

mechanism, with good proximity of the organic and inorganic catalytic centers, seems clear. It is a process with considerable synthetic potential beyond the examples reported here.

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Preparation, Characterization, and Structure of $\text{Fe}_4(\text{CO})_{12}[\text{Au}(\text{PPh}_3)]_2\text{BH}$: An Iron-Gold Borido Cluster Violating the H/AuPR₃ Structural Analogy

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Metallaboranes are predominantly exemplified by boron-rich rather than metal-rich clusters, and in a variety of cases, replacement of BH_2 for isoelectronic CH units in a metallaborane leads to a known organometallic cluster.¹ However, in contrast to metallaboranes, metal-carbon clusters also include a category of compound in which a carbon atom is fully or partially encapsulated by metal atoms: the so-called metal carbide clusters.^{2,3}

The replacement of metal cluster⁴⁻⁷ and, to a far lesser extent, borane cluster⁸ hydrogen atoms by gold(I) phosphine^{4,5,9} has been exploited to synthesize some novel compounds with structures often related to the parent hydrogen-containing species via direct H/AuL (L = PR₃) substitution. Indeed, it has been noted that the structures of transition-metal-gold clusters can be used directly to model the analogous transition-metal hydrides^{4,10} and to "isolate" isomers which are unstable as the hydride cluster but stable after H/AuL replacement.⁴ To our knowledge, no H/AuL replacement has been reported for a metallaborane. Here we report the synthesis of $\text{Fe}_4(\text{CO})_{12}[\text{Au}(\text{PPh}_3)]_2\text{BH}$ (I).

I was prepared by the addition of $[\text{HFe}_4(\text{CO})_{12}\text{BH}]\text{PPN}^{11}$ (II) (PPN = bis(triphenylphosphine)iminium) (0.04 mmol) in 4 mL of CH_2Cl_2 to an excess of $\text{Au}(\text{PPh}_3)\text{Cl}$. After 30 min of stirring at room temperature, solvent was removed and the product extracted from PPNCl and unreacted $\text{Au}(\text{PPh}_3)\text{Cl}$ with diethyl ether. The major product¹² was a green-brown, moderately air sensitive, neutral material collected as the first band after elution with hexanes/ CH_2Cl_2 (1:2) on a silica gel column. A single crystal suitable for X-ray diffraction was grown from CH_2Cl_2 layered with hexane.¹³

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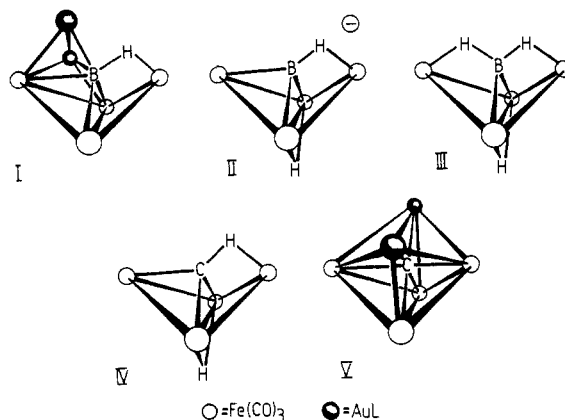
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(12) $\text{Fe}_4(\text{CO})_{12}[\text{Au}(\text{PPh}_3)]_2\text{BH}$: 28.7-MHz ¹¹B NMR ((CD₃)₂CO, 20 °C) δ +141.3 (br s, fwhm = 185 Hz, {¹H} fwhm = 110 Hz, $J_{\text{BH}} \approx 90$ Hz); 36.2-MHz ³¹P NMR ((CD₃)₂CO, -70 °C) δ +53.0; 89.56-MHz ¹H NMR ((CD₃)₂CO, 20 °C) δ +7.57-7.25 (m, 30 H, Ph), -9.1 (br, 1 H, FeHB); IR (CH₂Cl₂, cm⁻¹) ν_{CO} 2056 m, 2009 vs, 1996 vs, 1967 m, 1925 sh.

