Structural characterization of the trinuclear cluster compound $[Fe(CO)_4(AuPPh_3)_2]$ and isolation of its parent anion $[Fe(CO)_4(AuPPh_3)]^-$

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Abstract

A re-investigation of the reaction of $Au(PPh_3)Cl$ with $[Fe(CO)_4]^{2-}$ has shown that the $[Fe(CO)_4(AuPPh_3)]^-$ monoanion and $[Fe(CO)_4(AuPPh_3)_2]$ are obtained in sequence by using a 1:1 and 2:1 molar ratio, respectively. The complex $[Fe(CO)_4(AuPPh_3)_2]$ crystallizes in the monoclinic space group $P2_1/a$, $a=20.309(5)$, $b=18.379(3)$, $c=40.737(6)$ Å, $\beta=96.26(2)°$, $Z=16$, $R=0.0526$. There are four crystallographically independent but chemically equivalent molecules in the asymmetric unit. Each molecule consists of an Au_2Fe triangle with the two Au atoms bearing a PPh_3 ligand and the iron atom bound to four carbonyl groups. The feature of greatest interest in this molecule is the Au–Au interaction whose length is found in the range 2.897–2.941(1) Å, quite different from that quoted from a previous study (3.028(1) Å).

Introduction

The reaction of $Au(PPh_3)Cl$ with $[Fe(CO)_4]^{2-}$ was investigated several years ago in a pioneering study on the formation of M–M bonds and afforded the first gold mixed-metal cluster, that is $[Fe(CO)_4(AuPPh_3)_2]$ [1]. Later, it was reported that the related reactions of both Cu(dppe)Cl (dppe = 1,2-bis(diphenylphosphino)ethane) and $Cu(PPh_3)_2Cl$ with $Na_2[Fe(CO)_4]$ in a 2:1 molar ratio result in the quantitative formation of the $[Cu_6Fe_4(CO)_{16}]^{2-}$ cluster in its corresponding CuL_x^+ salts; however, when using $Cu(PPh_3)_2Cl$, crystallization of the reaction mixture afforded crystals of either the neutral $[Fe(CO)_4\{Cu(PPh_3)_2\}_2]$ or the salt $[Cu(PPh_3)_3]_2[Cu_6Fe_4(CO)_{16}]$, depending on the experimental conditions [2]. The former reverts into the latter when redissolved in organic solvents.

Recently we have found that the corresponding reaction of silver(I) phosphine complexes with $[Fe(CO)_4]^{2-}$ is much more complicated, and leads to the formation of several anionic Ag–Fe species, depending on the molar ratio between the reagents. Unfortunately, most of these anionic species are unstable and rapidly separate out silver metal, $Fe(CO)_{5-x}L_x$ ($x=1$, 2) complexes and minor amounts of the known $[Ag_{13}Fe_8(CO)_{32}]^{n-}$ ($n=3$, 4) clusters [3, 4], as their AgL_x^+ salts (L = tertiary phosphine). No evidence of a neutral $[Fe(CO)_4\{Ag(PPh_3)_x\}_2]$ ($x=1$ or 2), corresponding to either the gold or the copper congener, has been obtained. This prompted us to re-investigate the reaction of $Au(PPh_3)Cl$ with $[Fe(CO)_4]^{2-}$ with the hope of gaining a better understanding of the corresponding reaction of silver(I) phosphine complexes. So far, we have been able to isolate the $[Fe(CO)_4(AuPPh_3)]^-$ anion and the previously reported neutral cluster $[Fe(CO)_4(AuPPh_3)_2]$.

Although the structure of this molecule has already been determined [5], no account has ever appeared; however, the Au–Au distance has been quoted and discussed [6, 7]. The present structural study has been undertaken also in the hope of finding some new features in the molecular structure, as the unusually high number of formula units contained in the unit cell might suggest. Although our present work confirmed the known molecular structure, what follows is not a mere repetition of previous results. We report here the complete description of the molecular structure and take the opportunity of discussing the chemical significance and reliability of the metal–metal distances as obtained by X-ray diffraction experiments. As a matter of fact, an

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aspect of interest of this structural work is that the Au–Au bond distances are not equivalent to the previously reported one. Very probably we came across a new polymorph in which a significantly different molecular packing is present.

Results and discussion

The reaction of $Na_2[Fe(CO)_4]\cdot x$THF with $Au(PPh_3)Cl$ has been investigated by using different molar ratios. Owing to the low solubility of both reagents in tetrahydrofuran (THF), powdered samples of the two reagents were mixed and the reaction started by injection of THF and stirring. Equilibration of the reaction mixtures occurs in a few minutes, as shown by IR monitoring. The IR carbonyl absorptions are at variance depending on the adopted molar ratio between the two reagents. When using a 1:1 molar ratio, equilibration of the reaction mixture gives rise to a light brown solution which displays IR absorptions at 1935(m), 1870(sh), 1842(s) and 1790(sh) cm^{-1}, owing to almost quantitative formation of $[Fe(CO)_4(AuPPh_3)]^-$. This compound has been isolated as a microcrystalline solid by precipitation with bis (triphenylphosphine) iminium chloride and characterized by elemental analysis.

A mixture mainly containing this compound and minor amounts of a yet unknown species also results from the reaction of $[Fe(CO)_4]^{2-}$ with $Au(PPh_3)Cl$ in a 1:1.5 molar ratio. The resulting reaction solution is deeper in colour and shows additional IR absorptions at 1960(ms) and 1890(s) cm^{-1}, which can be attributed to the above unknown species. The IR pattern and the absorption frequencies are almost coincident with those of $[Cu_6Fe_4(CO)_{16}]^{2-}$ [2] and $[Ag_6Fe_4(CO)_{16}]^{2-}$ [4]. Unfortunately all attempts to drive the reaction towards the selective formation of this new species, as well as its separation from $[Fe(CO)_4(AuPPh_3)]^-$ by differential solubility in the miscellaneous solvents, have so far been unsuccessful.

