Moreover, in the case of monogold derivatives, the location of the $AuPR_3$ unit tends to mimic that of an endo-hydrogen atom in the parent neutral cluster.[1,5] The usual observation, then, is that the gold(I) phosphine retains its integrity. Contrast this with the situation in solutions of the simple gold(I) phosphine

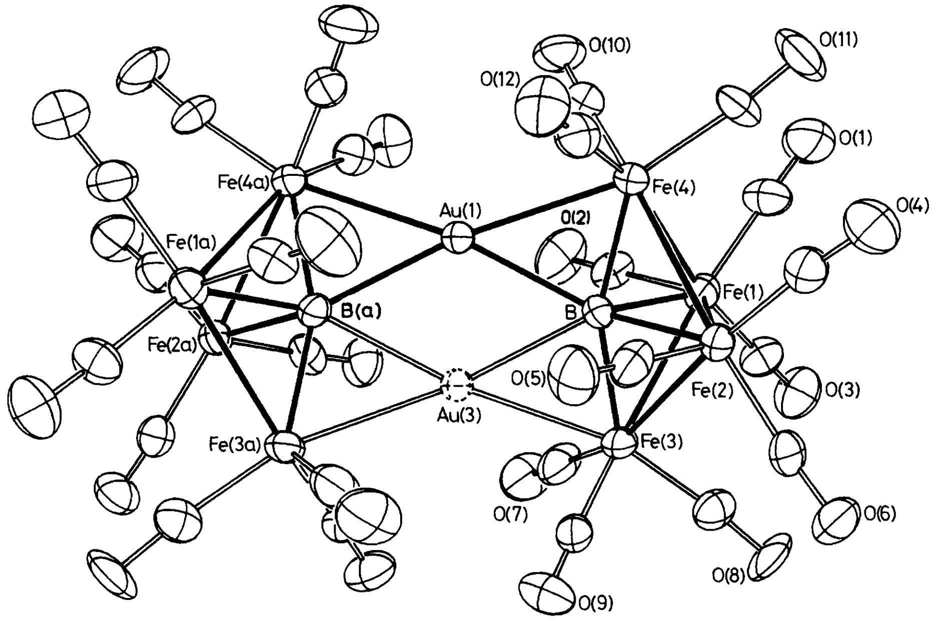

Figure 1. Molecular structure and labelling scheme for the $[\{HFe_4(CO)_{12}BH\}_2Au]^-$ anion. Au(1)–Fe(4) 2.615(1); Fe(1)–Fe(2) 2.630(2); Fe(1)–Fe(3) 2.649(2); Fe(1)–Fe(4) 2.660(2); Fe(2)–Fe(3) 2.650(2); Fe(2)–Fe(4) 2.668(2); Au(1)–B 2.300(12); Fe(1)–B 2.065(13); Fe(2)–B 2.082(12) Å; Fe(1)–B–Fe(2) 78.7(4); Fe(3)–B–Fe(4) 75.1(4); B–Au(1)–B(a) 25.8(6); B–Au(1)–Fe(4) 47.2(3); Fe(4)–Au(1)–Fe(4a) 143.4(1)°. Au(3) is a chemically equivalent site for Au(1) with a site occupancy of 0.098. Iron-butterfly internal dihedral angle = 116.6(3)°. Dihedral angle for the two [Fe–Au–B] planes = 30.9(5)°.

halides themselves; in the presence of even small amounts of excess of phosphine, L, equilibria arise which lead to the formation of the cations $[AuL_n]^+$ (n = 2—4).[6—14] However, at the cluster level, formation of this type of species appears to be a less recognised phenomenon. In one example, the cluster, $[HOs_3(CO)_{10}(AuPR_3)]$ (R = Ph; Et), undergoes cleavage of the Au–P bond in the presence of $[(Ph_3P)_2N]^+$ to form $[\{HOs_3(CO)_{10}\}_2Au][(Ph_3P)_2N]$;[15] however, in the first instance, the reaction of $[HOs_3(CO)_{10}]^-$ with $AuPR_3Cl$ (R = Ph; Et) proceeds smoothly to give $[HOs_3(CO)_{10}(AuPR_3)]$ as an isolable product,[16] and only when the compound is refluxed in a dichloromethane solution of $[(Ph_3P)_2N]Cl$ does cluster fusion occur.[15] Preparation of a similarly linked cluster anion, $[\{Pt_3(\mu\text{-}CO)_3(PPh_3)_3\}_2Au]^-$ uses Au(L)Cl (L = CO or Me_2S) rather than gold(I) phosphines.[17]