Table I. Selected Distances (Å) and Angles (deg) from I

Distances			
Au(1)-Au(2)	2.943 (1)	Fe(4)-C(12)	2.42 (1)
Au(1)-Fe(1)	2.630 (1)	Au(1)-B	2.36 (1)
Au(1)-Fe(2)	2.852 (2)	Au(2)-B	2.35 (1)
Au(2)-Fe(2)	2.606 (1)	Fe(1)-B	2.07 (1)
Fe(1)-Fe(2)	2.720 (2)	Fe(2)-B	2.00 (1)
Fe(1)-Fe(3)	2.671 (2)	Fe(3)-B	2.01 (1)
Fe(1)-Fe(4)	2.578 (2)	Fe(4)-B	2.13 (1)
Fe(2)-Fe(4)	2.708 (2)	Au(1)-P(1)	2.299 (3)
Fe(3)-Fe(4)	2.655 (3)	Au(2)-P(2)	2.302 (2)
Fe(1)-C(12)	1.75 (1)		
Angles			
Au(1)-Au(2)-B	51.4 (3)	Au(2)-B-Fe(4)	125.5 (6)
Au(1)-Au(2)-Fe(2)	61.5 (0)	Fe(1)-Fe(2)-Fe(4)	56.7 (1)
Au(2)-Au(1)-B	51.2 (3)	Fe(1)-Fe(2)-B	49.1 (3)
Au(2)-Au(1)-Fe(1)	98.0 (0)	Fe(1)-Fe(3)-Fe(4)	57.9 (1)
Au(2)-Au(1)-Fe(2)	53.4 (0)	Fe(1)-Fe(3)-B	50.1 (3)
Au(1)-Fe(1)-B	58.8 (3)	Fe(1)-Fe(4)-Fe(2)	61.9 (1)
Au(2)-Fe(2)-B	59.7 (3)	Fe(1)-Fe(4)-Fe(3)	61.3 (1)
Au(2)-B-Fe(1)	144.4 (5)	Fe(1)-Fe(4)-B	51.1 (3)
Au(2)-B-Fe(2)	73.0 (4)	Fe(1)-B-Fe(2)	83.8 (4)
Au(2)-B-Fe(3)	126.6 (5)		
Au(1)-Fe(1)-Fe(2)	64.4 (0)	Fe(1)-B-Fe(3)	81.8 (5)
Au(1)-Fe(1)-Fe(3)	84.4 (1)	Fe(1)-B-Fe(4)	75.7 (4)
Au(1)-Fe(1)-Fe(4)	110.8 (1)	Fe(2)-Fe(1)-Fe(3)	94.0 (1)
Au(1)-Fe(2)-B	54.8 (3)	Fe(2)-Fe(1)-Fe(4)	61.4 (1)
Au(1)-Fe(2)-Fe(1)	56.3 (0)	Fe(2)-Fe(1)-B	47.0 (4)
Au(1)-Fe(2)-Fe(4)	100.8 (1)	Fe(2)-Fe(4)-Fe(1)	61.9 (1)
Au(1)-B-Au(2)	77.3 (3)	Fe(2)-Fe(4)-Fe(3)	97.7 (1)
Au(1)-B-Fe(1)	72.5 (4)	Au(1)-B-Fe(3)	158.9 (6)
Au(1)-B-Fe(2)	81.3 (4)	Fe(2)-B-Fe(4)	81.8 (5)
Au(1)-B-Fe(3)	108.8 (6)	Fe(3)-Fe(1)-Fe(4)	60.7 (1)
Au(1)-B-Fe(4)	145.3 (5)	Fe(3)-Fe(1)-B	48.2 (3)
Au(2)-Fe(2)-Au(1)	65.1 (0)	Fe(3)-Fe(4)-B	48.2 (4)
Au(2)-Fe(2)-Fe(1)	104.4 (1)	Fe(4)-Fe(3)-B	52.1 (3)
Au(2)-Fe(2)-Fe(4)	97.2 (1)		