As expected, increased molar ratios between the reagents up to a ratio of 1:2 lead to progressive formation of the neutral complex $[Fe(CO)_4(AuPPh_3)_2]$. According to the previous report [1], this species shows IR absorptions in THF solution at 2044(w), 1996(s), 1930(s) and 1890(s) cm^{-1}. These are essentially invariant in most common organic solvents and the possible equilibria of $[Fe(CO)_4(AuPPh_3)_2]$ with anionic species corresponding to the above cited $[M_6Fe_4(CO)_{16}]^{2-}$ (M = Cu, Ag) or $[Ag_{13}Fe_8(CO)_{32}]^{n-}$ ($n = 3$, 4) do not occur. It is worth noting that the mean carbonyl absorption frequency of $[Fe(CO)_4(AuPPh_3)_2]$ (*c*. 1940 cm^{-1}) differs significantly from that of both $[Fe(CO)_4\{Cu(PPh_3)_2\}_2]$ (*c*. 1790 cm^{-1}) and $[Fe(CO)_4]^{2-}$ (*c*. 1780 cm^{-1}) [2]. This seems to imply a significant transfer of electron density from iron to gold, which occurs to a much lesser extent in the related copper derivative. In this connection, $[Fe(CO)_4\{Cu(PPh_3)_2\}_2]$ seems to be better regarded as a case of tight ion pairing; the suggested greater polarity of the heterometallic Cu–Fe bond, as compared to Au–Fe, and the minor reluctance of copper for higher coordination numbers, could be at the origin of the reported ready rearrangement in polar solutions of $[Fe(CO)_4\{Cu(PPh_3)_2\}_2]$ to $[Cu(PPh_3)_3]_2[Cu_6Fe_4(CO)_{16}]$ [2].

The yellow $[Fe(CO)_4(AuPPh_3)_2]$ does not show electrochemically reversible redox behaviour; however, by reduction with Na naphthalene in slight excess, it gives rise to the parent $[Fe(CO)_4(AuPPh_3)]^-$ monoanion, as the only carbonyl species detected in solution.

The crystal structure of $[Fe(CO)_4(AuPPh_3)_2]$ is quite exceptional from a crystallographic point of view in that the structural motif consists of four independent molecules. As a result we had to work out the geometries of four slightly different molecular objects and we could not avoid a fourfold determination of the molecular structure. That was a real nuisance in terms of experimental and computational work, but a unique opportunity of determining very reliable average values of bond lengths of chemical interest. At the same time the perturbing effects of the packing forces on the molecular geometry have been assessed in a situation in which the force field experienced by each molecule cannot be very different.

The four independent images of the molecule are shown in Fig. 1. The relevant bond lengths and angles are given in Table 1. The overall geometries are quite similar but an analysis of the differences is instructive. The phosphines in each molecule, when observed along their threefold axis, clearly show opposite chirality and are oriented around their own P–Au bond in such a way as to make the molecules asymmetric. The Fe–Au–P angles are in the range 169–177° (av. 173°) (Table 2), and reflect the deviations of the P atoms out of the Au_2Fe plane. The $Fe(CO)_4$ groups exhibit approximate C_{2v} symmetry with two ligands in the equatorial trimetal plane and the other two above and below that plane but tilted towards the Au atoms (C_{ax}–Fe–C_{ax} av. angle 147.8°) so that the resultant Au...C contacts are quite short (av. 2.74 Å). The phenomenon has repeatedly been observed and commented on [8] but no univocal explanation has been given. Very probably the CO groups adopt a distorted tetrahedral geometry in order to optimize the contacts between equatorial and axial carbon atoms (av. values $C_{eq}...C_{eq}$ 2.72, $C_{eq}...C_{ax}$ 2.70 Å), and this kind of geometry is made possible by the lack of axial ligands at the Au atoms. Attractive Au...C contacts can be seen as a concomitant effect and as a manifestation of the residual bonding ability of the

