

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.

Keywords: Structure; heterometallic; gold/iron; clusters; isomers;

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ABBREVIATIONS

<i>1,5-cod</i>	<i>1,5-cyclooctadiene</i>
<i>C₁₁H₁₉S</i>	<i>2,2,6,6-tetramethylcyclohexanthiocarbalddehyde</i>
<i>C₁₇H₂₈NP</i>	<i>1,1'-(1-dimethylamino-1,3-propanediyl)-2-diphenylphosphine-dicyclopentadienyl</i>
<i>C₅H₄CH₂NMe₂</i>	<i>N,N-dimethylaminomethylcyclopentadienyl</i>
<i>C₅H₄Me</i>	<i>methylcyclopentadienyl</i>
<i>C₅H₄P(Ph)C₅H₄</i>	<i>dicyclopentadienylphenylphosphine</i>
<i>C₅H₄PPh₂</i>	<i>diphenylphosphinocyclopentadienyl</i>
<i>C₆H₆</i>	<i>benzene</i>
<i>Cp</i>	<i>cyclopentadienyl</i>
<i>ddpca</i>	<i>(S*)-N,N-dimethyl-1-[R*]-1',2-(bis(diphenylphosphino) cyclopentadienyl)ethylamine</i>
<i>dppm</i>	<i>bis(diphenylphosphino)methane</i>
<i>dptpc</i>	<i>diphenylthiophosphoryl-cyclopentadienyl</i>
<i>m</i>	<i>monoclinic</i>
<i>Me</i>	<i>methyl</i>
<i>or</i>	<i>orthorhombic</i>
<i>P(OEt)₃</i>	<i>tris(ethyloxy)phosphine</i>
<i>PhC₂Ph</i>	<i>1,2-diphenylethenyl</i>
<i>PPh₂(tol)</i>	<i>tolyldiphenylphosphine</i>
<i>PPh₃</i>	<i>triphenylphosphine</i>
<i>PrⁱS</i>	<i>iso-propylthiolate</i>
<i>SiPh₂(Me)</i>	<i>methyldiphenylsilicium</i>
<i>tr</i>	<i>triclinic</i>

1. INTRODUCTION

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

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

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

2. STRUCTURAL CLASSIFICATION

2.1 Heterobinuclear Compounds

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

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

In another two yellow AuFe derivatives [8] bis(diphenylphosphino)methane (dppm) serve as a bridge between AuL (L= Me or Cl) and Fe(CO)₂(η⁴-C₅H₄Me) moieties in the manner LAu-P(Ph₂)CH₂CH₂(Ph₂)P-Fe(CO)₂(η⁴-C₅H₄Me). 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 $2.301(3)\text{Å}$ and $176.43(12)^\circ$ (molecule 1) and $2.284(3)\text{Å}$ 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 (AgClP) and iron atom is sandwiched (FeC_{10}).

The data in Table 1 indicates gold in two- AuPFe [5-7], AuCP [8,12,14], AuClP [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: 2.085Å (Me) < 2.268Å (PPh_3) < 2.305Å (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 2.210Å , 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: 2.059Å ($\text{L}=\text{O}^1\text{C}^{10}$) < 2.074Å ($\text{L}=\text{C}^1\text{C}^5$) < 2.240Å ($\text{L}=\text{P}^1\text{C}^{10}$) < 2.383Å ($\text{L}=\text{P}^1\text{C}^5$). 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 $2.605(2)\text{Å}$ and Au-Fe bond distances of $2.622(1)$ and $2.698(1)\text{Å}$. 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 ($2.621(2)\text{Å}$) 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 attached to each iron atom. The mean Au-Fe bond distance of $2.670(1)\text{Å}$ is about 0.010Å 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 $2.651(4)\text{Å}$ and Au-Fe bond distances of $2.683(4)$ and $2.700(3)\text{Å}$ in one molecule. The values in the other one are $2.644(4)$, $2.681(3)$ and $2.740(4)\text{Å}$, 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 AuFe_2 system with the Fe-Fe bond distance of $2.627(2)\text{Å}$ and Au-Fe bond distances of $2.627(2)$ and $2.761(2)\text{Å}$, respectively. The edge of Fe-Fe bond is bridged

by a carbonyl group and an σ,π -diphenylethenyl group.

In the remaining two orange AuFe_2 clusters [21,22], two (cp)Fe fragments are connected with $\text{Au}(\text{C}\equiv\text{CPh})$ [21] or AuCl [22] unit with $\text{C}_5\text{H}_4\text{P}(\text{Ph})\text{C}_5\text{H}_4$ ligand. Each gold atom is two-coordinated, AuCP [21] and AuClP [22] with P-Au-X bond angles of $174.3(4)^\circ$ ($\text{X}=\text{C}$) and $176.1(1)^\circ$ ($\text{X}=\text{Cl}$), respectively. Each iron atom is sandwiched, FeC_{10} .

There are eleven coloured Au_2Fe 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 is the only example in the series of heterotrinary clusters with such a number of independent molecules. The mean Au-Fe bond distance of $2.538(3)\text{\AA}$ (range from $2.509(3)$ to $2.553(2)\text{\AA}$) is about 0.363\AA shorter than Au-Au bond distances with the mean value of 2.901\AA ($2.872(2)$ - $2.928(1)\text{\AA}$).

In red Au_2Fe cluster [25] the $\text{Ph}_3\text{PAuAuPPh}_3$ fragment with Au-Au bond distance of $2.768(2)\text{\AA}$ is attached to $(\mu_3\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-cp})$ fragment via $\mu_3\text{-C}$ atom and, in addition, the iron atom is connected with one Au atom ($\text{Fe-Au } 2.818(2)\text{\AA}$). In two yellow Au_2Fe clusters [26] the $\text{Fe}(\text{C}_5\text{H}_4\text{PPh}_2)_2$ fragment coordinates to two AuX ($\text{X}=\text{Cl}$ 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 $177.0(2)^\circ$, respectively. The cyclopentadienyl rings adopts in staggered conformation. In orange Au_2Fe cluster [27] the $\text{Fe}(\text{C}_5\text{H}_4\text{PPh}_2)_2$ fragment is attached via P atoms to AuSAu fragment. The Au-Au bond distance is $2.882(1)\text{\AA}$ and Au-S-Au bridge angle is $77.57(9)^\circ$. The P-Au-S bond angles are $173.78(6)^\circ$. The iron atom is sandwiched (FeC_{10}).

In structure of yellow Au_2Fe cluster [28] the $\text{C}(\text{PPh}_2)_2$ ligand serves as a bridge between the $\text{Cl}(\text{PhNC})_3\text{Fe}$ unit and two $\text{Au}(\text{PPh}_3)$ fragments. Two phosphorous atoms of the bridging ligand are directly coordinated to the iron atom and complete pseudo-octahedral coordination about the iron atom ($\text{FeC}_3\text{P}_2\text{Cl}$). The C atom of the $\text{C}(\text{PPh}_2)_2$ ligand is bridging two $\text{Au}(\text{PPh}_3)$ fragments. The Au-Au distance is $2.891(4)\text{\AA}$ and Au-C-Au bridge angle is $74.1(15)^\circ$.

In the remaining four Au_2Fe clusters [29-32], the 1,1-bis(diphenylphosphino)ferrocene is singly bridging in [29] the $\text{Au}_2\{\mu\text{-}\eta^2\text{-S}(\text{CH}_2)_2\text{S}\}$ fragment,

in [30] two $\text{Au}(\eta^1\text{-F}_3\text{CCOO})$ fragments, in [31] two $\text{Au}(\eta^1\text{-C}_{16}\text{H}_9)$ fragments, and in [32] two AuCl fragments. Each gold atom is almost linearly coordinated and each iron is sandwiched (FeC_{10}) (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 heterotrinary (AuFe_2 , Au_2Fe) clusters crystallized in two crystal classes, monoclinic (x10) and triclinic (x6). The gold atoms are two- AuXP ($\text{X}=\text{C}$ [21-31], Cl [22, 26, 32], I [26], S [29] or O [30]), three- AuPFe_2 [17-20], AuPFeAu [23-24], AuSPAu [27], AuCPAu [28], and four- AuCPFeAu [25] coordinated.

For the iron atom the coordinations involved are six- FeC_4AuFe [17, 18], FeC_4Au_2 [23], FeC_3PAu_2 [24], $\text{FeC}_3\text{P}_2\text{Cl}$ [28], seven- FeC_4SAuFe [19], FeC_5AuFe [20], ten (sandwich) - FeC_{10} [21, 22, 26, 27, 29 - 32] and eleven- FeC_{10}Au [25] donor atoms of which the sandwiched is most common.

The Au-Fe bond distance range from $2.509(3)\text{\AA}$ [24] to $2.818(2)\text{\AA}$ [25] (mean 2.634\AA), Au-Au bond distance from $2.768(4)\text{\AA}$ [25] to $2.928(1)\text{\AA}$ [23] (mean 2.880\AA) and Fe-Fe bond distance from $2.615(2)\text{\AA}$ [17] to $2.651(4)\text{\AA}$ [19] (mean 2.630\AA). The mean Au-L (monodentate) bond distance elongates in the order: 2.036\AA (Cl) < 2.098\AA (OL) < 2.272\AA (PPh_3) < 2.285\AA (Cl) < 2.353\AA (I). There are two clusters, $(\text{Ph}_3\text{P})\text{AuFe}_2(\mu\text{-C}_{11}\text{H}_{19}\text{S})(\text{CO})_6$ [19] and $(\text{ClAu})_2(\mu\text{-}\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2\text{Fe}$ [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 $2.652(3)\text{\AA}$ and the Fe-Au-Fe bond angle is $64.3(1)^\circ$. 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 Fe₃Te tetrahedron with Au-Fe(1)-Fe(3) bond angle of 98.7(1)^o and Au-Fe(2)-Fe(3) bond angle of 99.4(1)^o.

The metal core in [(Ph₃P)AuFe₃(μ-CO)(CO)₁₀]⁻ anion [34] consists of a Fe₃Au „butterfly“ arrangement, where a triphenylphosphinylgold(I) cation forms a bridge at one edge of the Fe₃ triangle. The interplanar angle here is 59.7(1)^o. The average Fe-Fe distance is 2.655Å [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 AuFe₃ cluster [35] are approximate non-superimposable mirror of each other (Fig. 1). The triphenylphosphinylgold(I) cation bridging the Fe(1)-Fe(2) edge of the Fe₃ triangle. Furthermore, it is situated opposite side to the triangle to that occupied by the μ₃-HC=CBut ligand. The AuFe(2)Fe(3) dihedral angle in the two independent molecules differs significantly having the values 110.9 and 132.1^o.

In another AuFe₃ cluster [36] the metal core consists of an isosceles triangle of iron atoms, capped by a μ₃-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)^o. 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 Au₂Fe₂ clusters [37-39]. In the red Au₂Fe₂ 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)^o. 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 μ-η²-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 (FeC₄AuFe⁺). Each gold atom is three coordinated (AuPFeAu)(T shape).

