An Iron-57 and Gold-197 Mössbauer Spectroscopic Investigation of the Bonding in Two Gold–Iron Cluster Compounds

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Iron-57 and gold-197 Mössbauer spectroscopic data are reported for the compounds $[Fe(CO)_4\{Au[P(C_6H_{11})_3]\}_2]$ and $[Fe(CO)_4\{Au[P(C_6H_{11})_3]\}_3]PF_6$. The data are consistent with localised bonding for the former and four-centre two-electron cluster bonding for the latter.

Gold forms a wide variety of cluster compounds, both homo- and hetero-nuclear, for which the major characterisational technique is *X*-ray crystallography.[1,2] This is because, in many cases, structural data relating to the thermodynamically stable form can be obtained only from measurements on solid samples. Solid-state ^{31}P n.m.r.[3] and ^{197}Au Mössbauer data[2,4] have been shown to be consistent with established structures. In principle, both can detect non-equivalent ligand or gold sites but, for homonuclear clusters, ^{197}Au Mössbauer spectroscopy lacks sufficient resolution to distinguish crystallographically non-equivalent gold atoms which bear the same peripheral ligand. We have recently shown that such sites can be distinguished in gold–ruthenium clusters,[5] and that there is a good correlation between the Mössbauer parameters and the gold–ruthenium bond lengths and the connectivities of the gold atom to other metal atoms in the cluster.[6] No data have yet been reported in which two metals of a heteronuclear transition-metal cluster have both been investigated by Mössbauer spectroscopy, and we now present ^{57}Fe and ^{197}Au data for two gold–iron cluster compounds, $[Fe(CO)_4\{Au[P(C_6H_{11})_3]\}_2]$ and $[Fe(CO)_4\{Au[P(C_6H_{11})_3]\}_3]PF_6$.

Experimental

Mössbauer spectra were obtained as described previously, using ^{197}Pt and $^{57}Co/Rh$ sources.[7,8] For the ^{197}Au spectra, both source and sample were held at 4.2 K, while for the ^{57}Fe spectra the sample was cooled to *ca.* 80 K. Isomer shifts are quoted relative to the elemental metal in each case.

$[Fe(CO)_4\{Au[P(C_6H_{11})_3]\}_2]$ was prepared by stirring a suspension of $Na_2[Fe(CO)_4]\cdot 1.5diox$ (diox = 1,4-dioxane) (0.054 g, 0.16 mmol) in tetrahydrofuran (40 cm^3) with $[AuCl\{P(C_6H_{11})_3\}]$ (0.16 g, 0.32 mmol) for 2 h. The solvent was removed and the residue extracted with benzene (25 cm^3). Addition of ethanol (20 cm^3) to the extract, followed by concentration *in vacuo*, gave pale yellow crystals (0.14 g, 78%) (Found: C, 43.0; H 6.0. $C_{40}H_{66}Au_2FeO_4P_2$ requires C, 42.8; H, 5.9%). I.r.: ν(CO) at 1 985s, 1 915s, 1 890s, and 1 858s cm^{-1} (Nujol mull).

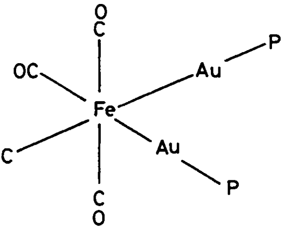
$[Fe(CO)_4\{Au[P(C_6H_{11})_3]\}_3]PF_6$ was obtained by stirring a benzene (30 cm^3) solution of $[Fe(CO)_4\{Au[P(C_6H_{11})_3]\}_2]$ (0.13 g, 0.12 mmol) with $[AuCl\{P(C_6H_{11})_3\}]$ (0.06 g, 0.12 mmol) and an excess of $TlPF_6$ (0.21 g, 0.6 mmol). A pale yellow solid was deposited over 4 h, which was filtered off and extracted with dichloromethane (20 cm^3). Addition of ethanol (20 cm^3) to the extract, followed by concentration *in vacuo* gave the product (0.15 g, 72%) (Found: C, 39.9; H, 5.7. $C_{58}H_{99}Au_3FeF_6O_4P_4$ requires C, 39.9; H, 5.7%). I.r.: ν(CO) at 2 018s and 1 901s,br cm^{-1} (Nujol mull). ^{31}P-$\{^1H\}$ N.m.r. gave a singlet at 62.3 p.p.m. to high frequency of $P(OMe)_3$.