The X-ray crystal structure of I (Figure 1) shows the near encapsulation of the boron by six metal atoms. Selected bond parameters are given in Table I. The "butterfly" of iron atoms present in II¹¹ and in its conjugate acid, III,¹⁴ is retained in I. The boron resides 0.37 (1) Å above the Fe(2)-Fe(3) wingtip axis.¹⁵



(13) Crystal data for I: $\text{C}_{48}\text{H}_{31}\text{Au}_2\text{BF}_4\text{P}_2\text{O}_{12}$, $M_r = 1489.8$, triclinic, $P\bar{1}$, $a = 10.870$ (3) Å, $b = 12.114$ (3) Å, $c = 20.466$ (6) Å, $\alpha = 80.23$ (2)°, $\beta = 83.17$ (2)°, $\gamma = 73.40$ (2)°, $V = 2537.9$ Å³, $Z = 2$, $D_c = 1.949$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 70.2$ cm⁻¹, green-black, $0.24 \times 0.30 \times 0.37$ mm, 293 K. Nicolet R3m/ μ diffractometer with graphite monochromator. Corrections for decay (linear, 4%) and absorption (empirical, $T_{\text{max}}/T_{\text{min}} = 2.23$). Of 8320 reflections collected (max $2\theta = 48^\circ$), 7942 were unique ($R_{\text{int}} = 1.2\%$), and 5474 were considered observed with $F_o \geq 3\sigma(F_o)$. Phenyl rings; rigid, planar constraint. All non-hydrogen atoms anisotropic; hydrogen atoms idealized; isotropic contributions (H atom on boron ignored). Refinement of 550 parameters: $R_F = 4.49\%$, $R_{\text{w}} = 5.20\%$, $\text{GOF} = 1.102$, $\Delta/\sigma = 0.08$, $\Delta\rho = 1.13$ e Å⁻³ (1.28 Å from Au(2)). All programs in SHELXTL and P3 program libraries (Nicolet Corp., Madison, WI).

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(15) In III, the boron lies 0.31 Å above the wingtip Fe-Fe axis.

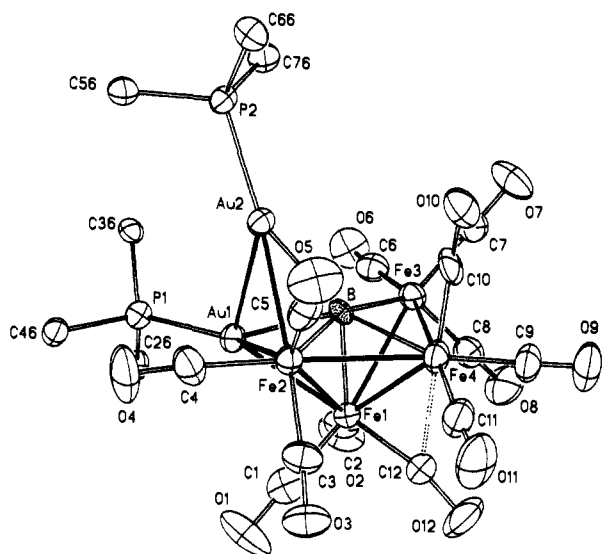


Figure 1. Molecular structure and labeling scheme for I. Phenyl rings depicted as ipso-carbon atoms only.

One AuL ($L = PPh_3$) unit, Au(1), caps the Fe(1)Fe(2)B face and the second AuL unit caps the Fe(2)Au(1)B face. The hydrogen atom on boron was not located, but its 1H NMR shift (-9.1 ppm) and observed coupling to boron implies an Fe-H-B bridge position. The cluster skeleton can be regarded as a pair of facially fused trigonal bipyramids if all metal atoms plus the boron are regarded as vertex atoms, although structural parameters (viz., position of B with respect to the iron butterfly and the latter's dihedral angle of 113.4 (1°)) suggest that a more appropriate description is an *arachno* cluster as previously presented for III.^{14,16,17}