In the colourless Au₂Fe₂ cluster [38], which has an approximate C₂ 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 μ-η²-dppm ligand, thus forming unusual twisted six-membered rings fused along the Au-Au edge. The average Au-Fe bond distance is 2.549Å. It is interesting to note that the complex forms also a 10-membered ring, where the Au-Au bond distance is 2.962(1)Å is reminiscent of the transannular interactions that occur in middle-sized organic rings.

In a yellow-orange Au₂Fe₂ cluster [39] two C₅H₄CH₂NMe₂ ligands act as bridges between two gold atoms and two Fe(η⁵-cp) moieties, thus forming a 10-membered ring (AuNC)₂ with Au...Au separation of 3.122(1)Å.

There are two Au₃Fe clusters [40,41] and the structure of orange Au₃Fe cluster [40] is shown in Fig. 2. The three gold atoms form a plane and an apical sulfur atom is situated 1.29Å out of this plane. The shortest Au-Au distance of 2.8889(8)Å is found between the atoms Au(1) and Au(2), and the remaining two distances are 3.404(1) and 3.759(1)Å between Au(1)-Au(2) and Au(2)-Au(3), respectively. Consequently, also the respective angles are dissimilar with the values of Au(1)-S-Au(2) = 76.36(10), Au(1)-S-Au(3) = 92.64(12) and Au(2)-S-Au(3) = 105.69(14)^o. 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)^o. The Au(III) cation has square-planar geometry (AuC₃S).

In colourless Au₃Fe cluster [41] the complex cation consists of two gold atoms bridged by two different ligands, namely C₅H₄PPh₂ 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)Å is significantly longer than that for the Au(1)-Au(3), 3.0965(12)Å. The cyclopentadienyl rings adopts coordination approximately midway the staggered and eclipsed ones.

Table 1. Crystallographic and structural data of heterobinuclear AuFe compoundsa

COMPLEX (colour)	Cr. cl. Sp.Gr Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo- phore	M - L [Å]	Au - Fe [Å]	L - M - L [°]	Ref
(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)		C,P 177.3(4) C,P 96.0(5,1.0) C,P 175.1(3) C,P 95.9(3,6)	8

					P 2.204(3)		
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 P $\bar{1}$ 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^1 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^1 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^1 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^1 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]1.5C ₆ H ₆ (yellow)	m P2 ₁ /c 4	9.285(3) 18.287(8) 19.427(6)	99.55(4)	AuClP 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

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

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: AuFe₂ (NEt ₄)(Ph ₃ P)Au. {Fe(μ -CO)(CO) ₃ } ₂] (orange)	m	10.079(2)		AuPFe ₂	Ph ₃ P ^b 2.264(2)	Fe 2.660(1,38)	P,Fe ^b 150.1(1,7.3)	17
	P2 ₁ /c 4	19.622(4) 18.743(4)	102.82(2)	FeC ₄ Au.Fe	OC 1.790(12,26) μ OC 2.001(11,22)	Fe 2.605(2) C 81.34(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)	
(Ph ₃ P)AuFe ₂ (μ -CO). (μ -SP ^r)(CO) ₆ (dark green)	m	11.373(1)		AuPFe ₂	Ph ₃ P 2.287(2)	Fe 2.670(1,26)	P,Fe 150.60(6,7.3)	18
	P2 ₁ /c 4	14.899(3) 17.997(3)	95.12(2)	FeC ₄ Au. Fe	OC 1.792(10,38) μ OC 1.937(9) 2.016(9) μ S 2.267(2,4)	Fe 2.621(2) C 83.0(3) S 70.66(8)	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)	
(Ph ₃ P)AuFe ₂ . (μ -C ₁₁ H ₁₉ S)(CO) ₆ ^c (red orange)	tr	14.640(3)	66.82(2)	AuPFe ₂	Ph ₃ P 2.284(6)	Fe 2.692(4,9)	P,Fe 150.3(2,7.7)	19
	P $\bar{1}$	15.156(4)	71.39(2)	FeC ₄ S.	OC not given	Fe 2.651(4)	Fe,Fe 59.0(1)	
	4	18.502(5)	71.79(2)	AuFe	μ C 2.014(25,5) μ S 2.209(7,4)	82.3(8) 73.7(2)	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)	
				AuPFe ₂	Ph ₃ P 2.294(7)	Fe 2.711(4,30)	P,Fe 150.7(1,2.6) Fe,Fe 58.4(1)	
			FeC ₄ S.	OC not given	Fe 2.644(4)	C,S 48.3(7)		

				AuFe	μ C 2.033(15,7) μ S 2.196(8,3)	C 81.0(7) S 74.0(2)	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)	
(Ph ₃ P)AuFe ₂ (μ -CO). (CO) ₆ (μ - η^2 -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)	AuClP 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}. Fe(CO) ₄ ^d (yellow)	m P2 ₁ /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)	23

							Au,Au 69.2(1)	
[[(Ph ₃ P)Au] ₂ Fe. (CO) ₃ {P(OEt) ₃ }. H ₂ O (yellow)]	m	10.385(3)		AuPFeAu	Ph ₃ P not given	Fe 2.535(3,26) Au 2.872(2)	P,Au not given	24
	P2 ₁ /n	35.422(10)	91.15(3)					
	4	13.648(6)		FeC ₃ PAu ₂	OC not given P 2.133(6)		C,C 145.9(8) C,P 99.7(7) Au,Au 69.0(1)	
[[(Ph ₃ P)Au] ₂ . (μ ₃ -η ¹ :η ¹ -η ⁵ -C ₅ H ₄). Fe(η ⁵ -cp)]BF ₄ (red)]	m	14.460(11)		AuCP.	μ ₃ C 2.25(4)	Fe 2.818(2)	C,P 174(1)	25
	P2 ₁ /a	30.539(27)	92.61(15)	FeAu	Ph ₃ P 2.283(12)	Au 2.768(2) C 78(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)	
	4	9.509(12)						
				AuCPAu	μ ₃ C 2.12(4) Ph ₃ P 2.275(15)			
				FeC ₁₀ Au	cpC 2.08(5,8) η ⁵ C 1.91(5) 2.10(5,3)		not given	
[(ClAu) ₂ (μ-η ¹ :η ⁵ - C ₅ H ₄ PPh ₂) ₂ Fe]CH ₂ Cl ₂ (yellow) (at 173 K)]	tr	8.671(2)	81.82(2)	AuPI	Cl 2.2815(13)	Fe 4.29(1)	Cl,P 179.59(5)	26
	Pī	9.867(2)	74.45(3)		η ¹ P 2.262(13)			
	1	12.359(3)	70.56(2)	FeC ₁₀	η ⁵ C 2.049(5,14)		not given	
[(IAu) ₂ (μ-η ¹ :η ⁵ - C ₅ H ₄ PPh ₂) ₂ Fe]CH ₂ Cl ₂ (yellow) (at 173 K)]	tr	11.955(3)	85.85(2)	AuPI	η ¹ P 2.244(9,4)		P,I 177.0(2,7)	26
	Pī	13.472(3)	70.16(2)		I 2.553(3,8)			
	2	14.596(2)	66.04(2)	FeC ₁₀	η ⁵ C not given		not given	
[(μ-S)Au ₂ (μ-η ¹ :η ⁵ - C ₅ H ₄ PPh ₂) ₂ Fe].2CHCl ₃ (orange) (at 143 K)]	m	12.571(4)		AuSPAu	μS 2.300(2)	Au 2.882(1)	S,P 173.78(6)	27
	P2 ₁ /n	10.579(4)	107.84(3)		η ¹ P 2.247(2)	S 77.57(9)	S,Au 51.21(4) P,Au 122.66(5)	
	2	15.212(4)		FeC ₁₀	η ⁵ C 2.039(7,17)		not given	
[[(Ph ₃ P)Au] ₂ (μ-η ¹ :η ² - C(PPh ₂)Fe(CNPh ₃ Cl)] (yellow)]	tr	19.325(4)	105.05(3)	AuCPAu	μC 2.16(5,7)	Au 2.89(4)	C,P 174.7(14,2.8)	28
	Pī	17.430(4)	104.62(3)		Ph ₃ P 2.25(2,2)	C 84.1(15)		
	2	11.906(3)	82.95(3)	FeC ₃ P ₂ Cl	PhNC 1.87(7,3) η ² P 2.25(2,2) Cl 2.38(2)		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)	
$(\eta^2\text{-S}(\text{CH}_2)_2\text{S})\text{Au}_2$ $(\mu\text{-}\eta^1:\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2\text{Fe}$ (yellow)	m P2 ₁ /n 4	10.263(2) 21.064(4) 16.259(3)		AuSP 97.06(2) FeC ₁₀	$\eta^2\text{S}$ 2.292(4,3) $\eta^1\text{P}$ 2.267(3,1) $\eta^5\text{cp}$ 1.633 1.645	Au 3.06	S,P 165.1(1,4) not given	29
$\{(\eta^1\text{-F}_3\text{CCOO})\text{Au}\}_2$ $(\mu\text{-}\eta^1:\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2\text{Fe}$ (yellow)	m C2 ₁ /c 4	15.325(1) 19.058(4) 15.373(3)		AuOP 95.98(3) FeC ₁₀	$\eta^1\text{O}$ 2.078(3) $\eta^1\text{P}$ 2.219(2) $\eta^5\text{C}$ 2.051(3)	Au 3.254(1)	O,P 177.1(1) not given	30
$\{(\text{C}_{16}\text{H}_9)\text{Au}\}_2(\mu\text{-}\eta^1:\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2\text{Fe}$ (orange)	tr P $\bar{1}$ 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) $\eta^1\text{P}$ 2.295(2) $\eta^5\text{C}$ 2.033(8)- 2.058(8)	Au 8.315	C,P 172.1(3) not given	31
$(\text{ClAu})_2(\mu\text{-}\eta^1:\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2\text{Fe}^c$ (yellow)	tr P $\bar{1}$ 3	16.192(4) 16.921(4) 10.878(5)	93.39(3) 94.28(2) 115.29(2)	AuCIP FeC ₁₀ AuCIP FeC ₁₀	Cl 2.287(4,14) $\eta^1\text{P}$ 2.331(3,9) $\eta^5\text{C}$ not given Cl 2.282(3) $\eta^1\text{P}$ 2.229(3) $\eta^5\text{C}$ not given		Cl,P 175.8(1,3) not given Cl,P 173.4(1) not given	32

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) clustersa

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)	Ph ₃ P ^b 2.290(4) OC 1.747(20,59) μ_3 Te 2.502(3,3)	Fe 2.667(3,15) Fe 2.620(3) 2.836(3) Te 69.1(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 ^t)(CO) ₆ ^c (deep red)	tr P1 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	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)	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)	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)	35

