

**STRUCTURAL CHARACTERIZATION OF HETEROMETALLIC GOLD –
IRON CLUSTERS**

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ABSTRACT

Structural survey of the clusters in Cambridge Structural Database was carried out to investigate the stereochemistry about gold and iron in their heterometallic clusters. Clusters ranging from heterobinuclear to polynuclear clusters were included in the survey. The gold atoms are surrounded from two to six donor atoms, and the iron atoms from six to ten donor atoms. The shortest Au-Fe, Fe-Fe and Au-Au bond distances are 2.438(3), 2.504(3) and 2.630(1)Å. There are few clusters, which contain two crystallographically independent molecules and another one which contains four such molecules. Those are classical examples of distortion isomerism. Correlations between structural parameters and donor atoms are given.

Key words: structure, heterometallic, gold/iron, clusters, isomers

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0. ABBREVIATIONS

1,5-cod

1,5-cyclooctadiene

50	C ₁₁ H ₁₉ S	2,2,6,6-tetramethylcyclohexanthiocarbaldehyde
51	C ₁₇ H ₂₈ NP	1,1'-(1-dimethylamino-1,3-propanediyl)-2-diphenylphosphine-
52		dicyclopentadienyl
53	C ₅ H ₄ CH ₂ NMe ₂	N,N-dimethylaminomethylcyclopentadienyl
54	C ₅ H ₄ Me	methylcyclopentadienyl
55	C ₅ H ₄ P(Ph)C ₅ H ₄	dicyclopentadienylphenylphosphine
56	C ₅ H ₄ PPh ₂	diphenylphosphinocyclopentadienyl
57	C ₆ H ₆	benzene
58	cp	cyclopentadienyl
59	ddpca	(S*)-N,N-dimethyl-1-[R*]-1',2-(bis(diphenylphosphino)
60		cyclopentadienyl)ethylamine
61	dppm	bis(diphenylphosphino)methane
62	dptpc	diphenylthiophosphoryl-cyclopentadienyl
63	m	monoclinic
64	Me	methyl
65	or	orthorhombic
66	P(OEt) ₃	tris(ethyloxy)phosphine
67	PhC ₂ Ph	1,2-diphenylethenyl
68	PPh ₂ (tol)	tolylidiphenylphosphine
69	PPh ₃	triphenylphosphine
70	Pr'S	iso-propylthiolate
71	SiPh ₂ (Me)	methyldiphenylsilicium
72	tr	triclinic

74 1. INTRODUCTION

76 Compounds containing metal-metal bonds are called cluster compounds. Clusters of
77 more than three metal atoms generally consist of polyhedral arrangements of the metal
78 atoms. They form the fascinating and rapidly growing branch of chemistry that we may call
79 „polyhedral cluster chemistry“. By applying the 18-electron rule to the polyhedral clusters
80 containing transition metal atoms the entire cluster can be usually and conveniently treated
81 as a unit.

82 The convention and reactivity of metal-metal bonds is an important aspect of metal
83 cluster chemistry [1]. The key role in the practical and theoretical behavior of the clusters is
84 played by the metal-metal bond opening and closing. Especially transition metal clusters that
85 are capped by a main group atom containing moieties (e.g. CR, PR or SR [2-4]) are good
86 candidates for the study of metal-metal bond cleavage and formation since the capping
87 group preserves the integrity of the molecule.

88 The aim of this article is to analyze Au-Fe bonds as well as no-bonds in a series of
89 compounds ranging from heterobinuclear compounds to heterooligonuclear compounds.

91 2. STRUCTURAL CLASSIFICATION

93 2.1 Heterobinuclear compounds

95 There are totally 12 coloured compounds, three with an Au-Fe bond [5-7] and
96 remaining nine without an Au-Fe bond [8-16]. Their crystallographic and structural data are
97 gathered in Table 1.

98 In three yellow AuFe derivatives, two non-equivalent units, (Ph₃P)Au and Fe(CO)₃(η³-
99 allyl) [5], {(tol)Ph₂P}Au and Fe(CO)₃{Si(Me)Ph₂}(PMe₃) [6], (Ph₃P)Au and Fe(CO)₃.
100 {Si(Me)Ph₂}(PPh₃) [7] are held together only by direct Au-Fe bond, with the distances of
101 2.519(1)Å [5], 2.527(3)Å [6] and 2.553(1)Å [7]. Each Au atom is almost linearly coordinated
102 (AuPFe) with the P-Au-Fe bond angles of 174.4(2), 178.1(2) and 177.51(6)°, respectively. In
103 [5] the iron atom is seven coordinated (FeC₆Au) and in the remaining two derivatives are six-
104 coordinated (FeC₃PSiAu).

In another two yellow AuFe derivatives [8] bis(diphenylphosphino)methane (dppm) serve as a bridge between AuL (L= Me or Cl) and $\text{Fe}(\text{CO})_2(\eta^4\text{-C}_5\text{H}_4\text{Me})$ moieties in the manner $\text{LAu-P}(\text{Ph}_2)\text{CH}_2\text{CH}_2(\text{Ph}_2)\text{P-Fe}(\text{CO})_2(\eta^4\text{-C}_5\text{H}_4\text{Me})$. The derivative when L is methyl, contains two crystallographically independent molecules, differ mostly by degree of distortion. Each gold atom is two-coordinated with the C-Au-P bond angles of $177.3(4)^\circ$ (molecule 1) and $175.1(3)^\circ$ (molecule 2) and the value of Cl-Au-P bond angle is $176.44(8)^\circ$. Each iron atom is seven coordinated (FeC_6P).

In orange triclinic AuFe derivative [9] pair of equivalent diphenylthiophosphoryl-cyclopentadienyl (dptpc) ligands are coordinated to iron atom via the cyclopentadienyl rings and form a sandwich (FeC_{10}) and to gold atom via the two S atoms (AuS_2). There are two crystallographically independent molecules, differ by degree of distortion. The mean Au-S bond distance and S-Au-S bond angle are $2.301(3)\text{\AA}$ and $176.43(12)^\circ$ (molecule 1) and $2.284(3)\text{\AA}$ and $178.26(11)^\circ$ (molecule 2).

Two monoclinic AuFe derivatives, orange [10] and yellow [11] are isostructural. In both a pair of $\text{C}_5\text{H}_4\text{PPh}_2$ ligands are coordinated to AuPPh_3 unit via P atoms (AuP_3) and to iron atom via the cyclopentadienyl rings and form a sandwich (FeC_{10}).

In another AuFe derivative [12] two units, Ph_3PAu and $\text{Fe}(\eta^5\text{-cp})$ are held together by hexadentate $\text{C}_5\text{H}_4\text{C}(\text{O})\text{C}(\text{H})\text{C}(\text{O})\text{Me}$ ligand in the $\text{C}^1\text{:C}^5$ -fashion. The gold atom is two-coordinated (AuCP) and iron atom is sandwiched (FeC_{10}). In orange AuFe derivative [13] the Ph_3PAu unit is connected with iron by multidentate $\text{C}_5\text{H}_4\text{C}(\text{O})\text{C}_6\text{H}_4\text{COO-1,2}$ in the $\text{O}^1\text{:C}^{10}$ -fashion. The gold atom is two coordinated (AuOP) and iron atom is sandwiched (FeC_{10}). The O-Au-P bond angle is $176.5(2)^\circ$. In another orange AuFe derivative [14] two non-equivalent moieties, Ph_3PAu and $\text{Fe}(\eta^5\text{-cp})$ and connected by the $\text{C}_5\text{H}_4\text{CH}_2\text{NMe}_2$ ligand in the $\text{N}^1\text{:C}^5$ -fashion and completed an almost linear coordination about gold atom (AuNP) and sandwich about iron atom (FeC_{10}). Finally, in yellow AuFe derivative [15] multidentate $\text{C}_{17}\text{H}_{28}\text{NP}$ ligand connected AuCl unit with iron in the $\text{P}^1\text{:C}^{10}$ -fashion. The gold atom is two-coordinated (AgCIP) and iron atom is sandwiched (FeC_{10}).

The data in Table 1 indicates gold in two- AuPFe [5-7], AuCP [8,12,14], AuCIP [8], AuS_2 [9] and AuOP [13] and three- AuP_3 [10,11] coordinated. The mean value of Au-L (monodentate) bond distance in the series of two-coordinated species elongated in the sequence: $2.085\text{\AA}$ (Me) < $2.268\text{\AA}$ (PPh_3) < $2.305\text{\AA}$ (Cl). There is only one homo-P,P'-bidentate ligand, which span between the respective moieties in two derivatives.

Gold and iron units [8] with the mean Au-P and Fe-P bond distances are of 2.267 and $2.210\text{\AA}$, respectively. The multidentate ligands include hetero-donor atoms one O plus ten C, one C plus five C, one P and five P, one P plus ten C donor atoms. All of the multidentate ligands bound to gold atom via one donor atom with the Au-L bond distance elongated in the sequence: $2.059\text{\AA}$ (L= O^1C^{10}) < $2.074\text{\AA}$ (L= C^1C^5) < $2.240\text{\AA}$ (L= P^1C^{10}) < $2.383\text{\AA}$ (L= P^1C^5). Multidentate C donor atoms bound the iron atoms.

The iron atoms are six- FeC_3PSiAu [6,7], seven- FeC_6Au [5], FeC_6P [8] and ten- FeC_{10} [9-15] coordinated. There are two AuFe derivatives [8,9] which contain two crystallographically independent molecules within the same crystal and are examples of distortion isomerism [16]. Noticeable, the AuFe derivatives by far prefer crystallized in the monoclinic space group (x10) with one example which is triclinic.

2.2 Heterotrinnuclear clusters

There are seventeen (six AuFe_2 and eleven Au_2Fe) trinuclear clusters and their crystallographic and structural parameters are summarized in Table 2. In orange AuFe_2 cluster [17] all three metal atoms form a triangle with Fe-Fe bond distance of $2.605(2)\text{\AA}$ and Au-Fe bond distances of $2.622(1)$ and $2.698(1)\text{\AA}$. Two carbonyl groups also bridge the two iron atoms. The core of dark green AuFe_2 cluster [18] consists of an almost equilateral metal triangle. The edge of Fe-Fe bond ($2.621(2)\text{\AA}$) is bridged by both an isopropylthiolate ligand and a carbonyl group. In addition the gold atom is coordinated by a triphenylphosphine ligand and three terminal carbonyls are attacked to each iron atom. The mean Au-Fe bond distance of $2.670(1)\text{\AA}$ is about $0.010\text{\AA}$ longer than that found in [17]. In red orange AuFe_2 cluster [19]

two crystallographically independent molecules within the same crystal are present. Two iron atoms and one gold atom form a triangle with the Fe-Fe bond distance of 2.651(4)Å and Au-Fe bond distances of 2.683(4) and 2.700(3)Å in one molecule. The values in the other one are 2.644(4), 2.681(3) and 2.740(4)Å, respectively. The **edge of** Fe-Fe bond is bridged by thioaldehyde ligand **via** carbon and sulfur atoms. The basic skeleton of green cluster [20] consists of a highly asymmetric triangular AuFe₂ system with the Fe-Fe bond distance of 2.627(2)Å and Au-Fe bond distances of 2.627(2) and 2.761(2)Å, respectively. The **edge of** Fe-Fe bond is bridged by a carbonyl group and an σ,π -diphenylethenyl group.

In the remaining two orange AuFe₂ clusters [21,22], two (cp)Fe fragments are connected with Au(C≡CPh) [21] or AuCl [22] unit with C₅H₄P(Ph)C₅H₄ ligand. Each gold atom is two-coordinated, AuCP [21] and AuClP [22] with P-Au-X **bond** angles of 174.3(4)° (X=C) and 176.1(1)° (X=Cl), respectively. Each iron atom is sandwiched, FeC₁₀.

There are eleven coloured Au₂Fe clusters [23-32]. Two yellow clusters [23-24] contain a triangular core of metal atoms. In [23] four crystallographically independent molecules within the same crystal are present, differing mostly by the degree of distortion, this in the only example in the series of heterotrinnuclear clusters with such a number of independent molecules. The mean Au-Fe bond distance of 2.538(3)Å (range from 2.509(3) to 2.553(2)Å) is about 0.363Å shorter than Au-Au bond distances with the mean value of 2.901Å (2.872(2) - 2.928(1)Å).

In red Au₂Fe cluster [25] the Ph₃PAuAuPPh₃ fragment with Au-Au bond distance of 2.768(2)Å is attached to (μ_3 -C₅H₄)Fe(η^5 -cp) fragment **via** μ_3 -C atom and **in addition**, the iron atom is connected with one Au atom (Fe-Au 2.818(2)Å). In two yellow Au₂Fe clusters [26] the Fe(C₅H₄PPh₂)₂ fragment coordinates **to two** AuX (X=Cl or I) centers in an open bridging mode. The P-Au-Cl and P-Au-I **bond** angles are very close to the linear with the values of 179.59(5) and 177.0(2)°, respectively. The cyclopentadienyl rings adopts in staggered conformation. In orange Au₂Fe cluster [27] the Fe(C₅H₄PPh₂)₂ fragment is attached **via** P atoms to AuSAu fragment. The Au-Au bond distance is 2.882(1)Å and Au-S-Au bridge angle is 77.57(9)°. The P-Au-S **bond** angles are 173.78(6)°. The iron atom is sandwiched (FeC₁₀).

In structure of yellow Au₂Fe cluster [28] the C(PPh₂)₂ ligand serves as a bridge between the Cl(PhNC)₃Fe **unit** and two Au(PPh₃) fragments. Two phosphorus atoms of the bridging ligand are directly coordinated to the iron atom and complete pseudo-octahedral coordination about the iron atom (FeC₃P₂Cl). The C atom of the C(PPh₂)₂ ligand is bridging two Au(PPh₃) fragments. The Au-Au distance is 2.891(4)Å and Au-C-Au bridge angle is 74.1(15)°.

In the remaining four Au₂Fe clusters [29-32], the 1,1-bis(diphenylphosphino)ferrocene is singly bridging in [29] the Au₂{ μ - η^2 -S(CH₂)₂S} fragment, in [30] two Au(η^1 -F₃CCOO) fragments, in [31] two Au(η^1 -C₁₆H₉) fragments, and in [32] two AuCl fragments. Each gold atom is almost linearly coordinated and each iron is sandwiched (FeC₁₀) (Table 2). In [32] two crystallographically independent molecules within the same crystal are present, **differing** mostly by the degree of distortion.

Inspection of the data in Table 2 reveals that the heterotrinnuclear (AuFe₂, Au₂Fe) clusters crystallized in two crystal classes, monoclinic (x10) and triclinic (x6). The gold atoms are two- AuXP (X=C [21-31], Cl [22, 26, 32], I [26], S [29] or O [30]), three- AuPFe₂ [17-20], AuPFeAu [23-24], AuSPAu [27], AuCPAu [28], and four- AuCPFeAu [25] coordinated.

For the iron atom the coordinations involved are six- FeC₄AuFe [17, 18], FeC₄Au₂ [23], FeC₃PAu₂ [24], FeC₃P₂Cl [28], seven- FeC₄SAuFe [19], FeC₅AuFe [20], ten (sandwich) - FeC₁₀ [21, 22, 26, 27, 29 - 32] and eleven- FeC₁₀Au [25] donor atoms of which the sandwiched is most common.

The Au-Fe bond distance range from 2.509(3)Å [24] to 2.818(2)Å [25] (mean 2.634Å), Au-Au bond distance from 2.768(4)Å [25] to 2.928(1)Å [23] (mean 2.880Å) and Fe-Fe bond distance from 2.615(2)Å [17] to 2.651(4)Å [19] (mean 2.630Å). The mean Au-L (monodentate) bond distance **elongates** in the order: 2.036Å (CL) < 2.098Å (OL) < 2.272Å (PPh₃) < 2.285Å (Cl) < 2.353Å (I). There are two clusters, (Ph₃P)AuFe₂(μ -C₁₁H₁₉S)(CO)₆ [19] and (ClAu)₂(μ - η^1 : η^5 -C₅H₄PPh₂)₂Fe [32] which contain two crystallographically independent

molecules within the same crystal and $\{(\text{Ph}_3\text{P})\text{Au}\}_2\text{Fe}(\text{CO})_4$ [23] contains even four such molecules. These are classical examples of distortion isomerism [16].

2.3 Heterotetranuclear clusters

There are six categories of clusters: AuFe_3 (4 examples), Au_2Fe_2 (3 examples), Au_3Fe (2 examples), Au_2FePt (1 example), $\text{AuM}_2\text{M}'$ (2 examples) and AuFeCoRu (1 example), and their crystallographic and structural parameters are gathered in Table 3. There are four red AuFe_3 clusters [33-36]. One of them [33] consists of an $\{\text{Fe}(\text{CO})_3\}_3$ triangular planes capped by a $\mu_3\text{-Te}^{2-}$ ion with one edge bridged by a triphenylphosphinylgold(I) cation. This moiety has approximately the same distances to two iron atoms. The Au-Fe bond distances are 2.681(3) and 2.652(3) Å and the Fe-Au-Fe bond angle is 64.3(1)°. The distance between the bridged Fe(1)-Fe(2) atoms is significantly longer (2.837(4) Å) than the corresponding distance between the non-bridged Fe(1)-Fe(3) and Fe(2)-Fe(3) distances of 2.623(4) Å. The triphenylphosphinylgold(I) cation lies below the plane of the Fe_3Te tetrahedron with Au-Fe(1)-Fe(3) bond angle of 98.7(1)° and Au-Fe(2)-Fe(3) bond angle of 99.4(1)°.

The metal core in $[(\text{Ph}_3\text{P})\text{AuFe}_3(\mu\text{-CO})(\text{CO})_{10}]^-$ anion [34] consists of a Fe_3Au „butterfly“ arrangement, where a triphenylphosphinylgold(I) cation forms a bridge at one edge of the Fe_3 triangle. The interplanar angle here is 59.7(1)°. The average Fe-Fe distance is 2.655 Å [2.632(1), 2.652(1) and 2.682(1) Å]. The mean Au-Fe bond distance is 2.643(1) Å.

The independent molecules in another AuFe_3 cluster [35] are approximate non- super imposable mirror of each other (Fig. 1). The triphenylphosphinylgold(I) cation bridging the Fe(1)-Fe(2) edge of the Fe_3 triangle. Furthermore, it is situated opposite side to the triangle to that occupied by the $\mu_3\text{-HC=CBu}^t$ ligand. The AuFe(2)Fe(3) dihedral angle in the two independent molecules differs significantly having the values 110.9 and 132.1°.