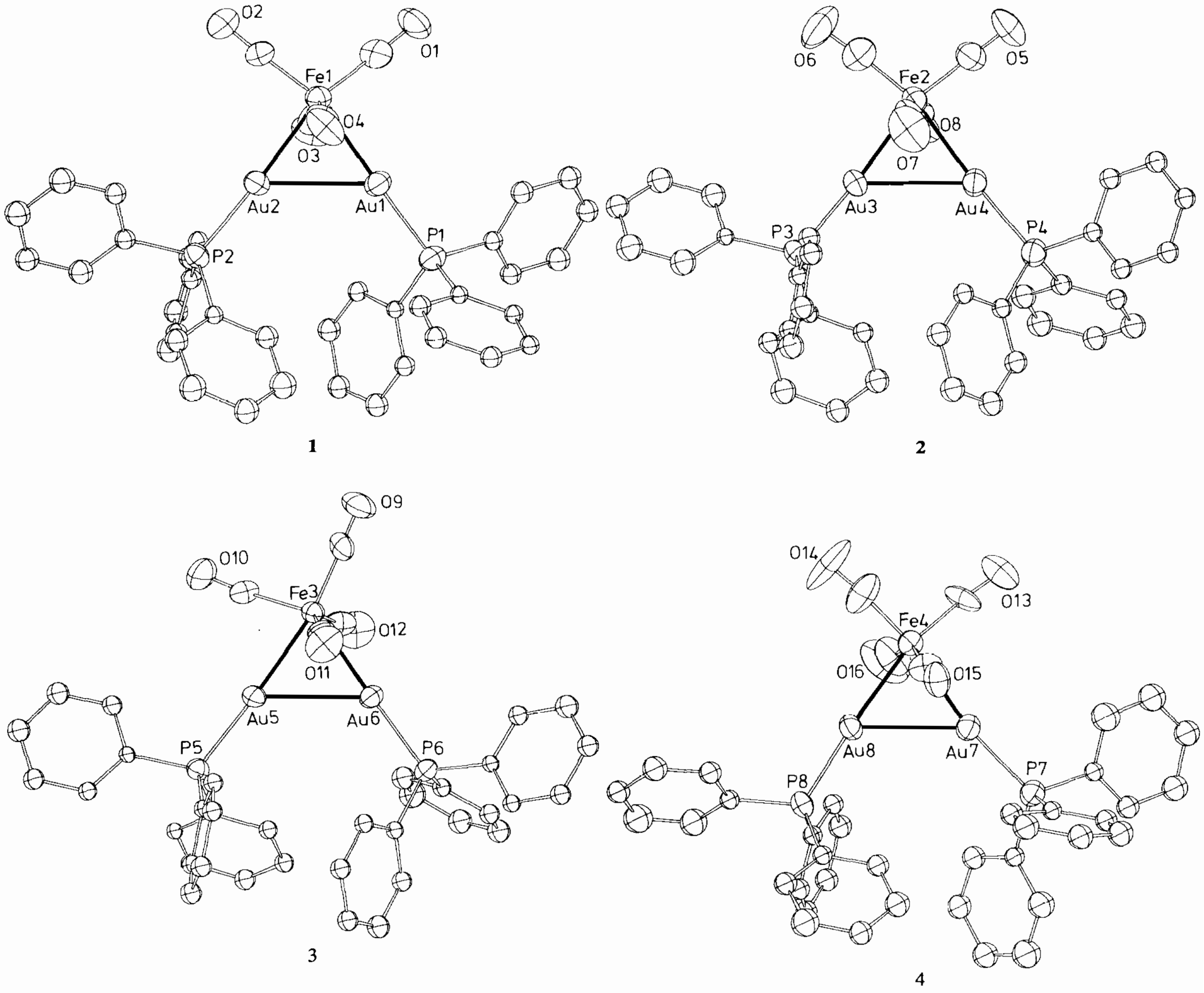

Fig. 1. ORTEP drawings of the four deformation conformers of $[Fe(CO)_4(AuPPh_3)_2]$ present in the crystal. Hydrogen atoms have been omitted for clarity.

two-coordinate Au(I) atoms better expressed by the Au–Au interactions (see later). This view is consistent with the observation that the $Fe(CO)_4$ group in molecule 3 is significantly rotated around a vertical axis (surely a packing effect and observed in at least another case [9]) with minor changes in its internal geometry.

While angular deformations are considered normal consequences of the packing forces, bond lengths variations have not received special attention as yet mainly because they are often not well discernible from fluctuations engendered by experimental errors. The variability of the bonds involving P, Fe and Au atoms, on the other hand, is much higher than the estimated standard deviations and, significantly increases with increasing softness of the bonding interactions. The following average bond distances and their corresponding range of values are very instructive: Au–P 2.275 (0.022), Au–Fe 2.538 (0.031), Au–Au 2.919 (0.044) Å. The Au–Au distance, averaged over four independent values, compares well with the corresponding distances in similar molecules: 2.872(2) Å in $[\{Fe(CO)_3P(OEt)_3\}(AuPPh_3)_2]$ [6], 2.977(1) Å in $[Fe(CO)_4Au_2(dppe)]_2$ [9], 2.929(1) Å in $[Os(CO)_4(AuPPh_3)_2]$ [7]. Quite surprisingly the reported value in the alleged polymorph of $[Fe(CO)_4(AuPPh_3)_2]$ [5], 3.028(1) Å, is the farthest from the present value, in spite of the strict chemical equivalence. The figures discussed above indicate that comparisons among metal–metal distances should be made with caution and that only average values should be taken as reference. Therefore the