				FeC ₄ Fe ₂	OC 1.73 μC 1.91(2)	C 79.7(1) Fe 2.560(3) 2.607(3)	Fe, Fe 62.2(1)	
				AuPFe ₂	Ph ₃ P 2.290(5)	Fe 2.659(2) 2.717(3)	P, Fe 150.8(1,3,1) Fe, Fe 58.6(1)	
				FeC ₃ N. AuFe ₂	OC 1.74 μN 1.97(1)	Au 2.659(2) Fe 2.635(3,8) N 81.9(4)	Au, Fe 61.8(1) 104.9(1) Fe, Fe 58.5(1)	
				TeC ₄ N. AuFe ₂	OC 1.74 μC 2.09(2) μN 2.04(1)	Au 2.717(3) Fe 2.574(3) 2.627(2)	Au, Fe 59.6(1) 105.1(1) Fe, Fe 61.1(1)	
				FeC ₄ Fe ₂	OC 1.74 μC 1.94(2)	C 79.4(6) Fe 2.574(3) 2.643(3)	Fe, Fe 60.5(1)	
(Ph ₃ P)AuFe ₃ . (μ ₃ -SPr ¹)(CO) ₉ (dark red)	m P2 ₁ /c 4	18.745(3) 10.638(2) 18.345(3)	111.57(3)	AuPFe ₂	Ph ₃ P 2.251(8)	Fe 2.649(3,4)	P, Fe 147.7(2,4,6) Fe, Fe 63.8(1)	36
				FeC ₃ S. AuFe ₂ (x2)	OC 1.76(4,7) 2.04(4) μ ₃ S 2.121(10,22)	Au 2.649(3,4) Fe 2.638(8,7) 2.800(6) S 76.6(4,0) 82.7(3)	S, Au 106.6(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 P2 ₁ /n 4	16.405(5) 17.031(8) 12.400(4)	95.64(2)	AuPFeAu (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)	37
				FeC ₄ AuFe (x2)	OC 1.77(1,1)	Au 2.531(2,4) Fe 2.900(1)	C, C 97.9(5,7,3) 150.6(5,9) Au, Fe 87.80(6,14)	
[Au(μ-η ² -dppm)Fe. (CO) ₃ {Si(OMe) ₃ } ₂ . CH ₂ Cl ₂ (colourless)	m P2 ₁ /a 4	21.930(9) 17.826(7) 11.297(5)	90.57(2)	AuPFeAu (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)	38
				FeC ₃ Si. Au (x2)	OC not given P 2.235(6,9) Si 2.275(8,7)	Au 2.962(1)	C, C 106(1,2) 147(1,4) P, Si 172.9(3,1,5)	
[Au(μ-η ² :η ⁵ - C ₅ H ₄ CH ₂ NMe ₂).	m P2/c	11.992(3) 12.804(3)	97.89	AuNC (x2)	η ² N 2.148(5) η ² C 2.021(6)	Au 3.122(1)	N, C 175.9(2)	39

Fe(η^5 -cp) ₂ (yellow orange)	4	16.428(4)		FeC ₁₀ (x2)	η^5 C not given		not given	
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 P2 ₁ /n 4	17.876(2) 18.559(2) 17.896(2)	104.07(1)	Au ^I PS (x2) Au ^{III} C ₃ S	η^1 P 2.245(4,1) μ_3 S 2.337(4,5) C 2.05(2,3) μ_3 S 2.374(4)	Au 2.8889(8) S 76.36(10) S 99.2(1,6.6)	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
[(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 P2 ₁ /n 4	13.831(3) 14.181(3) 31.059(7)	102.17(2)	FeC ₁₀ Au ^I SP (x2) Au ^I NP FeC ₁₀	η^5 C not given 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
D: Au₂FePt [(CO) ₃ Fe(μ -Pcy ₂). {Au(PPh ₃) ₂ Pt. (1,5- η^4 -cod)]PF ₆ (not given)	m P2 ₁ /n 4	22.479(6) 26.781(8) 10.254(3)	102.94(2)	AuPPtFe (x2) FeC ₃ PtAu ₂ PtC ₄ PAu ₂	Ph ₃ P 2.291(5,7) OC 1.76(2,6) μ P 2.197(6) η^4 C 2.20(2,2) 2.37(2,2) μ P 2.229(5)	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
E: AuM₂M' (CO) ₆ Fe ₂ AuCo. (μ_3 -COMe)(PPh ₃). (η^5 -cp) (black)	m P2 ₁ /n 4	13.669(3) 14.315(5) 16.665(4)	103.12(2)	AuPFe ₂ FeC ₄ Co. AuFe (x2) CoC ₇ Fe ₂	Ph ₃ P 2.293(2) OC 1.789(2,0) μ_3 C 1.906(5,19) OC 1.774(6) cpC 2.083(3) μ_3 C1.932(5)	Fe 2.690(1,9) Co 2.490(1,4) Au 2.690(1,9) Fe 2.643(1)	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

(CO) ₃ Fe(μ ₃ -CPh). Co ₂ (CO) ₆ Au(PPh ₃) (black)	or Pna2 ₁ 4	34.617(6) 8.793(2) 11.226(2)		AuPFFeCo 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 C1.953(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 P2 ₁ /c 4	12.962(4) 15.082(3) 17.264(4)	105.07(2)	AuPFFeRu 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

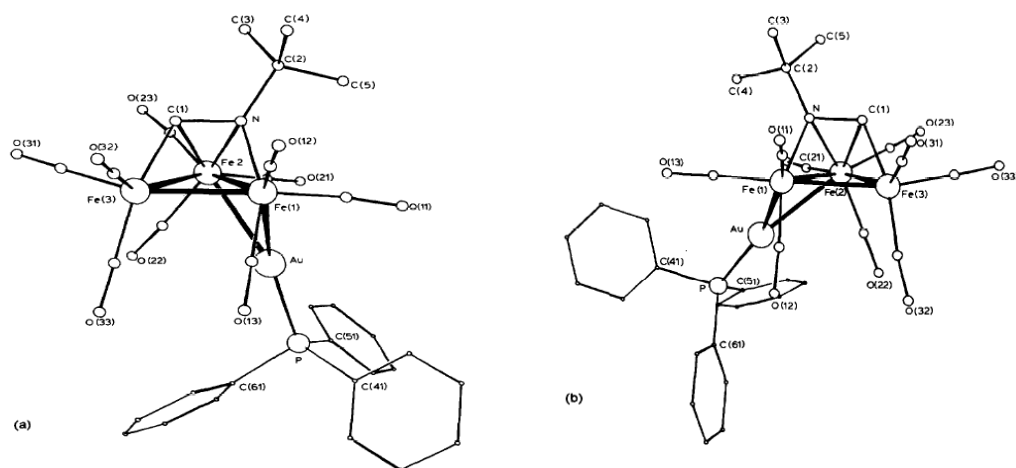


Fig. 1. Structure of two independent molecules of $[(\text{Ph}_3\text{P})\text{AuFe}_3(\mu_4\text{-HC=NBU}^h)(\text{CO})_6]$ [35]

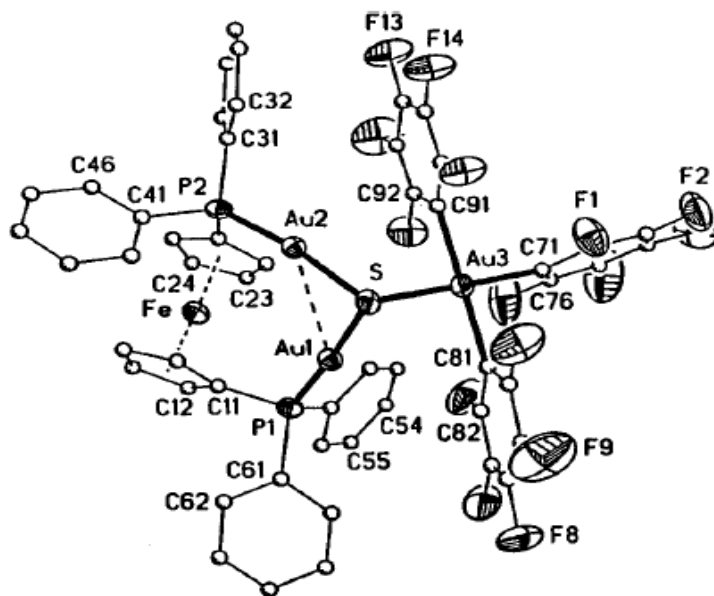


Fig. 2. Structure of $[(\text{F}_5\text{C}_6)_3\text{Au}(\mu_3\text{-S})\text{Au}_2\{(\mu\text{-dppcp})_2\text{Fe}\}]$ [40]

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)Å) 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.

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 $\mu_3\text{-COME}$ 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 $(\text{OC})_3\text{Fe}(\mu_3\text{-CPh})\text{Co}_2(\text{CO})_6\text{Au}(\text{PPh}_3)$ [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: $2.677(2)\text{Å}$ (Au-Fe) < $2.678(4)\text{Å}$ (Fe-Co) < $2.679(3)\text{Å}$ (Co-Ru) < $2.729(2)\text{Å}$ (Au-Ru) < $2.914(3)\text{Å}$ (Fe-Ru) < $2.957(3)\text{Å}$ (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 ($2.527(2)\text{Å}$ [37] – $2.717(3)\text{Å}$ [35]) < Co , $2.661(3)\text{Å}$ [44] < Ru , $2.729(2)\text{Å}$ [45] < Pt , 2.848Å ($2.821(1)$ – $2.875(1)\text{Å}$ [42]) < Au , 2.922Å ($2.8889(8)\text{Å}$ [40] – $2.962(1)\text{Å}$ [38]). The mean Fe-M bond distance elongated in the order: $M=Co$, 2.570Å ($2.486(1)\text{Å}$ [43] – $2.678(4)\text{Å}$ [45]) < Au , 2.633Å < Fe , 2.676Å ($2.574(2)\text{Å}$ [35] – $2.900(2)\text{Å}$ [37]) < Pt , $2.715(3)\text{Å}$ [42] < Ru , $2.914(3)\text{Å}$ [45]. The Co-M bond distance elongated in the order: $M=Co$, $2.492(4)\text{Å}$ [44] < Ru , $2.679(3)\text{Å}$ [45].

2.4 Heteropentanuclear Clusters

There are twenty one heteropentanuclear 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], Au_2Fe_2Ir [58], $AuFe_2M_2$ ($M=Ir$ [59], Rh [60]) and AuM_3Fe ($M=Co$ [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 2.655Å (range $2.604(2)$ – $2.680(2)\text{Å}$). The Au(I) atom has $AuPBF_e$ chromophore with the Au-Fe bond distance of $2.580(1)\text{Å}$.