Results and Discussion

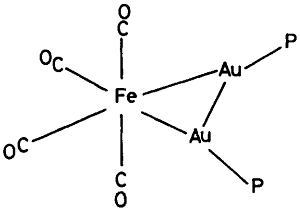
(*a*) $[Fe(CO)_4\{Au[P(C_6H_{11})_3]\}_2]$.—The molecular structure of $[Fe(CO)_4\{Au[P(C_6H_{11})_3]\}_2]$ is not known, but it may reasonably be presumed to be analogous to the corresponding triphenylphosphine derivative which embodies a distorted octahedral $Fe(CO)_4Au_2$ unit.[9] The observed i.r. spectrum is consistent with such a structure. In the PPh_3 derivative, the Au–Fe–Au bond angle is only 73°, which leads to an Au–Au distance of 302.8 pm, possibly indicating some bonding interaction between the two gold atoms. Such interactions are common even in compounds which appear to be monomeric.[10] Thus, it is not immediately clear whether $[Fe(CO)_4\{Au[P(C_6H_{11})_3]\}_2]$ should be treated as an $FeAu_2$ trimetallic cluster or whether the gold–gold interaction is incidental. In the latter case, the isolobal analogy[11] would suggest that only the Au–Fe bonds are electronically significant, and that the compound is analogous to other $[Fe(CO)_4X_2]$ cases, *e.g.* X = Cl or H. The iron atom would then be regarded as an essentially monomeric 18-electron system [model (**I**)]. A trinuclear cluster could be regarded as being composed of a neutral $Fe(CO)_4$ group and a $(C_6H_{11})_3P$–Au–Au–$P(C_6H_{11})_3$ unit, the latter being formed by pairing the single electron on each gold atom. Interaction of the Au–Au bond pair with an empty orbital on the iron atom would complete the cluster bonding. Such a system has some analogy with an $[Fe(CO)_4(\eta^2\text{-alkene})]$ complex. These complexes usually adopt an equatorially substituted trigonal-bipyramidal configuration with alkene-to-iron donation in a bond between the C–C π-bonding orbital and a σ-acceptor (dsp^3) orbital on iron plus, possibly, back-donation from a filled d_π orbital on iron to the π* orbital of the alkene. In the present case, forward- and back-donation would involve the Au–Au σ- and σ*-orbitals [model (**II**)]. In the limit of strong back-donation, this model becomes indistinguishable from model (**I**).

The ^{197}Au Mössbauer parameters (i.s.$_{Au}$ = 3.80 mm s^{-1}, q.s. = 7.76 mm s^{-1}) (i.s. = isomer shift, q.s. = quadrupole splitting) are similar to those for many other clusters,[2,4] although the i.s. is at the top of the range. Both parameters are consistent with effectively linear two-co-ordination and univalency,[12] which could be interpreted in favour of model (**I**). On the other hand, many systems are known in which a significant Au–Au interaction apparently has no effect on the Mössbauer parameters,[2] and such an interpretation is unsafe.

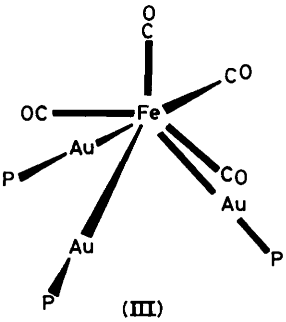
Distinction between the models can, however, be made on the basis of the ^{57}Fe parameters. The observed values (see Table) are much closer to those of *cis*-$[Fe(CO)_4X_2]$ systems than to those of $[Fe(CO)_4L]$. The latter always give substantial quadrupole splittings, which arise principally from the non-bonding d^8 configuration. In model (**I**), the iron has a six-co-ordinate d^6 configuration in which the non-bonding electrons



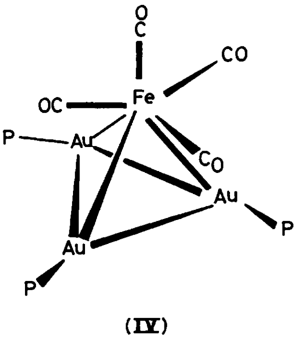
(I)



(II)



(III)



(IV)

