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Phosphinegold(I) derivatives of the metal-rich metallaborane, $HFe_4(CO)_{12}BH_2$: a novel phosphine exchange involving cation and cluster-bound phosphine ligands

Karen S. Harpp and Catherine E. Housecroft*
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain)

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Abstract

The preparation and characterisation of three new gold(I) phosphine derivatives of the ferraborane, $HFe_4(CO)_{12}BH_2$ are reported. In $HFe_4(CO)_{12}(AuPPh_3)BH$ (**2**), the $AuPPh_3$ fragment formally replaces an Fe–H–B bridging hydrogen atom in the parent compound $HFe_4(CO)_{12}BH_2$. A comparison between **2** and the structurally characterised di-gold derivative, $Fe_4(CO)_{12}(AuPPh_3)_2BH$ (**1**) is made to gain insight into the relative site preference for the heavy metal fragments in **1**. Preparation of the bis(triethylphosphine)gold(I) derivative of $HFe_4(CO)_{12}BH_2$ from the PPN^+ salt of its conjugate base illustrates a novel exchange reaction between the PPh_3 groups in the PPN^+ cation and the initially, gold-associated PEt_3 groups. This leads to a distribution of products $Fe_4(CO)_{12}(AuPR_3)(AuPR'_3)BH$ where $R = R' = Ph$ (**1**) or $R = R' = Et$ (**3**) or $R = Ph$ and $R' = Et$ (**4**).

Introduction

The success or failure of the isolobal principal when applied to the replacement of *endo*-hydrogen atoms by heavy metal fragments such as $AuPR_3$ appears to depend, at least in part, on the number of heavy metal fragments which are introduced into a cluster. To date, the vast majority of examples come from transition metal cluster chemistry. Mono-gold derivatives tend to exhibit structures in which formal structural substitution of $AuPR_3$ for H occurs [1–4]. In multi-gold derivatives, there is a tendency for the gold atoms to be in close proximity to one another [3]. The introduction of a main group atom into a transition metal cluster adds a new dimension to the problem. Protons and heavy metal fragments alike now have a choice between interactions with metal-only or metal-main group atom edges or faces on a cluster framework.

We recently reported the synthesis and structural characterisation of the first auraferraborane, $Fe_4(CO)_{12}(AuPPh_3)_2BH$ (**1**) [5,6]. The novel feature of this cluster

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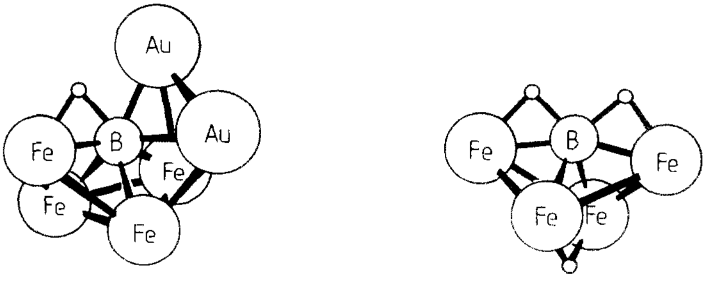

[a] [b]

Fig. 1. (a) The Fe_4Au_2BH core structure of **1**; the hydrogen atom was not located in the X-ray determination [5,6]. (b) The core structure of $HFe_4(CO)_{12}BH_2$ showing crystallographically located hydrogen atoms [7,8].