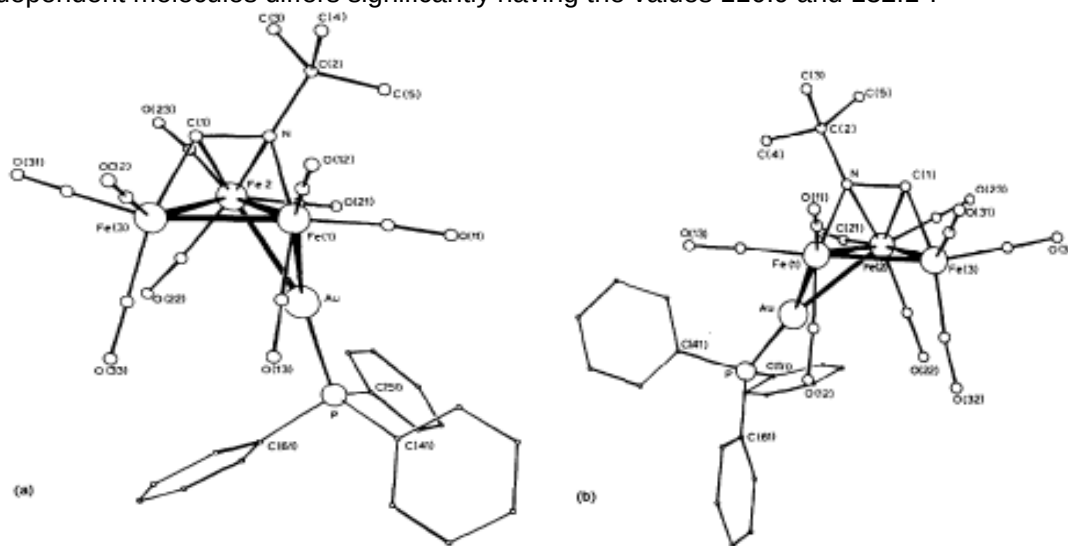


Fig.1 Structure of two independent molecules of $[(\text{Ph}_3\text{P})\text{AuFe}_3(\mu_4\text{-HC=NBu}^t)(\text{CO})_6]$ [35]

In another AuFe_3 cluster [36] the metal core consists of an isosceles triangle of iron atoms, capped by a $\mu_3\text{-SPr}^i$ ligand. The longest Fe-Fe bond (2.800(6) Å) is bridged by a triphenylphosphinylgold(I) cation. The resulting „butterfly“ angle is 123.9(2)°. The Au-Fe bond distances are 2.653(4) and 2.645(5) Å. The non-bridged Fe-Fe bond distances are 2.631(8) and 2.644(7) Å.

There is structural information on three complexes containing Au_2Fe_2 clusters [37-39]. In the red Au_2Fe_2 cluster [37] the square planar geometry is tetrahedrally distorted. The dihedral angle between two Au(1)-Au(2)-Fe(1) and Au(1)-Au(2)-Fe(2) planes is 24.7(1)°. The Au-Fe bond distances 2.527(2) and 2.534(2) Å are shorter than for Fe-Fe and Au-Au (2.900(2) and 2.915(1) Å, respectively). Both gold atoms are bonded to phosphorus atoms of

the bridging $\mu\text{-}\eta^2\text{-dppm}$ ligand. The coordination sphere around each iron atom displays a distorted octahedron with bridging to four carbonyl groups, one gold atom and the other iron atom (FeC_4AuFe). Each gold atom is three coordinated (AuPFeAu) (T shape).

In the colourless Au_2Fe_2 cluster [38], which has an approximate C_2 symmetry, the Fe-Au-Au-Fe chain is a zig-zag chain. Two pairs, of Fe(1) and Au(2) and of Fe(2) and Au(1), are bridged by a $\mu\text{-}\eta^2\text{-dppm}$ ligand, thus forming unusual twisted six-membered rings fused along the Au-Au edge. The average Au-Fe bond distance is $2.549\text{\AA}$. It is interesting to note that the complex forms also a 10-membered ring, where the Au-Au bond distance is $2.962(1)\text{\AA}$ is reminiscent of the trans-annular interactions that occur in middle-sized organic rings.

In a yellow-orange Au_2Fe_2 cluster [39] two $\text{C}_5\text{H}_4\text{CH}_2\text{NMe}_2$ ligands act as bridges between two gold atoms and two $\text{Fe}(\eta^5\text{-cp})$ moieties, thus forming a 10-membered ring ($\text{AuNC})_2$ with $\text{Au}\cdots\text{Au}$ separation of $3.122(1)\text{\AA}$.

There are two Au_3Fe clusters [40, 41] and the structure of orange Au_3Fe cluster [40] is shown in Fig. 2. The three gold atoms form a plane and an apical sulfur atom is situated $1.29\text{\AA}$ out of this plane. The shortest Au-Au distance of $2.8889(8)\text{\AA}$ is found between the atoms Au(1) and Au(2), and the remaining two distances are $3.404(1)$ and $3.759(1)\text{\AA}$ between Au(1)-Au(2) and Au(2)-Au(3), respectively. Consequently, also the respective angles are dissimilar with the values of $\text{Au}(1)\text{-S-Au}(2) = 76.36(10)$, $\text{Au}(1)\text{-S-Au}(3) = 92.64(12)$ and $\text{Au}(2)\text{-S-Au}(3) = 105.69(14)^\circ$. In this mixed-valence cluster the Au(I) and Au(2) atoms have the formal oxidation state of +1, whereas the Au(3) atom has the value +3. The Au(I) cations have an almost linear coordination (AuSP) with the S-Au-P angles of $175.94(14)$ and $171.72(12)^\circ$. The Au(III) cation has square-planar geometry (AuC_3S).

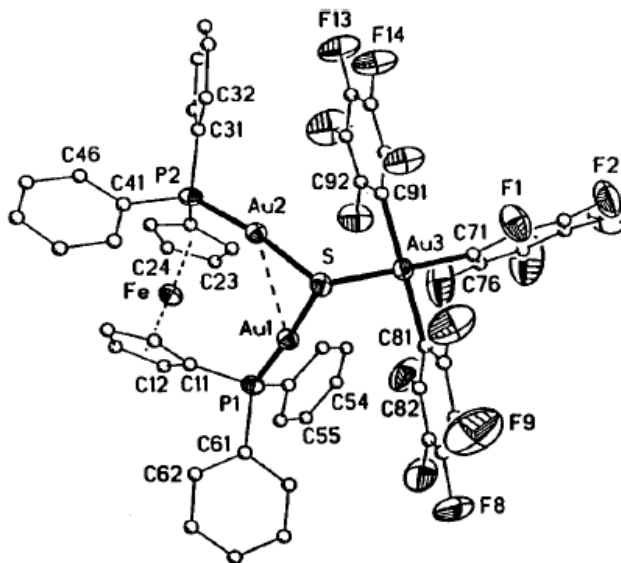


Fig. 2 Structure of $[(\text{F}_5\text{C}_6)_3\text{Au}(\mu_3\text{-S})\text{Au}_2\{(\mu\text{-dppcp})_2\text{Fe}\}]$ [40]

In colourless Au_3Fe cluster [41] the complex cation consists of two gold atoms bridged by two different ligands, namely $\text{C}_5\text{H}_4\text{PPh}_2$ and 2-pyridinethiolate. The third gold atom is bonded to a tertiary phosphine and to a sulfur atom of the 2-pyridinethiolate ligand. Accordingly, the sulfur atom in the 2-pyridinethiolate atoms acts as a terdentate bridging donor atom. The Au(1)-Au(2) separation of $3.2105(13)\text{\AA}$ is significantly longer than that for the Au(1)-Au(3), $3.0965(12)\text{\AA}$. The cyclopentadienyl rings adopts coordination approximately midway the staggered and eclipsed ones.

The structure of an Au_2FePt cluster [42] is illustrated in Fig. 3. As can be seen, the FePt atoms (Fe-Pt $2.715(3)\text{\AA}$) are bridged by a $\mu\text{-Pcy}_2$ fragment and by two $\text{Au}(\text{PPh}_3)$ fragments. The propeller-like core consists of three triangles sharing a Pt-Fe edge. The dihedral angles between the Fe-Pt-Au(1) and Pt-Fe-Au(2) are 134.6° . The average Au-Fe

distance of 2.595Å is much shorter than that for the Au-Pt distance of 2.848Å. The Au-Au distance of 4.333Å is too long to indicate a chemical bond.

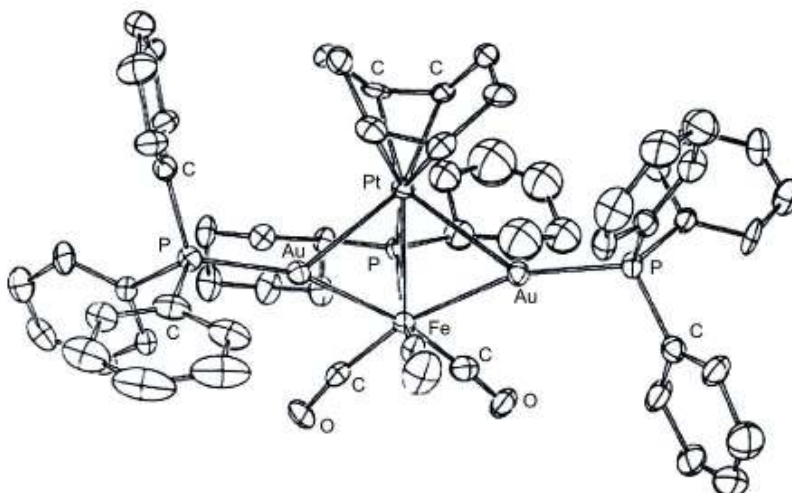


Fig. 3 Structure of $[(OC)_3Fe(\mu-Pcy_2)\{Au(PPh_3)\}_2Pt(1,5-cod)]^+$ [42]

In a black complex with an $AuFe_2Co$ cluster [43], a Fe_2Co triangle base is capped by an $AuPPh_3$ moiety from one side and by a μ_3-COMe ligand from the other side, resulting in a trigonal bipyramid. The average Fe-Co bond distance of 2.490Å is clearly shorter than the average value for the Au-Fe bond distances (2.690Å) or the Fe-Fe bond distance of 2.643(1)Å.

The structure of a black $(OC)_3Fe(\mu_3-CPh)Co_2(CO)_6Au(PPh_3)$ [44] contains a $FeCo_2AuC$ core, where a CPh fragment serves as a bridge between Fe and two Co atoms. The average Fe-Co bond distance of 2.566Å is shorter than that for Fe-Au or Co-Au distances of 2.615(3) and 2.661(3)Å, respectively. The Co-Co distance of 2.492(4)Å is the shortest one.

There are two more black compounds that have the formula $(OC)_3Fe(\mu_3-E)CoRuAu(CO)_6(PPh_3)$ ($E = S$ or PMe) [45]. Both cluster are isostructural displaying a „butterfly“ configuration of the metal atoms. While the cluster with μ_3-PMe crystallized in the monoclinic class, with the μ_3-S in triclinic. Unfortunately structural data are available only for the former. The metal-metal bond distance elongated in the order: 2.677(2)Å (Au-Fe) < 2.678(4)Å (Fe-Co) < 2.679(3)Å (Co-Ru) < 2.729(2)Å (Au-Ru) < 2.914(3)Å (Fe-Ru) < 2.957(3)Å (Co-Ru).

Inspection of the data in Table 3 reveals that the heterotetranuclear clusters crystallized in the following crystal classes: monoclinic (x11), triclinic (x2) and orthorhombic (x1). Mostly clusters are red (x5) and black (x4) of colours with two examples of orange and colourless. Gold atoms are two- $AuNC$ [39, 41], $AuSP$ [40, 41], three- $AuPFe_2$ [33-36, 43], $AuPFeM$ ($M=Au'$ [37,38], Pt [42], Co [44] or Ru [45]) and four- AuC_3S [40] coordinated.

The iron atoms are found six- [33-38, 42], seven- [33-36, 43-45], and ten (sandwiched) [39, 41] coordinated, cobalt atoms are six- [44, 45], seven- [44] and nine- [43] coordinate, gold seven- [42] as well as ruthenium [45].

The series of heterotetranuclear clusters is rich on the direct metal-metal bonds. The mean Au-M bond distance elongated in the order: ($M=Fe$, 2.633Å (2.527(2)Å [37] – 2.717(3)Å [35]) < Co, 2.661(3)Å [44] < Ru, 2.729(2)Å [45] < Pt, 2.848Å (2.821(1) – 2.875(1)Å [42]) < Au, 2.922Å (2.8889(8)Å [40] – 2.962(1)Å [38]). The mean Fe-M bond distance elongated in the order: $M=Co$, 2.570Å (2.486(1)Å [43] – 2.678(4)Å [45]) < Au, 2.633Å < Fe, 2.676Å (2.574(2)Å [35] – 2.900(2)Å [37]) < Pt, 2.715(3)Å [42] < Ru, 2.914(3)Å [45]. The Co-M bond distance elongated in the order: $M=Co$, 2.492(4)Å [44] < Ru, 2.679(3)Å [45].

2.4 Heteropentanuclear clusters

There are twenty one heteropentannuclear clusters of the eight categories, AuFe_4 [46-49], Au_2Fe_3 [11, 50-53], Au_3Fe_2 [54,55], Au_4Fe [27,56], AuFe_3Co [57], $\text{Au}_2\text{Fe}_2\text{Ir}$ [58], AuFe_2M_2 ($\text{M}=\text{Ir}$ [59], Rh [60]) and AuM_3Fe ($\text{M}=\text{Co}$ [61-62], Ru [63]), and their crystallographic and structural data are gathered in Table 4. There are five coloured AuFe_4 clusters [46-49] for which X-ray data are available. In dark brown AuFe_4 cluster [46], the internal dihedral angle of the Fe_4 butterfly framework is 114.6° . The mean Fe-Fe bond distance is $2.655\text{\AA}$ (range $2.604(2) - 2.680(2)\text{\AA}$). The Au(I) atom has AuPBFfe chromophore with the Au-Fe bond distance of $2.580(1)\text{\AA}$.

Dark green AuFe_4 cluster [47] contains well-separated $(\text{NMe}_3\text{CH}_2\text{Ph})^+$ cations, $[(\text{OC})_{16}\text{Fe}_4\text{Au}]^-$ anion and chloride anion. The gold(III) atom sits on a center of symmetry. Two $[\text{Fe}_2(\text{CO})_8]^{2-}$ anions linked to a central gold(III) atom adopts a square-planar coordination with the mean Au-Fe bond distance of $2.595\text{\AA}$. The Fe-Fe bond distance is $2.711(2)\text{\AA}$. Black $(\text{OC})_{12}\text{Fe}(\mu_4\text{-COMe})\text{Au}(\text{PEt}_3)$ [48a] has a butterfly core. The Fe-Fe bond distances in the butterfly core range from $2.606(3)$ to $2.687(4)\text{\AA}$ and average $2.638\text{\AA}$. Interestingly, the presence of Et_3PAu bridge across the hinge causes by a $0.05\text{\AA}$ between in the $\text{Fe}(2)\text{-Fe}(3)$ bond distance ($2.687(4)\text{\AA}$) when compared to the average Fe-Fe bond distance. The Au-Fe(2) and Au-Fe(3) bond distances are $2.666(2)$ and $2.675(2)\text{\AA}$.

In green AuFe_4 cluster [48b], the four iron atoms are also in a butterfly arrangement while the gold atom bridges the two-wingtip iron atoms. The internal dihedral angle of Fe_4 butterfly framework is $107.3(1)\text{\AA}$. The carbide atom occupies the cavity of the Fe_4Au metal core and is bonded to all five metal atoms. The mean Au-Fe and Fe-Fe bond distances are 2.843 and $2.617\text{\AA}$, respectively. The four iron atoms define a „butterfly“ configuration and the gold atom bridges the two „wingtip“ iron atoms to give an overall „bridged – butterfly“ metal framework for another green cluster [49]. The internal dihedral angle of Fe_4 butterfly framework of 71.7° is the smallest one in the series of AuFe_4 clusters.

There are also five coloured Au_2Fe_3 clusters [11, 50-53]. The black $\{(\text{Ph}_3\text{P})\text{Au}\}_2\text{Fe}_3(\mu_3\text{O})(\text{CO})_9$ [50] contains a Au_2Fe_3 trigonal bipyramidal moiety with $\text{Au}(1)$ and $\text{Fe}(5)$ atom in the axial positions and $\text{Au}(2)$, $\text{Fe}(3)$ and $\text{Fe}(4)$ atoms in the equatorial positions. The molecule of the cluster has C_5 noncrystallographic symmetry, with the mirror plane passing through the atoms $\text{Au}(1)$, $\text{Au}(2)$ and $\text{Fe}(5)$. The $(\mu_3\text{-O})(1)$ atom is bonded with three iron atoms with the average Fe-O bond distance of $1.876\text{\AA}$ and Fe-O-Fe bond angles of 88° . The $\text{Fe}(3)\text{-Fe}(4)$ bond distance between two equatorial iron atoms ($2.700(2)\text{\AA}$) is substantially longer than the corresponding values for $\text{Fe}(3)\text{-Fe}(5)$ ($2.537(2)\text{\AA}$) and $\text{Fe}(4)\text{-Fe}(5)$ ($2.578(2)\text{\AA}$) bonds between axial and equatorial iron atoms. The same tendency was found for Fe-Au bond lengths $2.782(2)\text{\AA}$ ($\text{Au}(2) - \text{Fe}(3)$) and $2.749(2)\text{\AA}$ ($\text{Au}(2) - \text{Fe}(4)$) for two atoms in equatorial positions and $2.699(2)\text{\AA}$ ($\text{Au}(1) - \text{Fe}(3)$), $2.714(2)\text{\AA}$ ($\text{Au}(1) - \text{Fe}(4)$) for atoms in equatorial and axial positions. The Au-Au distance is $2.9915(9)\text{\AA}$.

Structure of deep red Au_2Fe_3 cluster [51] consists of $\{\text{HFe}_3(\text{CO})_9(\mu_3\text{-P})\}^{2-}$ cluster frame coordinated to $\text{Au}\cdots\text{Au}$ bonded $\{\text{Au}_2(\text{PPh}_3)_2\}^{2+}$ unit (Fig. 4). Distinct coordination can be seen for each $\{(\text{Ph}_3\text{P})\text{Au}\}^+$ fragment. The Fe-Fe bond distances in the Fe_3 triangular range from $2.645(3)$ to $2.693(3)\text{\AA}$ and Fe-Fe-Fe bond angles from $59.26(7)$ to $61.06(7)^\circ$. The $\text{Fe}(2)\text{-Au}(2)$ bond length is $2.678(2)\text{\AA}$ and $\text{Au}(1)\text{-Au}(2)$ is $2.991(1)\text{\AA}$.

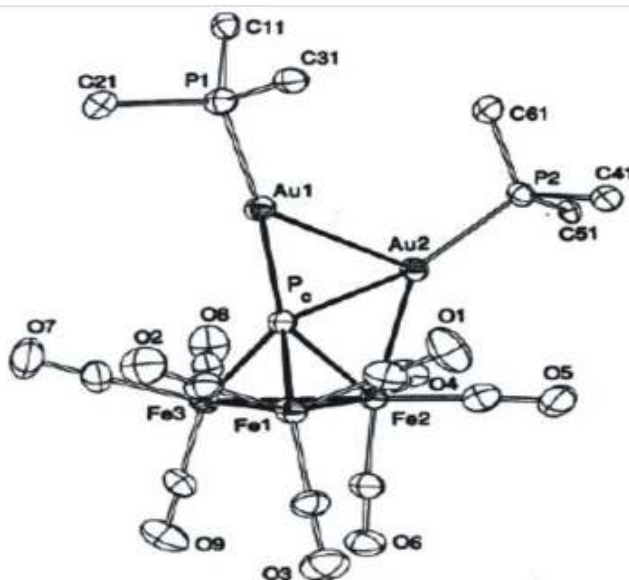


Fig. 4 Structure of $[(\text{Ph}_3\text{P})\text{Au}]_2(\mu_3\text{-P})\text{Fe}_3(\mu\text{-H})(\text{CO})_9$ [51]

Structure of black $\{(\text{Ph}_3\text{P})\text{Au}\}_2\text{Fe}_3(\mu_3\text{-S})(\text{CO})_9$ [52] is similar to that of black $\{(\text{Ph}_3\text{P})\text{Au}\}_2\text{Fe}_3(\mu_3\text{-O})(\text{CO})_9$ [50]. Both contain a Fe_3Au_2 trigonal bipyramidal moiety. The M-M bond distances differ from each other, while the mean $\text{Fe}_{\text{eq}}\text{-Au}_{\text{eq}}$ bond distance in [52] of $2.734\text{\AA}$ is about $0.031\text{\AA}$ shorter than that in [50], all remaining mean M-M bond distances are somewhat longer in [52] than those in [50]. The $\text{Fe}_{\text{eq}}\text{-Fe}_{\text{eq}}$ bond distances are $2.864(4)\text{\AA}$ [52] vs $2.700(2)\text{\AA}$ [50], av. $\text{Fe}_{\text{eq}}\text{-Fe}_{\text{ax}}$ $2.696\text{\AA}$ [52] vs $2.557\text{\AA}$ [50], av. $\text{Fe}_{\text{eq}}\text{-Au}_{\text{ax}}$ $2.706\text{\AA}$ [52] vs $2.700\text{\AA}$ [50], and Au-Au $3.020(1)\text{\AA}$ [52] vs $2.9915(9)\text{\AA}$ [50].