Dark green $AuFe_4$ cluster [47] contains well-separated $(NMe_3CH_2Ph)^+$ cations, $[(OC)_{16}Fe_4Au]^-$ anion and chloride anion. The gold(III) atom sits on a center of symmetry. Two $[Fe_2(CO)_8]^{2-}$ anions linked to a central gold(III) atom adopts a square-planar coordination with the mean Au-Fe bond distance of 2.595Å . The Fe-Fe bond distance is $2.711(2)\text{Å}$. Black $(OC)_{12}Fe(\mu_4-COMe)Au(PEt_3)$ [48a] has a butterfly core. The Fe-Fe bond distances in the butterfly core range from $2.606(3)$ to $2.687(4)\text{Å}$ and average 2.638Å . Interestingly, the presence of Et_3PAu bridge across the hinge causes by a 0.05Å between in the Fe(2)-Fe(3) bond distance ($2.687(4)\text{Å}$) when compared to the average Fe-Fe bond distance. The Au-Fe(2) and Au-Fe(3) bond distances are $2.666(2)$ and $2.675(2)\text{Å}$.

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 $107.3(1)\text{Å}$. 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 2.617Å , 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 $\{(Ph_3P)Au\}_2. Fe_3(\mu_3O)(CO)_9$ [50] contains a Au_2Fe_3 trigonal bipyramidal moiety with Au(1) and Fe(5) atom in the axial positions and Au(2), Fe(3) and 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 Au(1), Au(2) and Fe(5). The $(\mu_3-O)(1)$ atom is bonded with three iron atoms with the average Fe-O bond distance of 1.876Å and Fe-O-Fe bond angles of 88° . The Fe(3)-Fe(4) bond distance between two equatorial iron atoms ($2.700(2)\text{Å}$) is substantially longer than the corresponding values for Fe(3)-Fe(5) ($2.537(2)\text{Å}$) and Fe(4)-Fe(5) ($2.578(2)\text{Å}$) bonds between axial and equatorial iron atoms. The same tendency was

found for Fe-Au bond lengths 2.782(2)Å (Au(2) – Fe(3) and 2.749(2)Å (Au(2) – Fe(4)) for two atoms in equatorial positions and 2.699(2)Å (Au(1) – Fe(3)), 2.714(2)Å (Au(1) – Fe(4)) for atoms in equatorial and axial positions. The Au-Au distance is 2.9915(9)Å.

Structure of deep red Au₂Fe₃ cluster [51] consists of {HFe₃(CO)₉(μ₃-P)}²⁻ cluster frame coordinated to Au···Au bonded {Au₂(PPh₃)₂}²⁺ unit (Fig. 4). Distinct coordination can be seen for each {(Ph₃P)Au}⁺ fragment. The Fe-Fe bond distances in the Fe₃ triangular range from 2.645(3) to 2.693(3)Å and Fe-Fe-Fe bond angles from 59.26(7) to 61.06(7)°. The Fe(2)-Au(2) bond length is 2.678(2)Å and Au(1)-Au(2) is 2.991(1)Å.

Structure of black {(Ph₃P)Au}₂Fe₃(μ₃-S)(CO)₉ [52] is similar to that of black {(Ph₃P)Au}₂Fe₃(μ₃-O)(CO)₉ [50]. Both contain a Fe₃Au₂ trigonal bipyramidal moiety. The M-M bond distances differ from each other, while the mean Fe_{eq}-Au_{eq} bond distance in [52] of 2.734Å is about 0.031Å shorter than that in [50], all remaining mean M-M bond distances are somewhat longer in [52] than those in [50]. The Fe_{eq}-Fe_{eq} bond distances are 2.864(4)Å [52] vs 2.700(2)Å [50], av. Fe_{eq}-Fe_{ax} 2.696Å [52] vs 2.557Å [50], av. Fe_{eq}-Au_{ax} 2.706Å [52] vs 2.700Å [50], and Au-Au 3.020(1)Å [52] vs 2.9915(9)Å [50].

Two yellow Au₂Fe₃ [11, 53] contain [Fe₃(μ-η⁵:η¹-C₅-H₄PPh₂)₆Au₂]²⁺ cations and ClO₄⁻ [11] or Cl⁻ [53] anions. The geometry around the gold atom is in a distorted trigonal pyramidal coordination environment. The gold atom lays 0.073Å [11] and ~0.3Å [53] out of the plane of the three phosphorus atoms. The mean Ag-P bond

distances are 2.365Å [11] and 2.380Å [53]. The Fe···Au separations over 4.0Å ruled out direct metal-metal bond.

Structure of two orange Au₃Fe₂ clusters [54,55] differs from each other. The structure of [(OC)₄Fe]₂Au₃(μ-η²-dppm)]⁻ anion [54] consists of an isosceles Au₃ triangle with two shorter edges, Au(1)-Au(3) and Au(2)-Au(3), 2.921(2)Å, spanned by Fe(CO)₄ groups, and a longer one (Au(2)···Au(3), 3.578(2)Å, bridged by a μ-η²-dppm ligand. The mean Au-Fe bond length is 2.562Å. In the structure of the other orange Au₃Fe₂ cluster [55], two satellite {ClAu(μ-η¹:η⁵-ddpea)Fe((μ-η¹:η⁵-C₅H₄PPh₂))} moieties are held together by the central AuCl group. The central gold atom has a trigonal-planar (AuP₂Cl) structure and the satellite gold atoms are linearly (AuClP) coordinated. Both iron atoms are sandwiched (FeC₁₀).

The Au₄Fe core is found in two orange clusters [27,56]. The structure which is isostructural contains a trigonal bipyramidal Au₄S 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)Å. 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)°, these values differ from the ideal 120°, which may be a 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)°.

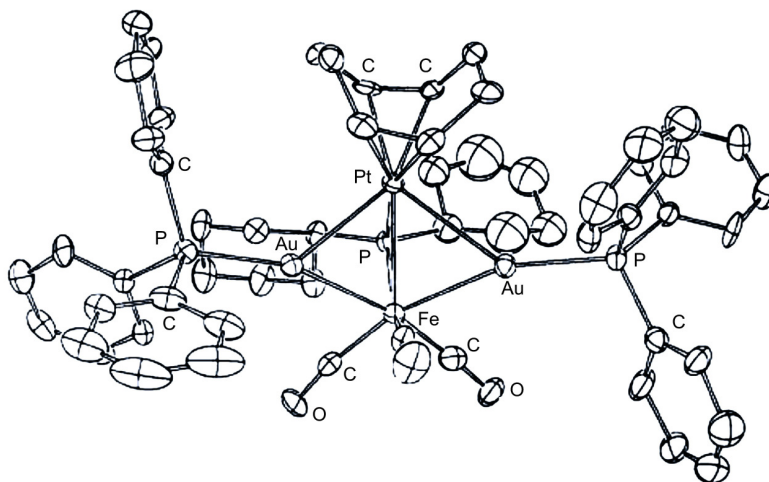


Fig. 3. Structure of [(OC)₃Fe(μ-Pcy₂){Au(PPh₃)₂Pt(1,5-cod)}]⁺ [42]

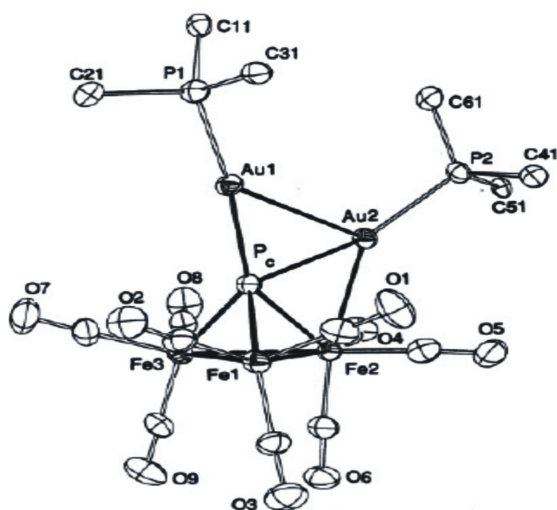
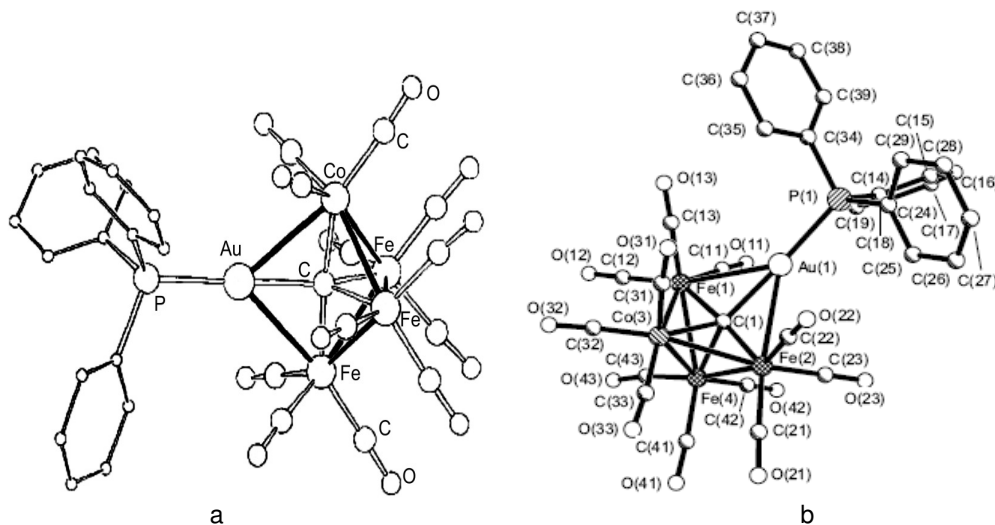


Fig. 4. Structure of $[(\text{Ph}_3\text{P})\text{Au}]_2(\mu_3\text{-P})\text{Fe}_3(\mu\text{-H})(\text{CO})_9$ [51]

Structure of 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 Fe(2)-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



**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]**

wingtip iron atoms. Such differences reflect the metal-metal bonds (Table 4).

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 Ir(1) Fe(1) Fe(2) and Ir(1) Au(1) Au(2) triangles. The dihedral angle between the planes is 86.0° . The metal-metal bonds are Fe-Fe, 2.501(5)Å, Fe-Ir, 2.709(3) and 2.744(4)Å and Ir-Au, 2.726(1)Å. 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)Å.

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)Å, $\text{Fe}_{\text{ap}}\text{-Rh}$, 2.634(1) and 2.640(1)Å; $\text{Fe}_{\text{eq}}\text{-Rh}$, 2.732(1), 2.750(1) and 2.760(1)Å, $\text{Fe}_{\text{eq}}\text{-Au}$, 2.793(1)Å and Au-Rh , 2.781(1) and 2.782(1)Å.

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, 2.715Å, Co-Fe, 2.59Å and Co-Co, 2.52Å.

Structure of a red AuRu_3Fe cluster [63] contains four $\text{M}(\text{CO})_3$ (M=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 Ru(3)-Ru(4) bond. The mean of Au-Ru bonds is of the value 2.760Å. The gold bridged hinge Ru-Ru bond is lengthened (2.839(2)Å) compared to have non-bridged Ru-Ru bonds (av. 2.788Å). The Fe-Ru(3) and Fe-Ru(4) bonds are 2.717(2) and 2.639(2)Å.