TABLE 1. Relevant bond lengths (Å) and angles (°) for $[Fe(CO)_4(AuPPh_3)_2]$

Molecule 1		Molecule 2		Molecule 3		Molecule 4	
Au(1)–Au(2)	2.928(1)	Au(3)–Au(4)	2.941(1)	Au(5)–Au(6)	2.897(1)	Au(7)–Au(8)	2.909(1)
Fe(1)–Au(1)	2.523(3)	Fe(2)–Au(3)	2.533(3)	Fe(3)–Au(5)	2.547(3)	Fe(4)–Au(7)	2.537(3)
Fe(1)–Au(2)	2.546(3)	Fe(2)–Au(4)	2.522(3)	Fe(3)–Au(6)	2.553(2)	Fe(4)–Au(8)	2.544(3)
Au(1)–P(1)	2.269(5)	Au(3)–P(3)	2.272(5)	Au(5)–P(5)	2.276(5)	Au(7)–P(7)	2.274(5)
Au(2)–P(2)	2.278(5)	Au(4)–P(4)	2.281(6)	Au(6)–P(6)	2.274(5)	Au(8)–P(8)	2.273(5)
Fe(1)–C(1)	1.76(2)	Fe(2)–C(5)	1.75(2)	Fe(3)–C(9)	1.78(2)	Fe(4)–C(13)	1.73(2)
C(1)–O(1)	1.17(3)	C(5)–O(5)	1.17(3)	C(9)–O(9)	1.13(3)	C(13)–O(13)	1.14(2)
Fe(1)–C(2)	1.76(2)	Fe(2)–C(6)	1.76(3)	Fe(3)–C(10)	1.79(2)	Fe(4)–C(14)	1.75(2)
C(2)–O(2)	1.16(3)	C(6)–O(6)	1.17(3)	C(10)–O(10)	1.14(2)	C(14)–O(14)	1.14(3)
Fe(1)–C(3)	1.78(2)	Fe(2)–C(7)	1.76(2)	Fe(3)–C(11)	1.76(2)	Fe(4)–C(15)	1.77(2)
C(3)–O(3)	1.13(3)	C(7)–O(7)	1.12(3)	C(11)–O(11)	1.14(2)	C(15)–O(15)	1.15(3)
Fe(1)–C(4)	1.75(2)	Fe(2)–C(8)	1.77(2)	Fe(3)–C(12)	1.75(2)	Fe(4)–C(16)	1.75(2)
C(4)–O(4)	1.14(2)	C(8)–O(8)	1.13(2)	C(12)–O(12)	1.15(2)	C(16)–O(16)	1.15(3)
C(1)...C(2)	2.81	C(5)...C(6)	2.76	C(9)...C(10)	2.71	C(13)...C(14)	2.58
C(1)...C(3)	2.72	C(5)...C(7)	2.67	C(9)...C(11)	2.63	C(13)...C(15)	2.70
C(1)...C(4)	2.65	C(5)...C(8)	2.65	C(9)...C(12)	2.62	C(13)...C(16)	2.64
C(2)...C(3)	2.70	C(6)...C(7)	2.69	C(10)...C(11)	2.94	C(14)...C(15)	2.65
C(2)...C(4)	2.69	C(6)...C(8)	2.69	C(10)...C(12)	2.78	C(14)...(C16)	2.72
Au(1)...C(1)	3.13	Au(4)...C(5)	3.12	Au(6)...C(9)	3.80	Au(7)...C(13)	3.18
Au(2)...C(2)	3.13	Au(3)...C(6)	3.18	Au(5)...C(12)	3.16	Au(8)...C(14)	3.34
Au(1)...C(3)	2.73	Au(3)...C(7)	2.71	Au(5)...C(11)	2.90	Au(7)...C(15)	2.60
Au(2)...C(3)	2.71	Au(4)...C(7)	2.79	Au(6)...C(11)	2.64	Au(8)...C(15)	2.87
Au(1)...C(4)	2.73	Au(3)...C(8)	2.87	Au(5)...C(10)	2.61	Au(7)...C(16)	2.94
Au(2)...C(4)	2.82	Au(4)...C(8)	2.74	Au(6)...C(12)	2.54	Au(8)...C(16)	2.63
Au(2)–Fe(1)–Au(1)	70.6(1)	Au(4)–Fe(2)–Au(3)	71.2(1)	Au(5)–Fe(3)–Au(6)	69.2(1)	Au(7)–Fe(4)–Au(8)	69.9(1)
Fe(1)–Au(1)–P(1)	171.7(1)	Fe(2)–Au(3)–P(3)	170.9(1)	Fe(3)–Au(5)–P(5)	177(1)	Fe(4)–Au(7)–P(7)	168.8(2)
Fe(1)–Au(2)–P(2)	174.3(1)	Fe(2)–Au(4)–P(4)	171.4(2)	Fe(3)–Au(6)–P(6)	177(1)	Fe(4)–Au(8)–P(8)	173.6(2)
C(1)–Fe(1)–Au(1)	91.9(7)	C(5)–Fe(2)–Au(4)	91.8(7)	C(9)–Fe(3)–Au(6)	121.4(7)	C(13)–Fe(4)–Au(7)	94.6(7)
C(2)–Fe(1)–Au(2)	91.4(7)	C(6)–Fe(2)–Au(3)	93.9(9)	C(10)–Fe(3)–Au(5)	71.8(6)	C(14)–Fe(4)–Au(8)	100.6(8)
C(1)–Fe(1)–C(2)	106.1(9)	C(5)–Fe(2)–C(6)	103(1)	C(9)–Fe(3)–C(10)	98(1)	C(13)–Fe(4)–C(14)	96(1)
C(3)–Fe(1)–C(4)	148(1)	C(7)–Fe(2)–C(8)	152(1)	C(11)–Fe(3)–C(12)	141(1)	C(15)–Fe(4)–C(16)	150(1)

TABLE 2. Relevant average bond distances (Å) and angles (°) with the respective dispersion of values in parentheses for $[Fe(CO)_4(AuPPh_3)_2]$

Au–Au	2.919 (2.897–2.941)
Au–Fe	2.538 (2.522–2.553)
Au–P	2.275 (2.269–2.281)
Fe–C_{eq}	1.76 (1.73–1.79)
C–O_{eq}	1.15 (1.13–1.17)
Fe–C_{ax}	1.76 (1.75–1.78)
C–O_{ax}	1.14 (1.12–1.15)
C_{ax}–Fe–C_{ax}	147.8 (141.2–151.7)
C_{eq}–Fe–C_{eq}	100.9 (98.4–106.1)
Fe–Au–P	173.0 (168.8–177.0)
Au–Fe–Au	70.2 (69.2–71.2)

Au–Au interactions in the Au_2M clusters, in which M is a Group 8 metal, are substantially equivalent. The deformability of this distance agrees well with an estimated bond energy of 7–8 kcal/mol [10]. A recent database analysis [11] of the Au...Au interactions confirms that the values in the Au_2Fe systems lie on the bonded side of the wide range of observed Au...Au contacts, also considering that the Au–Au distance in the metal is 2.89 Å [12].

Experimental

All manipulations were carried out with standard Schlenk techniques under nitrogen in dried solvents. The $Na_2[Fe(CO)_4]\cdot x$THF and $Au(PPh_3)Cl$ compounds were prepared according to literature methods [13, 14]. Analyses of Au and Fe were performed by atomic absorption. IR spectra were recorded on a Perkin-Elmer 1605 interferometer using CaF_2 cells.