Recently, we reported Au–P bond cleavage leading to the exchange reaction between the cluster bound triethylphosphine ligands of $[Fe_4(CO)_{12}(AuPEt_3)_2BH]$, and the triphenylphosphine ligands of the cation $[(Ph_3P)_2N]^+$.[18] We now report the synthesis and crystal structure of a novel, metal-rich metallaborane, $[\{HFe_4(CO)_{12}BH\}_2Au][Au(PPh_2Me)_2]$ (**1**), the formation of which relies upon Au–P bond rupture, and is reminiscent of solution reactions of gold(I) phosphine halides. When LAuCl (L = $MePh_2P$ or Me_2PhP) and $[HFe_4(CO)_{12}BH][(Ph_3P)_2N]$ react together for 45 min at room temperature in CH_2Cl_2 in the presence of $TlPF_6$, a colour change from brown to dark green is observed. After removal of solvent *in vacuo*, extraction with Et_2O, and centrifugal chromatographic separation, (**1**)† is obtained in ~20% yield. Crystals of (**1**) suitable for *X*-ray analysis were obtained by using a fortuitous mix of Me_2PhP and $MePh_2P$ (~1 to 2 ratio) and were grown from CH_2Cl_2 layered with hexane.‡ The structure of the $[\{HFe_4(CO)_{12}BH\}_2Au]^-$ anion contained in (**1**) is shown in Figure 1. The product anion is readily described as consisting of two $[HFe_4(CO)_{12}BH]^-$ units, linked *via* an Au^+ cation; indeed the structural parameters of each tetrairon butterfly $HFe_4(CO)_{12}BH$ fragment in (**1**) vary little from those of the neutral cluster $[HFe_4(CO)_{12}BH_2]$.[19] The two $HFe_4(CO)_{12}BH$ fragments are related by a two-fold axis which passes through the gold atom of the $[\{HFe_4(CO)_{12}BH\}_2Au]^-$ anion. Co-ordination about the Au atom deviates from planarity by a 30.9(5)° spiro-twist

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† $[\{HFe_4(CO)_{12}BH\}_2Au]^-$: 250 MHz ^1H n.m.r. (CD_2Cl_2) δ −6.5 (br., Fe–H–B), −24.9 (s, Fe–H–Fe); 128 MHz ^{11}B n.m.r. (CD_2Cl_2) δ 135.4; i.r. (CH_2Cl_2, cm^{-1}) ν_{CO} 2066 m, 2034 vs, 2003 m, 1980 s.

‡ *Crystal data* for (**1**): $C_{50}H_{26}B_2O_{24}P_2Au_2Fe_8$, monoclinic, space group *C*2/*c*, a = 21.704(3), b = 9.542(2), c = 29.717(6) Å, β = 97.50(1)°, U = 6102.0(19) Å³, Z = 4, D_c = 2.106 g cm⁻³, μ(Mo-K_α) = 69.7 cm⁻¹, T = 293 K. Of 5220 reflections collected (Nicolet R3m diffractometer, 4° ≤ 2θ ≤ 48°), 4785 were independent (R_{int} = 2.6%) and corrected for absorption. At the $4\sigma(F_o)$ level, 3050 reflections were observed. The Au atom locations were observed from a Patterson synthesis, and the remaining non-hydrogen atoms from subsequent difference Fourier syntheses. The asymmetric unit consists of half of the $[Au(PR_3)_2]^+$ cation with the Au atom on an inversion centre, and half of the $[\{HFe_4(CO)_{12}BH\}_2Au]^-$ anion with the Au atom on a two-fold rotational axis. The cation phosphine molecules are a mixture of PPh_2Me and $PPhMe_2$ with the former found, from occupancy refinement, to consist of 63(1)% of the mixture. The anion contains two chemically equivalent Au-atom sites, Au(1) and Au(3), with occupancies of 0.402(1) and 0.098(1), respectively. Both sites are on the two-fold axis. At convergence, with all non-hydrogen atoms anisotropic except the carbon atoms of the partially occupied phenyl rings (which were additionally constrained to planar hexagons to conserve data), and cation hydrogen atoms incorporated as idealised contributions, R_F = 4.59%, R_{wF} = 6.22%, GOF = 1.032, Δ/σ = 0.13, Δ(ρ) = 1.02 e Å⁻³ [1.06 Å from Au(2)]. All computations used SHELXTL(5.1) written by G. Sheldrick, and distributed by Nicolet XRD, Madison, WI. 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.

angle between the [Au,B,Fe] planes. The Au(1)–B and Au(1)–Fe(4) bond lengths are similar to those observed in related compounds.[20—22] Hydrogen atoms were not crystallographically located. However, ^{1}H n.m.r. resonances at δ −6.4 and −24.9 imply hydrogen atoms bridging Fe–B and Fe–Fe edges respectively, and the observed carbonyl ligand orientations§ are in keeping with Fe(3)–H–B and Fe(1)–H–Fe(2) bridges.

The synthesis of (**1**) provides a novel departure from the more generally exemplified routes to neutral gold(I) phosphine cluster derivatives. The driving force for the formation of (**1**) is therefore of interest. We note that the stoicheiometry of (**1**) is equivalent to that of a monogold derivative of formula $HFe_4(CO)_{12}(AuPPh_2Me)BH$ or $HFe_4(CO)_{12}(AuPPhMe_2)BH$. For the phosphines PPh_3,[18] $P(p\text{-}Me\text{-}C_6H_4)$,[23] and $P(C_6H_{11})_3$,[23] such a monogold derivative has indeed been isolated, but for $PPhMe_2$, PPh_2Me, PMe_3, and PEt_3, the ionic product is observed. It is tempting to suggest that $HFe_4(CO)_{12}(AuL)BH$ is an intermediate in the formation of (**1**) and that a ligand redistribution reaction then leads to (**1**). Cluster mediated Au–P bond fission, and the interaction of the $\{HFe_4(CO)_{12}(Au)BH\}$ fragment with starting anion, $[HFe_4(CO)_{12}BH]^-$, are considered to be crucial steps in the formation of (**1**).

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§ Compare with CO ligand orientations in $[HFe_4(CO)_{12}BH_2]$.[19]