Two yellow Au_2Fe_3 [11, 53] contain $[\text{Fe}_3(\mu\text{-}\eta^5\text{:}\eta^1\text{-C}_5\text{H}_4\text{PPh}_2)_6\text{Au}_2]^{2+}$ cations and ClO_4^- [11] or Cl^- [53] anions. The geometry around the gdd atom is in a distorted trigonal pyramidal coordination environment. The gold atom lays $0.073\text{\AA}$ [11] and $\sim 0.3\text{\AA}$ [53] out of the plane of the three phosphorus atoms. The mean Ag-P bond distances are $2.365\text{\AA}$ [11] and $2.380\text{\AA}$ [53]. The $\text{Fe}\cdots\text{Au}$ separations over $4.0\text{\AA}$ ruled out direct metal-metal bond.

Structure of two orange Au_3Fe_2 clusters [54,55] differs from each other. The structure of $[\{(\text{OC})_4\text{Fe}\}_2\text{Au}_3(\mu\text{-}\eta^2\text{-dppm})]^-$ anion [54] consists of an isosceles Au_3 triangle with two shorter edges, $\text{Au}(1)\text{-Au}(3)$ and $\text{Au}(2)\text{-Au}(3)$, $2.921(2)\text{\AA}$, spanned by $\text{Fe}(\text{CO})_4$ groups, and a longer one ($\text{Au}(2)\cdots\text{Au}(3)$, $3.578(2)\text{\AA}$, bridged by a $\mu\text{-}\eta^2\text{-dppm}$ ligand. The mean Au-Fe bond length is $2.562\text{\AA}$. In the structure of the other orange Au_3Fe_2 cluster [55], two satellite $\{\text{ClAu}(\mu\text{-}\eta^1\text{:}\eta^5\text{-ddpea})\text{Fe}((\mu\text{-}\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4\text{PPh}_2))\}$ moieties are held together by the central AuCl group. The central gold atom has a trigonal-planar (AuP_2Cl) structure and the satellite gold atoms are linearly (AuClP) coordinated. Both iron atoms are sandwiched (FeC_{10}).

The Au_4Fe core is found in two orange clusters [27,56]. The structure which is isostructural contains a trigonal bipyramidal Au_4S fragment with one Au and S atom at the axial positions. There are intramolecular Au-Au contacts, the shortest are between the equatorial gold atoms and the gold atom perpendicular to them with the values of $2.9047(12)$, $2.9210(12)$ and $2.9775(14)\text{\AA}$. The Au-S-Au angles for the three gold atoms located in the equatorial plane are $124.4(2)$, $109.8(2)$ and $108.1(2)^\circ$, these values differ from the ideal 120° , which may be is consequence of the interaction with the other gold atom. The Au-S-Au angles between the gold atom in the apical position and the gold atoms in the plane are very narrow, $74.1(2) - 78.1(2)^\circ$.

Structure of red $(\text{OC})_9\text{Fe}_3\text{Co}(\text{CO})_3(\mu_5\text{-C})\text{Au}(\text{PPh}_3)$ was investigated at room temperature [57a] and at 173K [57b]. The structures are shown in Fig. 5. As it can be seen the structures differ from each other. While at room temperature the Fe_3Co butterfly moiety, with a carbide atom C(1) inside it, is linked to an Au atom by one $\text{Fe}(2)\text{-Au}$ and Co-Au bond through the wingtip iron atoms (Fig. 5a), at 173K (Fig. 5b) the Fe_3Co butterfly moiety with

a carbide atom C(1) inside it is linked to an Au atom by two Fe-Au bonds through the wingtip iron atoms. Such differences reflect the metal-metal bonds (Table 4).

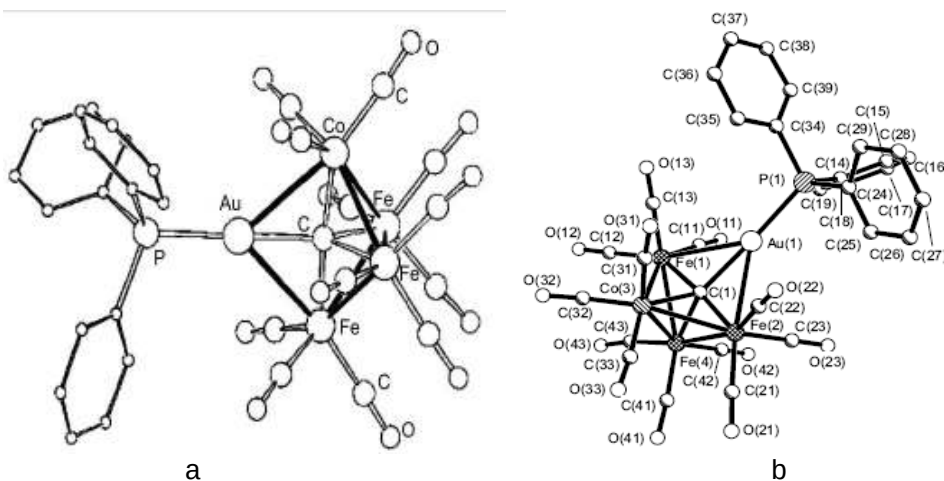


Fig 5 Structure of $[(\text{CO})_9\text{Fe}_3\text{Co}(\text{CO})_3(\mu_5\text{-C})\text{Au}(\text{PPh}_3)]$
a) at room temperature [57a]; b) at 173 K [57b]

The cluster core of orange $\text{Au}_2\text{Fe}_2\text{Ir}$ comprises [58] a spiro or „bow-tie“ arrangement of the five metal atoms with the two halves of the tie defined by the $\text{Ir}(1)\text{Fe}(1)\text{Fe}(2)$ and $\text{Ir}(1)\text{Au}(1)\text{Au}(2)$ triangles. The dihedral angle between the planes is 86.0° . The metal-metal bonds are Fe-Fe, $2.501(5)\text{\AA}$, Fe-Ir, $2.709(3)$ and $2.744(4)\text{\AA}$ and Ir-Au, $2.726(1)\text{\AA}$. The distances are all comparable to those found in $[(\text{OC})_5\text{Fe}_2(\mu\text{-CO})_2\text{Ir}_2(\mu\text{-CO})(\text{CO})_4\text{Au}(\text{PPh}_3)]^-$ [59]. In the anion, the $\text{Au}(\text{PPh}_3)$ group caps a FeIr_2 face, with Au-Fe, $2.806(1)$, Au-Ir, $2.797(1)$ and $2.829(1)$, and Fe-Ir, $2.668(1)$ and $2.776(1)\text{\AA}$.

Structure of orange AuFe_2Rh_2 cluster [60] consists of discrete $[\text{PPh}_4]^+$ cations and $[(\text{OC})_5\text{Fe}_2(\mu\text{-CO})_3\text{Rh}_2(\text{CO})_4\text{Au}(\text{PPh}_3)]^-$ anions, with normal van der Waals contacts. The metallic framework can be described as a trigonal bipyramid, with $\text{Fe}(\text{CO})_3$ and $\text{Au}(\text{PPh}_3)$ fragments occupying the apical vertices, whilst two rhodium and the remaining iron atom are located in the equatorial positions, each being connected to only two terminal CO ligands. Bridging CO groups span all the edges of the equatorial plane. The metal-metal bonds are: $\text{Fe}_{\text{ap}}\text{-Fe}_{\text{eq}}$, $2.656(1)\text{\AA}$, $\text{Fe}_{\text{ap}}\text{-Rh}$, $2.634(1)$ and $2.640(1)\text{\AA}$; $\text{Fe}_{\text{eq}}\text{-Rh}$, $2.732(1)$, $2.750(1)$ and $2.760(1)\text{\AA}$, $\text{Fe}_{\text{eq}}\text{-Au}$, $2.793(1)\text{\AA}$ and Au-Rh, $2.781(1)$ and $2.782(1)\text{\AA}$.

Structure of three purple AuCo_3Fe clusters [61, 62] consists of a trigonal bipyramidal array of metal atoms, with the gold and iron atoms at apical positions. The mean metal-metal bonds are: Au-Co, $2.715\text{\AA}$, Co-Fe, $2.59\text{\AA}$ and Co-Co, $2.52\text{\AA}$.

Structure of a red AuRu_3Fe cluster [63] contains four $\text{M}(\text{CO})_3$ ($\text{M}=\text{Fe}$ and Ru) groups in a butterfly arrangement, with the nitrogen atom coordinated to all four metal atoms. The gold atom symmetrically bridges the hinge $\text{Ru}(3)\text{-Ru}(4)$ bond. The mean of Au-Ru bonds is of the value $2.760\text{\AA}$. The gold bridged hinge Ru-Ru bond is lengthened ($2.839(2)\text{\AA}$) compared to have non-bridged Ru-Ru bonds (av. $2.788\text{\AA}$). The Fe-Ru(3) and Fe-Ru(4) bonds are $2.717(2)$ and $2.639(2)\text{\AA}$.

Inspection of the data in Table 4 reveals that the clusters crystallized in three crystal classes orthorhombic (x5), tridinic (x8) and monoclinic (x9). The clusters covered wide range of colours: yellow, green, purple, brown each (x2), red, black each (x3) and orange (x6). The gold atoms are found in coordination number two- $\text{AuP}(\text{Cl})$ [55], three- AuP_3 [11, 53], AuPM_2 ($\text{M}=\text{Fe}$ [48a, 52], Ir [59], Co [62], Ru [63], AuBPFe [46], AuP_2Au [51], AuPFeAu [54], AuP_2Cl [55], AuSPAu [56], $\text{AuP}(\text{IrAu})$ [58]; four- AuSPAu_2 [27], AuFe_4 [47], AuCPFe_2 [48b, 49, 57b], AuP_2FeAu [51], AuPM_3 ($\text{M}=\text{Fe}$ [52], Co [61]), AuFe_2Au_2 [54], AuC_3S [56], AuSPCoFe [57a], $\text{AuCP}(\text{IrAu})$ [58], AuPRh_2Au [60], and five- AuPFe_3Au [50] coordinated. The iron atoms are five- [48b], six- [46-48, 51, 52, 54, 59-60], eight- [50, 52, 57, 59, 60] and ten (sandwiched)

[11, 27, 53, 55, 56] coordinated. Remaining heterometal partners are coordinated: six- Ru [63], seven- Co [57], Ir [58], and eight- Ir [59], Rh [60], Co [61, 62] and Ru [63].

The mean Au-M bond distance elongated in the sequence: 2.702Å (2.545(4) – 2.880(1)Å) (M=Fe) < 2.724Å (2.633(1) – 2.829(1)Å) (M=Ir) < 2.754Å (2.710(3) – 2.873(1)Å) (M=Co) < 2.760Å (2.754(1) – 2.766(1)Å) (M=Ru) < 2.782Å (2.781(1) – 2.783(1)Å) (M=Rh) < 2.936Å (2.847(1) – 2.991(1)Å) (M=Au). The mean Fe-M bond distance elongated in the order: 2.545Å (M=Au) < 2.582Å (M=Co) < 2.640Å (M=Fe) < 2.689Å (M=Rh) < 2.705Å (M=Ru) < 2.729Å (M=Ir). The mean Co-Co and Ru-Ru bonds are 2.52 and 2.813Å, respectively.

2.5 Heterohexa- and heteroheptanuclear clusters

In total, twenty one (ten heterohexa- and eleven heteroheptanuclear) clusters have been included in this chapter (Table 5).

There are seven colored Fe₄Au₂ derivatives [21, 64 - 68], for which X-ray data are available. In the green complex [64], the four Fe atoms define a butterfly configuration while the Au(1) atom bridges the two single metal atoms Fe(1) and Fe(2), and the Au(2) atom asymmetrically bridges the butterfly created by the Fe(1), Fe(2) and Fe(4) face and the Au(1) atom. The carbido (C1) atom lies approximately at the center of the distorted square defined by the Fe(1), Fe(2), Fe(3), and Au(1) atoms. The Au(2)-Fe(4) distance (2.560(2)Å) is markedly shorter than those for Au(1)-Fe(2) and Au(1)-Fe(1) (2.825(2) and 2.831(2)Å), respectively. The Au-Au bond length is 2.860(2)Å. In addition the dppm ligand bridged two gold atoms. In another four Fe₄Au₂ clusters [65 - 67] the boron atom, lying approximately at the center of a distorted octahedron formed by six metal atoms.

Structure of orange (cp)Fe(C₅H₄)(Ph)PAuC≡CAuP(Ph)(C₅H₄)Fe(cp) [21], is centrosymmetric with respect to the C≡C bond. The P-Au-C≡C unit is basically linear, with an angle at C(1) of 178(1)° and at Au(1) at 175.9(2)°. Each of the ferrocenyl moieties has an eclipsed geometry with only small in-plane rotations of the ring with respect to each other (6.4° for C(11) and C(20) and 9.7° for C(21) and C(30)). The cyclopentadienyl rings within to each ferrocenyl unit are not perfectly parallel, with mean interplanar angles of 2.4 and 3.6°, respectively. The two substituent ferrocenyl units are oriented essentially orthogonal with respect to each other with a dihedral angle of 88° between the mean planes of C(11)-C(15) and C(21)-C(25).

The molecule of Fe₄Au₂ cluster [68] lies on a crystallographic 2-fold axis which bisects the Au(1)-Au(1') and Fe(2)-Fe(2') bonds and passes through the carbido C(1) atom. The four iron atoms define butterfly geometry with a dihedral angle between the „rings“ of 72.9°. The two gold atoms lie above but slightly skewed respect to the with Fe(2)-Fe(2') „hinge“ bond and bridge the „using-tip“ Fe(1) and Fe(1') atoms. The six metal atoms define a distorted octahedron with the carbido C(1) atom, lying approximately at its center.

Structure of dark red Fe₃Au₃ cluster [51] is shown in Fig. 6. The structure consists of a {Fe₃(CO)₉(μ₃-P)}³⁻ unit frame coordinated to a triangular {Au₃(PPh₃)₃}³⁺ unit. The Au₃ plane makes a dihedral angle of 46° with respect to the Fe₃ plane. The mean Fe-Au and Fe-Fe bond distances are 2.716 and 2.652Å, are much shorter than that of Au-Au distance with the mean value of 3.207Å.

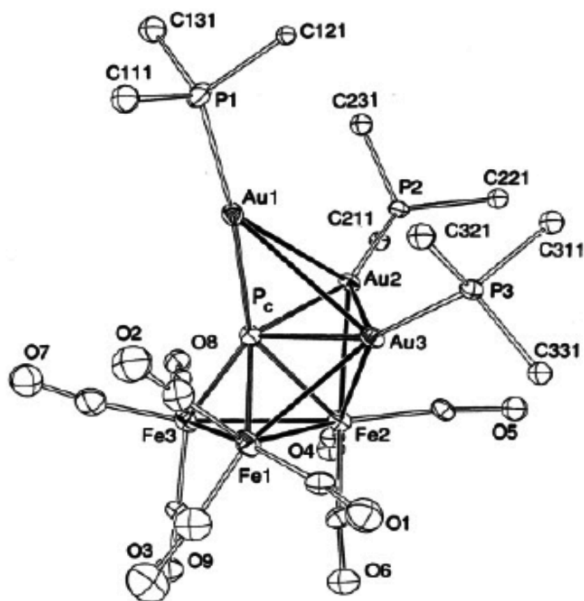


Fig 6 Structure of $[(\text{CO})_9\text{Fe}_3(\mu_5\text{-P})\{\text{Au}(\text{PPh}_3)\}_3]$ [51]

There are two yellow Fe_2Au_4 complexes, which crystallize in the same space group C2/c, as dimeric $[(\text{CO})_4\text{FeAu}_2(\mu\text{-}\eta^2\text{-L})]_2$ (L = dpmm or dppe), but since the former lies on a crystallographically imposed two fold axis, and the latter on a center of symmetry the structures differ markedly [69]. In the latter, two virtually parallel P-CH₂-CH₂-P moieties function as bridging ligands between two well separated ($>6.0\text{\AA}$) $\text{Au}_2\text{Fe}(\text{CO})_4$ fragments leading to a fourteen-membered ring in a pseudo-chair conformation. In the Au_2Fe triangle Au(1)-Au(2) distance is $2.977(1)\text{\AA}$ and the mean Au-Fe bond distance is $2.530\text{\AA}$. In contrast the structure of the former contains an approximate rhombus of gold atoms, which is folded about the Au(1)-Au(1') diagonal of length $3.041(2)\text{\AA}$. Tetrahedral angle between Au(1)-Au(2)-Au(1') and Au(1)-Au(2')-Au(1') planes is $158.3(3)^\circ$. The $\text{Fe}(\text{CO})_4$ and dpmm ligands span the four edges of the rhombus lying alternately above and below the Au_4 mean plane.

Structure of yellow FeAu_5 cluster [70] contains well separated $[(\text{ox})_3\text{FeAu}_5(\text{PPh}_3)_5]^+$ cations and PF_6^- anions. The cationic FeAu_5 cluster form bi capped FeAu_3 tetrahedron with Fe-Au bond distances from $2.590(1)$ to $2.65(1)\text{\AA}$ to all five Au atoms. The Au-Au distances range from $2.7760(4)$ to $3.0880(4)\text{\AA}$.

In black Fe_6Au cluster [48b] the $\{\text{Au}(\text{PPh}_3)\}^+$ unit caps one of the two triangular faces of the $\{\text{Fe}_6(\mu_6\text{-C})(\mu\text{-CO})_3(\text{CO})_{13}\}^{2-}$ anion lacking bridging CO ligands. The mean of the three Fe-Au bond distances is $2.750\text{\AA}$. The Fe-Fe bonds range from $2.562(4)$ to $2.801(4)\text{\AA}$. In orange red Fe_6Au derivative [71] the ppn^+ cations and $[(\text{CO})_9(\mu_3\text{-PMe})\text{Fe}_3(\mu_3\text{-P})_2\text{Au}]^-$ anions are well separated. In the complex anion, two identical $[(\text{CO})_9(\mu_3\text{-PMe})\text{Fe}_3(\mu_3\text{-P})]$ units are held together by Au(1) atom, with the central P-Au-P angle of 177° .

Structure of black Fe_5Au_2 cluster [72] contains two $\text{Au}(\text{PET}_3)$ groups, which display different bonding modes. The five iron atoms lie at the vertices of a square-based pyramid with the carbide atom lying $0.11\text{\AA}$ below the square base. One $\text{Au}(\text{PET}_3)$ group symmetrically bridges the Fe(1)-Fe(4) basal edge, the other three basal edges being asymmetrically bridge by carbonyls. The Au atom of the second $\text{Au}(\text{PET}_3)$ group caps the square base of the Fe_5 square pyramid to give a distorted octahedral metal arrangement and is also within bonding distance of the carbide atom. The remaining eleven carbonyls are terminally coordinated two of each of the basal iron atoms and three to the apical iron atom. The Fe-Au distances range from $2.696(2)$ to $3.036(3)\text{\AA}$, and Fe-Fe distances from $2.573(3)$ to $2.941(3)\text{\AA}$.

