A Metal Encapsulated Boron Atom: Preparation and Structure of $[Fe_4(CO)_{12}B\{AuPPh_3\}_3]$

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The preparation and structural characterisation of the heterometallic cluster $[Fe_4(CO)_{12}B\{AuPPh_3\}_3]$ are described: the new compound is the first example of a structurally characterised cluster containing a naked boron atom, *i.e.* a discrete metal boride cluster; the boron atom is within bonding contact of all seven metal atoms and this unique environment is reflected by an exceptional downfield n.m.r. shift for the ^{11}B resonance.

The chemistry of *metal*-rich as opposed to *boron*-rich metallaboranes is an interesting area, largely because of changes in reactivity patterns of the boron atom as B–H interactions are replaced by B–M interactions.[1] Recently, we reported the structural characterisation of the metal-rich auraferraborane $Fe_4(CO)_{12}(AuPPh_3)_2BH$.[2] This cluster has an unprecedented core structure consisting of a boron atom associated with an irregular array of four iron and two gold atoms. The related cluster compounds $Fe_4(CO)_{12}(AuPEt_3)_2BH$ and the two isomers of $Fe_4(CO)_{12}(AuPPh_3)(AuPEt_3)BH$ have also been prepared, and spectroscopic characterisation suggests that these compounds are isostructural with the bis(triphenylphosphine) derivative.[3] Each of these compounds, however, still retains a B–H bond. Although the anion $[Fe_4(CO)_{12}B]^{3-}$ has recently been described, and represents the first example of a cluster with an exposed boride atom,[4] and the cluster $[Co_6(CO)_{18}B]$ has been described by Schmid *et al.*,[5] no fully characterised example of a discrete metal cluster containing an *enclosed* boride atom has previously been reported. This is quite surprising in view of the number of metal carbide clusters which are known[6,7] and the growing number of metal clusters containing nitrogen,[8,9] phosphorus[10,11] and, recently, oxygen atoms[12] which have been characterised.

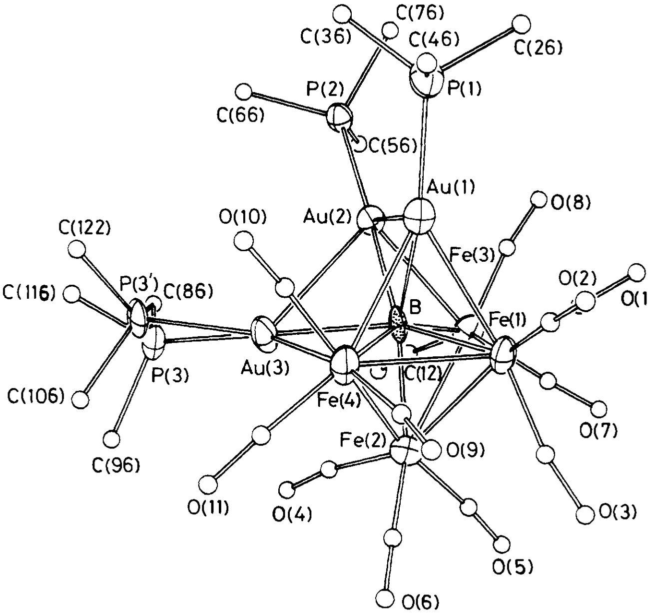

Figure 1. Molecular structure of (2). Selected bond lengths (Å): Au(1)–Au(2) 2.877(1), Au(2)–Au(3) 2.858(1), Au(1)–Fe(1) 2.693(4), Au(1)–Fe(4) 2.711(3), Au(2)–Fe(3) 2.625(4), Au(3)–Fe(4) 2.616(3), Au(1)–B 2.34(2), Au(2)–B 2.27(2), Au(3)–B 2.32(2), Fe(1)–B 2.09(2), Fe(2)–B 2.16(2), Fe(3)–B 1.98(2), Fe(4)–B 2.13(2). Phenyl rings are shown as *ipso* atoms only. P(3) is disordered; P(3) and P(3') have C(86) in common to both.

The reaction of $[N(PPh_3)_2][HFe_4(CO)_{12}BH]$[13] with an excess of $AuPPh_3Cl$ in CH_2Cl_2 at room temperature for 40 min leads to the cluster $HFe_4(CO)_{12}(AuPPh_3)_2BH$, (**1**), in good yield as previously reported.[2] This compound is characterised in the ^{11}B n.m.r. spectrum by a downfield resonance at δ 137 (CD_2Cl_2).[3] Longer reaction times give rise to small quantities of a second product, (**2**), which is characterised by an ^{11}B n.m.r. resonance at δ 183. This shift, being significantly further downfield than that of (**1**), implied a greater degree of boron–metal interaction in (**2**) than in (**1**). Syntheses of other trigold derivatives of metal clusters[14—20] have made use of the cation $[(Ph_3PAu)_3O]^+$ as a source of gold(I) as well as, or instead of, the mononuclear gold(I) species exemplified here. Indeed, the synthesis of (**2**) is greatly improved by reacting $[N(PPh_3)_2][HFe_4(CO)_{12}BH]$ with $[(Ph_3PAu)_3O][BF_4]$ in tetrahydrofuran (thf) at room temperature, and >70% yield of (**2**) is obtained *via* this route. An interesting feature of the new auraferraborane systems is that, in the presence of an alcohol, the clusters $Fe_4(CO)_{12}(AuPPh_3)_{3-n}BH_n$ (n = 1,2) gradually transform completely to (**2**), (n = 0), suggesting that this is the thermodynamically preferred product.