is the unusual arrangement of six metal atoms surrounding a single boron atom. The core structure of the crystallographically characterised isomer of **1** is shown in Fig. 1a. Compound **1** is related to $HFe_4(CO)_{12}BH_2$ [7,8], (the core structure of which is given in Fig. 1b), by the formal replacement of two *endo*-hydrogen atoms by two gold(I) triphenylphosphine groups. However, although the Fe_4B cluster core geometries in $HFe_4(CO)_{12}BH_2$ and **1** are virtually identical, Fig. 1 emphasises that **1** is not isostructural with $HFe_4(CO)_{12}BH_2$ in terms of the location of the three *endo*-hydrogen atoms in $HFe_4(CO)_{12}BH_2$ versus the location of one *endo*-hydrogen atom and two gold(I) fragments in **1** [5,6]. Consideration of the geometrical parameters and the electronic structure of **1** indicate that both gold(I) phosphine fragments are bonded to the cluster core primarily via Fe–Au(PPh_3)–B interactions [6]. There is no evidence for structural isomerism to give an isomer of **1** with a gold fragment bridging an iron–iron edge. We have suggested [6] that charge effects may play a rôle in determining whether the proton or gold(I) phosphine adopts a metal associated or main-group associated site in the cluster. We considered it to be of interest to probe further two areas of the aurination of $HFe_4(CO)_{12}BH_2$. Firstly, we have investigated the relative preference for bridging the two Fe–B edge types (viz. Fe_{wing}–B and Fe_{hinge}–B) because in **1**, the $AuPPh_3$ units each bridge an Fe–B edge of a different type. Secondly, we have probed the importance of steric effects in determining the location of the $AuPR_3$ units, and whether other isomers of $Fe_4(CO)_{12}(AuPR_3)_2BH$ could be formed by altering the steric requirements of the phosphine group.

Experimental

General

All reactions and manipulations were performed under argon or nitrogen by standard Schlenk techniques [9]. Solvents were dried, freshly distilled under nitrogen, and were freeze-thaw degassed prior to use. $HAuCl_4$, PPh_3, PPNCl, and $AuPEt_3Br$ (Aldrich) were used as received. Product separation was performed by column chromatography using Kieselgel 70–230 mesh (Merck). Compound **1** [5,6] and PPN[$HFe_4(CO)_{12}BH$] [10] were prepared as previously reported. $AuPPh_3Cl$ and $AuPEt_3Cl$ were prepared by published routes [11].

Spectra

IR spectra were obtained using a Perkin–Elmer 983 spectrophotometer. FAB mass spectra were recorded on an MS 902 instrument. Infrared spectra were recorded on a Perkin–Elmer 283B or FT-1710 spectrophotometer. ^1H, ^{31}P and ^{11}B NMR spectra were recorded on a Bruker WM 250 or AM 400 spectrometer. ^1H NMR shifts are relative to TMS, $\delta = 0$, ^{11}B NMR shifts are relative to $BF_3 \cdot Et_2O$, $\delta = 0$, and ^{31}P NMR shifts and relative to H_3PO_4, $\delta = 0$. All downfield chemical shifts are at positive δ.

Synthesis of $HFe_4(CO)_{12}(AuPPh_3)BH$ (2)

A solution of PPN[$HFe_4(CO)_{12}BH$] (0.16 mmol) in CH_2Cl_2 (4 cm^3) was added to solid $AuPPh_3Cl$ (0.08 g, 0.16 mmol). The mixture was stirred at room temperature for 40 min and then solvent was removed under vacuum. The crude neutral product was extracted with Et_2O (2 × 3 cm^3). Dark green-brown $HFe_4(CO)_{12}(AuPPh_3)BH$ was separated as the first fraction, (72% yield by ^{11}B NMR), by column chromatography using dichloromethane/hexane (2/1). $HFe_4(CO)_{12}(AuPPh_3)BH$ (**2**): 128 MHz $^{11}B\{^1H\}$ NMR (CD_2Cl_2) δ 137.3; 162 MHz $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 52.2; 250 MHz ^1H NMR (CD_2Cl_2) δ 7.6–7.3(m, 15H), −7.4(br. 1H), −24.9(s, 1H). IR (CH_2Cl_2, cm^{-1}) ν(CO) 2078w, 2060sh, 2034vs, 2030ws, 2011s, 1994m.