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- AuPCl [55], three- AuP_3 [11, 53], AuPM_2 (M=Fe [48a, 52], Ir [59], Co [62], Ru [63], AuBPFe [46], AuP_2Au [51], AuPF₂Au [54], AuP_2Cl [55], AuSPAu [56], AuPIrAu [58]; four- AuSPAu_2 [27], AuFe_4 [47], AuCPFe₂ [48b, 49, 57b], AuP_2FeAu [51], AuPM_3 (M=Fe [52], Co [61]), AuFe_2Au_2 [54], AuC_3S [56], AuSPCoFe [57a], AuCPIrAu [58], AuPRh₂Au [60], and five- AuPF₃Au [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 Fe_4Au_2 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 dpmm ligand bridged two gold atoms. In another four Fe_4Au_2 clusters [65 - 67] the boron atom, lying approximately at the center of a distorted octahedron formed by six metal atoms.

Structure of orange $(\text{cp})\text{Fe}(\text{C}_5\text{H}_4)(\text{Ph})\text{PAu}\text{C}\equiv\text{CAuP}(\text{Ph})(\text{C}_5\text{H}_4)\text{Fe}(\text{cp})$ [21], is centrosymmetric with respect to the $\text{C}\equiv\text{C}$ bond. The P-Au-C \equiv C unit is basically linear, with an angle at C(1) of 178(1) $^\circ$ and at Au(1) at 175.9(2) $^\circ$. 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 $^\circ$ for C(11) and C(20) and 9.7 $^\circ$ 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 $^\circ$, respectively. The two substituent ferrocenyl units are oriented essentially orthogonal with respect to each other with a dihedral angle of 88 $^\circ$ between the mean planes of C(11)-C(15) and C(21)-C(25).

The molecule of Fe_4Au_2 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 $^\circ$. 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 Fe_3Au_3 cluster [51] is shown in Fig. 6. The structure consists of a $\{\text{Fe}_3(\text{CO})_9(\mu_3\text{-P})\}^{3-}$ unit frame coordinated to a triangular $\{\text{Au}_3(\text{PPh}_3)_3\}^{3+}$ unit. The Au_3 plane makes a dihedral angle of 46 $^\circ$ with respect to the Fe_3 plane. The mean Fe-Au and Fe-Fe bond

distances are 2.716 and 2.652 Å, are much shorter than that of Au-Au distance with the mean value of 3.207 Å.

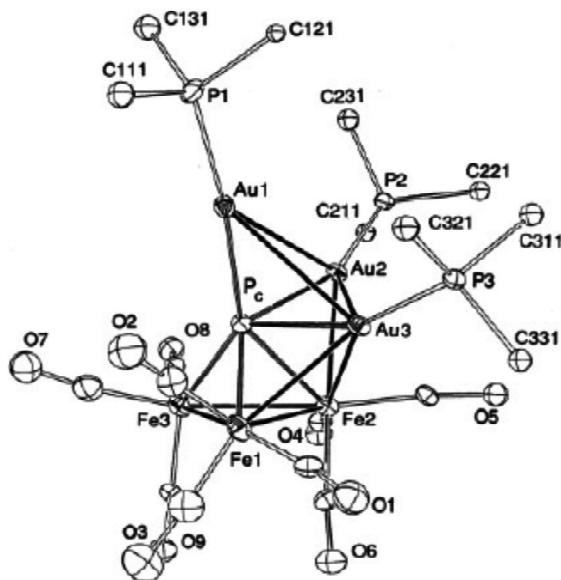


Fig. 6. Structure of [(CO)₉Fe₃(μ₅-P){Au(PPh₃)₃}] [51]

There are two yellow Fe₂Au₄ complexes, which crystallize in the same space group C2/c, as dimeric [(CO)₄FeAu₂(μ-η²-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 Å) Au₂Fe(CO)₄ fragments leading to a fourteen-membered ring in a pseudo-chair conformation. In the Au₂Fe triangle Au(1)-Au(2) distance is 2.977(1) Å and the mean Au-Fe bond distance is 2.530 Å. 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) Å. Tetrahedral angle between Au(1)-Au(2)-Au(1') and Au(1)-Au(2')-Au(1') planes is 158.3(3)°. The Fe(CO)₄ and dpmm ligands span the four edges of the rhombus lying alternately above and below the Au₄ mean plane.

Structure of yellow FeAu₅ cluster [70] contains well separated [(ox)₃FeAu₅(PPh₃)₅]⁺ cations and PF₆⁻ anions. The cationic FeAu₅ cluster form is capped FeAu₃ tetrahedron with Fe-Au bond distances from 2.590(1) to 2.65(1) Å to all five Au

atoms. The Au-Au distances range from 2.7760(4) to 3.0880(4) Å.

In black Fe₆Au cluster [48b] the {Au(PPh₃)⁺} unit caps one of the two triangular faces of the {Fe₆(μ₆-C)(μ-CO)₃(CO)₁₃}²⁻ anion lacking bridging CO ligands. The mean of the three Fe-Au bond distances is 2.750 Å. The Fe-Fe bonds range from 2.562(4) to 2.801(4) Å. In orange red Fe₆Au derivative [71] the ppn⁺ cations and [(CO)₉(μ₃-PMe)Fe₃(μ₃-P)₂Au]⁻ anions are well separated. In the complex anion, two identical [(CO)₉(μ₃-PMe)Fe₃(μ₃-P)] units are held together by Au(1) atom, with the central P-Au-P angle of 177°.

Structure of black Fe₅Au₂ cluster [72] contains two Au(PEt₃) 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 Å below the square base. One Au(PEt₃) 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 Au(PEt₃) group caps the square base of the Fe₅ 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) Å, and Fe-Fe distances from 2.573(3) to 2.941(3) Å.

Structure of Fe₄Au₃ 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) Å above the Fe_{ring}⁻ Fe_{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 $[\{(\text{OC})_4\text{Fe}\}_2\text{Au}_5(\eta^2\text{-dppm})_2]^{2+}$ 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 $\mu\text{-}\eta^2\text{-dppm}$ 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 $[\{\text{Fe}(\mu\text{-dppcp})_2\}_2\cdot\{\text{Au}^{\text{I}}_2(\mu_3\text{-S})\}_2\text{Au}^{\text{III}}(\text{C}_6\text{F}_5)_2]^{+}$ 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 [75] 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 0.168Å shorter than that of Ru-Ru bond distances (2.863(5)Å). The Au-Au bond distance is 2.818(2)Å.

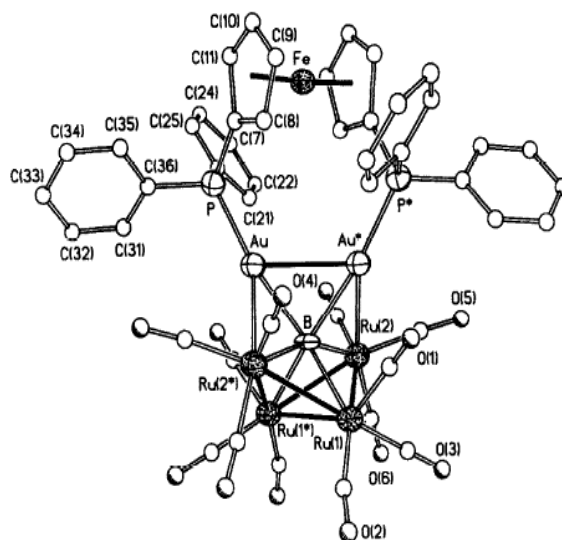


Fig. 7. STRUCTURE of $[\text{Fe}(\mu\text{-}\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{PPh}_2)_2\text{Au}_2(\mu_6\text{-B})\text{Ru}_4(\text{H})(\text{CO})_{12}]$ [76]

The red FeRu₄CuAu 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 [Ru(1)Ru(2)Ru(3)] capped by a copper atom and one of the faces of the CuRu₃ 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)Å (Au-Cu) < 2.795(1)Å (av.) (Au-Ru) < 2.807(2)Å (av.) (Cu-Ru) < 2.885(1)Å (av.) (Ru-Ru). Interestingly, that the metal-metal bond distances elongated while the sum of the covalent radii of the respective metals diminishes: 2.81Å (Au+ Cu) > 2.69Å (Au+Ru) > 2.64Å (Cu+Ru) > 2.52Å (Ru+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: 2.646Å (Fe-Fe) < 2.709Å (Fe-Au) < 2.857Å (Au-Au). In the series of heptanuclear clusters the order is: 2.660Å (Au-Mn) < 2.670Å (Fe-Fe) < 2.700Å (Au-Fe) < 2.773Å (Au-Ru) < 2.857Å (Au-Au). The gold atoms are two- AuCIP [21], AuPS [40], AuPFe [69, 70], AuP₂ [51, 71], three- AuP₂Fe

[51], AuPFeAu [64], AuPMn₂ [74], four- AuC₂S₂ [40], AuPFe₃ [48b], AuPFeAu₂ [54], AuCPFe₂ [64, 68], AuBEFeAu, (E=As [65], P [66, 67]), AuP₂Au₂ [74], AuBPRuAu [76], five- AuHPFeAu₂ [73], AuBPFe₂Au [73], AuHPRu₂Au [77], AuPRu₂Au₂ [77], and six- AuFe₂Au₄ [54], AuCIPFe₄ [72], AuP₂Fe₂Au₂ [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 Fe₈Au cluster [46] consists of $[\text{Au}(\text{PMePh}_2)_2]_2^+$ cation and $[\{(\text{CO})_{12}(\mu\text{-H})\text{Fe}_4(\mu_3\text{-BH})\}_2\text{Au}]^-$ anion. Complex anion contains two $\{\text{HFe}_4(\text{CO})_{12}\text{BH}\}$ 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 Fe₄ skeleton is 116.6(3)^o. The two clusters subunits are twisted with respect to one another with a spiro twist angle of 30.9(3)^o at the gold(I) atom. The Au-Fe bond distance is 2.615(1)Å. The Fe-Fe bond distances range from 2.630(2) to 2.688(2)Å (av. 2.651Å). In complex cation $[\text{Au}(\text{PMePh}_2)_2]^+$, the geometry is unexceptional with linear coordination of the Au(I) center, (P-Au-P = 180.0(1)^o).

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 2.689Å is about 0.083Å longer than the mean Fe-Fe bond distance (2.606Å). Structure of yellow $[\{\text{Fe}(\text{C}_5\text{H}_4\text{PPh}_2)\}_3\{(\mu_3\text{-S})\text{Au}_3\}_2].8\text{CHCl}_3$ [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 $[\text{Au}_2\text{dppt}]^{2+}$ fragment that are bonded to the same sulfur atoms. The shortest Au...Fe separation is 4.284Å.