Synthesis of $[N(PPh_3)_2][Fe(CO)_4(AuPPh_3)]$

$Na_2[Fe(CO)_4]\cdot x$THF ($x \sim 1$; 1.2 g) and $Au(PPh_3)Cl$ (2.1 g) were charged in a Schlenk tube under a nitrogen atmosphere and THF (30 ml) was added. The mixture was stirred for 30 min, filtered and evaporated to dryness under vacuum. The residue was dissolved in methanol and precipitated by addition of $[N(PPh_3)_2]Cl$. The resulting microcrystalline precipitate was filtered, washed with isopropyl alcohol and dried under vacuum. Yield 3.7 g. *Anal.* Found: Fe, 4.6; Au, 16.2. Calc. for $[N(PPh_3)_2][Fe(CO)_4(AuPPh_3)]$: Fe, 4.79; Au, 16.91%.

Synthesis of $[Fe(CO)_4(AuPPh_3)_2]$

$Na_2[Fe(CO)_4]\cdot x$THF ($x \sim 1$; 0.82 g) and $Au(PPh_3)Cl$ (2.8 g) were charged in a Schlenk tube under a nitrogen atmosphere and THF (30 ml) was added. The mixture was stirred for 30 min, filtered and evaporated to dryness under vacuum. The residue was dissolved in toluene (40 ml) and the solution was filtered. Crystallization by layering of hexane (60 ml) gave 2.2 g of well-shaped yellow crystals of $[Fe(CO)_4(AuPPh_3)_2]$. *Anal.* Found: Fe, 5.2; Au, 36.7. Calc. for $[Fe(CO)_4(AuPPh_3)_2]$: Fe, 5.40; Au, 38.03%.

X-ray data collection and structure refinement of $[Fe(CO)_4(AuPPh_3)_2]$

Cell constants and details of the data collection for $[Fe(CO)_4(AuPPh_3)_2]$ are given in Table 3. The diffraction experiments were carried out at room temperature on a fully automated Enraf-Nonius CAD-4 diffractometer using a crystal mounted on a glass fibre. Graphite monochromated Mo Kα radiation ($\lambda = 0.71067$ Å) was used. The cell dimensions were determined from 25 randomly selected strong reflections by using automatic search, indexing and least-squares routines. Intensity data were corrected for Lorentz and polarization effects. Decay was observed (39%) and a linear decay correction was applied. An empirical absorption correction was applied by using the azimuthal scan method [15]. All calculations were performed using the SHELX 76 package of programs [16]. The metal atom positions were determined by direct methods and all non-hydrogen atoms located from difference Fourier syntheses. Four independent molecules were found in the asymmetric unit. The C_6H_5 groups of the PPh_3 ligands were treated as rigid groups (C–C 1.395, C–H 1.08 Å, C–C–C 120°). The final refinement of the positional and thermal parameters proceeded using anisotropic thermal parameters for all non-hydrogen atoms except the phenyl C atoms. The final difference Fourier map showed peaks not exceeding 1.1 e Å^{-3} in the vicinity of the gold atoms. Final positional and equivalent isotropic thermal parameters with their estimated standard deviations corresponding to the final least-squares refinement cycles are given in Table 4.

TABLE 3. Crystal data and experimental details for $[Fe(CO)_4(AuPPh_3)_2]$

Complex	$[Fe(CO)_4(AuPPh_3)_2]$
Formula	$C_{40}H_{30}Au_2FeO_4P_2$
M	1086.4
Crystal size (mm)	$0.15 \times 0.20 \times 0.45$
System	monoclinic
Space group	$P2_1/a$ (No. 14)
a (Å)	20.309(5)
b (Å)	18.379(3)
c (Å)	40.737(6)
β (°)	96.26(2)
V (Å^3)	15114.5
Z	16
D_c (g/cm^3)	1.91
$F(000)$	8256
Radiation (graphite monochromated (λ, Å)	Mo Kα (0.71067)
μ(Mo Kα) (cm^{-1})	79.27
Diffractometer	Enraf-Nonius CAD-4
Scan mode	ω
θ Limits (°)	2.5–23
ω Scan width (°)	$0.6 + 0.35 \mathrm{tg}\theta$
Prescan rate (° min^{-1})	5
Prescan acceptance $\sigma(I)/I$	0.5
Required $\sigma(I)/I$	0.01
Maximum scan time (s)	100
Standard reflections	3, remeasured periodically
Reflections collected	17223
Unique observed reflections ($F_o > 4\sigma(F_o)$)	10424
No. refined parameters	768
R^a, R_w^b	0.0526, 0.0574
K, g^c	1.95, 0.00590
Quality-of-fit-indicator[d]	1.21

[a] $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. [b] $R_w = [\Sigma w(F_o - F_c)^2/\Sigma w F_o^2]^{1/2}$. [c] $w = K/[\sigma^2(F) + |g|F^2]$. [d] Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{para})]^{1/2}$.

TABLE 4. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å^2) for [Fe(CO)$_4$(AuPPh$_3$)$_2$]