Synthesis of $Fe_4(CO)_{12}(AuPEt_3)_2BH$ (3)

A solution of PPN[$HFe_4(CO)_{12}BH$] (0.4 mmol) in dichloromethane (15 cm^3) was added via cannula to solid $AuPEt_3Cl$ (0.35 g, 1.0 mmol) or to $AuPEt_3Br$ (0.40 g, 1.0 mmol) at room temperature. After 1 h stirring at room temperature, the solvent was removed in vacuo. The product was extracted with Et_2O (3 × 5 cm^3) and was separated by column chromatography (hexane/dichloromethane = 3/1) as the major, dark-green fraction, in 65% yield by ^{11}B NMR. $Fe_4(CO)_{12}(AuPEt_3)_2BH$ (**3**): 128 MHz $^{11}B\{^1H\}$ NMR (CD_2Cl_2) δ 142.4; 162 MHz $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 197 K) δ 52.9(1P), 51.5(1P); 250 MHz ^1H NMR (CD_2Cl_2) δ 2.02 (dq, *J*(HH) 7.5, *J*(PH) 8.0 Hz, 18H), 1.34(dt, *J*(HH) 7.5, *J*(PH) 18.5 Hz, 12H), −10.4(br, 1H). IR (CH_2Cl_2, cm^{-1}) ν(CO) 2057m, 2018vs, 1993vs, 1970sh. FAB-MS *m/e* P^+ 1202.

Synthesis of $Fe_4(CO)_{12}(AuPEt_3)(AuPPh_3)BH$ (4)

A solution of PPN[$HFe_4(CO)_{12}BH$] (0.3 mmol) in dichloromethane (15 cm^3) was added through a cannula to solid $AuPEt_3Cl$ (0.28 g, 0.8 mmol) at room temperature. After 2 h stirring at room temperature, the solvent was removed in vacuo. The dark green product was extracted with Et_2O (3 × 5 cm^3). The product was separated from a small amount of unchanged starting material by column chromatography with hexane/dichloromethane (2/1) eluant. TLC showed the presence of at least two dark green products with extremely close R_f values. Attempts to separate these products further by chromatographic techniques, (column and centrifugal) failed. For mixture: 128 MHz $^{11}B\{^1H\}$ NMR (CD_2Cl_2) δ 142.4 ($Fe_4(CO)_{12}(AuPEt_3)_2BH$), 140.7 ($Fe_4(CO)_{12}(AuPPh_3)(AuPEt_3)BH$), 137.7 ($Fe_4(CO)_{12}Au(PPh_3)_2BH$ [12*];

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* Reference number with asterisk indicates a note in the list of references.

162 MHz $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 298 K) δ 51.6 ($Fe_4(CO)_{12}(AuPEt_3)_2BH$), 51.0 ($Fe_4(CO)_{12}(AuPPh_3)(AuPEt_3)BH$), 50.6 ($Fe_4(CO)_{12}(AuPPh_3)_2BH$) [12*]; 400 MHz ^{1}H NMR (CD_2Cl_2) δ 7.30–7.75 ($Fe_4(CO)_{12}(AuP\mathit{Ph}_3)(AuPEt_3)BH$ and $Fe_4(CO)_{12}(AuP\mathit{Ph}_3)_2BH$), 2.02(dq, *J*(HH) 7.5, *J*(PH) 8.0 Hz, $Fe_4(CO)_{12}(AuP\mathit{Et}_3)_2BH$), 1.34(dt, *J*(HH), 7.5, *J*(PH) 18.5 Hz, $Fe_4(CO)_{12}(AuP\mathit{Et}_3)_2BH$), 1.75(dq, *J*(HH) 7.5, *J*(PH) 8.0 Hz, $Fe_4(CO)_{12}(AuP\mathit{Et}_3)(AuPPh_3)BH$), 1.09(dt, *J*(HH) 7.5, *J*(PH) 18.5 Hz, $Fe_4(CO)_{12}(AuP\mathit{Et}_3)(AuPPh_3)BH$), -10.4(br., $Fe_4(CO)_{12}(AuPEt_3)_2B\mathit{H}$), -10.0(br., $Fe_4(CO)_{12}(AuPEt_3)(AuPPh_3)B\mathit{H}$), -9.1 (br., $Fe_4(CO)_{12}(AuPPh_3)_2B\mathit{H}$).