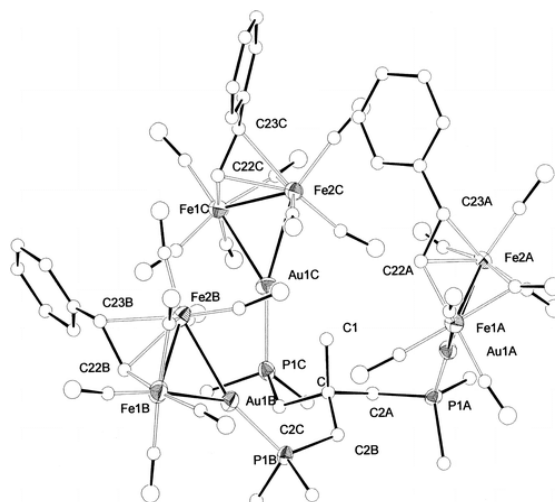


Fig. 8. Structure of $[\{(\text{CO})_6(\mu\text{-CO})(\mu\text{-HC}\equiv\text{CPhH})\text{Fe}_2\text{Au}\}_3(\mu\text{-}\eta^3\text{-triphos})]$ [78]

In black Fe₈Au₂ cluster [48a] two „butterfly“ clusters $\{(\mu\text{-CO})(\text{CO})_{11}(\mu_3\text{-CO})\text{Fe}_4\text{Au}(\text{PET}_3)\}$ are connected by $\{\text{K}(18\text{-crown-6})\}$ 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. 2.642Å) and Au-Fe bond distance is 2.666(1)Å.

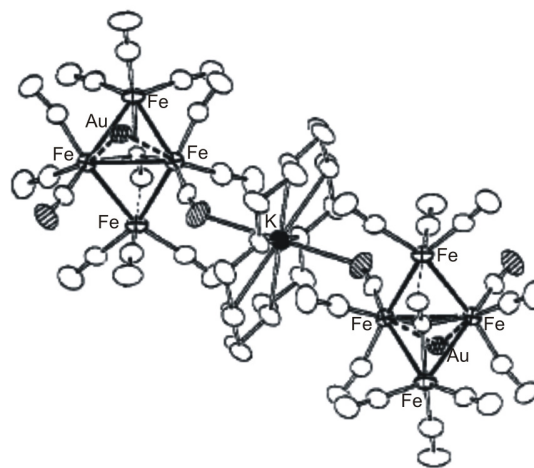


Fig. 9. Structure of $[\text{K}(\eta^6\text{-18-crown-6})\{(\mu\text{-CO})(\text{CO})_{11}(\mu_3\text{-CO})\text{Fe}_4\text{Au}(\text{PET}_3)_2\}]$ [48a]

Table 4. Crystallographic and structural data for heteropentanuclear (gold, iron) clustersa

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	10.223(2)	104.02(2)	AuBPFe	μ_5 B ^b 2.310(10)	Fe 2.580(1)	B,P ^b 149.2(2)	46
	P $\bar{1}$	12.814(3)	90.47(2)		P 2.321(2)		B,Fe 47.0(2)	
	2	15.231(4)	90.13(2)	FeC ₃ B. AuFe ₂	OC not given μ_5 B 1.964(9)	Au 2.580(1) B 73.8(3) Fe 2.678(2,3) B 83.6(4)	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)	
(NMe ₃ CH ₂ Ph) ₂ . [(CO) ₁₆ Fe ₄ Au]Cl (dark green)	or	23.618(4)		Au ^{III} Fe ₄		Fe 2.595(1,12)	Fe,Fe not given	47
	Pccn	16.600(3)		FeC ₄ AuFe (x4)	OC 1.78(1,2)	Fe 2.771(2)	C,C 158.9(6,7.3)	
	4	11.594(3)						
(CO) ₁₂ Fe ₄ (μ_4 -COMe). Au(PEt ₃) (black)	tr	14.764(2)	87.26(1)	AuPFe ₂	Et ₃ P 2.278(5)	Fe2.671(3,5)	P,Fe 149.7(2,3,2)	48a
	P $\bar{1}$	9.574(1)	82.33(2)			Au 2.671(3,5)	Fe,Fe 60.40(8)	
	2	11.094(2)	112.131	FeC ₄ AuFe ₂ (x2)	OC not given μ_4 C 1.98(2,1)	Fe 2.638(4,49)	Au,Fe 76.95(9,20) 110.90(11,10) Fe,Fe 59.24(10,36) 97.38(12,43)	
				FeC ₄ Fe ₂	OC not given μ_4 C 1.86(2)		Fe,Fe 61.63(9)	
				FeC ₄ OFe ₂	OC not given μ_4 C 2.14(2) μ_4 O 2.029(9)	C 159.5(8)	Fe,Fe 61.49(9)	
(CO) ₁₁ (ON)Fe ₄ . (μ_5 -C)Au(PPh ₃) (green)	m	17.142(5)		AuCPFe ₂	μ_5 C 2.095(9)	Fe 2.843(2,23)	C,P 176.5(2)	48b
	P2 ₁ /n	15.738(2)	108.63(2)		Ph ₃ P 2.273(3)		Fe,Fe 81.03(1)	
	4	13.771(4)		FeC ₄ AuFe (x2)	OC not given μ_5 C 1.853(7,8)	Au 2.843(2,23) C 91.9(4,1.2) Fe 2.636(2,21) C 88.6(4,1.0) 176.1(5)	Fe,Fe 58.6(1,2)	

				FeC ₄ Fe ₂	OC not given μ ₅ C 1.915(9)	Fe 2.578(2)	Fe,Fe 61.2(1,3) 89.7(1)	
				FeC ₃ NFe	OC not given μ ₅ C 1.926(8) ON not given		Fe,Fe 60.3(1) 88.8(1)	
(CO) ₁₂ (μ-H)Fe ₄ .	tr	9.855(4)	103.46(2)	AuCPFe ₂	μ ₄ C 2.077(5)	Fe 2.867(1,13)	Fe,Fe 80.5(1)	49
(μ ₄ -C)Au(PPh ₃)	Pī	12.495(6)	98.47(2)		Ph ₃ P not given			
(green brown)	2	14.938(7)	99.74(2)	FeC ₄ AuFe ₂ (x2)	OC not given	Au 2.867(1,13) C 93.5(2,1.1) Fe 2.634(1,10)	not given	
				FeC ₄ HFe ₂ (x2)	OC not given μ ₄ C 1.954(5,3) μH 1.91(8,2)	Fe 2.618(1) H 87(3)	not given	
{(Ph ₃ P)Au} ₂ Fe ₃ .	m	8.872(2)		AuPFe ₃ Au (x2)	Ph ₃ P 2.297(3,8)	Fe 2.678(2,10) 2.748(2,34) Au 2.9915(9)	Fe,Fe 57.52(5,92) Fe,Au 55.59(5,66) 99.66(4)	50
(μ ₃ -O)(CO) ₉ (black)	P ₂ /n 4	12.136(2) 41.568(9)	90.15(3)	FeC ₃ O. Au ₂ Fe ₂ (x2)	OC not given μ ₃ O 1.878(7,3)	Au 2.669(2) 2.748(2,34) Fe 2.558(2,21) 2.700(2) O 88.0(3,3.9)	Au,Au 66.46(4,7) Fe,Fe 58.15(6,75) Au,Fe 60.40(5,98) 111.70(7,4.39)	
				FeC ₃ O. AuFe ₂	OC not given μ ₃ O 1.871(7)	Au 2.688(2) Fe 2.558(2,21) O 86.1(3,1.0)	not given	
{[(Ph ₃ P)Au] ₂ (μ ₅ -P). Fe ₃ (μ-H)(CO) ₉ . 1.5C ₆ H ₆ (deep red)	m C ₂ /c 8	20.422(9) 15.434(6) 34.135(11)	93.29(3)	AuP ₂ FeAu	Ph ₃ P 2.295(3) μ ₅ P 2.428(3)	Fe 2.678(2) Au 2.991(1)	P,μ ₃ 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,Au137.4(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)	51
				AuP ₂ Au	Ph ₃ P 2.301(3) μ ₅ P 2.316(3)			
				FeC ₃ P. AuFe ₂	OC 1.76(1,1) μ ₅ P 2.278(4)	Au 2.678(2) P 69.3(1) Fe 2.651(3,6) P 72.6(1,2)		

				FeC ₃ PFe ₂ (x2)	OC1.77(1,2) μ ₅ P 2.197(4,3)	Fe 2.664(3,29) P 74.2(1,1.4)	C,C98.4(7,5.5) C,P 98.0(5,3.5) 153.3(5,1.7) Fe,Fe 101.91(5)	
{(Ph ₃ P)Au} ₂ Fe ₃ . (μ ₃ -S)(CO) ₉ (black)	tr Pī 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) Fe2.642(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)	η ¹ P 2.345(3) 2.398(3,7) Cl 2.929(2)	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
				FeC ₁₀ (x3)	η ⁵ C not given		not given	
[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 Pī 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)		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). (μ-η ⁵ :η ¹ -ddpca)] ₂ . (AuCl) ₃ .Et ₂ O (orange) (at 190 K)	or Pbcn 4	12.791 17.792 36.966		AuPCL (x2) AuP ₂ Cl FeC ₁₀ (x2)				55
[Fe(μ-η ⁵ :η ¹ -C ₅ H ₄ PPh ₂) ₂ . Au ₂ (μ ₄ -S){Au(PPh ₃) ₂] ₂ . 3CH ₂ Cl ₂ (orange) (at 173 K)	tr Pī 2	13.727(2) 15.925(3) 17.763(2)	71.738(12) 73.264(4) 75.96(2)	AuSPAu ₂ (x4)	μ ₄ S 2.338(5,29) 2.410(5,6) Ph ₃ P2.268(6,12)	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
				FeC ₁₀	η ⁵ C not given		not given	
[Fe(μ-η ⁵ :η ¹ -C ₅ H ₄ PPh ₂) ₂ . AuSPAu	tr	13.321(2)	86.707(8)	AuSPAu	μ ₄ S 2.34(3,2)	Au 2.956(7)	S,P 170.39(11)	56