Atom	x	y	z	U_{eq}
Molecule 1				
Au(1)	0.34728(4)	0.19934(4)	0.34022(2)	0.0633(6)
Au(2)	0.44667(4)	0.17984(4)	0.29401(2)	0.0562(5)
Fe(1)	0.37198(14)	0.08058(14)	0.31298(7)	0.0590(19)
C(1)	0.3107(8)	0.0345(10)	0.3324(6)	0.081(16)
O(1)	0.2715(8)	0.0017(8)	0.3453(5)	0.122(15)
C(2)	0.4078(11)	0.0151(10)	0.2889(5)	0.078(16)
O(2)	0.4307(9)	-0.0297(9)	0.2737(5)	0.129(16)
C(3)	0.3214(11)	0.1276(12)	0.2815(5)	0.084(18)
O(3)	0.2871(8)	0.1554(9)	0.2615(4)	0.104(14)
C(4)	0.4329(9)	0.0845(11)	0.3470(5)	0.065(15)
O(4)	0.4721(8)	0.0831(10)	0.3692(4)	0.110(15)
P(1)	0.3125(3)	0.3076(3)	0.3589(1)	0.060(3)
C(47)	0.2247(5)	0.3063(7)	0.3627(3)	0.064(5)
C(48)	0.1838(5)	0.3647(7)	0.3523(3)	0.076(6)
C(49)	0.1163(5)	0.3622(7)	0.3560(3)	0.095(7)
C(50)	0.0897(5)	0.3012(7)	0.3702(3)	0.085(7)
C(51)	0.1306(5)	0.2428(7)	0.3806(3)	0.092(7)
C(52)	0.1981(5)	0.2453(7)	0.3769(3)	0.084(7)
C(47A)	0.3518(6)	0.3397(6)	0.3977(2)	0.055(5)
C(48A)	0.4209(6)	0.3363(6)	0.4020(2)	0.079(6)
C(49A)	0.4558(6)	0.3646(6)	0.4305(2)	0.083(7)
C(50A)	0.4217(6)	0.3962(6)	0.4548(2)	0.079(6)
C(51A)	0.3526(6)	0.3995(6)	0.4506(2)	0.062(5)
C(52A)	0.3177(6)	0.3712(6)	0.4220(2)	0.060(5)
C(47B)	0.3241(6)	0.3789(5)	0.3298(3)	0.051(5)
C(48B)	0.3159(6)	0.3625(5)	0.2962(3)	0.068(6)
C(49B)	0.3227(6)	0.4170(5)	0.2730(3)	0.090(7)
C(50B)	0.3377(6)	0.4880(5)	0.2834(3)	0.085(7)
C(51B)	0.3459(6)	0.5044(5)	0.3171(3)	0.090(7)
C(52B)	0.3391(6)	0.4498(5)	0.3402(3)	0.068(6)
P(2)	0.5098(2)	0.2655(3)	0.2718(1)	0.053(3)
C(17)	0.4615(6)	0.3161(7)	0.2394(3)	0.066(5)
C(18)	0.4787(6)	0.3870(7)	0.2316(3)	0.079(6)
C(19)	0.4436(6)	0.4232(7)	0.2051(3)	0.105(8)
C(20)	0.3912(6)	0.3884(7)	0.1864(3)	0.096(8)
C(21)	0.3739(6)	0.3174(7)	0.1942(3)	0.090(7)
C(22)	0.4091(6)	0.2813(7)	0.2207(3)	0.062(5)
C(17A)	0.5464(7)	0.3319(6)	0.2996(3)	0.056(5)
C(18A)	0.5041(7)	0.3704(6)	0.3181(3)	0.090(7)
C(19A)	0.5295(7)	0.4242(6)	0.3401(3)	0.120(9)
C(20A)	0.5972(7)	0.4394(6)	0.3436(3)	0.108(8)
C(21A)	0.6395(7)	0.4009(6)	0.3252(3)	0.120(9)
C(22A)	0.6141(7)	0.3471(6)	0.3032(3)	0.092(7)
C(17B)	0.5778(6)	0.2279(7)	0.2518(3)	0.070(6)
C(18B)	0.6089(6)	0.2683(7)	0.2290(3)	0.101(8)
C(19B)	0.6624(6)	0.2389(7)	0.2148(3)	0.094(7)
C(20B)	0.6849(6)	0.1690(7)	0.2234(3)	0.110(9)
C(21B)	0.6539(6)	0.1286(7)	0.2463(3)	0.117(9)
C(22B)	0.6003(6)	0.1580(7)	0.2605(3)	0.079(6)
Molecule 2				
Au(3)	0.49458(4)	0.33899(4)	0.04814(2)	0.0597(5)
Au(4)	0.39503(4)	0.30335(4)	0.09294(2)	0.0673(6)
Fe(2)	0.41904(14)	0.42912(15)	0.07255(8)	0.0628(19)
C(5)	0.3562(10)	0.4673(11)	0.0932(6)	0.080(17)
O(5)	0.3108(7)	0.4917(10)	0.1047(4)	0.109(13)
C(6)	0.4532(14)	0.5052(12)	0.0540(7)	0.120(24)
O(6)	0.4784(10)	0.5521(11)	0.0404(6)	0.162(20)
C(7)	0.3701(9)	0.3939(14)	0.0380(5)	0.090(19)
O(7)	0.3377(10)	0.3734(12)	0.0157(4)	0.130(17)