Results and discussion

$HFe_4(CO)_{12}(AuPPh_3)BH$

The reaction of $[HFe_4(CO)_{12}BH]^-$ with one equivalent of $AuPPh_3Cl$ gives, as expected, a mono-gold(I) derivative which can, from spectroscopic evidence, be unambiguously unidentified as $HFe_4(CO)_{12}(AuPPh_3)BH$ (**2**). Changes in the ^{11}B and ^{1}H NMR spectra during the reaction are minor and thus suggest that the HFe_4BH fragment of the starting cluster remains intact after the addition of the $AuPPh_3^+$ electrophile; the ^{11}B NMR resonance shifts from δ 150.0 to 137.3, while ^{1}H NMR resonances at δ -7.4 and -24.9 in the product compare favourably with those at δ -8.5 and -24.9 in $[HFe_4(CO)_{12}BH]^-$ assigned to Fe_{wing}–H–B and Fe_{hinge}–H–Fe_{hinge} protons respectively [10]. The ^{11}B NMR shift δ 137.7 [2*] for $Fe_4(CO)_{12}(AuPPh_3)_2BH$ illustrates that the presence of gold(I) phosphine fragments adjacent to the boron atom does not result in significant perturbation of the ^{11}B NMR spectrum [5]. The observation that two *endo*-hydrogens remain in **1** still leaves both Fe_{wing}–B and Fe_{hinge}–B edges unbridged and, apparently, able to accept the $AuPPh_3$ fragment into a μ-bonding mode. However, the presence of a Fe_{hinge}–H–Fe_{hinge} proton means that the hinge iron carbonyl ligands will be arranged so as to block the Fe_{hinge}–B site (Fig. 2). We have previously noted [6] that electrophile location and carbonyl ligand orientation are mutually related; an electrophile which bridges an Fe_{hinge}–B edge would produce a rotation of the carbonyl ligands on the hinge iron atom, rendering one CO semi-bridging along the Fe_{hinge}–Fe_{hinge} edge. This is the case in **1** [6]. Thus, we suggest that the structure of **2** is that shown in Fig. 3. This is as expected, since it is a common phenomenon that singly substituted $AuPR_3^+$ fragments mimic protons in their location on a cluster surface [1–4].

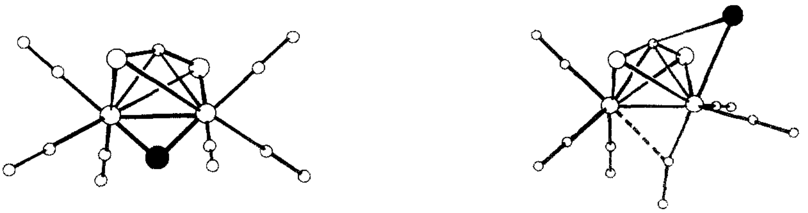

Fig. 2. Schematic representation of the change in carbonyl ligand orientations at the hinge iron atoms which accompanies relocation of an electrophile from Fe_{hinge}–Fe_{hinge} to Fe_{hinge}–B edge.

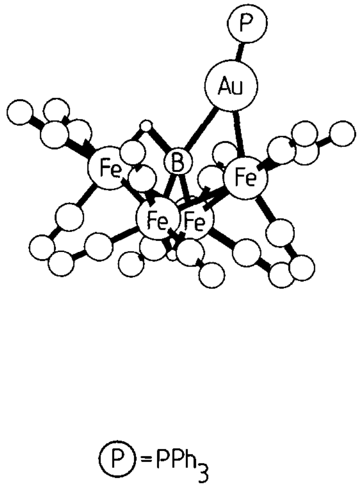

Fig. 3. Proposed structure of **2**.