Although I is prepared from anion II, it is formally derived from III by replacing two H atoms by AuL fragments. However, in contrast to many previous examples of H/AuL replacement,⁴⁻⁷ this turns out not to be a straightforward structural analogy. Taking the H/AuL isolobal analogy at face value, the increased degree of boron encapsulation in going from III to I is brought about by the migration of one "proton" (in the form of Au(PPh_3)) from the base of the iron skeleton toward the boron. A similar situation arises in comparing $HFe_4(CO)_{12}CH^{18}$ (IV) with $Fe_4(CO)_{12}(AuL)_2C$ ($L = PEt_3, PPh_3$)¹⁹ (V). Again, although the preparative route to V is not via direct H/AuL substitution in IV, the net result is a "proton" migration toward the main-group element and away from the metal framework. In V, however, the carbide is sited within a near octahedron of metal atoms. Whether or not the structural difference between I and V is due entirely to the requirements of the additional proton in I is currently under investigation.

It is noteworthy that, compared to III, one of the hinge $Fe(CO)_3$ units in I is twisted through 60° and forms a semibridging CO along the Fe(1)-Fe(4) hinge bond, the site occupied by a bridging hydride in II and III. The steric requirements of the Fe(1)Fe(2)B face bridging Au(PPh_3) group presumably cause the hinge $Fe(CO)_3$ rearrangement. It is interesting, however, that in a closely related butterfly cluster, $[Fe_4(CO)_{13}(AuL)]^-$ ($L = PPh_3, PEt_3$), the AuL fragment occupies the hinge position,²⁰ just as the hydrogen atom did in the analogous $[HFe_4(CO)_{13}]^-$.²¹

(16) Previous Fenske-Hall calculations on III indicate that the BH_2 unit is strongly perturbed upon interaction with the metal butterfly, allowing each of the boron and hydrogens to bond directly to the cluster.

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The positions of the Au(PPh_3) groups in the solid-state structure of I are inequivalent (Figure 1). However, at $-70^\circ C$, the ^{31}P NMR spectrum exhibits only one resonance. Assuming an intramolecular process, this equivalence can be explained by either a simple site exchange or a "rocking" motion of the $[Au(PPh_3)]_2$ unit across the Fe(2)-B bond. A related dynamic skeletal rearrangement involving the $[Pt(PMe_2Ph)_2]$ unit in $PtOs_3(CO)_9(PMe_2Ph)_2(\mu_3-S)_2$ has been invoked by Adams et al.²²

Finally, whereas the ^{11}B NMR shift is very sensitive to the presence of B-H or Fe-H-B vs. direct Fe-B bonds,^{11,23} it does not appear sensitive to association of the boron with Au PR_3 moieties. Thus in going from II to I no prominent change in ^{11}B NMR shift is observed, even though the boron is increasing its degree of metal encapsulation.

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Supplementary Material Available: Tables of atomic coordinates, bond distances and angles, anisotropic temperature factors, and hydrogen atom coordinates for I (7 pages); table of observed and calculated structure factors for I (33 pages). Ordering information is given on any current masthead page.

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Enzyme-Catalyzed Regioselective Deacylation of Protected Sugars in Carbohydrate Synthesis

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Selective deprotection of acylated sugars and nucleosides or nucleotides has been a problem and an area of extensive research.¹ The preparation of protected sugars with free primary hydroxyl group, for example, is very often carried out through several steps including selective tritylation, esterification, and acid-catalyzed detriylation (which may cause complicated acyl migration) followed by tedious chromatographic purifications.^{2,3}

As part of our interest in the application of enzymes in organic synthesis, particularly in carbohydrate synthesis,⁴ we wish to report here the regioselective deacylation of methyl 2,3,4,6-tetra-*O*-acyl-D-hexopyranosides to give the 6-OH derivatives in high yields (80-90%) using the lipase from *Candida cylindracea* (Scheme I). Enzymatic approaches to this type of reactions were attempted but yielded a mixture of products.⁵

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