Structural Studies on Mixed Iron–Gold Clusters with Bidentate Tertiary Phosphine Ligands

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Structural analyses on $[Fe(CO)_4Au_2(dppm)]_2$ (**1a**) [dppm = $(Ph_2P)_2CH_2$] and $[Fe(CO)_4Au_2(dppe)]_2$ (**1b**) [dppe = $(Ph_2P)_2C_2H_4$] have demonstrated that the bite angle of the phosphine ligands exerts a profound influence on the cluster geometry, since (**1a**) has a rhomboid of gold atoms with μ_2-$Fe(CO)_4$ moieties, and (**1b**) has well separated Au_2Fe triangles.

Lewis, Stone, and their co-workers[1,2] have demonstrated that the $AuPR_3$ fragment (R = phenyl or alkyl) can be readily introduced into metal carbonyl clusters and *X*-ray crystallographic studies on the resultant mixed metal clusters have demonstrated that this fragment is capable of forming multicentre bridge bonds either with other metal atoms or with

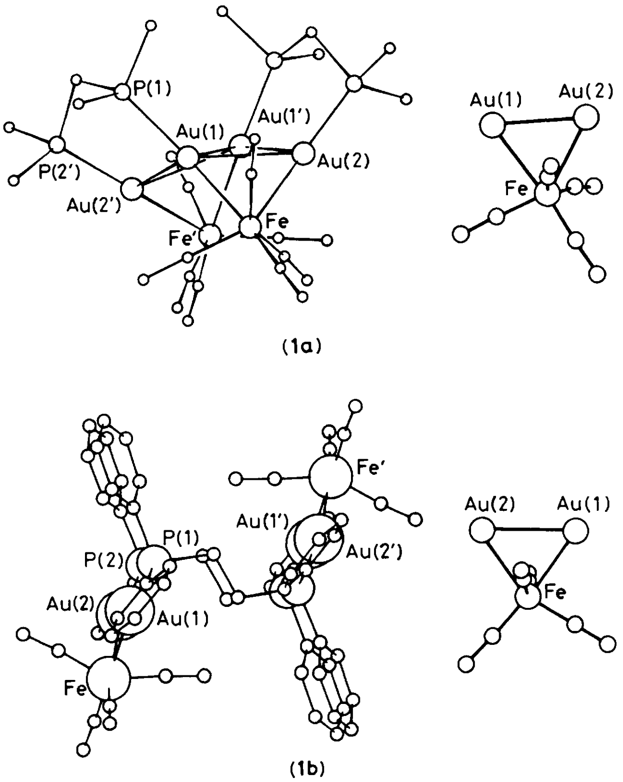

Figure 1. The molecular structures of $[Fe(CO)_4Au_2(dppm)]_2$ (**1a**) and $[Fe(CO)_4Au_2(dppe)]_2$ (**1b**). On the right hand side the inner co-ordination geometries about the iron atoms are shown which emphasise the rotational distortion of the $Fe(CO)_4$ fragment in (**1a**).

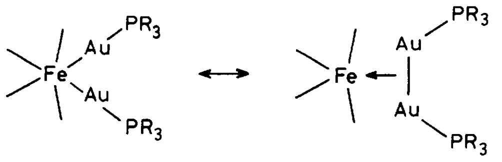

Figure 2

other $AuPR_3$ fragments.[3] Consequently the initial view that the $AuPR_3$ fragment forms structures directly analogous to hydrido-cluster compounds[4] has been superceded by a more general analysis of the bonding capabilities of this fragment which permits the occurrence of multicentre two-electron interactions.[5] To date the structural analyses on gold–transition metal cluster compounds have concentrated on derivatives based on monodentate phosphine ligands.[3] It is the purpose of this communication to demonstrate the interesting structural complications which arise when the PR_3 ligands are replaced by bidentate phosphine ligands.

$[Fe(CO)_4Au_2(PPh_3)_2]$

(**1c**)

The complexes $[Fe(CO)_4Au_2(dppm)]$ (**1a**) and $[Fe(CO)_4Au_2(dppe)]$ (**1b**) were synthesised from $Na_2Fe(CO)_4$ and Au_2Cl_2-(L–L) [L–L = dppm, $(Ph_2P)_2CH_2$, or dppe, $(Ph_2P)_2C_2H_4$] in a manner reported by Nyholm *et al.*[6] for $[Fe(CO)_4Au_2(PPh_3)_2]$ (**1c**). Complexes (**1b**) and (**1c**) are both yellow crystalline solids with similar i.r. characteristics [ν(CO) ($CHCl_3$) (**1b**) 1885, 1932, and 1996 cm^{-1}, (**1c**) 1888, 1928, and 2000 cm^{-1}], but (**1a**) is a red crystalline solid with somewhat different i.r. characteristics [ν(CO) ($CHCl_3$) 1933 and 1994 cm^{-1}]. *X*-Ray crystallographic studies on (**1a**) and (**1b**) have demonstrated that these differences in physical properties originate from quite different solid state structures.†