$Fe_4(CO)_{12}(AuPEt_3)_2BH$

Preparation of pure $Fe_4(CO)_{12}(AuPEt_3)_2BH$ (**3**) from $[HFe_4(CO)_{12}BH]PPN$ and excess $AuPEt_3X$ ($X = Cl$ or Br) can only be achieved if the reaction time is carefully controlled. For a 0.4 mmol scale reaction, reaction times of between 40 min and 1 h produce the desired bis(triethylphosphine)gold(I) product in high yield. NMR spectra are consistent with **3** possessing a structure analogous to that of **1**. This structure is shown in Fig. 4. At 197 K, there are two phosphorus environments on the 162 MHz NMR time scale, but at room temperature only one signal is observed. Previously [5,6] we reported that for **1**, in the 36 MHz ^{31}P NMR, a single resonance persisted to 203 K. On this basis, we proposed a facile "rocking" of the $\{AuPPh_3\}_2$

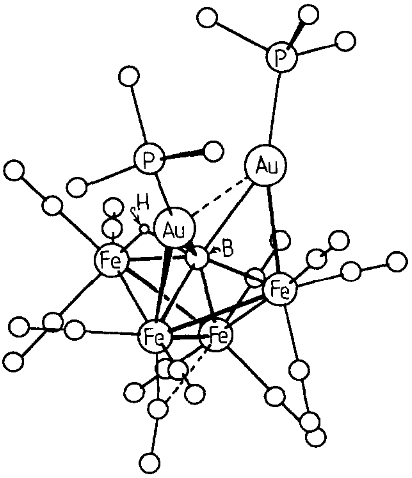

Fig. 4. Structure of $Fe_4(CO)_{12}(AuPR_3)_2BH$, $R = Ph$ [5,6] or Et.

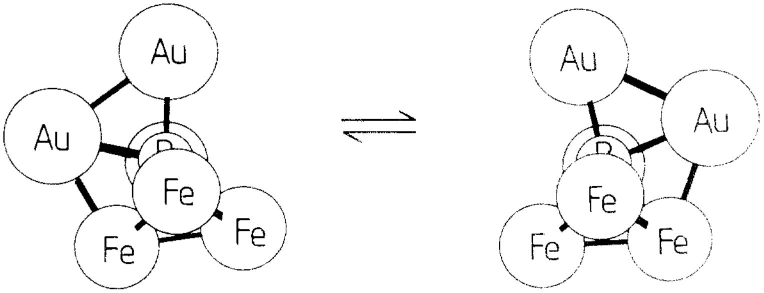

Fig. 5. Proposed mechanism for fluxionality in $Fe_4(CO)_{12}(AuPR_3)_2BH$ leading to phosphorus site equivalence. For convenience, only the Fe_4Au_2B core is shown.

unit across the Fe_4B cluster (Fig. 5). We have recently repeated variable temperature ^{31}P NMR studies on **1**, but at 162 rather than 36 MHz. The increased field strength allows us to observe the two inequivalent phosphorus environments which an X-ray study [5,6] shows exist in the static structure of **1**.

Formation of $Fe_4(CO)_{12}(AuPPh_3)(AuPEt_3)BH$ via phosphine exchange

Attempts to prepare pure **3** by treating $[HFe_4(CO)_{12}BH]PPN$ with excess $AuPEt_3X$ (X = Cl or Br) with a reaction time of between 1 and 2 h led to a mixture of products, two of which are identified as **1** and **3**. The third product, **4**, shows similar spectral characteristics to those of **1** and **3**; the ^{11}B NMR resonance at 298 K for **4** is midway between those of **1** and **3**, and there is a highfield ^1H NMR resonance at δ −10.0 compared to δ −9.1 in **1** and δ −10.4 in **3** corresponding to an Fe_{wing}–H–B bridging proton. The variable temperature ^{31}P NMR spectra of the mixture are shown in Fig. 6. Resonances a and b are assigned to **1** and **3** respectively. The appearance of **1** as a product in the reaction of $[HFe_4(CO)_{12}BH]$ PPN with $AuPEt_3X$ caused us some surprise, since the only possible source of phenyl substituent is the PPN^+ cation. (The purity of the $AuPEt_3X$ had been established). Synthesis of a gold(I) phosphine derivative of a transition metal cluster via the reaction of a cluster anion with gold(I) phosphine halide is a well documented procedure. However, to the best of our knowledge, there has been no report of a phosphine ligand from the cluster's counter-ion exchanging with the gold(I) bound phosphine, and resulting in a substantial product redistribution.