C(8)	0.4788(10)	0.4190(11)	0.1072(4)	0.064(15)
O(8)	0.5174(8)	0.4131(10)	0.1293(4)	0.110(15)
P(3)	0.5543(2)	0.2639(3)	0.0184(1)	0.054(3)
C(23)	0.6183(6)	0.3093(7)	-0.0012(3)	0.052(5)
C(24)	0.6465(6)	0.3726(7)	0.0130(3)	0.102(8)
C(25)	0.6944(6)	0.4101(7)	-0.0023(3)	0.115(9)
C(26)	0.7141(6)	0.3844(7)	-0.0319(3)	0.097(8)
C(27)	0.6859(6)	0.3211(7)	-0.0462(3)	0.126(10)
C(28)	0.6380(6)	0.2836(7)	-0.0309(3)	0.121(10)
C(23A)	0.5946(6)	0.1880(6)	0.0403(3)	0.059(5)
C(24A)	0.6601(6)	0.1674(6)	0.0382(3)	0.081(6)
C(25A)	0.6860(6)	0.1059(6)	0.0550(3)	0.110(8)
C(26A)	0.6463(6)	0.0649(6)	0.0739(3)	0.095(7)
C(27A)	0.5807(6)	0.0854(6)	0.0760(3)	0.097(8)
C(28A)	0.5548(6)	0.1470(6)	0.0592(3)	0.070(6)
C(23B)	0.5012(6)	0.2217(7)	-0.0145(3)	0.065(5)
C(24B)	0.4467(6)	0.2609(7)	-0.0289(3)	0.081(6)
C(25B)	0.4044(6)	0.2303(7)	-0.0545(3)	0.091(7)
C(26B)	0.4166(6)	0.1603(7)	-0.0657(3)	0.096(8)
C(27B)	0.4712(6)	0.1211(7)	-0.0513(3)	0.111(9)
C(28B)	0.5135(6)	0.1518(7)	-0.0258(3)	0.071(6)
P(4)	0.3577(3)	0.1922(3)	0.1076(1)	0.069(4)
C(29)	0.3702(6)	0.1236(7)	0.0765(3)	0.068(6)
C(30)	0.3645(6)	0.1467(7)	0.0437(3)	0.074(6)
C(31)	0.3707(6)	0.0966(7)	0.0185(3)	0.097(8)
C(32)	0.3826(6)	0.0235(7)	0.0261(3)	0.105(8)
C(33)	0.3883(6)	0.0004(7)	0.0589(3)	0.104(8)
C(34)	0.3821(6)	0.0505(7)	0.0841(3)	0.087(7)
C(29A)	0.2706(4)	0.1944(7)	0.1116(3)	0.065(5)
C(30A)	0.2314(4)	0.1323(7)	0.1062(3)	0.075(6)
C(31A)	0.1641(4)	0.1351(7)	0.1103(3)	0.084(7)
C(32A)	0.1361(4)	0.2001(7)	0.1198(3)	0.077(6)
C(33A)	0.1753(4)	0.2622(7)	0.1251(3)	0.084(7)
C(34A)	0.2426(4)	0.2593(7)	0.1211(3)	0.080(6)
C(29B)	0.3960(7)	0.1527(7)	0.1460(3)	0.077(6)
C(30B)	0.3609(7)	0.1183(7)	0.1692(3)	0.073(6)
C(31B)	0.3950(7)	0.0864(7)	0.1972(3)	0.110(9)
C(32B)	0.4640(7)	0.0891(7)	0.2019(3)	0.098(8)
C(33B)	0.4991(7)	0.1235(7)	0.1787(3)	0.115(9)
C(34B)	0.4650(7)	0.1554(7)	0.1508(3)	0.102(8)
Molecule 3				
Au(5)	0.07704(4)	0.80864(4)	0.45686(2)	0.0463(4)
Au(6)	0.18586(4)	0.77082(4)	0.41962(2)	0.0525(5)
Fe(3)	0.15569(12)	0.90032(13)	0.43504(7)	0.0482(16)
C(9)	0.2060(10)	0.9760(12)	0.4264(5)	0.063(14)
O(9)	0.2370(8)	1.0254(9)	0.4214(4)	0.101(13)
C(10)	0.0887(8)	0.9493(9)	0.4499(5)	0.050(12)
O(10)	0.0513(8)	0.9862(8)	0.4605(5)	0.110(14)
C(11)	0.2108(9)	0.8662(10)	0.4678(5)	0.063(14)
O(11)	0.2448(8)	0.8454(9)	0.4898(4)	0.097(13)
C(12)	0.1264(10)	0.8821(11)	0.3937(4)	0.067(15)
O(12)	0.1047(9)	0.8730(10)	0.3667(4)	0.105(14)
P(5)	0.0060(2)	0.7308(2)	0.4785(1)	0.047(3)
C(35)	-0.0595(5)	0.7734(6)	0.4974(3)	0.047(4)
C(36)	-0.0936(5)	0.7360(6)	0.5202(3)	0.062(5)
C(37)	-0.1459(5)	0.7697(6)	0.5338(3)	0.079(6)
C(38)	-0.1640(5)	0.8407(6)	0.5248(3)	0.093(7)
C(39)	-0.1299(5)	0.8781(6)	0.5020(3)	0.088(7)
C(40)	-0.0776(5)	0.8444(6)	0.4884(3)	0.070(6)