Both complexes (**1a**) and (**1b**) crystallise in the same space group, *C*2/*c*, as dimeric $[Fe(CO)_4Au_2(L\text{–}L)]_2$ molecules, but since the former lies on a crystallographically imposed two-fold axis, and the latter on a centre of symmetry the structures differ markedly as illustrated in Figure 1. In (**1b**) the two virtually parallel $P\text{–}CH_2\text{–}CH_2\text{–}P$ moieties function as bridging ligands between two well separated (>6.0 Å) $Au_2Fe(CO)_4$ fragments leading to a fourteen-membered ring in a *pseudo*-chair conformation. The Au(1)–Au(2) distance of 2.977(1) Å in (**1b**) suggests a weak gold–gold interaction since it is longer than the Au–Au distances found in elemental gold (2.884 Å) but lies within the range commonly found in cluster compounds of gold (2.60—3.10 Å).[3] Therefore, the bonding in the Au_2Fe triangle is perhaps best described as intermediate between the 2-centre 2-electron and 3-centre 2-electron representations illustrated in Figure 2.[5]

In contrast the structure of (**1a**) contains an approximate rhombus of gold atoms, which is folded about the Au(1)–Au(1′) diagonal of length 3.041(2) Å. The dihedral angle between the Au(1)–Au(2)–Au(1′) and Au(1)–Au(2′)–Au(1′) planes is 158.3(3)°. The $Fe(CO)_4$ and dppm ligands span the four edges of the rhombus lying alternately above and below the Au_4 mean plane in a manner reminiscent of that reported for $Au_4(S_2CMe)_4$.[7] The Au(1)–Au(2) bond which is bridged by $Fe(CO)_4$ is shorter than the corresponding bond in (**1b**) suggesting a greater contribution from the 3-centre 2-electron representation illustrated in Figure 2. The Au(1)–Au(2′) edge, which is bridged by dppm, has a length of 3.163(1) Å, is longer than that generally associated with Au–Au bonds, and approximately 0.2 Å longer than that reported for $[Au_2(dppm)_2Cl_2]$.[8]

The disposition of the dppm and $Fe(CO)_4$ moieties in (**1a**) about the Au_4 rhomboid results in substantial steric crowding. This has its most dramatic manifestation in the relative orientations of the $Fe(CO)_4$ fragments with respect to the Au(1)–Au(2) bonds. The $Fe(CO)_4$ fragments have similar local geometries in (**1a**) and (**1b**) and can be described as intermediate between tetrahedral and C_{2v} *cis*-divacant octahedral, with the C–Fe–C angles varying between 92(1) and 144(1)° in (**1a**) and 99(1) and 147(1)° in (**1b**). In (**1b**), where the $Fe(CO)_4$ units are well separated, the overall $Fe(CO)_4Au_2$ geometry can be described as bicapped tetrahedral (see Figure 1) and in that respect resembles closely those reported for $Fe(CO)_4H_2$[9] and $Fe(CO)_4[Au(PPh_3)]_2$.[10] In (**1a**) the steric overcrowding pre-

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† *Crystal data:* (**1a**), $C_{58}H_{44}Au_4Fe_2O_8P_4\cdot C_3H_8O$, M = 1951.5, monoclinic, space group *C*2/*c*, a = 14.250(5), b = 19.431(4), c = 24.810(11) Å, β = 103.44(3)°, U = 6681.2 Å³, Z = 4, D_c = 1.94 g cm^{-3}, $\mu(\text{Mo-K}_{\bar{\alpha}})$ = 95.96 cm^{-1}, λ = 0.71069 Å. The 2274 observed reflections $[I \geqslant 3\sigma(I)]$ having $2\theta \leqslant 46°$ were measured on an ENRAF-NONIUS CAD4-F automatic diffractometer. The structure was solved by heavy atom methods and refined by blocked matrix least squares (Au,Fe,P anisotropic; C,O isotropic; H's calculated) to a final residual R = 0.042, R_w = 0.045. The asymmetric unit also contains a disordered molecule of isopropyl alcohol. (**1b**), $C_{60}H_{48}Au_4Fe_2O_8P_4\cdot C_4H_8O$, M = 1988.6, monoclinic, space group *C*2/*c*, a = 15.823(3), b = 15.858(4), c = 25.708(3) Å, β = 95.88(2)°, U = 6416 Å³, Z = 4, D_c = 2.06 g cm^{-3}, μ $(\text{Mo-K}_{\bar{\alpha}})$ = 99.91 cm^{-1}, λ = 0.71069 Å. 2485 reflections having $2\theta \leqslant 40°$. The data were collected and the structure solved as described above and refined to a final residual of R = 0.035, R_w = 0.046. The asymmetric unit also contains a molecule of tetrahydrofuran. The molecules of isopropyl alcohol and tetrahydrofuran found in the asymmetric units originated from the solvents used to recrystallise the compounds. Atomic coordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

cludes this geometry and the steric repulsions between the carbonyl ligands are minimised by the rotation of the $Fe(CO)_4$ fragment towards Au(2) illustrated in Figure 1. This leads to a most unusual edge bridged trigonal bipyramidal geometry about the iron and an asymmetry in the Fe–Au bond lengths, *viz* Fe–Au(1) 2.608(3) and Fe–Au(2) 2.539(3) Å; *cf.* 2.524(2) and 2.535(2) Å in (**1b**).‡

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‡ A referee has indicated an alternative representation for the structures (**1a**) and (**1b**) based on the view that the Au_2 unit occupies a single co-ordination site, as in the 3-centre 2-electron representation. The geometry in (**1a**) then approximates to square pyramidal, with the Au_2 unit in the basal plane, and that in (**1b**) approximates to trigonal bipyramidal. The geometries therefore reflect the alternative geometries available to five-co-ordinate d^8 transition metal complexes.

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