A crystal of (**2**) suitable for *X*-ray analysis was grown from CH_2Cl_2/propan-2-ol. The structure of (**2**)† is shown in Figure 1, and is based upon a butterfly array of iron atoms; the metal atom–boron atom core of (**2**) is shown in Figure 2. The Fe_4B unit is common to compound (**1**),[2] and to the parent compound $[HFe_4(CO)_{12}BH_2]$.[21] In (**2**), the boron atom lies 0.457(1) Å above the Fe_{wing}–Fe_{wing} [*i.e.* Fe(3)–Fe(4)] axis. The transformation from digold[2] to trigold derivative, therefore draws the boron atom out of the iron butterfly by a further 0.087 Å. The three $AuPPh_3$ fragments are asymmetrically sited over the surface of the Fe_4B core; Au(1) caps the Fe(1)–Fe(4)–B face, Au(2) bridges the Fe(3)–B edge, and Au(3) bridges both Fe(4)–B and Au(2)–B. Two of the Au–Au

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† *Crystal data* for $[Fe_4(CO)_{12}B\{AuPPh_3\}_3]$ (**2**): triclinic, $P\bar{1}$, a = 13.404(3), b = 13.338(3), c = 20.493(7) Å, α = 79.37(3), β = 71.88(3), γ = 73.94(3)°, U = 3327(1) Å^3, Z = 2, D_c = 1.945 g cm^{-3}, μ(Mo-K_α) = 75.5 cm^{-1}, T = 294 K. Of 10 111 reflections collected (Nicolet R3m diffractometer, 4° ≤ 2θ ≤ 48°), 9201 were independent (R_{int} = 1.34%) and corrected for absorption. At the $5\sigma(F_o)$ level, 5800 reflections were observed. The Au atom locations were observed from a Patterson synthesis, and the remaining non-hydrogen atoms from subsequent difference Fourier syntheses. P(3) is disordered over two sites [refined occupancy, P(3) = 63 and P(3') = 37%] with overlapping substituent phenyl rings. At covnergence, with all non-hydrogen atoms anisotropic except the carbon atoms of the phenyl rings (which were additionally constrained to planar hexagons to conserve data), R_F = 6.83%, R_{wF} = 7.03%, G.O.F. = 1.311, Δ/σ = 0.03, $\Delta(\rho)$ = 2.8e Å^{-3} [between Au(3) and Au(1)]. All computations used SHELTXTL(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.

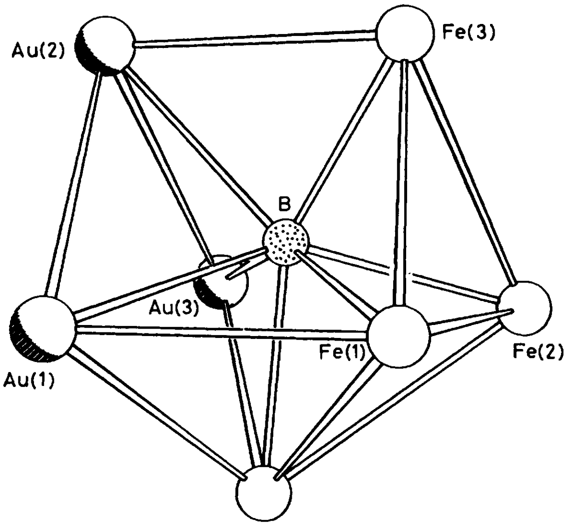

Figure 2. A skeletal view of (**2**), showing the Fe_4Au_3B core.

contacts, [*viz.* Au(1)–Au(2) and Au(2)–Au(3)], should probably be classed as bonding.

Despite the asymmetry of (**2**), the ^{31}P n.m.r. shows only one resonance at room temperature, indicating a fluxional process[2,3,22] which exchanges all three $AuPPh_3$ units.‡ Corresponding to this, the ^{13}C n.m.r. spectrum at room temperature exhibits two signals of equal intensity for the carbonyls; this suggests equivalence of the wing-tip COs, and of the hinge COs. Variable temperature n.m.r. studies are in progress.

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‡ *Selected data* for $[Fe_4(CO)_{12}B(AuPPh_3)_3]$: 250 MHz ^{1}H n.m.r. (CD_2Cl_2) δ 7.1—7.7 (m); 162 MHz ^{31}P n.m.r. (CD_2Cl_2), δ 52.8; 128 MHz ^{11}B n.m.r. (CD_2Cl_2) δ 183 (s, $W_{\frac{1}{2}} \simeq 190$ Hz); 100 MHz ^{13}C n.m.r. (CD_2Cl_2) δ 220.2 (s), 216.4 (s) ($I = 1:1$), 134.5—129.0 (Ph); i.r. [$(CH_2Cl_2\,cm^{-1})$ ν_{CO} 2035m, 1994vs, 1971vs, 1930sh. FAB-MS P^+ 1948 (12 CO loss observed). Satisfactory elemental analysis obtained for $Au_3BC_{66}H_{45}O_{12}P_3$.