(*continued*)

TABLE 4. (*continued*)

Atom	x	y	z	U_{eq}
C(35A)	−0.0347(5)	0.6711(5)	0.4475(2)	0.046(4)
C(36A)	0.0056(5)	0.6338(5)	0.4276(2)	0.059(5)
C(37A)	−0.0229(5)	0.5897(5)	0.4020(2)	0.067(6)
C(38A)	−0.0916(5)	0.5830(5)	0.3963(2)	0.075(6)
C(39A)	−0.1319(5)	0.6204(5)	0.4162(2)	0.069(6)
C(40A)	−0.1035(5)	0.6645(5)	0.4418(2)	0.048(4)
C(35B)	0.0471(6)	0.6716(6)	0.5097(2)	0.053(5)
C(36B)	0.0220(6)	0.6029(6)	0.5159(2)	0.063(5)
C(37B)	0.0514(6)	0.5614(6)	0.5422(2)	0.080(6)
C(38B)	0.1059(6)	0.5887(6)	0.5623(3)	0.077(6)
C(39B)	0.1310(6)	0.6574(6)	0.5561(2)	0.072(6)
C(40B)	0.1016(6)	0.6988(6)	0.5298(2)	0.067(6)
P(6)	0.2112(2)	0.6572(2)	0.4028(1)	0.049(3)
C(41)	0.1881(6)	0.5863(6)	0.4296(3)	0.054(5)
C(42)	0.1984(6)	0.6004(6)	0.4634(3)	0.064(5)
C(43)	0.1838(6)	0.5472(6)	0.4860(3)	0.074(6)
C(44)	0.1589(6)	0.4799(6)	0.4747(3)	0.074(6)
C(45)	0.1485(6)	0.4658(6)	0.4409(3)	0.091(7)
C(46)	0.1631(6)	0.5190(6)	0.4184(3)	0.071(6)
C(41A)	0.2980(4)	0.6427(6)	0.3981(3)	0.052(5)
C(42A)	0.3326(4)	0.5810(6)	0.4103(3)	0.056(5)
C(43A)	0.4003(4)	0.5749(6)	0.4077(3)	0.076(6)
C(44A)	0.4335(4)	0.6303(6)	0.3929(3)	0.083(7)
C(45A)	0.3989(4)	0.6920(6)	0.3807(3)	0.097(8)
C(46A)	0.3312(4)	0.6982(6)	0.3833(3)	0.068(6)
C(41B)	0.1674(6)	0.6353(7)	0.3634(3)	0.063(5)
C(42B)	0.1934(6)	0.5860(7)	0.3421(3)	0.072(6)
C(43B)	0.1558(6)	0.5652(7)	0.3129(3)	0.093(7)
C(44B)	0.0924(6)	0.5936(7)	0.3049(3)	0.101(8)
C(45B)	0.0664(6)	0.6428(7)	0.3262(3)	0.128(10)
C(46B)	0.1040(6)	0.6637(7)	0.3554(3)	0.092(7)
Molecule 4				
Au(7)	0.65662(4)	−0.21541(4)	0.16607(2)	0.0582(5)
Au(8)	0.77305(4)	−0.14696(4)	0.20104(2)	0.0561(5)
Fe(4)	0.67943(13)	−0.07967(14)	0.16719(7)	0.0534(17)
C(13)	0.6028(8)	−0.0566(12)	0.1473(5)	0.080(16)
O(13)	0.5514(7)	−0.0455(10)	0.1339(4)	0.103(13)
C(14)	0.7137(12)	0.0077(10)	0.1661(6)	0.107(20)
O(14)	0.7393(14)	0.0632(10)	0.1681(9)	0.292(33)
C(15)	0.7181(11)	−0.1182(11)	0.1345(5)	0.080(17)
O(15)	0.7406(6)	−0.1395(8)	0.1116(4)	0.080(11)
C(16)	0.6587(13)	−0.0844(16)	0.2077(4)	0.105(21)
O(16)	0.6390(11)	−0.0862(13)	0.2331(4)	0.156(19)
P(7)	0.6267(3)	−0.3328(3)	0.1549(1)	0.062(4)
C(59)	0.6600(7)	−0.3657(7)	0.1183(3)	0.064(5)
C(60)	0.7246(7)	−0.3470(7)	0.1130(3)	0.087(7)
C(61)	0.7512(7)	−0.3716(7)	0.0849(3)	0.118(9)
C(62)	0.7131(7)	−0.4150(7)	0.0620(3)	0.112(9)
C(63)	0.6485(7)	−0.4337(7)	0.0672(3)	0.116(9)
C(64)	0.6220(7)	−0.4091(7)	0.0954(3)	0.084(7)
C(59A)	0.5392(5)	−0.3413(8)	0.1463(4)	0.065(5)
C(60A)	0.5039(5)	−0.2814(8)	0.1327(4)	0.144(12)
C(61A)	0.4351(5)	−0.2847(8)	0.1264(4)	0.136(11)
C(62A)	0.4015(5)	−0.3479(8)	0.1337(4)	0.117(9)
C(63A)	0.4368(5)	−0.4078(8)	0.1473(4)	0.118(9)
C(64A)	0.5057(5)	−0.4045(8)	0.1536(4)	0.093(7)
C(59B)	0.6532(7)	−0.4001(8)	0.1852(3)	0.070(6)
C(60B)	0.6596(7)	−0.4733(8)	0.1771(3)	0.122(9)
C(61B)	0.6795(7)	−0.5239(8)	0.2018(3)	0.141(11)
C(62B)	0.6929(7)	−0.5012(8)	0.2345(3)	0.116(9)
C(63B)	0.6864(7)	−0.4280(8)	0.2426(3)	0.103(8)
C(64B)	0.6665(7)	−0.3774(8)	0.2180(3)	0.095(7)
P(8)	0.8478(2)	−0.2135(3)	0.2341(1)	0.056(3)
C(53)	0.9179(6)	−0.1652(7)	0.2540(4)	0.069(6)
C(54)	0.9536(6)	−0.1211(7)	0.2344(4)	0.090(7)
C(55)	1.0096(6)	−0.0840(7)	0.2485(4)	0.110(9)
C(56)	1.0301(6)	−0.0911(7)	0.2822(4)	0.091(7)
C(57)	0.9944(6)	−0.1352(7)	0.3018(4)	0.149(12)
C(58)	0.9383(6)	−0.1723(7)	0.2877(4)	0.133(11)
C(53A)	0.8818(7)	−0.2870(6)	0.2130(3)	0.067(6)
C(54A)	0.9496(7)	−0.3006(6)	0.2141(3)	0.092(7)
C(55A)	0.9721(7)	−0.3591(6)	0.1966(3)	0.139(11)
C(56A)	0.9268(7)	−0.4038(6)	0.1779(3)	0.097(8)
C(57A)	0.8590(7)	−0.3901(6)	0.1768(3)	0.109(9)
C(58A)	0.8365(7)	−0.3317(6)	0.1944(3)	0.086(7)
C(53B)	0.8101(6)	−0.2567(7)	0.2668(3)	0.068(6)
C(54B)	0.8408(6)	−0.3144(7)	0.2487(3)	0.079(6)
C(55B)	0.8113(6)	−0.3452(7)	0.3107(3)	0.083(7)
C(56B)	0.7510(6)	−0.3182(7)	0.3189(3)	0.091(7)
C(57B)	0.7202(6)	−0.2605(7)	0.3011(3)	0.095(7)
C(58B)	0.7498(6)	−0.2297(7)	0.2750(3)	0.072(6)

Supplementary material

Additional data available from the Cambridge Crystallographic Data Centre comprise Tables of positional parameters, calculated hydrogen coordinates, anisotropic thermal parameters and complete bond distances and angles.

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