Clearly, if the reaction of $[HFe_4(CO)_{12}BH]PPN$ with $AuPEt_3X$ produces the bis(triphenylphosphine) derivative as well as the bis(triethylphosphine) derivative, then the mixed phosphine derivative $Fe_4(CO)_{12}(AuPPh_3)(AuPEt_3)BH$ should also be formed. Product **4** is identified as this mixed species. Figure 7 illustrates schematically the products formed in the reaction. The ^{31}P NMR is consistent with this; at 197 K, the resonances labelled c and d in Fig. 6 can be assigned to the two isomers of **4**. At temperatures above 263 K, the two isomers are rendered indistinguishable due to the fluxional process illustrated in Fig. 5. The ^{31}P NMR data illustrate two consequences of the different steric requirements of the ethyl and phenyl substituents. Firstly, the coalescence temperature of **3** is lower than that of **4** which is in turn is lower than that of **1**. Thus, as expected, the "rocking" mechanism (Fig. 5) is most facile for the bis(triethylphosphine) derivative. Secondly, there is not a statistical distribution of the two isomers of **4**. Inspection of molecular models of

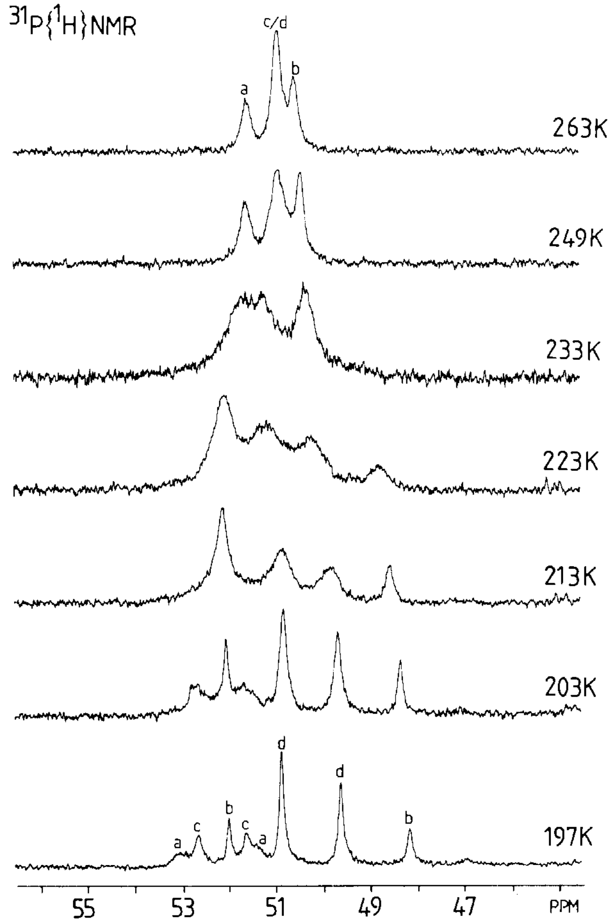

Fig. 6. Variable temperature 162 MHz ^{31}P NMR spectra of the mixture of products from the reaction of $[HFe_4(CO)_{12}BH]$PPN and excess $AuPEt_3$ with a reaction time of 2 h. Resonances labelled a and b refer to compounds **1** and **3** respectively. Resonances c and d refer to the two isomers of compound **4**.

the systems indicates that the isomer with the $AuPPh_3$ group bridging the Fe_{wing}–B edge and the $AuPEt_3$ group bridging the Fe_{hinge}–B edge (Fig. 7d) is probably preferred on steric grounds.