Structure of Fe_4Au_3 derivative [73] is based upon a butterfly array in iron atoms containing a naked boron atom. The boron atom is within bonding contact of all seven metal atoms. The boron atom lies $0.457(1)\text{\AA}$ above the $\text{Fe}_{\text{ring}}\text{-Fe}_{\text{ring}}$ (i.e. Fe(3)-Fe(4)) axis. The

three Au(PPh₃) fragments are asymmetrically sited over the surface of the Fe₄B 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. The Fe-Au bond distances range from 2.616(3) to 2.711(5) Å.

Structure of purple Fe₃Au₄ cluster [74] consists of a slightly distorted square-planar [Au₄(PPh₃)₄]⁴⁺ unit (Au-Au = 2.976(1)-3.224(2) Å) coordinated to the [Fe₃(CO)₉P]³⁻ (Fe-Fe = 2.632(5)-2.670(5) Å) cluster framework. The dihedral angle between the Fe₃ plane and the Au₄ plane is 30°. The phosphorus atom is within bonding contact of all seven metal atoms. Three of the four Au(1) atoms in the Au₄ square also interact with Fe1 and Fe2 in the Fe₃ triangle. Au₃ bridges the Fe1-Fe2 edge, while Au2 and Au4 interact with Fe2 and Fe1, respectively. The Fe-Au bond distances range from 2.690(3) to 2.830(4) Å.

X-ray structure of red Fe₂Au₅ derivative [54] shows well separated [(OC)₄Fe]₂Au₅(η²-dppm)₂²⁺ cation and BF₄⁻ anions. There are two crystallographically independent molecules, differing mostly by degree of distortion. The metal frameworks of the cations consists of a „low-tic“ of gold atoms whose tips are bridged by μ-η²-dppm ligands, whereas the Fe(CO)₄ units are triply bridging the central Au(1) and two apical gold (Au(2), Au(3)) atoms. The central atoms sit on inversion centers, and the gold frames are therefore planar. The Fe(CO)₄ units adopt idealized C_s symmetry with the two iron atoms pointing upward and downward with the respect to the Au₅ plane (distances from the plane ±0.92 Å). The Fe-Au bond distances are in the range of 2.438(3) – 2.750(3) Å and Au-Au distances are rather scattered (Au(center) – Au(periphery) range, 2.630(1) – 2.924(1) Å; Au(periphery) – Au(periphery), 3.051(2) and 3.312(2) Å).

Structure of orange Fe₂Au₅ derivative [40] contains well separated [{Fe(μ-dppcp)₂]₂. {Au^I₂(μ₃-S)}₂Au^{III}(C₆F₅)₂]⁺ cations, SO₃CF₃⁻ anions and CH₂Cl₂ molecules. In the complex cation trigonal pyramidal geometry about each sulfur atom is created by the three gold atoms with common Au(III) atom. There are several gold-gold interactions, the shortest are those for Au(I)-Au(I) in the [SAu₂(dppcp)₂Fe] units (2.9158(9) and 2.9511(9) Å). There is also a further Au(I)-Au(I) contact of 3.0436(8) Å between two gold atoms of different [SAu₂(dppcp)₂Fe] units. The Au(I)-Au(III) interactions are 3.2195(8) and 3.3661(10) Å.

Structure of red FeMn₄Au₂ cluster [35] is centrosymmetric with iron in Fe(C₅H₄PPh₂)₂ at a crystallographic inversion center, consists of a ferrocenylphosphine bringing two heterometallic triangles (AuMn₂) with Au-Mn bond distance of 2.660(1) and 2.776(1) Å and Mn-Mn of 3.049(2) Å. An alternative view of the cluster is that two Mn-Mn bonded dimers are bridged by a heterometallic fragment {Au-P(Ph₂)C₅H₄FeC₅H₄(Ph₂)P-Au}. In addition each of the PPh₂ ligands serves as a bridge between two Mn atoms and created four-membered bimetallic rings {PMnMnP}.

Structure of orange red FeRu₄Au₂ cluster [76] is shown in Fig. 7. The six metal atoms encapsulate the boron atom rendering it interstitial although the geometry of Ru₄Au₂ core is non-octahedral; the Au-Au(*) vector lies at 46° to Ru(1)-Ru1(*) vector. The two Au atoms are related by a molecular C₂ rings are locked in an approximately mutually eclipsed position. The mean Au-Ru bond distance of 2.695(2) Å is about 0.168 Å shorter than that of Ru-Ru bond distances (2.863(5) Å). The Au-Au bond distance is 2.818(2) Å.

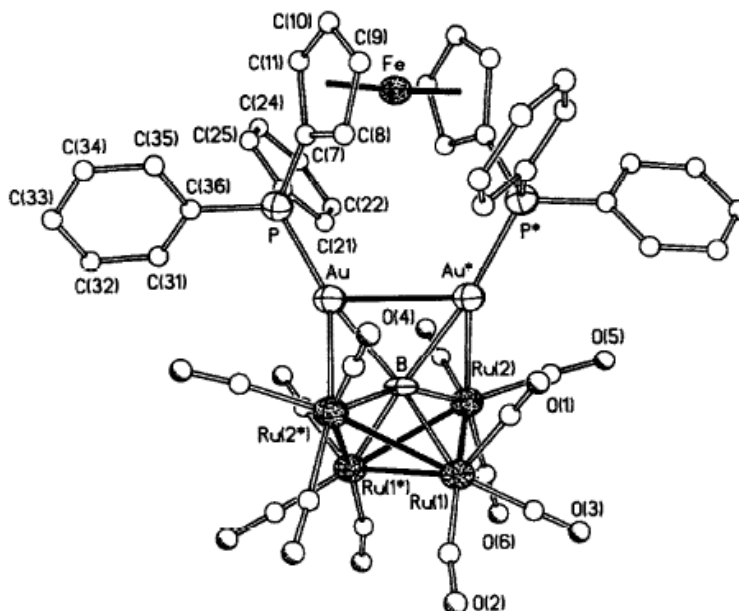


Fig 7 Structure of $[\text{Fe}(\mu\text{-}\eta^5\text{:}\eta^1\text{-C}_5\text{H}_4\text{PPh}_2)_2\text{Au}_2(\mu_6\text{-B})\text{Ru}_4(\text{H})(\text{CO})_{12}]$ [76]

The red FeRu_4CuAu cluster [77] is only example, which contains four different metal atoms. The metal skeleton to the cluster consists of a tetrahedron of ruthenium atoms, with one face $[\text{Ru}(1)\text{Ru}(2)\text{Ru}(3)]$ capped by a copper atom and one of the faces of the CuRu_3 tetrahedron so formed further capped by a gold atom to give an overall capped trigonal-bipyramidal metal-core geometry. The metal-metal bond distances elongated in the order: $2.641(1)\text{\AA}$ (Au-Cu) < $2.795(1)\text{\AA}$ (av.) (Au-Ru) < $2.807(2)\text{\AA}$ (av.) (Cu-Ru) < $2.885(1)\text{\AA}$ (av.) (Ru-Ru). Interestingly, that the metal-metal bond distances elongated while the sum of the covalent radii of the respective metals diminishes: $2.81\text{\AA}$ ($\text{Au} + \text{Cu}$) > $2.69\text{\AA}$ ($\text{Au} + \text{Ru}$) > $2.64\text{\AA}$ ($\text{Cu} + \text{Ru}$) > $2.52\text{\AA}$ ($\text{Ru} + \text{Ru}$).

Inspection of the data in Table 5 reveals that in the series of hexanuclear clusters the mean M-M bond distance elongated in the order: $2.646\text{\AA}$ (Fe-Fe) < $2.709\text{\AA}$ (Fe-Au) < $2.857\text{\AA}$ (Au-Au). In the series of heptanuclear clusters the order is: $2.660\text{\AA}$ (Au-Mn) < $2.670\text{\AA}$ (Fe-Fe) < $2.700\text{\AA}$ (Au-Fe) < $2.773\text{\AA}$ (Au-Ru) < $2.857\text{\AA}$ (Au-Au). The gold atoms are two- AuClP [21], AuPS [40], AuPFe [69, 70], AuP_2 [51, 71], three- AuP_2Fe [51], AuPFeAu [64], AuPMn_2 [74], four- AuC_2S_2 [40], AuPFe_3 [48b], AuPFeAu_2 [54], AuCPFe_2 [64, 68], AuBEFeAu , ($\text{E}=\text{As}$ [65], P [66, 67]), AuP_2Au_2 [74], AuBPRuAu [76], five- AuHPFeAu_2 [73], AuBPFe_2Au [73], AuHPRu_2Au [77], $\text{AuPRu}_2\text{Au}_2$ [77], and six- AuFe_2Au_4 [54], AuClPFe_4 [72], $\text{AuP}_2\text{Fe}_2\text{Au}_2$ [74] coordinated. The iron atoms are from six- to ten- coordinated, manganese five- and ruthenium from seven- to nine- coordinated. The clusters crystallized in two crystal classes triclinic (x7) and monoclinic (x14). Red $[\{(\text{CO})_4\text{Fe}\}_2\text{Au}_5(\eta^2\text{-dppm})_2](\text{BF}_4)_2$ [54] contains two crystallographically independent molecules differ mostly by degree of distortion.

2.6 Heterooligo- and heteropolynuclear clusters

Structural parameters for these clusters are gathered in Table 6. Structure of the dark orange Fe_3Au cluster [46] consists of $[\text{Au}(\text{PMePh}_2)_2]_2^+$ cation and $[\{(\text{CO})_{12}(\mu\text{-H})\text{Fe}_4(\mu_5\text{-BH})\}_2\text{Au}]^-$ anion. Complex anion contains two $\{\text{HFe}(\text{CO})_{12}\text{BH}\}$ fragments fused in „face-to-face“ manner via a single gold(I) atom which bridges one Fe wingtip – B edge of each cluster unit. The geometry of each butterfly fragment varies little. The internal dihedral angle of the Fe_4 skeleton is $116.6(3)^\circ$. The two clusters subunits are twisted with respect to one another with a spiro twist angle of $30.9(3)^\circ$ at the gold(I) atom. The Au-Fe bond distance is $2.615(1)\text{\AA}$. The Fe-Fe bond distances range from $2.630(2)$ to $2.688(2)\text{\AA}$ (av. $2.651\text{\AA}$). In complex cation

[Au(PMePh₂)₂]⁺, the geometry is unexceptional with linear coordination of the Au(I) center, (P-Au-P = 180.0(1)°).

In dark green Au₃Fe₆ cluster [78] three Fe₂Au units are linked by the three – legged propeller – like structure of the triphos ligand (Fig. 8). Interestingly, the gold atoms are placed at the corners of an almost equilateral triangle. The mean Au-Fe bond distance of 2.689 Å is about 0.083 Å longer than the mean Fe-Fe bond distance (2.606 Å). Structure of yellow [{Fe(C₅H₄PPh₂)₃}{(μ₃-S)Au₃}₂].8CHCl₃ [27] consists of an S₂Au₆ core with Au-Au distances vary from 2.905(2) to 3.272(2) Å. The shortest contacts, Au(1)-Au(4) 2.905(2) Å, Au(1)-Au(2) 2.922(2) Å and Au(4)-Au(5) 2.920(2) Å, involve gold atoms of the [Au₂dppf]²⁺ fragment that are bonded to the same sulfur atoms. The shortest Au...Fe separation is 4.284 Å.

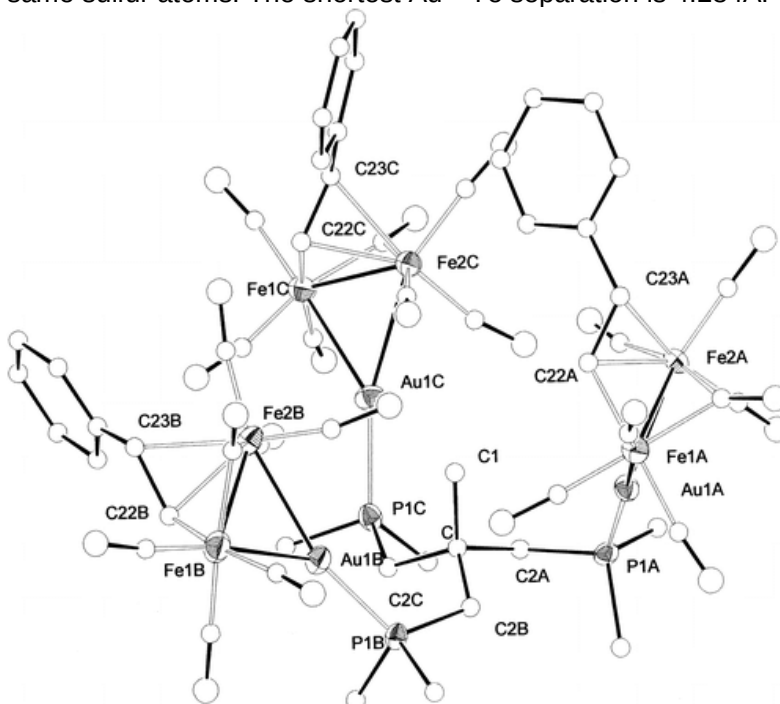


Fig. 8 Structure of [(CO)₆(μ-CO)(μ-HC≡CPhH)Fe₂Au]₃(μ-η³-triphos)] [78]

In black Fe₈Au₂ cluster [48a] two „butterfly“ clusters {(μ-CO)(CO)₁₁(μ₃-CO)Fe₄Au(PEt₃)} are connected by {K(18 – crown – 6)} unit (Fig. 9). The potassium is coordinated to the six oxygens of the crown ether in a planar array and also axially to two carbonyl oxygen of two „butterfly“ clusters. The Fe-Fe bond distances in butterfly range from 2.623(1) to 2.654(1) Å (av. 2.642 Å) and Au-Fe bond distance is 2.666(1) Å.

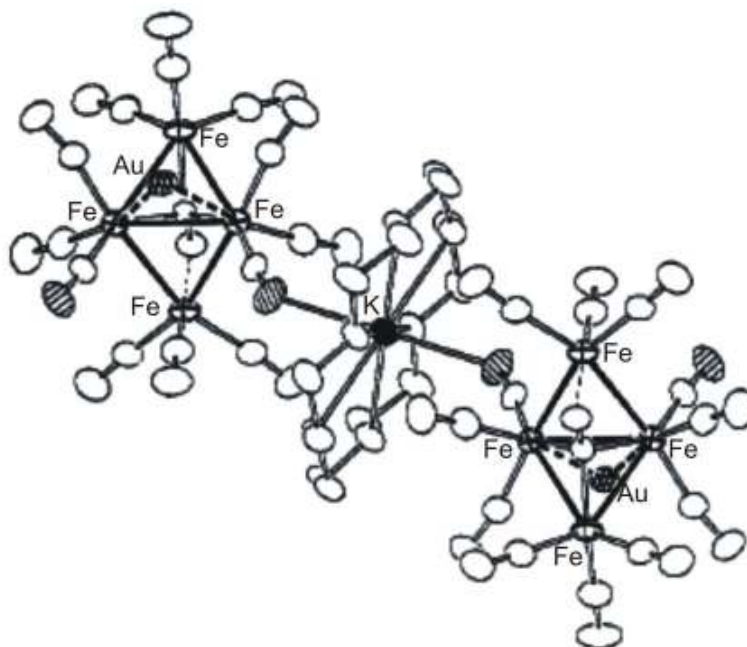


Fig 9 Structure of $[K(\eta^6\text{-18-crown-6})\{(\mu\text{-CO})(\text{CO})_{11}(\mu_3\text{-CO})\text{Fe}_4\text{Au}(\text{PEt}_3)\}_2]$ [48a]

There are three yellow $[\text{Fe}(\text{C}_5\text{H}_4\text{PPh}_2)\text{AuCl}]\cdot\text{S}$ ($\text{S} = 0.4 \text{ CH}_2\text{Cl}_2$ [79], 0.48 CHCl_3 [79] and CH_2Cl_2 [80]), which are isostructural. All three compounds comprise polymeric chain structures involving bridging ferrocenylphosphine units linking trigonal (P_2AuCl) groups. The $\text{Au}\cdots\text{Au}$, $\text{Au}\cdots\text{Fe}$ and $\text{Fe}\cdots\text{Fe}$ separations of 4.2, 8.4 and $11.2\text{\AA}$, ruled out a direct bond.

Inspection of the data in Table 6 reveals, that the clusters crystallized in three crystal classes: monoclinic (x3), triclinic and orthorhombic each (x2). The clusters are coloured, yellow (x4), and orange, green and black each (x1). The gold atoms are three- AuSPAu [27], AuPFe_2 [48a], AuP_2Cl [79, 80] and four- AuB_2Fe_2 [46], and AuPFe_3 [78] coordinated. The iron atoms are five-, six-, seven-, eight- and ten (sandwich) coordinated.

The mean M-M bond distance elongated in the order: $2.633\text{\AA}$ (Fe-Fe) < $2.707\text{\AA}$ (Au-Fe) < $2.917\text{\AA}$ (Au-Au).

3. CONCLUSIONS

There are almost one hundred heterometallic gold iron clusters in this review. From the nuclearity point of view, there are di- (x12), tri- (x7), tetra- (x14), penta- (x23), hexa- (x10), hepta- (x11), nona- (x4) and poly- (x3) nuclear clusters. The clusters cover wide variety of colours where yellow, orange and red by far prevail. The clusters crystallized in three crystal classes orthorhombic (x8), triclinic (x28) and monoclinic (x58). The gold atoms are two-, three-, four-, five- and even six- coordinated. The iron atoms are surrounded from five- to ten donor atoms. There are six clusters [8, 9, 19, 32, 35, 54] which contain two crystallographically independent molecules and $\{(\text{Ph}_3\text{P})\text{Au}\}_3\text{Fe}(\text{CO})_4$ [23] contains four such molecules, which are differ by degree of distortion in the M-L, M-M bond distances and L-M-L bond angles. Such examples are typical of the general class of distortion isomerism [16]. A summary of the M-M and M-M' bond distances is given in Table 7, where the shortest are $2.438(3)\text{\AA}$ for Au-Fe [54], $2.504(3)\text{\AA}$ for Fe-Fe [58], and $2.630(1)\text{\AA}$ for Au-Au [54]. There is also wide variety of another metal-metal bond distances.

Heterometallic compounds are important both from a chemical and biological point of view and structural information are crucial for the understanding of their role in both areas. This represents the first overview of structural data for heterometallic gold iron clusters. It is hoped that this review will serve to draw together common structural trends and stimulate activity in areas of particular interest.