Au ₂ (μ ₄ -S){Au(C ₆ F ₅) ₃] ₂ . CH ₂ Cl ₂ (orange) (at 173 K)	P $\bar{1}$ 2	13.829(2) 20.145(2)	79.431(8) 78.421(10)	(x2) AuC ₃ S (x2) FeC ₁₀	η ¹ P 2.253(3,1) C 2.050(13,27) μ ₄ S 2.35(3,1) η ⁵ C not given	S 78.30(9) Au 3.333(1)- 4.250(1) S 96.84(11- 126.22(13)	S,Au 50.85(7,6) P,Au121.57(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	
(CO) ₉ Fe ₃ Co(CO) ₃ . (μ ₅ -C)Au(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	μ ₅ C 2.069(3) Ph ₃ P 2.267(1) OC not given μ ₅ C 1.940(3,6) OC not given μ ₅ C 1.845(5) OC not given μ ₅ 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 not given	57a
(CO) ₉ Fe ₃ Co(CO) ₃ . (μ ₅ -C)Au(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	μ ₅ C 2.086(10) Ph ₃ P 2.276(1) OC 1.77-1.84 μ ₅ C 1.846(10,9) OC 1.77-1.84 μ ₅ C 1.924(10) OC 1.77-1.81 μ ₅ 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) C87.6(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
(CO) ₆ Fe ₂ Ir(CO). (PPh ₃)(μ ₃ -η ² -C ₂ Ph). Au ₂ (PPh ₃) ₂ (orange)	m Cc 4	12.956(1) 26.604(4) 19.190(2)	97.14(1)	AuPIrAu AuCPIrAu	Ph ₃ P 2.269(2) μ ₃ C 2.39(2) Ph ₃ P 2.269(6)	Ir 2.635(1) Au 2.847(1) Ir 2.726(1) Au 2.847(1)	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)	58

				IrC ₂ PAu ₂ Fe ₂	OC not given μ ₃ C 1.96(2) Ph ₃ P 2.287(2)	Au 2.635(1) 2.726(1) Fe 2.727(4,18) Ir 2.727(4,18)	Au,Au 64.1(1) Au,Fe 88.4(1,1.9) 107.1(1) 144.8(1)	
				FeC ₅ IrFe (x2)	OC not given μC 2.10(2,4) μ ₃ C 2.075(20,5)	Fe 2.501(5) C not given μ ₃ C not given	not given	
(PPh ₄)[(OC) ₅ Fe ₂ (μ-CO) ₂ - Ir ₂ (μ-CO)(CO) ₄ Au(PPh ₃)] (orange)	m P ₂ /c 4	10.990(3) 13.693(2) 35.883(3)	97.99(2)	AuPIr ₂ Fe	Ph ₃ P not given	Ir 2.813(1,16) Fe 2.806(3) Ir 2.756(1,21) C 83.2(1) Au 2.806(3)	Ir,Ir 58.70(1) Ir,Fe 58.73(1,2) Ir,Au 60.77(1,15) Ir,Fe 59.44(2,43)	59
				FeC ₄ Ir ₂ . AuFe	OC 1.776(x2) μOC 1.996(x2)	Ir 2.679(1,7) Fe 2.645(1) Au 2.813(1,16) Ir 2.786(1) C 83.2(3)	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)	
				FeC ₃ Ir ₂ Fe	OC 1.776			
				IrC ₄ Fe ₂ . AuIr (x2)	OC 1.845 μOC 2.133			
(PPh ₄)[(CO) ₅ Fe ₂ . (μ-CO) ₃ Rh ₂ (CO) ₄ . Au(PPh ₃)] (orange)	m P ₂ /c 4	10.992(3) 13.724(3) 35.982(6)	97.6(2)	AuPRh ₂ Fe	Ph ₃ P 2.283(2)	Rh 2.782(1,1) Fe 2.793(1) Au 2.782(1,1) Fe 2.637(1,3) 2.755(1,5) Rh 2.732(1)	not given C,Fe 175.9(1,5)	60
				RhC ₄ Fe ₂ . AuRh (x2)	OC 1.851(6,45) μOC 2.098(5,83)	Rh 2.755(1,5) Au 2.793(1) Fe 2.656(1)	C,Fe 175.8(2)	
				FeC ₄ Rh ₂ . AuFe	OC 1.815(5,10) μOC 2.018(5,25)	Rh 2.637(1) Fe 2.656(1)	not given	
				FeC ₃ Rh ₂ Fe	OC 1.759(2) 1.788(5,2)			
(CO) ₃ FeCo ₃ (μ-CO) ₃ . (CO) ₆ Au(PPh ₃) (purple)	m P ₂ 2	9.174(2) 15.103(2) 12.708(3)	108.08(2)	AuPCo ₃	Ph ₃ P not given	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
				CoC ₄ Fe. AuCo ₂ (x3) FeC ₃ Co ₃	OC 1.75(-,6) μOC 1.94(-,7) OC 1.79(-,14)			
(CO) ₃ FeCo ₃ (μ-CO) ₃ . (CO) ₅ (PMe ₂ Ph).	m P ₂ /c	22.863(5) 13.232(4)	95.28(9)	AuPCo ₂	Ph ₃ P 2.283(3)	Co 2.72(3,0) Au 2.72(3)	Co,Co 54.8(4) C,C 95(1)	62
				CoC ₄ Fe.	OC 1.74(5)			

Au(PPh ₃) (purple)	8	28.598(6)	AuCo ₂ (x2)	μOC 1.92(5)	Co 2.50(2) C 139(4)	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)	
(CO) ₃ FeCo ₃ (μ-CO) ₃ .	or	21.566(5)	AuPCo ₂	Ph ₃ P 2.28(3)	Co 2.71(3)	not given	62
(CO) ₄ {P(OMc) ₃ } ₂ .	Pn2 ₁	13.356(3)	CoC ₃ P.	OC 1.72(9)	Au 2.71(3)	C,P 90(2,6)	
Au(PPh ₃) (purple)	4	15.141(2)	FeAuCo ₂ (x2)	μOC 1.88(10) P 2.24(9)	Fe 2.60(3) Co 2.53(2) C 137(7)	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)	
(CO) ₃ Fe(μ ₄ -N).	or	16.977(4)	AuPRu ₂	Ph ₃ P 2.287(4)	Ru 2.876(1,6)	not given	63
Ru ₃ (CO) ₉ Au(PPh ₃) (red)	Pbca 8	16.980(4) 24.872(25)	RuC ₃ NFe.	OC 1.90(2,3)	Ru2.788(2,10)	not given	
			AuRu ₂ (x2)	μ ₄ N 2.06(1,2)	2.839(2)		
			RuC ₃ NRu ₂	OC 1.86(2,2) μ ₄ N 1.89(1)	Ru 2.788(2,10)	not given	
			FeC ₄ NRu ₂	OC 1.76(2,2) μ ₄ N 1.81(1)	Ru 2.705(2,12)	not given	

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)].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 AuPFeAu AuCPFe ₂	OC ^b not given μ_5 C 1.860(13) OC not given μ OC not given μ_5 C 1.973(14) OC not given μ OC not given μ_5 C 1.922 η^2 P 2.282(4) μ_5 C 2.070(12) η^2 P 2.271(3)	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) C 86.8(5,4.2) Fe 2.560(2) Au 2.860(2) Fe 2.828(2,3)	Au,Fe ^b 84.78(8,7.14) 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) P,Fe 169.64(1) P,Au 93.65(1) Fe,Au 78.34(5) C,P 170.2(4) P,Fe 137.73(10,3.9) Fe,Fe 82.16(7)	64
[(CO) ₁₁ (μ -CO)HFe ₄ . (μ_6 -B){Au(AsPh ₃) ₂ }] (dark brown)	tr P $\bar{1}$ 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 FeC ₄ BAuFe ₂ FeC ₄ BFe ₂ FeC ₄ BFe ₃	OC not given μ_6 B 1.999(14) OC not given μ OC not given μ_6 B 2.068(11) OC not given μ OC not given μ_6 B 2.114(13) OC not given μ_6 B 2.031(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 2.613(1) B 72.4,144.3(6) Fe 2.586(2) 2.709(2,25) B 79.1(5,2.7) Fe 2.668(3) 2.717(2) B 81.3(5,1.3) Fe 2.586(2) 2.668(2)	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) B,Fe 48.8(4,2.2) Fe,Fe 57.8(1) B,Fe 50.5(4,89)	65

				AuBAsFeAu	μ_6 B 2.342(12,2) Ph ₃ As 2.408(1,0)	2.717(2) 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 PT 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)	
				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)	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) Ph ₃ P 2.301(3,2)	Au 2.943(1) B 77.3(3)		
[(OC) ₁₂ HFe ₄ (μ_6 -B). {Au(PEt ₃) ₂] (black)	m I2/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)		
				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 ₁ /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)	Au,Au 66.3(1) Fe,Fe 56.7(1) B,Au 56.9(6,9) B,Fe 50.7(6,7)	67

						2.741(4) B 82.2(8,1.0) 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) Au,Fe 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)		not given	21
				AuCP	C 2.002(6) P 2.276(2)		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)	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)	51
				FeC ₃ PAuFe ₂	OC 1.72(5,8) μ ₆ P 2.32(1)	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 96(2,2) C,P 89(2) 132(2,0) Au,Fe' 62.3(2) 106.3(2)	
				FeC ₃ PFe ₂	OC 1.79(4,4) μ ₆ P 2.18(1)	Fe 2.655(7,4)	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)
				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)			
				AuP ₂ Fe	Ph ₃ P 2.314(9) μ ₆ P 2.455(9)	Au' 3.206(2,39) P 82.6(2,3.2) Fe 2.665(5)			
[(OC) ₄ FeAu ₂ (μ-η ² - dppp)] 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 ² - 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(-,52) 3.0880(4)	not given		
(NEt ₄)[(CO) ₁₃ (μ-CO) ₃ . Fe ₆ (μ ₆ -C)Au(PPh ₃) 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 μOC 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 174.6(9,4.4) C 79.6(7)	not given		48b
				FeC ₄ Fe ₃ (x3)	OC not given μOC not given μ ₆ C 1.901(-,15)		not given		
				AuPFe ₃	Ph ₃ P 2.295(4)		not given		
(ppn)[{(OC) ₉ (μ ₃ -PMe)Fe ₃ . (μ ₃ -P) ₂ Au] (orange red)	m C2/c 4	21.272(2) 20.153(1) 17.020(1)	107.535(6)	FeC ₃ P ₂ Fe	OC not given μ ₃ MeP 2.200(2,23)	Fe 2.693(2,2) 3.549(2)	not given		71
				AuP ₂	μ ₃ P 2.263(2,6) μ ₃ P 2.305(2,0)		P,P 177		
[(CO) ₁₁ (μ-CO) ₃ Fe ₅ (μ ₆ -C). (μ ₄ -AuPEt ₃)(μ-AuPEt ₃) (black)	m P2 ₁ /c 4	12.934(5) 18.879(6) 16.425(9)	106.86(4)	FeC ₃ Au ₂ Fe ₃	OC not given μ ₃ C 1.876(18)	Au 2.696(2) 2.828(3) Fe 2.617(2,6) 2.941(3)	not given		72
				FeC ₄ Au ₂ Fe ₃	OC not given μOC not given	Au 2.701(3) 2.871(2)	not given		
				FeC ₄ Fe ₃	μ ₆ C 1.916(14) OC not given	Fe 2.640(3,12) Fe 2.573(3)	not given		