In an effort to understand at what stage in the reaction phenyl groups are introduced into the product, we carried out several room temperature test reactions. (i) Prolonged stirring of PPNCl with $AuPEt_3Cl$ monitored by ^{1}H NMR produced no exchange of the ethyl and phenyl substituents. (ii) Trace quantities of $[HFe_4(CO)_{12}BH]$PPN were added to a stirred solution of PPNCl with $AuPEt_3Cl$. Monitoring with ^{1}H NMR showed no indication that the iron cluster catalysed phenyl–ethyl exchange. (iii) The ^{31}P NMR spectrum of an aged CD_2Cl_2 solution of PPNCl showed no traces of free PPh_3. (iv) The ^{31}P NMR spectrum of a CD_2Cl_2 solution of pure **3** stirred at room temperature for 1 h, with PPNCl showed the formation of both **1** and **4**. Thus, we conclude that phosphine exchange takes place after the initial formation of **3**. Hence, the method of reacting $AuPR_3X$ with a transition metal cluster anion, the counter ion of which contains a phosphine PR'_3,

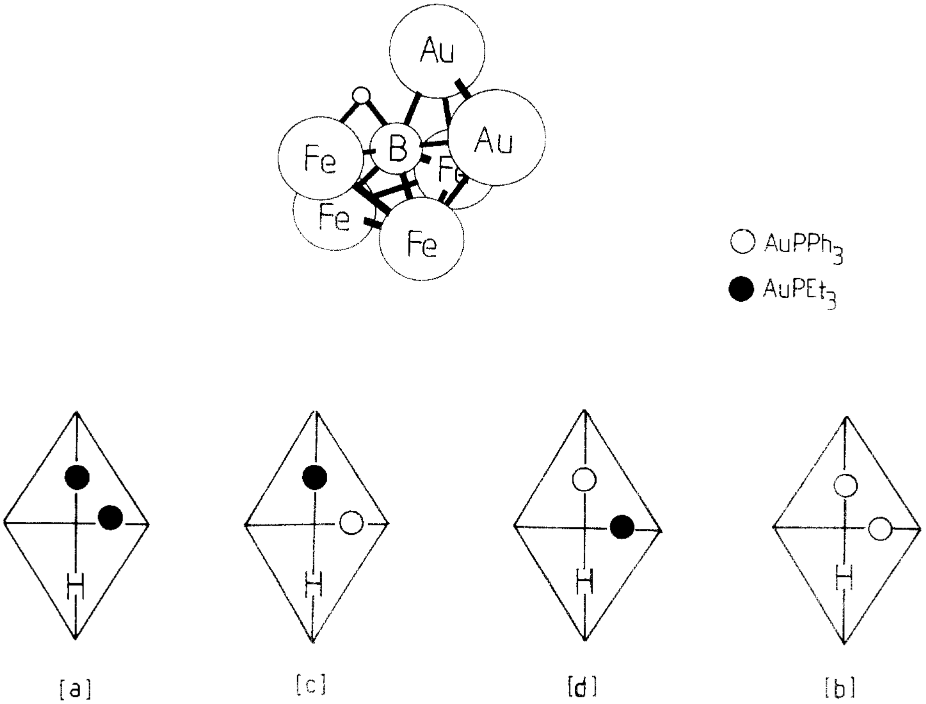

Fig. 7. Schematic representation of the structures of the products from the reaction of $[HFe_4(CO)_{12}BH]PPN$ and excess $AuPEt_3$ (t 2 h); (a) = **1**, (b) = **3**, (c) and (d) = the two isomers of **4**.

is, indeed, a suitable general synthetic route, providing that the reaction times are carefully controlled.

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