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Table 1. Crystallographic and structural data of heterobinuclear AuFe compounds^a

COMPLEX	Cr. cl. Sp.Gr	a [Å] b [Å]	α [°] β [°]	Chromo -phore	M - L [Å]	Au - Fe [Å]	L - M - L [°]	Ref
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(colour)	Z	c [Å]	γ [°]					
(Ph ₃ P)AuFe(CO) ₃ ⁻ (η^3 -allyl) (yellow)	m C2/c 8	30.76(1) 11.60(1) 13.54(2)	110.38(1)	AuPFe FeC ₆ Au	Ph ₃ P ^b 2.273(5) OC 1.778(9,11) η^3 C 1.99(1,0)	Fe 2.519(1)	P,Fe ^b 174.4(2) C,C 95.8(3,3) 142.9(3) C,Au 71.5(2,6) 106.0(3,4,4) 134.4(6) 163.2(3)	5
{{(tol)Ph ₂ P}AuFe(CO) ₃ . {Si(Me)Ph ₂ }(PMe ₃) (light yellow)	m P2 ₁ /n 4	10.513(7) 16.137(6) 22.106(5)	90.75(3)	AuPFe FeC ₃ P. SiAu	Ph ₃ P 2.282(7) OC 1.78(3,10) P 2.231(9) Si 2.35(1)	Fe 2.527(3)	P,Fe 178.1(2) C,C 143(1) P,Si 177.2(4) C,Au 73.2(7,9) 177(1) P,Au 85.7(2) S,Au 95.9(2)	6
(Ph ₃ P)AuFe(CO) ₃ . {Si(Me)Ph ₂ }(PPh ₃) (light yellow)	m P2 ₁ /n 4	11.772(3) 23.094(5) 18.922(5)	117.51(2)	AuPFe FeC ₃ P. SiAu	Ph ₃ P 2.283(2) OC 1.761(8,14) P 2.244(2) Si 2.357(3)	Fe 2.533(1)	P,Fe 177.51(6) C,C 106.0(4,6,8) 143.8(4) P,Si 173.95(9) C,Si 83.6(3,3,1) C,Au 73.7(3,5,2) 167.7(3) C,P 95.8(3,3,8) P,Au 90.4(6) Si,Au 94.96(7)	7
(Me)Au(μ - η^1 : η^1 -dppm). Fe(CO) ₂ (η^4 -C ₅ H ₄ Me) ^c (bright yellow)	n P2 ₁ /n 8	16.606(2) 18.886(3) 21.629(5)	100.60(1)	AuCP FeC ₆ P AuCP FeC ₆ P	MeC 2.053(11) P 2.291(3) OC 1.731(14,3) η^4 C 2.058(15,38) P 2.212(3) Me,C 2.112(10) P 2.284(3) OC 1.732(11,17) η^4 C 2.075(10,35) P 2.204(3)		C,P 177.3(4) C,P 96.0(5,1,0) C,P 175.1(3) C,P 95.9(3,6)	8
ClAu(μ - η^1 : η^1 -dppm). Fe(CO) ₂ (η^4 -C ₅ H ₄ Me) (yellow)	m P2 ₁ /n 4	10.896(2) 21.064(5) 15.212(3)	101.86(2)	AuClP FeC ₆ P	Cl 2.290(2) P 2.226(2) OC 1.756(9,45) η^4 C 2.075(9,45) P 2.217(3)		Cl,P 176.44(8) C,C 101.5(4) C,P 96.0(3,6)	8
[Au(μ - η^1 : η^5 -dptpc) ₂ Fe]. CHCl ₃ ^c (orange) (at 173 K)	tr P1 4	12.924(2) 17.485(3) 20.458(3)	64.985(8) 74.296(8) 70.575(12)	AuS ₂ FeC ₁₀ AuS ₂ FeC ₁₀	S 2.301(3,1) η^5 C not given S 2.284(3,8) η^5 C not given		S,S 176.43(12) not given S,S 178.26(11) not given	9
[(Ph ₃ P)Au(μ - η^1 : η^5 - C ₅ H ₄ PPh ₂) ₂ Fe]2CH ₂ Cl ₂ (orange) (at 173 K)	m P2 ₁ /c 4	14.275(2) 16.997(2) 21.219(3)	96.76(2)	AuP ₃ FeC ₁₀	η^4 P 2.464(1,25) Ph ₃ P 2.4(12) η^5 C not given		P,P 114.4(-,4,0) 131.2(4) not given	10
[(Ph ₃ P)Au(μ - η^1 : η^5 - C ₅ H ₄ PPh ₂) ₂ Fe]ClO ₄ (yellow)	m P2 ₁ /c 4	14.239(6) 16.889(4) 20.866(3)	95.81(3)	AuP ₃ FeC ₁₀	η^4 P 2.383(2,2) Ph ₃ P 2.343(2) η^5 C 2.019(8)- 2.068(9)		P,P 109.5(1)- 132.0(1) not given	11
(Ph ₃ P)Au(μ - η^1 : η^5 - C ₅ H ₄ C(O)C(H)C. (O)Me)Fe(η^5 -cp) (not given)	not given			AuCP FeC ₁₀	η^5 C 2.120 Ph ₃ P 2.274 η^5 C not given		not given not given	12
(Ph ₃ P)Au(μ - η^1 : η^{10} - C ₅ H ₄ C(O)C ₆ H ₄ COO- 1,2)Fe (orange)	m P2 ₁ /c 4	17.313(6) 8.379(2) 24.358(8)	91.97	AuOP FeC ₁₀	η^4 O 2.059(9) Ph ₃ P 2.207(3) η^{10} C 2.03(2,4) C not given		O,P 176.5(2) not given	13
(Ph ₃ P)Au(μ - η^1 : η^5 - C ₅ H ₄ CH ₂ NMe ₂)Fe(η^5 - cp) (orange) (at 153 K)	m P2 ₁ /c 4	11.502(1) 21.272(4) 11.290(2)	98.70(1)	AuCP FeC ₁₀	μ C 2.027(6) Ph ₃ P 2.287(2) μ C not given η^5 C not given cpC not given		C,P 174.5(2) not given	14

[ClAu{ μ - η^1 - η^{10} -C ₁₇ -H ₂₈ NP}Fe] ₂ 1.5C ₆ H ₆ (yellow)	m P2 ₁ /c 4	9.285(3) 18.287(8) 19.427(6)	99.55(4)	AuCIP FeC ₁₀	Cl 2.32(1) η^1 P 2.24(1) η^{10} C not given	Cl,P 176.5(5) not given	15
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Footnotes: a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated.

The first number in parenthesis is e.s.d., and the second is the maximum deviation from the mean

b. The chemical identity of coordinated atom / ligand is specified in these columns.

c. There are two crystallographically independent molecules.

Table 2. Crystallographic and structural data for heterotrinnuclear AuFe₂ and Au₂Fe clusters^a

COMPOUND (colour)	Cr. cl. Sp.Gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	M - L [Å]	M - M [Å] M - L - M [°]	L - M - L [°]	Ref.
A: AuFe₂ (NEt ₄)[(Ph ₃ P)Au. {Fe(μ -CO)(CO) ₃ }] ₂ (orange)	m P2 ₁ /c 4	10.079(2) 19.622(4) 18.743(4)	102.82(2)	AuPFe ₂ FeC ₄ Au.Fe	Ph ₃ P ^b 2.264(2) OC 1.790(12,26) μ OC 2.001(11,22)	Fe 2.660(1,38) Fe 2.605(2) C 81.34(3)	P,Fe ^b 150.1(1,7,3) Fe,Fe 58.6(1) μ C,Fe 49.4(3,7) C,Fe 118.0(3,5,4) μ C,Au 88.9(3,6,9) C,Au 77.4(3,2,8) 174.2(4,8) Au,Fe 60.4(1,1,8)	17
(Ph ₃ P)AuFe ₂ (μ -CO). (μ -SPH)(CO) ₆ (dark green)	m P2 ₁ /c 4	11.373(1) 14.899(3) 17.997(3)	95.12(2)	AuPFe ₂ FeC ₄ Au. Fe	Ph ₃ P 2.287(2) OC 1.792(10,38) μ OC 1.937(9) 2.016(9) μ S 2.267(2,4)	Fe 2.670(1,26) Fe 2.621(2) C 83.0(3) S 70.66(8)	P,Fe 150.60(6,7,3) Fe,Fe 58.80(4) C,C 93.6(4,6,8) 165.8(4,1) μ C,S 80.5(3,9) C,S 95.6(3,1,6) μ C,Au 94.6(3,2) C,Au 75.9(3,5,7) μ C,Fe 48.5(3,1,3) C,Fe 111.8-132.0(3) Au,Fe 60.60(4,97)	18
(Ph ₃ P)AuFe ₂ . (μ -C ₁₁ H ₁₉ S)(CO) ₆ ^c (red orange)	tr P1 4	14.640(3) 15.156(4) 18.502(5)	66.82(2) 71.39(2) 71.79(2)	AuPFe ₂ FeC ₄ S. AuFe AuPFe ₂ FeC ₄ S. AuFe	Ph ₃ P 2.284(6) OC not given μ C 2.014(25,5) μ S 2.209(7,4) Ph ₃ P 2.294(7) OC not given μ C 2.033(15,7) μ S 2.196(8,3)	Fe 2.692(4,9) Fe 2.651(4) 82.3(8) 73.7(2) Fe 2.711(4,30) Fe 2.644(4) C 81.0(7) S 74.0(2)	P,Fe 150.3(2,7,7) Fe,Fe 59.0(1) C,S 48.1(5) Au,Fe 60.5(1,3) C,Au 105.7(4,2) S,Au 104.6(2,4) C,Fe 48.9(5,2) S,Fe 53.6(1,3) P,Fe 150.7(1,2,6) Fe,Fe 58.4(1) C,S 48.3(7) Au,Fe 60.8(1,1,0) C,Au 101.5(7,8) S,Au 110.0(2,1,0) C,Fe 49.5(2,3) S,Fe 53.0(2,1)	19
(Ph ₃ P)AuFe ₂ (μ -CO). (CO) ₆ (μ - η^1 - PhC=CPhH) (green)	m P2 ₁ /n 4	18.334(8) 15.374(3) 13.430(4)	102.27(2)	AuPFe ₂ FeC ₅ Au. Fe	Ph ₃ P 2.288(2) OC 1.802(16,29) μ OC 1.896(12) μ C 2.015(10) C 2.058(10,57) μ C 2.253(12)	Fe 2.627(2) 2.761(2) Fe 2.627(2) C 80.8(4,2,5)	P,Fe 151.0(1,5,4) C,C 37.5(4) 145.5-171.4(5) μ C,Fe 49.6(3,3,2)	20
(η^1 -PhC=C)Au{ μ - η^1 - η^{10} - C ₅ H ₄ P(Ph)C ₅ H ₄ }. {Fe(η^5 -cp)} ₂ (orange)	m P2 ₁ /a 4	12.141(7) 19.053(1) 12.458(8)	92.62(2)	AuCP FeC ₁₀	η^1 C 2.011(15) η^1 P 2.274(4) C 1.977(20,11) 2.029(27,24)		C,P 174.3(4) not given	21
ClAu{ μ - η^1 - η^{10} - C ₅ H ₄ P(Ph)C ₅ H ₄ }. {Fe(η^5 -cp)} ₂ (orange red)	m P2 ₁ /n 4	10.205(2) 18.014(4) 12.680(3)	98.29(2)	AuCIP FeC ₁₀	Cl 2.289(2) η^1 P 2.234(2) C 2.041(8,17)		Cl,P 176.1(1) not given	22

B: Au₂Fe {(Ph ₃ P)Au} ₂ . Fe(CO) ₄ ^d (yellow)	m P ₂ /a 16	20.309(5) 18.379(3) 40.737(6)	96.26(2)	AuPFeAu FeC ₄ Au ₂ AuPFeAu FeC ₄ Au ₂ AuPFeAu FeC ₄ Au ₂ AuPFeAu FeC ₄ Au ₂	Ph ₃ P 2.277(6,5) OC 1.76(2,1) Ph ₃ P 2.274(5,5) OC 1.76(2,1) Ph ₃ P 2.274(5,1) OC 1.75(2,2) Ph ₃ P 2.275(5,1) OC 1.77(2,2)	Fe 2.548(3,6) Au 2.897(1) Fe 2.535(3,12) Au 2.928(1) Fe 2.541(3,4) Au 2.909(1) Fe 2.550(2,3) Au 2.897(1)	P, Fe 177(1) C, C 98(1), 141(1) Au, Au 69.2(1) P, Fe 173.0(1,1,3) C, C 106(1), 148(1) Au, Au 70.6(1) P, Fe 171.2(2,2,4) C, C 96(1), 150(1) Au, Au 69.9(1) P, Fe 177(1) C, C 98(1), 141(1) Au, Au 69.2(1)	23
[(Ph ₃ P)Au] ₂ Fe. (CO) ₃ [P(OEt) ₃]. H ₂ O (yellow)	m P ₂ /n 4	10.385(3) 35.422(10) 13.648(6)	91.15(3)	AuPFeAu FeC ₃ PAu ₂	Ph ₃ P not given OC not given P 2.133(6)	Fe 2.535(3,26) Au 2.872(2)	P, Au not given C, C 145.9(8) C, P 99.7(7) Au, Au 69.0(1)	24
[(Ph ₃ P)Au] ₂ . (μ ₃ -η ¹ -η ¹ -η ⁵ -C ₅ H ₄). Fe(η ¹ -cp)]BF ₄ (red)	m P ₂ /a 4	14.460(11) 30.539(27) 9.509(12)	92.61(15)	AuCP. FeAu AuCPAu FeC ₁₀ Au	μ ₃ C 2.25(4) Ph ₃ P 2.283(12) μ ₃ C 2.12(4) Ph ₃ P 2.275(15) cpC 2.08(5,8) η ⁵ C 1.91(5) 2.10(5,3)	Fe 2.818(2) Au 2.768(2) C 78(1)	C, P 174(1) C, Fe 49(1) P, Fe 135.5(4) C, Au 49(1) P, Au 126.3(4) F, Au 97.6(2) C, P 169(1) C, Au 53(1) P, Au 135.6(3) not given	25
[(ClAu) ₂ (μ-η ¹ :η ⁵ - C ₅ H ₄ PPh ₂) ₂ Fe]CH ₂ Cl ₂ (yellow) (at 173 K)	tr P ₁ 1	8.671(2) 9.867(2) 12.359(3)	81.82(2) 74.45(3) 70.56(2)	AuPI FeC ₁₀	Cl 2.2815(13) η ¹ P 2.262(13) η ⁵ C 2.049(5,14)	Fe 4.29(1)	Cl, P 179.59(5) not given	26
[(IAu) ₂ (μ-η ¹ :η ⁵ - C ₅ H ₄ PPh ₂) ₂ Fe]CH ₂ Cl ₂ (yellow) (at 173 K)	tr P ₁ 2	11.955(3) 13.472(3) 14.596(2)	85.85(2) 70.16(2) 66.04(2)	AuPI FeC ₁₀	η ¹ P 2.244(9,4) I 2.553(3,8) η ⁵ C not given		P, I 177.0(2,7) not given	26
[(μ-S)Au ₂ (μ-η ¹ :η ⁵ - C ₅ H ₄ PPh ₂) ₂ Fe].2CHCl ₃ (orange) (at 143 K)	m P ₂ /n 2	12.571(4) 10.579(4) 15.212(4)	107.84(3)	AuSPAu FeC ₁₀	μS 2.300(2) η ¹ P 2.247(2) η ⁵ C 2.039(7,17)	Au 2.882(1) S 77.57(9)	S, P 173.78(6) S, Au 51.21(4) P, Au 122.66(5) not given	27
[(Ph ₃ P)Au] ₂ (μ-η ¹ :η ² - C(PPh ₂)Fe(CNPh) ₃ Cl)] (yellow)	tr P ₁ 2	19.325(4) 17.430(4) 11.906(3)	105.05(3) 104.62(3) 82.95(3)	AuCPAu FeC ₃ P ₂ Cl	μC 2.16(5,7) Ph ₃ P 2.25(2,2) PhNC 1.87(7,3) η ² P 2.25(2,2) Cl 2.38(2)	Au 2.89(4) C 84.1(15)	C, P 174.7(14,2,8) C, C 90.9(31,3,9) 174.3(34) P, P 69.8(8) C, Cl 90.0(29,5,6) C, P 92.7(22,1) 164.2(28) P, Cl 100.1(8) 169.9(8)	28
(η ² -S(CH ₂) ₂ S)Au ₂ . (μ-η ¹ :η ⁵ -C ₅ H ₄ PPh ₂) ₂ Fe (yellow)	m P ₂ /n 4	10.263(2) 21.064(4) 16.259(3)	97.06(2)	AuSP FeC ₁₀	η ² S 2.292(4,3) η ¹ P 2.267(3,1) η ⁵ cp 1.633 1.645	Au 3.06	S, P 165.1(1,4) not given	29
{(η ¹ -F ₃ CCOO)Au} ₂ . (μ-η ¹ :η ⁵ -C ₅ H ₄ PPh ₂) ₂ Fe (yellow)	m C ₂ /c 4	15.325(1) 19.058(4) 15.373(3)	95.98(3)	AuOP FeC ₁₀	η ¹ O 2.078(3) η ¹ P 2.219(2) η ⁵ C 2.051(3)	Au 3.254(1)	O, P 177.1(1) not given	30
{(C ₁₆ H ₉)Au} ₂ (μ-η ¹ :η ⁵ - C ₅ H ₄ PPh ₂) ₂ Fe (orange)	tr P ₁ 1	11.255(4) 13.484(4) 9.406(2)	104.92(2) 91.99(3) 114.50(2)	AuCP FeC ₁₀	C 2.061(8) η ¹ P 2.295(2) η ⁵ C 2.033(8)- 2.058(8)	Au 8.315	C, P 172.1(3) not given	31
(ClAu) ₂ (μ-η ¹ :η ⁵ -	tr	16.192(4)	93.39(3)	AuClP	Cl 2.287(4,14)		Cl, P 175.8(1,3)	32

$C_5H_4PPh_2)_2Fe^c$ (yellow)	PT 3	16.921(4) 10.878(5)	94.28(2) 115.29(2)	FeC ₁₀ AuCIP FeC ₁₀	η^1P 2.331(3,9) η^5C not given Cl 2.282(3) η^1P 2.229(3) η^5C not given	not given Cl,P 173.4(1) not given
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Footnotes: a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is maximum deviation from the mean
b. The chemical identity of the coordinated atom/ ligand is specified in these columns.
c. There are two crystallographically independent molecules.
d. There are four crystallographically independent molecules.