				(x2)	μ OC not given μ_6 C 1.924(18,12)	2.625(3,3) 2.673(3,13) Au 3.021(3,15)		
				FeC ₄ Fe ₄	OC not given μ_6 C 1.961(14)	Fe 2.612(3) 2.666(3,20)	not given	
				AuCPFe ₄	μ_6 C 2.117(14) Et ₃ P 2.268(4)	Fe 2.849(2,22) 3.021(3,15)	C,P 176.7(4)	
				AuPFe ₂	Et ₃ P 2.276(5)	Fe 2.698(2,3)	P,Fe 146.9(2,1.9)	
[(OC) ₁₂ Fe ₄ (μ_7 -B). {Au(PPh ₃) ₃ } ₃]	tr PT 2	13.404(3) 13.338(3) 20.493(7)	79.37(3) 71.88(3) 73.94(3)	FeC ₃ BAu ₂ Fe ₂	OC not given μ_7 B 2.13(2)	Au 2.616(3) 2.711(3)	not given	73
				FeC ₃ BAuFe ₃	OC not given μ_7 B 2.09(2)	Au 2.693(4) Fe not given	not given	
				FeC ₃ BAuFe ₂	OC not given μ_7 B 1.98(2)	Au 2.625(4) Fe not given	not given	
				FeC ₃ BFe ₃	OC not given μ_7 B 2.16(2)	Fe not given	not given	
				AuPBFe ₂ Au	Ph ₃ P not given μ_7 B 2.34(2)	Fe 2.702(3,9) 2.877(1)	not given	
				AuPBFeAu ₂	Ph ₃ P not given μ_7 B 2.27(2)	Fe 2.625() Au 2.867(1,10)	not given	
				AuP ₂ BFeAu	Ph ₃ P not given μ_7 B 2.32(2)	Fe 2.616(3) Au 2.858(1)	not given	
[(OC) ₉ Fe ₃ (μ_7 -P). {Au(PPh ₃) ₄ } ₄ . [B{3,5(CF ₃) ₂ C ₆ H ₃ } ₄ . 1.5Et ₂ O (purple) (at 123K)	tr PT 2	12.918(3) 19.863(9) 23.256(4)	89.94(2) 91.57(2) 94.31(3)	FeC ₃ PAu ₂ Fe ₂ (x2)	OC not given μ_7 P 2.287(7,9)	Au 2.709(3,20) 2.808(3,22) Fe 2.632(5) 2.672(5,2)	not given	74
				FeC ₃ PFe ₂	OC not given μ_7 P 2.220(7)	Fe 2.632(5) 2.670(5)	not given	
				AuP ₂ Fe ₂ Au ₂	Ph ₃ P 2.287(3) μ_7 P 2.694(6)	Fe 2.690(4) 2.830(4) Au 2.980(1) 3.224(2)	not given	
				AuP ₂ FeAu ₂ (x2)	Ph ₃ P 2.297(6,2) μ_7 P 2.419(6,7)	Fe 2.729(3) 2.786(3) Au 2.984(1,8) 3.224(2)	not given	
				AuP ₂ Au ₂	Ph ₃ P 2.302(6) μ_7 P 2.357(6)	Au 2.984(1,8)	not given	
[[{(OC) ₄ Fe] ₂ Au ₅ .	tr PT	10.051(4) 10.086(2)	87.79(1) 111.60(2)	FeC ₄ Au ₃	OC not given	Au 2.533(3) 2.607(3)	not given	54

$(\eta^2\text{-dppm})_2(\text{BF}_4)_2^d$ (red)	2	33.284(6)	82.17(2)	AuFe ₂ Au ₄		2.750(4)			
						Fe 2.533(3,0)	not given		
				AuPFeAu ₂ (x4)	P 2.329(6) 2.398(6)	2.624(1)- 2.924(1)	P,Fe 168.1(2,2.1)		
				FeC ₄ Au ₃	OC not given	Fe 2.607(3) 2.750(4)	not given		
			AuFe ₂ Au			Au 2.438(3) 2.650(4) 2.751(3)		not given	
			AuPFeAu ₂ (x4)	P 2.139(6) 2.277(7)		Fe 2.751(3,0) Au 2.630(1)- 2.840(1) Fe 2.438(3) 2.650(4)		P,Fe 167.4(2,1.5)	
[Fe($\mu\text{-}\eta^5\text{-}\eta^1\text{-dppcp}$) ₂] {Au ₂ ($\mu_3\text{-S}$) 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)	$\eta^5\text{C}$ not given			not given	40
				Au'PS (x4)	$\eta^1\text{P}$ 2.255(4,12)	Au' 2.933(1,17)	P,S 173.5(1,2.8)		
				Au ^{III} C ₂ S ₂	$\mu_3\text{S}$ 2.342(4,26) C 2.058(14,5) $\mu_3\text{S}$ 2.392(4,5)	S 77.5(1,6) Au' 3.219(8) 3.3661(10) S 106.4(2,7)	C,C 88.6(5) S,S 95.19(13) C,S 88.2(3,2.9) 174.9(4,1.2)		
[Fe($\mu\text{-}\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{PPh}_2$) ₂] {AuMn ₂ ($\mu\text{-PPh}_2$)(CO) ₈ } ₂ (red)	m P2 ₁ /c 2	14.592(2) 14.675(2) 16.658(2)	91.46(1)	FeC ₁₀	$\eta^5\text{cpC}$ 2.049(7)			not given	75
				AuPMn ₂	$\eta^1\text{P}$ 2.318(2)	Mn 2.660(1) 2.776(1)	P,Mn 145.88(5,3.5) Mn,Mn 68.20(3)		
				MnC ₃ PAu	OC 1.82(1,3) μP 2.283(2,3)	Mn 3.049(2)	P,Au 48.09(6,7) 103.01(6,1.84)		
[Fe($\mu\text{-}\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{PPh}_2$) ₂] Au ₂ ($\mu_6\text{-B}$)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	$\eta^5\text{cpC}$			not given	76
				AuBPRuAu	2.048(25,24) $\mu_6\text{B}$ 2.292(20) $\eta^1\text{P}$ 2.300(6)	Ru 2.695(2) B 74.9(3) Au 2.818(2) B 75.9(8)	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)		
				RuC ₃ BAuRu ₂ (x2)	OC not given $\mu_6\text{B}$ 2.133(5)	Ru 2.853(2) B 81.4(6) Ru 2.854(2) B 157.4	B,Au 55.2(6) B,Ru 51.0(5) Ru,Ru 60.9(1)		
				RuC ₃ BRu ₃ (x2)	OC not given $\mu_6\text{B}$ 2.242(19)	Ru 2.854(2,1) B 80.4(8)	B,Ru 48.4(1,1.4) Ru,Ru 59.5(1,1) 94.3(1)		

[Fe(μ - η^5 - η^1 -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 cpC 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 μ H not given OC 1.840(18)- 1.902(21) μ H 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)	P,Ru 146.4(1,5.0) P,Au 126.2(1) Ru,Ru 64.9(1) Ru,Au 59.0,76.5(1) P,Ru 146.5(1,6.1) P,Au 113.1(1) Ru,Ru 63.8(1) Ru,Au 58.2,101.9(1) Au,Au 62.8(1) Ru,Ru 58.4(1,1.6) Au,Ru 58.4(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
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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 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 . (μ_5 -BH) ₂ Au] (dark orange)	m C2/c 4	21.704(3) 9.542(2) 29.717(6)	97.50(6)	AuB ₂ Fe ₂ FeC ₃ B. AuFe ₂ (x2) FeC ₃ BFe ₂ (x6) AuP ₂	μ_5 B ^b 2.300(12) OC not given μ_5 B 1.990(12) OC not given μ_5 B 2.054(12,39) Ph ₂ MeP 2.300(4)	Fe 2.615(1) B 74.7(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)	B, B ^b 125.8(6) Fe, Fe 143.4(1) B, Fe 47.2(3) 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)	46
[{(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) L 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^6 -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^6 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].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].2.85CHCl 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]			Heteronuclearity	
	Shortest [ref.]	Longest [ref.]	Average		
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]	2.962(1) [38]	2.922	Tetranuclear	
	2.847(1) [58]	2.991(1) [51]	2.936	Pentanuclear	
	2.776(1) [70]	2.971(1) [67]	2.867	Hexanuclear	
	2.630(1) [54]	2.992(2) [74]	2.857	Heptanuclear	
	2.905(2) [27]	2.929(2) [27]	2.917	Nonanuclear	
Fe - Fe	2.605(2) [17]	2.651(4) [19]	2.630	Trinuclear	
	2.574(2) [35]	2.900(2) [37]	2.676	Tetranuclear	
	2.504(3) [58]	2.782(2) [50]	2.640	Pentanuclear	
	2.571(3) [64]	2.741(4) [67]	2.646	Hexanuclear	
	2.562(4) [48b]	2.941(3) [72]	2.670	Heptanuclear	
	2.594(2) [78]	2.922(2) [68]	2.726	Nonanuclear	
	2.623(2) [48a]	2.654(2) [48a]	2.692	Decanuclear	
Au-Co	2.661(3) [44]			Tetranuclear	
	- Pt	2.821(1) [42]	2.875(1) [42]	2.848	Tetranuclear
	- Ru	2.729(2) [45]			Tetranuclear
	- Ir	2.633(1) [58]	2.829(1) [59]	2.724	Pentanuclear
	- Co	2.710(3) [62]	2.873(1) [57a]	2.754	Pentanuclear
	- Ru	2.754(1) [63]	2.766(1) [63]	2.760	Pentanuclear
	- Rh	2.781(1) [60]	2.783(1) [60]	2.782	Pentanuclear
	- Mn	2.660(1) [74]	2.776(1) [74]	2.718	Heptanuclear
	- Ru	2.641(2) [77]	2.846(1) [77]	2.773	Heptanuclear
Fe - Co	2.486(1) [43]	2.678(1) [45]	2.570	Tetranuclear	
	- Pt	2.715(3) [42]			Tetranuclear
	- Ru	2.914(3) [45]			Tetranuclear
	- Co	2.517(1) [57b]	2.633(1) [57a]	2.582	Pentanuclear
	- Rh	2.634(1) [60]	2.750(1) [60]	2.689	Pentanuclear
	- Ru	2.693(2) [63]	2.717(2) [63]	2.705	Pentanuclear
	- Ir	2.686(1) [59]	2.776(1) [59]	2.729	Pentanuclear
Co - Co	2.492(4) [44]			Tetranuclear	
	2.44 [81]	2.60 [61]	2.52	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	

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 Å, 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], AuPF_2 [48a], AuP_2Cl [79,80] and four- AuB_2Fe_2 [46], and AuPF_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: 2.633Å (Fe-Fe) < 2.707Å (Au-Fe) < 2.917Å (Au-Au).

3. CONCLUSION

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 $\{(Ph_3P)Au\}_3Fe(CO)_4$ [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 above, where the shortest are 2.438(3)Å for Au-Fe [54], 2.504(3)Å for Fe-Fe [58], and 2.630(1)Å 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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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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