Table 3. Crystallographic and structural data for heterotetranuclear (gold, iron) clusters^a

COMPOUND (colour)	Cr. cl. Sp.Gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo- phore	M - L [Å]	M - M [Å] M - L - M [°]	L - M - L [°]	Ref.
A: AuFe₃ (PPh ₄)[(Ph ₃ P)Au. Fe ₃ (μ_3 -Te)(CO) ₉] (red)	m P2 ₁ /c 4	16.970(5) 12.966(4) 21.108(8)	95.25(3)	AuPFe ₂ FeC ₃ Te. AuFe ₂ (x2) FeC ₃ TeFe ₂	Ph ₃ P ^b 2.290(4) OC 1.747(20,59) μ_3 Te 2.502(3,3) OC 1.733(24,1) 1.819(22) μ_3 Te 2.457(3)	Fe 2.667(3,15) Fe 2.620(3) 2.836(3) Te 69.1(1) Fe 2.621(4,1) Te 63.8(1,1)	P,Fe ^b 147.8(1,8) Fe,Fe 64.3(1,8) C,C 98.5(10,8.8) C,Te 95.2(7,6.1) 153.3(7,2.5) C,Au 74.2(6,8.1) 158.1(8,1.2) C,Fe 100.9(7,9.9) 149.0(6,7.4) Te,Au 111.0(1,6) Au,Fe 57.9(1,5) 99.1(1,4) Fe,Fe 57.3(1,1) C,C 99.6(10,1.7) C,Te 104.5(7,1.2) 141.6(4) C,Fe 93.3(7,5.1) 160.0(7,1) Te,Fe 88.9(1,1) Fe,Fe 65.6(1)	33
(PPh ₄)[(Ph ₃ P)Au. Fe ₃ (μ -CO)(CO) ₁₀] (dark red)	m P2 ₁ /c 4	17.532(2) 13.433(1) 21.373(3)	95.01(2)	AuPFe ₂ FeC ₄ Au. Fe ₂ (x2) FeC ₄ Fe ₂	Ph ₃ P 2.28(1) OC 1.759(3,44) μ OC 1.954(2,30) OC 1.753(3,30)	Fe 2.643(1,11) Fe 2.655(1,27) C 84.7(1)	P,Fe 150.5(1,1.1) Fe,Fe 59.7(1) Au,Fe 59.7(1) 97.0(1) Fe,Fe 59.9(1)	34
(Ph ₃ P)AuFe ₃ . (μ_3 - η^2 - HC=NBu [†])(CO) ₆ ^c (deep red)	tr PT 4	12.815(3) 16.265(4) 19.106(3)	67.15(2) 73.46(2) 73.12(2)	AuPFe ₂ FeC ₃ N. AuFe ₂ FeC ₄ N. AuFe ₂ FeC ₄ Fe ₂ AuPFe ₂ FeC ₃ N. AuFe ₂ TeC ₄ N. AuFe ₂ FeC ₄ Fe ₂	Ph ₃ P 2.286(5) OC 1.73 μ N 1.96(1) OC 1.73 μ C 2.08(2) μ N 2.02(1) OC 1.73 μ C 1.91(2) Ph ₃ P 2.290(5) OC 1.74 μ N 1.97(1) OC 1.74 μ C 2.09(2) μ N 2.04(1) OC 1.74 μ C 1.94(2)	Fe 2.675(3,4) Au 2.671(3) Fe 2.635(3,28) N 83.8(6) Au 2.679(1) Fe 2.560(3) 2.662(3) C 79.7(1) Fe 2.560(3) 2.607(3) Fe 2.659(2) 2.717(3) Au 2.659(2) Fe 2.635(3,8) N 81.9(4) Au 2.717(3) Fe 2.574(3) 2.627(2) C 79.4(6) Fe 2.574(3) 2.643(3)	P,Fe 149.9(1,2.5) Fe,Fe 59.7(1) Au,Fe 60.2(1) 90.1(1) Fe,Fe 88.1(1) Au,Fe 60.0(1) 90.9(1) Fe,Fe 59.9(1) Fe,Fe 62.2(1) P,Fe 150.8(1,3.1) Fe,Fe 58.6(1) Au,Fe 61.8(1) 104.9(1) Fe,Fe 58.5(1) Au,Fe 59.6(1) 105.1(1) Fe,Fe 61.1(1) Fe,Fe 60.5(1)	35
(Ph ₃ P)AuFe ₃ . (μ_3 -SP [†])(CO) ₉ (dark red)	m P2 ₁ /c 4	18.745(3) 10.638(2) 18.345(3)	111.57(3)	AuPFe ₂ FeC ₃ S.	Ph ₃ P 2.251(8) OC 1.76(4,7)	Fe 2.649(3,4) Au 2.649(3,4)	P,Fe 147.7(2,4.6) Fe,Fe 63.8(1) S,Au 106.6(3)	36

				AuFe ₂ (x2)	2.04(4) μ_3 S 2.121(10,22)	Fe 2.638(8,7) 2.800(6) S 76.6(4,0) 82.7(3)	S, Fe 51(3,3) Au, Fe 57.9(1) 97(4,0) Fe, Fe 58(2,0) S, Fe 51.4(2,2) Fe, Fe 64.1(2)	
				FeC ₃ SFe ₂	OC 1.80(4,0) 1.87(5) μ_3 S 2.14(1)			
B: Au₂Fe₂ Au ₂ (μ - η^2 -dppm). Fe ₂ (CO) ₈ (red)	m P ₂ /n 4	16.405(5) 17.031(8) 12.400(4)	95.64(2)	AuPF ₂ Au (x2)	P 2.276(2,2)	Fe 2.531(2,4) Au 2.915(1)	P, Fe 175.04(9,2.36) P, Au 91.20(8,6) Fe, Au 87.46(5,2.28) C, C 97.9(5,7.3) 150.6(5,9) Au, Fe 87.80(6,14)	37
				FeC ₄ AuFe (x2)	OC 1.77(1,1)	Au 2.531(2,4) Fe 2.900(1)		
[Au(μ - η^2 -dppm)Fe. (CO) ₃ [Si(OMe) ₃] ₂ . CH ₂ Cl ₂ (colourless)	m P ₂ /a 4	21.930(9) 17.826(7) 11.297(5)	90.57(2)	AuPF ₂ Au (x2)	P 2.280(6,14)	Fe 2.549(3,14) Au 2.962(1)	P, Fe 162.9(2,1.2) P, Au 88.0(1,7) Fe, Au 106.0(1,1.2) C, C 106(1,2) 147(1,4) P, Si 172.9(3,1.5)	38
				FeC ₃ Si. Au (x2)	OC not given P 2.235(6,9) Si 2.275(8,7)	Au 2.962(1)		
[Au(μ - η^2 - η^5 - C ₅ H ₄ CH ₂ NMe ₂). Fe(η^5 -cp) ₂ (yellow orange)	m P ₂ /c 4	11.992(3) 12.804(3) 16.428(4)	97.89	AuNC (x2)	η^1 N 2.148(5) η^2 C 2.021(6) η^5 C not given	Au 3.122(1)	N, C 175.9(2) not given	39
				FeC ₁₀ (x2)				
C: Au₃Fe (F ₅ C ₆) ₃ Au(μ_3 -S). Au ₂ {(μ - η^1 - η^5 - C ₅ H ₄ PPh ₂) ₂ Fe} (orange) (at 173 K)	m P ₂ /n 4	17.876(2) 18.559(2) 17.896(2)	104.07(1)	Au ^I PS (x2)	η^1 P 2.245(4,1) μ_3 S 2.337(4,5)	Au 2.8889(8) S 76.36(10)	P, S 173.4(1,1.7) P, Au 122.7(1,1.9) S, Au 51.82(9,1.5) C, C 90.1(5,3.0) 179.5(4) C, S 89.9(2,2.7) 176.0(3) not given	40
				Au ^{III} C ₃ S	C 2.05(2,3) μ_3 S 2.374(4)	S 99.2(1,6.6)		
				FeC ₁₀	η^5 C not given			
[(Ph ₂ MeP)Au(μ - η^2 - C ₅ H ₄ NS-2)Au ₂ . (μ - η^1 - η^5 -C ₅ H ₄ PPh ₂) ₂ . Fe].(otf) ₂ (colourless) (at 173 K)	m P ₂ /n 4	13.831(3) 14.181(3) 31.059(7)	102.17(2)	Au ^I SP (x2)	μ S 2.339(6,2) P 2.249(4,3) N 2.065(14) P 2.239(5) η^5 C not given	Au 3.0985(12) S 83.0(2) Au 3.2105(13)	S, P 177.4(2,6) N, P 173.3(5) not given	41
				Au ^I NP				
				FeC ₁₀				
D: Au₂FePt [(CO) ₃ Fe(μ -Pcy ₂). {Au(PPh ₃) ₂ Pt. (1,5- η^4 -cod)]PF ₆ (not given)	m P ₂ /n 4	22.479(6) 26.781(8) 10.254(3)	102.94(2)	AuPPtFe (x2)	Ph ₃ P 2.291(5,7)	Fe 2.595(3,19) Pt 2.848(1,27) Au 2.595(3,19) Pt 2.715(3) P 75.6(2) Au 2.848(1,27)	P, Fe 51.6(2) Pt, Fe 59.61(3,17) C, C 97(1,2) Au, Au 113.2(1) Pt, Au 64.83(7,93) C, P 103.9(7,3.2) 160.9(6,4) Au, Au 99.07(3)	42
				FeC ₃ PtAu ₂	OC 1.76(2,6) μ P 2.197(6)			
				PtC ₄ PAu ₂	η^4 C 2.20(2,2) 2.37(2,2) μ P 2.229(5)			
E: AuM₂M' (CO) ₆ Fe ₂ AuCo. (μ_3 -COMe)(PPh ₃). (η^5 -cp) (black)	m P ₂ /n 4	13.669(3) 14.315(5) 16.665(4)	103.12(2)	AuPF ₂	Ph ₃ P 2.293(2)	Fe 2.690(1,9)	P, Fe 150.1(1,3.7) Fe, Fe 58.9(1) C, C 97.4(3,6.6) C, Fe 58.0(1,2) Au, Fe 60.6(1,4) Fe, Fe 64.1(7)	43
				FeC ₄ Co. AuFe (x2)	OC 1.789(2,0) μ_3 C 1.906(5,19)	Co 2.490(1,4) Au 2.690(1,9) Fe 2.643(1)		
				CoC ₇ Fe ₂	OC 1.774(6) cpC 2.083(3) μ_3 C 1.932(5)			

(CO) ₃ Fe(μ ₃ -CPh). Co ₂ (CO) ₆ Au(PPh ₃) (black)	or Pna ₂₁ 4	34.617(6) 8.793(2) 11.226(2)		AuPF ₂ Co FeC ₄ Co ₂ Au CoC ₄ Fe. AuCo CoC ₄ FeCo	Ph ₃ P 2.272(5) OC 1.772(26,8) 1.854(31) μ ₃ C 1.872(18) OC 1.788(26,34) μ ₃ C 1.959(21) OC 1.817(34,27) μ ₃ C 1.953(17)	Fe 2.615(3) Co 2.661(3) Co 2.566(4,45) Au 2.615(3) C 68.9(8) Fe 2.621(4) Au 2.661(3) Co 2.492(4) C 73.9(8) Fe 2.512(4)	not given C,C 97.9(11,6.2) C,μ ₃ C 146.0(8) C,Co 95.8(1) 121.1(8) Co,Au 92.3(1) C,C 98.6(11,6.8) C,μ ₃ C 150.3(10) C,Fe 118.7(8) C,Co 100.6(8) Au,Co 91.7(1) C,C 101.4(17,3.0) C,μ ₃ C 141.9(9) C,Fe 102.9(7) C,Co 97.9(10)	44
(CO) ₃ Fe(μ ₃ -PMe). CoRuAu(CO) ₆ (PPh ₃) (black)	m P ₂₁ /c 4	12.962(4) 15.082(3) 17.264(4)	105.07(2)	AuPF ₂ Ru FeC ₃ PCo. AuRu CoC ₃ P. RuFe RuC ₃ P. FeCoAu	Ph ₃ P not given OC not given μ ₃ P not given OC not given μ ₃ P not given OC not given μ ₃ P not given	Fe 2.677(2) Ru 2.729(2) Co 2.678(4) Au 2.677(2) Ru 2.914(3) Ru 2.679(3) Au 2.957(3)	not given not given not given not given	45
(CO) ₃ Fe(μ ₃ -S)Co. RuAu(CO) ₆ (PPh ₃) (black)	tr Pī 2	11.971(2) 14.483(3) 9.228(2)	93.45(2) 101.24(2) 77.55(1)					45

Footnotes: a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is maximum deviation from the mean
b. The chemical identity of the coordinated atom or ligand is specified in these columns.
c. There are two crystallographically independent molecules.

Table 4. Crystallographic and structural data for heteropentamuclear (gold, iron) clusters^a

COMPOUND (colour)	Cr. cl. Sp.Gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo- phore	M - L [Å]	M - M [Å] M - L - M [°]	L - M - L [°]	Ref.
{P(2-MeC ₆ H ₄) ₃ }Au. (μ ₅ -BH)Fe ₄ (μ- H)(CO) ₁₂ (dark brown)	tr Pī 2	10.223(2) 12.814(3) 15.231(4)	104.02(2) 90.47(2) 90.13(2)	AuBPFe FeC ₃ B. AuFe ₂ FeC ₃ BFe ₂ (x3)	μ ₅ B ^D 2.310(10) P 2.321(2) OC not given μ ₅ B 1.964(9) OC not given μ ₅ B 1.964(9) 2.052(9,4)	Fe 2.580(1) Au 2.580(1) B 73.8(3) Fe 2.678(2,3) B 83.6(4) Fe 2.655(2,51) B 81.9(4,3,1)	B,P ^D 149.2(2) B,Fe 47.0(2) P,Fe 163.9(1) B,Au 59.3(3) B,Fe 49.6(3,1) Au,Fe 99.9(1,1,3) Fe,Fe 58.2(1) B,Fe 49.1(3,5,2) Fe,Fe 60.1(1,1,4) 94.5(1,1)	46
(NMe ₃ CH ₂ Ph) ₂ . [(CO) ₁₆ Fe ₄ Au]Cl (dark green)	or Pccn 4	23.618(4) 16.600(3) 11.594(3)		Au ^{III} Fe ₄ FeC ₄ AuFe (x4)	OC 1.78(1,2)	Fe 2.595(1,12) Fe 2.771(2)	Fe,Fe not given C,C 158.9(6,7,3)	47
(CO) ₁₂ Fe ₄ (μ ₄ - COMe). Au(PEt ₃) (black)	tr Pī 2	14.764(2) 9.574(1) 11.094(2)	87.26(1) 82.33(2) 112.131	AuPF ₂ FeC ₄ AuFe ₂ (x2) FeC ₄ Fe ₂ FeC ₄ OFe ₂	Et ₃ P 2.278(5) OC not given μ ₄ C 1.98(2,1) OC not given μ ₄ C 1.86(2) OC not given μ ₄ C 2.14(2) μ ₄ O 2.029(9)	Fe 2.671(3,5) Au 2.671(3,5) Fe 2.638(4,49) C 159.5(8)	P,Fe 149.7(2,3,2) Fe,Fe 60.40(8) Au,Fe 76.95(9,20) 110.90(11,10) Fe,Fe 59.24(10,36) 97.38(12,43) Fe,Fe 61.63(9) Fe,Fe 61.49(9)	48a
(CO) ₁₁ (ON)Fe ₄ . (μ ₅ -C)Au(PPh ₃) (green)	m P ₂₁ /n 4	17.142(5) 15.738(2) 13.771(4)	108.63(2)	AuCPFe ₂ FeC ₄ AuFe (x2)	μ ₅ C 2.095(9) Ph ₃ P 2.273(3) OC not given μ ₅ C 1.853(7,8)	Fe 2.843(2,23) Au 2.843(2,23) C 91.9(4,1,2)	C,P 176.5(2) Fe,Fe 81.03(1) Fe,Fe 58.6(1,2)	48b

				FeC ₄ Fe ₂ FeC ₃ NFe	OC not given μ_5 C 1.915(9) OC not given μ_5 C 1.926(8) ON not given	Fe 2636(2,21) C 88.6(4,10) 176.1(5) Fe 2.578(2)	Fe, Fe 61.2(1,3) 89.7(1) Fe, Fe 60.3(1) 88.8(1)	
(CO) ₁₂ (μ -H)Fe ₄ . (μ_4 -C)Au(PPh ₃) (green brown)	tr P $\bar{1}$ 2	9.855(4) 12.495(6) 14.938(7)	103.46(2) 98.47(2) 99.74(2)	AuCPFe ₂ FeC ₄ AuFe ₂ (x2) FeC ₄ HFe ₂ (x2)	μ_4 C 2.077(5) Ph ₃ P not given OC not given OC not given μ_4 C 1.954(5,3) μ H 1.91(8,2)	Fe 2867(1,13) Au 2867(1,13) C 93.5(2,1,1) Fe 2634(1,10) Fe 2.618(1) H 87(3)	Fe, Fe 80.5(1) not given not given	49
{(Ph ₃ P)Au} ₂ Fe ₃ . (μ_3 -O)(CO) ₉ (black)	m P2 ₁ /n 4	8.872(2) 12.136(2) 41.568(9)	90.15(3)	AuPFe ₃ Au (x2) FeC ₃ O. Au ₂ Fe ₂ (x2) FeC ₃ O. AuFe ₂	Ph ₃ P 2.297(3,8) OC not given μ_3 O 1.878(7,3) OC not given μ_3 O 1.871(7)	Fe 2678(2,10) 2.748(2,34) Au 2.9915(9) Au 2.669(2) 2.748(2,34) Fe 2.558(2,21) 2.700(2) O 88.0(3,3,9) Au 2.688(2) Fe 2.558(2,21) O 86.1(3,1,0)	Fe, Fe 57.52(5,92) Fe, Au 55.59(5,66) 99.66(4) Au, Au 66.46(4,7) Fe, Fe 58.15(6,75) Au, Fe 60.40(5,98) 111.70(7,4,39) not given	50
{[(Ph ₃ P)Au] ₂ (μ_5 -P). Fe ₃ (μ -H)(CO) ₉ . 1.5C ₆ H ₆ (deep red)	m C2/c 8	20.422(9) 15.434(6) 34.135(11)	93.29(3)	AuP ₂ FeAu AuP ₂ Au FeC ₃ P. AuFe ₂ FeC ₃ PFe ₂ (x2)	Ph ₃ P 2.295(3) μ_5 P 2.428(3) Ph ₃ P 2.301(3) μ_5 P 2.316(3) OC 1.76(1,1) μ_5 P 2.278(4) OC 1.77(1,2) μ_5 P 2.197(4,3)	Fe 2.678(2) Au 2.991(1) Au 2.678(2) P 69.3(1) Fe 2.651(3,6) P 72.6(1,2) Fe 2.664(3,29) P 74.2(1,1,4)	P, μ_5 P 160.67(12) P, Fe 144.9(1) μ_5 P, Fe 52.72(8) Fe, Au 101.91(5) P, μ_5 P 165.90(12) P, Au 137.4(1) μ_5 P, Au 52.61(8) C, C 97.0(7,1,0) C, P 114.2(5,1,5) 131.6(5) Fe, Fe 61.06(7) Fe, Au 100.58(8,3,93) C, C 98.4(7,5,5) C, P 98.0(5,3,5) 153.3(5,1,7) Fe, Fe 101.91(5)	51
{(Ph ₃ P)Au} ₂ Fe ₃ . (μ_3 -S)(CO) ₉ (black)	tr P $\bar{1}$ 2	14.065(2) 16.917(3) 10.864(2)	97.57(1) 109.53(1) 67.64(1)	AuPFe ₃ AuPFe ₂ FeC ₃ S. Au ₂ Fe ₂ (x2) FeC ₃ S. AuFe	Ph ₃ P 2.305(6) Ph ₃ P 2.301(6) OC 1.80(3,4) μ_3 S 2.203(4,15) OC 1.80(3,4) μ_3 S 2.194(5)	Fe 2.722(4,24) Au 3.020(1) Fe 2.711(4,40) Au 2.697(3,26) Fe 2.642(5) 2.807(5,57) Au 2.698(4) Fe 2.642(3)	not given not given not given not given	52
[Au ₂ (μ - η^1 : η^5 - C ₅ H ₄ PPh ₂) ₆ . Fe ₃ Cl ₂ .CH ₂ Cl ₂ (yellow)	or Pbca 4	19.142(8) 20.759(4) 23.645(10)		AuP ₃ (Cl) (x2) FeC ₁₀ (x3)	η^1 P 2.345(3) 2.398(3,7) Cl 2.929(2) η^5 C not given	Fe 4.280(5) 4.850(5)	P, P 104.6(1) 125.1(1,1,1) P, Cl 86.1(1) 103.4(1,2,9) not given	53
[Au(μ - η^1 : η^5 - C ₅ H ₄ PPh ₂) ₆ . Fe ₃ (ClO ₄) ₂ .2CH ₂ Cl ₂ (yellow) (at 173 K)	m C2/c 4	32.858(6) 14.821(3) 26.399(5)	128.48(2)	AuP ₃ (x2) FeC ₁₀ (x3)	η^1 P 2.332(4) 2.381(3,4) η^5 C not given		P, P 108.8(1) 125.6(1,3) not given	11
(NEt ₄)[{(CO) ₄ Fe] ₂ . Au ₃ (μ - η^2 -dppm)] (orange red)	tr P $\bar{1}$ 2	10.051(4) 10.086(2) 33.284(6)	87.79(1) 111.60(2) 82.17(2)	AuFe ₂ Au ₂ AuPFeAu (x2) FeC ₄ Au ₂ (x2)	 P 2.271(7,4) OC not given	Fe 2.574(4,2) Au 2.921(2,0) Fe 2.550(4,5) Au 2.662(4,17)	Fe, Fe 172.7(2) Au, Au 75.53(4) P, Fe 168.3(2,2,6) not given	54
{[Fe(μ - η^5 : η^1 - C ₅ H ₄ PPh ₂)	or Pbcn	12.791 17.792		AuPCL (x2)				55

$(\mu-\eta^5-\eta^1\text{-ddpca})_2$. (AuCl) ₃ .Et ₂ O (orange) (at 190 K)	4	36.966		AuP ₂ Cl FeC ₁₀ (x2)				
$[\text{Fe}(\mu-\eta^5-\eta^1\text{-C}_5\text{H}_4\text{PPh}_2)_2$. $\text{Au}_2(\mu_4\text{-S})(\text{Au}(\text{PPh}_3)_2)_2$. $3\text{CH}_2\text{Cl}_2$ (orange) (at 173 K)	tr P $\bar{1}$ 2	13.727(2) 15.925(3) 17.763(2)	71.738(12) 73.264(4) 75.96(2)	AuSPAu ₂ (x4) FeC ₁₀	$\mu_4\text{S}$ 2.338(5,29) 2.410(5,6) Ph ₃ P2.268(6,12) $\eta^5\text{C}$ not given	Au 2.913(1,8) 2.965(1,13) S 75.8(2,2,3) 109.0(2,9) 124.4(2)	S,P 172.7(2,3,0) S,Au 52.09(13,2,74) 83.02(13,4,56) P,Au 103.8(2,2,2) 120.5(2,3,2) 132.8(2,2,1) not given	27
$[\text{Fe}(\mu-\eta^5-\eta^1\text{-C}_5\text{H}_4\text{PPh}_2)_2$. $\text{Au}_2(\mu_4\text{-S})(\text{Au}(\text{C}_6\text{F}_5)_3)_2$. CH_2Cl_2 (orange) (at 173 K)	tr P $\bar{1}$ 2	13.321(2) 13.829(2) 20.145(2)	86.707(8) 79.431(8) 78.421(10)	AuSPAu (x2) AuC ₃ S (x2) FeC ₁₀	$\mu_4\text{S}$ 2.34(3,2) $\eta^1\text{P}$ 2.253(3,1) C 2.050(13,27) $\mu_4\text{S}$ 2.35(3,1) $\eta^5\text{C}$ not given	Au 2.956(7) S 78.30(9) Au 3.333(1)- 4.250(1) S 96.84(11)- 126.22(13)	S,P 170.39(11) S,Au 50.85(7,6) P,Au 121.57(8,20) C,C 89.5(4,2,8) 177.3(3,1,5) C,S 90.6(3,9) 175.9(4,1,9) not given	56
$(\text{CO})_9\text{Fe}_3\text{Co}(\text{CO})_3$. $(\mu_5\text{-C})\text{Au}(\text{PPh}_3)$ (red)	tr P $\bar{1}$ 2	11.095(2) 12.787(3) 13.721(3)	79.54(3) 81.49(3) 64.73(3)	AuCP. CoFe FeC ₄ CoFe ₂ (x2) FeC ₄ Au. CoFe ₂ CoC ₄ AuFe ₂	$\mu_5\text{C}$ 2.069(3) Ph ₃ P 2.267(1) OC not given $\mu_5\text{C}$ 1.940(3,6) OC not given $\mu_5\text{C}$ 1.845(5) OC not given $\mu_5\text{C}$ 1.847(5)	Co 2.873(1) Fe 2.818(1) Co 2.615(1,1) Fe 2.518(1) 2.630(1,3) Au 2.818(1) Fe 2.630(1,3) Au 2.873(1) Fe 2.615(1,1)	not given not given not given not given	57a
$(\text{CO})_9\text{Fe}_3\text{Co}(\text{CO})_3$. $(\mu_5\text{-C})\text{Au}(\text{PPh}_3)$ (red) (at 173 K)	tr P $\bar{1}$ 2	11.039(2) 12.725(3) 13.647(4)	79.00(2) 81.09(2) 64.83(2)	AuCPFe ₂ FeC ₄ Au. CoFe ₂ (x2) FeC ₄ CoFe ₂ CoC ₄ Fe ₃	$\mu_5\text{C}$ 2.086(10) Ph ₃ P 2.276(1) OC 1.77-1.84 $\mu_5\text{C}$ 1.846(10,9) OC 1.77-1.84 $\mu_5\text{C}$ 1.924(10) OC 1.77-1.81 $\mu_5\text{C}$ 1.941(10)	Fe 2.846(1,33) C 92.5(5,1,1) Au 2.846(1,33) C 92.5(5,1,1) Co 2.623(1,8) C 87.6(5,6) Fe 2.623(1,7) C 174.6(5) Co 2.517(1) C 81.3(5) Fe 2.623(1,7) C 87.2(1,5) Fe 2.517(1) 2.623(1,8)	not given not given not given not given	57b
$(\text{CO})_6\text{Fe}_2\text{Ir}(\text{CO})$. $(\text{PPh}_3)(\mu_3-\eta^2\text{-C}_2\text{Ph})$. $\text{Au}_2(\text{PPh}_3)_2$ (orange)	m Cc 4	12.956(1) 26.604(4) 19.190(2)	97.14(1)	AuPIrAu AuCPIrAu IrC ₂ PAu ₂ Fe ₂ FeC ₅ IrFe (x2)	Ph ₃ P 2.269(2) $\mu_3\text{C}$ 2.39(2) Ph ₃ P 2.269(6) OC not given $\mu_3\text{C}$ 1.96(2) Ph ₃ P 2.287(2) OC not given μC 2.10(2,4) $\mu_3\text{C}$ 2.075(20,5)	Ir 2.635(1) Au 2.847(1) Ir 2.726(1) Au 2.847(1) Au 2.635(1) 2.726(1) Fe 2.727(4,18) Ir 2.727(4,18) Fe 2.501(5) C not given $\mu_3\text{C}$ not given	P,Ir 66.0(2) P,Au 132.7(2) Ir,Au 59.5(1) P,Ir 170.0(2) P,Au 122.4(1) C,Au 66.3(1) Au,Au 64.1(1) Au,Fe 88.4(1,1,9) 107.1(1) 144.8(1) not given	58
$(\text{PPh}_4)[(\text{CO})_5\text{Fe}_2(\mu\text{-CO})_2$. $\text{Ir}_2(\mu\text{-CO})(\text{CO})_4\text{Au}(\text{PPh}_3)]$ (orange)	m P2 ₁ /c 4	10.990(3) 13.693(2) 35.883(3)	97.99(2)	AuPIr ₂ Fe FeC ₄ Ir ₂ . AuFe FeC ₃ Ir ₂ Fe IrC ₄ Fe ₂ . AuIr (x2)	Ph ₃ P not given OC 1.776(x2) μOC 1.996(x2) OC 1.776 OC 1.845 μOC 2.133	Ir 2.813(1,16) Fe 2.806(3) Ir 2.756(1,21) C 83.2(1) Au 2.806(3) Ir 2.679(1,7) Fe 2.645(1) Au 2.813(1,16) Ir 2.786(1) C 83.2(3)	Ir,Ir 58.70(1) Ir,Fe 58.73(1,2) Ir,Au 60.77(1,15) Ir,Fe 59.44(2,43) Ir,Ir 61.96(2) Ir,Fe 62.34(2,60) Fe,Fe 58.23(2,18) Fe,Au 60.49(1,42) Fe,Ir 59.02(2,24) Au,Ir 60.71(1,54)	59
$(\text{PPh}_4)[(\text{CO})_5\text{Fe}_2$. $(\mu\text{-CO})_3\text{Rh}_2(\text{CO})_4$.	m P2 ₁ /c	10.992(3) 13.724(3)	97.6(2)	AuPRh ₂ Fe	Ph ₃ P 2.283(2)	Rh 2.782(1,1) Fe 2.793(1)	not given	60

Au(PPh ₃) (orange)	4	35.982(6)		Rh ₄ Fe ₂ . AuRh (x2) FeC ₄ Rh ₂ . AuFe FeC ₃ Rh ₂ Fe	OC 1.851(6,45) μOC 2.098(5,83) OC 1.815(5,10) μOC 2.018(5,25) OC 1.759(2) 1.788(5,2)	Au 2.782(1,1) Fe 2.637(1,3) 2.755(1,5) Rh 2.732(1) Rh 2.755(1,5) Au 2.793(1) Fe 2.656(1) Rh 2.637(1) Fe 2.656(1)	C, Fe 175.9(1,5) C, Fe 175.8(2) not given	
(CO) ₃ FeCo ₃ (μ-CO) ₃ . (CO) ₆ Au(PPh ₃) (purple)	m P2 ₁ 2	9.174(2) 15.103(2) 12.708(3)	108.08(2)	AuPCo ₃ CoC ₄ Fe. AuCo ₂ (x3) FeC ₃ Co ₃	Ph ₃ P not given OC 1.75(-,6) μOC 1.94(-,7) OC 1.79(-,14)	Co 2.714(7,0) Fe 2.56(-,8) Co 2.52(-,8) Co 2.56(-,8)	Co, Co 55.3(3) Fe, Au 112.9(15) Fe, Co 60.5(13) C, C 96(2) Co, Co 59.0(2)	61
(CO) ₃ FeCo ₃ (μ-CO) ₃ . (CO) ₅ (PMe ₂ Ph). Au(PPh ₃) (purple)	m P2/c 8	22.863(5) 13.232(4) 28.598(6)	95.28(9)	AuPCo ₂ CoC ₄ Fe. AuCo ₂ (x2) CoC ₃ PFe. AuCo ₂ FeC ₃ Co ₃	Ph ₃ P 2.283(3) OC 1.74(5) μOC 1.92(5) OC 1.74(5) μOC 1.92(5) PhMe ₂ P 2.16(2) OC 1.71(9)	Co 2.72(3,0) Au 2.72(3) Co 2.50(2) C 139(4) Co 2.60(3)	Co, Co 54.8(4) C, C 95(1) Fe, Co 61.0(11) Co, Co 60.6(6) Co, Au 62.4(14) C, C 172(5) P, Fe 169(4) P, Au 78(4) P, Co 128(3) C, C 97(3) Co, Co 57.3(7) C, Co 100(3) 154(3)	62
(CO) ₃ FeCo ₃ (μ-CO) ₃ . (CO) ₄ [P(OMe) ₃] ₂ . Au(PPh ₃) (purple)	or Pn2 ₁ 4	21.566(5) 13.356(3) 15.141(2)		AuPCo ₂ CoC ₃ P. FeAuCo ₂ (x2) CoC ₄ Fe. AuCo ₂ FeC ₃ Co ₃	Ph ₃ P 2.28(3) OC 1.72(9) μOC 1.88(10) P 2.24(9) OC 1.72(9) μOC 1.88(10) OC 1.77(7)	Co 2.71(3) Au 2.71(3) Fe 2.60(3) Co 2.53(2) C 137(7) Co 2.60(3)	not given C, P 90(2,6) P, Fe 166.8(3) P, Au 81.7(3) P, Co 130(2) C, C 95(1) Fe, Co 61.0(6) Co, Co 60.0(6) Co, Au 62.1(6) C, C 99(1) Co, Co 58.1(1) C, Co 100, 155(3)	62
(CO) ₃ Fe(μ ₄ -N). Ru ₃ (CO) ₉ Au(PPh ₃) (red)	or Pbca 8	16.977(4) 16.980(4) 24.872(25)		AuPRu ₂ RuC ₃ NFe. AuRu ₂ (x2) RuC ₃ NRu ₂ FeC ₄ NRu ₂	Ph ₃ P 2.287(4) OC 1.90(2,3) μ ₄ N 2.06(1,2) OC 1.86(2,2) μ ₄ N 1.89(1) OC 1.76(2,2) μ ₄ N 1.81(1)	Ru 2.876(1,6) Ru 2.788(2,10) 2.839(2) Ru 2.788(2,10) Ru 2.705(2,12)	not given not given not given not given	63

Footnotes: a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is e.s.d., and the second is maximum deviation from the mean value.
b. The chemical identity of the coordinated atom or ligand is specified in these columns.

Table 5 . Crystallographic and structural data for heterohexa- and heptanuclear (gold, iron) clusters^a

COMPOUND (colour)	Cr. cl. Sp.Gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo- phore	M - L [Å]	M - M [Å] M - L - M [°]	L - M - L [°]	Ref.
A: Heterohexa- [(CO) ₁₁ (μ-O)Fe ₄ (μ ₅ -C). Au ₂ (μ-η ² -dppm)] ₂ .tol (green) (at 150(2) K)	m P2 ₁ /c 4	20.210(8) 12.761(7) 17.835(8)	110.48(5)	FeC ₄ AuFe ₂ (x2) FeC ₄ AuFe ₃ FeC ₄ Fe ₃	OC ^b not given μ ₆ C 1.860(13) OC not given μOC not given μ ₆ C 1.973(14) OC not given μOC not given	Au 2.828(2,3) C 92.4(5) Fe 2.648(3,5) C 88.6(6,1.1) Au 2.560(2) C 116.1(6) Fe 2.571(3) 2.658(3,5) C 85.1(5,2.6) Fe 2.571(3) 2.649(3,2)	AuFe ^b 84.78(8,14) Fe, Fe 58.08(8,4) Au, Fe 88.77(7,28) Fe, Fe 60.96(8,12) Fe, Fe 60.95(8,16) 89.13(9)	64

				AuPFeAu	μ_5 C 1.922 η^2 P 2.282(4)	C 86.8(5,4,2) Fe 2.560(2) Au 2.860(2)	P, Fe 169.64(1) P, Au 93.65(1) Fe, Au 78.34(5) C, P 170.2(4) PFe 137.73(10,39) Fe, Fe 82.16(7)	
				AuCPFe ₂	μ_5 C 2.070(12) η^2 P 2.271(3)	Fe 2828(2,3)		
[(CO) ₁₁ (μ -CO)HFe ₄ . (μ_6 -B){Au(AsPh ₃) ₂] (dark brown)	tr P† 2	10.498(2) 12.239(2) 20.718(5)	79.68(2) 83.00(2) 73.42(1)	FeC ₃ BAu ₂ Fe ₂	OC not given μ_6 B 1.999(14)	Au 2.590(1) 2.680(2) B 77.3(5,4,7) Fe 2.725(2,9) B 82.65(5) 160.1(7)	Au, Au 64.9(1) Fe, Fe 56.6(1) Au, Fe 55.6(1) 100.2(1,3,9) B, Au 55.4(4,1,2) B, Fe 49.6(3,9) Au, Fe 64.6; 83.5(1); 110.2(1) Fe, Fe 61.0(1,4) 94.2(1) B, Au 58.6(4) B, Fe 49.3(4,3,3) Fe, Fe 56.7(1,5,6) 95.0(1)	65
				FeC ₄ BAuFe ₂	OC not given μ OC not given μ_6 B 2.068(11)	Au 2.613(1) B 724,144.3(6) Fe 2.586(2) 2.709(2,25) B 79.1(5,2,7)	B, Fe 48.8(4,2,2) Fe, Fe 57.8(1) B, Fe 50.5(4,89)	
				FeC ₄ BFe ₂	OC not given μ OC not given μ_6 B 2.114(13)	Fe 2.668(3) 2.717(2) B 81.3(5,1,3)	Fe, Fe 56.7(1,5,6) 95.0(1)	
				FeC ₄ BFe ₃	OC not given μ_6 B 2.031(14)	Fe 2.586(2) 2.668(2) 2.717(2)	Fe, Fe 57.8(1) B, Fe 50.5(4,89)	
				AuBAsFeAu	μ_6 B 2.342(12,2) PhAs 2.408(1,0)	Au 2.931(1) B 77.4(1)	B, As 151.5(3,4,6) B, Fe 46.4(4,2,6) As, Fe 153.1(1,9,3) Fe, Au 53.1; 98.4(1)	
[(CO) ₁₁ (μ -CO)HFe ₄ . (μ_6 -B){Au(PPh ₃) ₂] (green black)	tr P† 2	10.870(3) 12.114(3) 20.466(6)	80.23(2) 83.17(2) 73.40(2)	FeC ₃ BAu ₂ Fe ₂	OC not given μ_6 B 2.00(1)	Au 2.606(1) 2.852(2) B 77.1(4,3,9) Fe 2.714(2,6) B 82.8(5,1,0) 158.9(6)	Au, Au 65.1(0) Fe, Fe 56.7(1) Au, Fe 56.3(0) 100.8(1,3,6) B, Au 57.3(3,2,4) B, Fe 49.1(3)	66
				FeC ₄ BAuFe ₂	OC not given μ OC 1.75(1) μ_6 B 2.07(1)	Au 2.630(1) B 72.5(4) Fe 2.578(2) 2.695(2,25) B 80.4(4,4,7)	Au, Au 64.4; 84.4(1) Fe, Fe 110.8(1) Au, Fe 61.0(1,4) 94.0(1) B, Au 58.8(3) B, Fe 47.6(3,6) Fe, Fe 61.9(1) 97.7(1) B, Fe 4 9.6(4,5) B, Au 1.3(3,1) Fe, Au 57.4(0,4,1) 98.0(0)	
				FeC ₄ BFe ₃	OC not given μ OC 2.42(1) μ_6 B 2.13(1)	Fe 2.578(2) 2.681(2,27) B 78.7(5,3,1)	Fe, Fe 61.9(1) 97.7(1) B, Fe 4 9.6(4,5) B, Au 1.3(3,1) Fe, Au 57.4(0,4,1) 98.0(0)	
				AuBPFeAu	μ_6 B 2.36(1,1) PhP 2.301(3,2)	Au 2.943(1) B 77.3(3)	Fe, Au 56.9(3) B, Fe 49.7(3) Au, Fe 81.1(1) 106.3(1) Fe, Fe 58.3(1) B, Fe 48.3(1,2,3) Fe, Fe 60.8(1,1)	
[(OC) ₁₂ HFe ₄ (μ_6 -B). {Au(PEt ₃) ₂] (black)	m l2/a 4	17.783(5) 11.277(3) 18.084(7)	106.26(3)	FeC ₃ BAuFe ₂ (x2)	OC 1.780(13,11) μ_6 B 1.989(3)	Fe 2.615(1) B 75.6(1) Fe 2.689(2,1) B 93.9(1)	B, Au 56.9(3) B, Fe 49.7(3) Au, Fe 81.1(1) 106.3(1) Fe, Fe 58.3(1) B, Fe 48.3(1,2,3) Fe, Fe 60.8(1,1)	67
				FeC ₃ BFe ₂	OC 1.799(13,23) μ_6 B 2.065(11)	Fe 2.621(2) 2.689(2,1) B 81.7(5,2,9)	B, P 157.1(1) B, Fe 47.4(1) P, Fe 152.8(1) Fe, Au 83.6(1) B, Au 50.5(2) P, Au 121.5(1)	
				AuBPFeAu	μ_6 B 2.262(11) Et ₃ P 2.293(3)	Au 2.880(1) B 79.1(5)	B, P 157.1(1) B, Fe 47.4(1) P, Fe 152.8(1) Fe, Au 83.6(1) B, Au 50.5(2) P, Au 121.5(1)	
[(OC) ₁₂ HFe ₄ (μ_6 -B). {AuP(<i>p</i> -tol) ₃] ₂ .CH ₂ Cl ₂ (brown black)	m P2/n 4	28.891(6) 13.367(4) 23.441(7)	110.82(3)	FeC ₃ BAu ₂ Fe ₂	OC not given μ_6 B 2.008(24)	Au 2.627(2) 2.808(3) B 77.0(8,2,1) Fe 2.688(4,4) 2.741(4) B 82.2(8,1,0)	Au, Au 66.3(1) Fe, Fe 56.7(1) B, Au 56.9(6,9) B, Fe 50.7(6,7)	67

				FeC ₃ BAuFe ₃	OC not given μ_6 B 2.114(19)	Au 2.635(2) B 58.6(5) Fe 2.580(4) 2.712(4,29) B 79.7(5,4.7) Fe 2.680(5,5) 80.2(7) Fe 2.580(4) 2.683(5,9) B 78.8(7,3.8) Au 2.975(1) B 79.1(5)	B, Au 58.6(1) Fe, Fe 60.9(1,2) 93.7(1) AuFe 62.9, 84.9(1) 109.6(1) B, Fe 51.3(6,3) Fe, Fe 57.6(1) B, Fe 49.3(6,3,0) Fe, Fe 62.0(1,6) 95.1(1) P, B 155.5(5,6,0) Fe, Au 56.81(3,0) 97.7(1)	
(OC) ₁₂ Fe ₄ (μ_6 -C)Au ₂ (PEt ₃) ₂	m C2/c 4	21.502(9) 11.457(5) 17.679(9)	125.977(32)	FeC ₄ AuFe ₂	OC not given μ_6 C 1.929(2,29)	Au 2.770(1) 2.991(2,9) C 87.0(3) Fe 2.562(2) 2.685(2,6) C 175.2(9)	not given	68
				AuCPFe ₂	μ_6 C 2.119(11) Et ₃ P not given		Fe, Fe 82.2(1)	
{[(cp)Fe] ₂ (μ - η^{10} , η^1 -C ₅ H ₄ P(Ph)C ₅ H ₄) ₂ . AuC≡CAu}.4EtOH (orange)	tr Pī 1	10.951(5) 11.368(5) 13.106(10)	69.08(5) 79.41(5) 75.31(4)	FeC ₁₀	C 1.997(6,1) 2.032(13,27) C 2.002(6) P 2.276(2)		not given	21
				AuCP			C, P 175.9(2)	
[(OC) ₉ Fe ₃ (μ_6 -P). {Au(PPh ₃) ₃ }. 0.3CH ₂ Cl ₂ .0.7Et ₂ O (dark red) (at 123 K)	m P2 ₁ /n 4	16.260(1) 20.363(7) 19.526(5)	93.45(5)	FeC ₃ PAu ₂ Fe ₂	OC 1.80(3,3) μ_6 P 2.31(1)	Au 2.665(5) 2.772(5) P 69.2(3,1.1) 145.4(4) Fe' 2.652(7,7) P 72.6(3) Au 2.711(5) P 68.3(3) 127.4(4,6.0) Fe 2.649(7,4) P 70.9(3,1.2)	C, C 97(2,0) C, P 120(1,5) Au, Au' 71.2(1) Fe, Fe' 60.0(2) Au, Fe 60.0(2) 102.8(2,10) C, C 96(2,2) C, P 89(2) 132(2,0) Au, Fe' 62.3(2) 106.3(2) Fe, Fe' 60.3(2) C, C 99(2,4) C, P 100(1,1) 151(1) Fe, Fe' 59.8(2) P, P 157.0(3) Fe, Fe' 57.7(2) Au, Au' 60.61(5,56) P, P 60.61(5,56) Au, Au' 170.9(3) 58.78(5)	51
				FeC ₃ PAuFe ₂	OC 1.72(5,8) μ_6 P 2.32(1)			
				FeC ₃ PFe ₂	OC 1.79(4,4) μ_6 P 2.18(1)	Fe 2.655(7,4)		
				AuP ₂ Fe ₂ (x2)	Ph ₃ P 2.267(3) μ_6 P 2.502(8)	Fe 2.742(5,31) Au' 3.188(2,21) P 81.5(2,2.1) Au' 3.206(2,39) P 82.6(2,3,2) Fe 2.665(5)		
				AuP ₂ Fe	Ph ₃ P 2.314(9) μ_6 P 2.455(9)			
[(OC) ₄ FeAu ₂ (μ - η^{12} -dppe)] ₂ . C ₃ H ₈ O (yellow)	m C2/c 4	15.823(3) 15.858(4) 25.708(3)	95.88(2)	FeC ₄ Au ₂	OC not given	Au 2.524(2) 2.535(2)	not given	69
				AuPFe	η^2 P not given	Au 2.977(1) 3.163(1)	not given	
[(OC) ₄ FeAu ₂ (μ - η^{12} -dppm)] ₂ (yellow)	m C2/c 4	14.250(5) 19.431(4) 24.810(11)	103.44(3)	FeC ₄ Au ₂	OC not given	Au 2.539(3) 2.608(3)	not given	69
				AuPFe	Ph ₃ P not given	Au 3.041(2)	not given	
B: Heterohepta- [(OC) ₃ FeAu ₅ (PPh ₃) ₅]PF ₆ (yellow) (at 203 K)	m P2 ₁ /c 4	22.300(7) 16.550(6) 24.627(8)	94.14(5)	FeC ₃ Au ₅	OC 1.749(7,20) 1.812(5)	Au 2.620(1,30)	not given	70
				AuPFe	Ph ₃ P 2.282(2,13)	Au 2.821(-5,2) 3.0880(4)	not given	
(NEt ₄)[(CO) ₁₃ (μ -CO) ₃ . Fe ₅ (μ_6 -C)Au(PPh ₃)] (black)	m P2 ₁ /c 4	10.233(2) 22.464(4) 21.530(5)	92.78(2)	FeC ₄ AuFe ₃ (x3)	OC not given μ OC not given μ_6 C 1.901(-,15)	Au 2.733(2,1) 2.785(2) Fe' 2.562- 2.801(4) C 82.4(8,4) μ_6 C 1746(9,44) C 79.6(7)	not given	48b
				FeC ₄ Fe ₃ (x3)	OC not given μ OC not given		not given	

				AuPF ₆ Au ₂ (x4)	P 2.139(6) 2.277(7)	2.840(1) Fe 2.438(3) 2.650(4)	P,Fe 167.4(2,1.5)	
[[Fe(μ-η ⁵ -dppcp) ₂] {Au ₂ (μ ₃ -S) ₂ Au(C ₆ F ₅) ₂ }. SO ₃ CF ₃ .3CH ₂ Cl ₂ (orange) (at 173 K)	m P2 ₁ /n 4	18.214(3) 22.444(3) 24.081(3)	105.611(12)	FeC ₁₀ (x2) AuPS (x4) Au ^{II} C ₂ S ₂	η ⁵ C not given η ¹ P 2.255(4,12) μ ₃ S 2.342(4,26) C 2.058(14,5) μ ₃ S 2.392(4,5)	Au 2.933(1,17) S 77.5(1,6) Au 3.219(8) 3.3661(10) S 106.4(2,7)	P,S 173.5(1,2.8) C,C 88.6(5) S,S 95.19(13) C,S 88.2(3,2.9) 174.9(4,1.2)	40
[Fe(μ-η ⁵ -C ₅ H ₄ PPh ₂) ₂ . {AuMn ₂ (μ-PPh ₂)(CO) ₈ } ₂] (red)	m P2 ₁ /c 2	14.592(2) 14.675(2) 16.658(2)	91.46(1)	FeC ₁₀ AuPMn ₂ MnC ₃ PAu	η ⁵ qC 2.049(7) η ¹ P 2.318(2) OC 1.82(1,3) μP 2.283(2,3)	Mn 2.660(1) 2.776(1) Mn 3.049(2)	P,Mn 145.88(5,35) Mn,Mn 68.20(3) P,Au 48.09(6,7) 103.01(6,1.84)	75
[Fe(μ-η ⁵ -C ₅ H ₄ PPh ₂) ₂ . Au ₂ (μ ₆ -B)Ru ₄ (H)(CO) ₁₂]. 2CHCl ₃ (orange red)	m C2/c 4	16.819(3) 12.988(2) 26.993(6)	104.11(2)	FeC ₁₀ AuBPRuAu RuC ₃ BAuRu ₂ (x2) RuC ₃ BRu ₃ (x2)	η ⁵ qC 2.048(2,24) μ ₆ B 2.292(20) η ¹ P 2.300(6) OC not given μ ₆ B 2.133(5) OC not given μ ₆ B 2.242(19)	Ru 2.695(2) B 74.9(3) Au 2.818(2) B 75.9(8) Ru 2.853(2) B 81.4(6) Ru 2.854(2) B 157.4 Ru 2.854(2,1) B 80.4(8)	not given B,P 160.6(2) B,Au 50.9(4,1.2) P,Au 117.0(2) 148.8(2) Ru,Au 90.6(1) B,Au 55.2(6) B,Ru 51.0(5) Ru,Ru 60.9(1) B,Ru 48.4(1,1.4) Ru,Ru 59.5(1,1) 94.3(1)	76
[Fe(μ-η ⁵ -C ₅ H ₄ PPh ₂) ₂ . Au ₂ (μ ₃ -H)Ru ₄ (μ ₃ -H)- (CO) ₁₂].CH ₂ Cl ₂ (red)	tr P-1 2	13.675(2) 16.999(2) 13.094(2)	110.69(2) 112.47(2) 87.99(2)	FeC ₁₀ AuPRu ₂ Au AuHPRu ₂ Au RuC ₃ HAuRu ₄ RuC ₃ H ₂ AuRu ₂ RuC ₃ HAuPRu ₃ RuC ₃ Ru ₃	η ⁵ qC 2.019(8)- 2.071(11) η ¹ P 2.305(4) μ ₃ H not given η ¹ P 2.282(5) OC 1.840(18)- 1.902(21) μ ₃ H not given OC 1.840(18)- 1.902(21) μ ₃ H not given μH not given OC 1.840(18)- 1.902(21) μH not given OC 1.840(18)- 1.902(21)	Ru 2.771(1) 2.846(1) Au 2.901(1) Ru 2.778(1) 2.796(2) Au 2.771(1) 3.016(1) Au 2.788(1) Ru 2.775(2) 2.950(1) Au 2.846(1) Ru 2.886(2)- 3.016(1) Ru 2.775(2)- 2.886(2)	not given P,Ru 146.4(1,5,0) P,Au 126.2(1) Ru,Ru 64.9(1) RuAu 59.0,76.5(1) P,Ru 146.5(1,6,1) P,Au 113.1(1) Ru,Ru 63.8(1) RuAu 58.2,101.9(1) Au,Au 62.8(1) Ru,Ru 58.4(1,1,6) Au,Ru 58.4(1,1,4) 75.4; 106.7(1,5,7) Au,Ru 56.3(1) 98.8(1) Ru,Ru 60.4(1) Au,Ru 54.2(1,5,3) 93.6(1) Ru,Ru 57.4(1,1,0) Ru,Ru 63.1(1,3)	77

Footnotes: a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is e.s.d., and the second is maximum deviation from the mean value.
b. The chemical identity of the coordinated atom or ligand is specified in these columns.
c. There are two crystallographically independent molecules.

Table 6. Crystallographic and structural data for heterooligo- and heteropolynuclear (gold, iron) clusters^a

COMPOUND (colour)	Crys.cl. Sp.Gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo- phore	M - L [Å]	M - M [Å] M - L - M [°]	L - M - L [°]	Ref.
[Au(MePh ₂) ₂]. {[(CO) ₁₂ (μ-H)Fe ₄]	m C2/c 4	21.704(3) 9.542(2) 29.717(6)	97.50(6)	AuB ₂ Fe ₂	μ ₆ B ^b 2.300(12)	Fe 2.615(1) B 74.7(4)	B,B ^b 125.8(6) Fe,Fe 143.4(1) B,Fe 47.2(3)	46

(μ_5 -BH) $_2$ Au] (dark orange)				FeC ₃ B. AuFe ₂ (x2) FeC ₃ BFe ₂ (x6) AuP ₂	OC not given μ_5 B 1.990(12) OC not given μ_5 B 2.054(12,39) Ph ₂ MeP2.300(4)	Au 2.615(1) B 74.7(4) Fe 2.664(2,4) B 81.9(4,1) Fe 2.651(2,21) B 90.1(4,1,4)	164.9(3) B,Au 58.0(3) B,Fe 50.4(3,2) Au,Fe 99.5(1,6) Fe,Fe 59.1(1) B,Fe 49.4(3,1,8) Fe,Fe 60.2(1,7) 95.4(1,2) P,P 180.0(1)	
{[(CO) $_6$ (μ -CO). (μ - HC=CPhH)Fe ₂ . Au] ₃ (μ - η^3 - triphos)]. 0.5CH ₂ Cl ₂ (dark green)	tr P1 2	14.632(4) 14.768(4) 21.750(6)	88.71(2) 77.75(2) 83.76(2)	AuPFe ₃ (x3) FeC ₄ AuFe (x6)	μ P 2.276(12) 2.294(11,3) OC not given μ OC not given LC 2.28(4,3) μ C 1.96(4,4) 2.14(4,2)	Fe 2.634(7) 2.687(6,20) 2.726(6,2) Au 2.634(7) 2.687(6,20) 2.726(6,2) Fe 2.606(8,12) C 81(2,4)	P,Fe 151.0(3,10.1) Fe,Fe 57.9(2,3) not given	78
{[Fe(μ - η^5 - η^1 - C ₅ H ₄ PPh ₂) ₂] ₃ . {Au(μ_3 -S)Au] ₃ . 8CHCl ₃ (yellow) (at 173 K)	tr P1 2	15.177(3) 18.408(4) 27.894(8)	88.83(2) 84.46(2) 67.78(2)	AuSPAu (x6) FeC ₁₀ (x3)	μ_3 S 2.331(9,17) 2.368(9) P 2.266(9,16) η^5 C not given	Fe 2.917(2,12) 3.255(2,28) S 77.3(2,3) 88.3(3,3) Au 4.284	S,P 171.6(3,4.0) S,Au 47.7(2,4.5) 87.3(2,3.6) P,Au 101.2(2,1.4) 123.3(2,2.5) 136.2(3,3.7) not given	27
[K(η^5 -18-crown- 6). {(μ - CO)(CO) $_{11}$ (μ_3 - CO). Fe ₄ Au(PEt ₃) ₂ . CH ₂ Cl ₂ (black)	or Pnma 4	20.916(3) 19.361(2) 11.511(2)		AuPFe ₂ (x2) FeC ₄ Au. Fe ₃ (x4) FeC ₃ OFe ₃ (x2) FeC ₃ Fe ₂ (x2) KO ₈	Et ₃ P 2.278(2) OC 1.767(6,17) OC 1.778(9,21) μ_3 O 2.137(9) μ CO 1.996(5) OC 1.808(9,34) μ_3 OC 1.851(9) η^5 O 2.782(4,36) μ CO 2.770(4,0)	Fe 2.666(1) Au 2.666(1) Fe 2.642(1,10) C 155.8(4)	P,Fe 150.18(2) Fe,Fe 59.57(4) Au,Fe 80.76(3) 111.92(3) Fe,Fe 95.31(4) Fe,Fe 59.86(4) Fe,Fe 60.64(4) not given	48a
[ClAu(μ - η^1 - η^5 - C ₅ H ₄ PPh ₂). Fe] ₂ .0.4CH ₂ Cl ₂ (yellow)	or F2dd 16	11.096(4) 31.507(10) 39.71(3)		AuP ₂ Cl FeC ₁₀	η^1 P 2.303(6,6) Cl 2.624(9) η^5 C not given		P,P 143.0(2) P,Cl 108.4(2,4.4) not given	79
[ClAu(μ - η^1 - η^5 - C ₅ H ₄ PPh ₂). Fe] ₂ .2.85CHCl ₃ (yellow)	m P2 ₁ /c 4	12.917(6) 18.321(6) 16.242(4)	110.11(2)	AuP ₂ Cl FeC ₁₀	η^1 P 2.315(2,0) Cl 2.580(3) η^5 C not given		P,P 136.5(1) P,Cl 111.7(1,1.0)	79
[ClAu(μ - η^1 - η^5 - C ₅ H ₄ PPh ₂). Fe].CH ₂ Cl ₂ (yellow)	m P2 ₁ /c 4	11.059(7) 24.154(9) 13.122(4)	128.94(4)	AuP ₂ Cl FeC ₁₀	η^1 P 2.308(2,15) Cl 2.709(2) η^5 C 2.046(6,3)		P,P 155.2(1) P,Cl 102.4(1,11.2) not given	80

Footnotes: a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is e.s.d., and the second is maximum deviation from the mean.
b. The chemical identity of the coordinated atom or ligand is specified in these columns.

Table 7. Summary of the M-M and M-M' bond distances

M - M	Distances [Å]			
	Shortest [ref.]	Longest [ref.]	Average	Heteronuclearity
Au - Fe	2.519(1) [5]	2.553(1) [7]	2.533	Binuclear
	2.507(3) [24]	2.818(2) [25]	2.634	Trinuclear
	2.527(2) [37]	2.717(3) [35]	2.633	Tetranuclear
	2.545(4) [54]	2.880(1) [40]	2.702	Pentanuclear
	2.776(1) [70]	2.975(1) [67]	2.867	Hexanuclear
	2.438(3) [54]	2.871(2) [72]	2.699	Heptanuclear
	2.615(1) [46]	2.922(2) [27]	2.707	Nonanuclear
	2.666(1) [48a]			Decanuclear
Au - Au	2.768(4) [25]	2.928(1) [23]	2.880	Trinuclear

	2.889(1) [40] 2.847(1) [58] 2.776(1) [70] 2.630(1) [54] 2.905(2) [27]	2.962(1) [38] 2.991(1) [51] 2.971(1) [67] 2.992(2) [74] 2.929(2) [27]	2.922 2.936 2.867 2.857 2.917	Tetranuclear Pentanuclear Hexanuclear Heptanuclear Nonanuclear
Fe - Fe	2.605(2) [17] 2.574(2) [35] 2.504(3) [58] 2.571(3) [64] 2.562(4) [48b] 2.594(2) [78] 2.623(2) [48a]	2.651(4) [19] 2.900(2) [37] 2.782(2) [50] 2.741(4) [67] 2.941(3) [72] 2.922(2) [68] 2.654(2) [48a]	2.630 2.676 2.640 2.646 2.670 2.726 2.692	Trinuclear Tetranuclear Pentanuclear Hexanuclear Heptanuclear Nonanuclear Decanuclear
Au-Co - Pt - Ru - Ir - Co - Ru - Rh - Mn - Ru	2.661(3) [44] 2.821(1) [42] 2.729(2) [45] 2.633(1) [58] 2.710(3) [62] 2.754(1) [63] 2.781(1) [60] 2.660(1) [74] 2.641(2) [77]	2.875(1) [42] 2.829(1) [59] 2.873(1) [57a] 2.766(1) [63] 2.783(1) [60] 2.776(1) [74] 2.846(1) [77]	2.848 2.724 2.754 2.760 2.782 2.718 2.773	Tetranuclear Tetranuclear Tetranuclear Pentanuclear Pentanuclear Pentanuclear Pentanuclear Heptanuclear Heptanuclear
Fe - Co - Pt - Ru - Co - Rh - Ru - Ir	2.486(1) [43] 2.715(3) [42] 2.914(3) [45] 2.517(1) [57b] 2.634(1) [60] 2.693(2) [63] 2.686(1) [59]	2.678(1) [45] 2.633(1) [57a] 2.750(1) [60] 2.717(2) [63] 2.776(1) [59]	2.570 2.582 2.689 2.705 2.729	Tetranuclear Tetranuclear Tetranuclear Pentanuclear Pentanuclear Pentanuclear Pentanuclear
Co - Co	2.492(4) [44] 2.44 [81]	2.60 [61]	2.52	Tetranuclear Pentanuclear
Co - Ru	2.679(3) [45]	2.957(3) [45]	2.818	Tetranuclear
Ru - Ru	2.778(2) [63]	2.798(2) [63]	2.788	Pentanuclear

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