Table. ^{57}Fe Mössbauer data for iron–carbonyl complexes

Complex	i.s.$_{\text{Fe}}$/mm s^{-1}	q.s./mm s^{-1}	Ref.
$[Fe(CO)_4\{Au[P(C_6H_{11})_3]\}_2]$	−0.01	0.16	*a*
$[Fe(CO)_4\{Au[P(C_6H_{11})_3]\}_3]PF_6$	−0.01	1.48	*a*
$[Fe(CO)_4Cl_2]$	0.05	0.26	*b*
$[Fe(CO)_4Br_2]$	0.06	0.31	*b*
$[Fe(CO)_4I_2]$	0.06	0.32	*b*
$[Fe(CO)_4H_2]$	−0.18	0.55	*c*
$[Fe(CO)_4(SnCl_3)_2]$	0.03	0.45	*d*
$[Fe(CO)_4(SnBr_3)_2]$	0.01	0.46	*d*
$[Fe(CO)_4(SnI_3)_2]$	0.03	0.38	*d*
$Na_2[Fe(CO)_4]$	−0.18	0.00	*e*
$[Fe(CO)_5]$	−0.09	2.57	*e*
$[Fe(CO)_4(PPh_3)]$	−0.07	1.36	*f*
$[NEt_4][Fe(CO)_4H]$	−0.17	1.41	*e*
$[Fe(CO)_4(MeO_2CCH{=}CHCO_2Me)]$	0.01	1.54	*g*
$[Fe(CO)_4\{H_2C{=}CHCO(NMe_2)\}]$	0.00	1.65	*g*
$[Fe(CO)_4(PhCH{=}CHCHO)]$	−0.01	1.75	*f*
$[Fe(CO)_4(anapth)]$[h]	−0.01	1.78	*f*

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contribute nothing to the electric-field gradient (e.f.g.), and the quadrupole splitting arises entirely from the dissimilarity in iron–ligand bonds. Quadrupole splittings in such systems are modest.

For the data listed in the Table, there is almost certainly a change in sign of the e.f.g. for *cis*-$[Fe(CO)_4X_2]$ between X = Cl, Br or I and X = H. On the assumption that the sign of the e.f.g. for the digold compound is the same as that for the dihydride, both the i.s. and the q.s. indicate that the $Au\{P(C_6H_{11})_3\}$ group acts as a ligand of donor power intermediate between these extremes. The ^{197}Au parameters also suggest considerable polarity for the Fe–Au bond, since they are comparable with data for complexes of the type $[AuX(PR_3)]$ in which X is a very weak donor.[12]

(*b*) $[Fe(CO)_4\{Au[P(C_6H_{11})_3]\}_3]PF_6$.—The structure of the $[Fe(CO)_4\{Au[P(C_6H_{11})_3]\}_3]^+$ cation is not known, but is probably analogous to that of $[V(CO)_5\{Au(PPh_3)\}_3]$, which has a tetrahedral VAu_3 skeleton.[13] The observed i.r. spectrum is consistent with effective C_{3v} symmetry at the iron atom. In this case, the formation of three localised Fe–Au bonds [model (**III**)] would give the iron atom an 18-electron configuration, but would involve seven-co-ordination which is without precedent for iron–carbonyl complexes involving only monodentate ligands. A more plausible description [model (**IV**)] is in terms of an association between a neutral $Fe(CO)_4$ fragment and an $[\{Au[P(C_6H_{11})_3]\}_3]^+$ unit. The latter could be bonded by overlap of three (Au)sp_z hybrids pointing towards the centre of the triangular unit, which would give rise to one occupied bonding orbital (a_1') and a degenerate pair of antibonding orbitals (e').[11] Overlap between the a_1' orbital and a vacant dsp^3 hybrid orbital on $Fe(CO)_4$ would then complete the cluster bonding. Such a description is equivalent to that of a monosubstituted iron pentacarbonyl in which the Au_3 unit acts as a single ligand. In principle, back-donation could occur between filled (Fe)d_π orbitals and the vacant e' antibonding orbitals of the Au_3 triangle; if this were significant, the description would approach that of model (**III**), except that Au–Au bonding would be retained.

The ^{197}Au Mössbauer parameters (i.s.$_{\text{Au}}$ = 3.26 mm s^{-1}, q.s. = 7.22 mm s^{-1}) are not inconsistent with either model, but the i.s. is rather low compared to the q.s. Such behaviour is seen in gold(I) systems with co-ordination numbers greater than two,[12] and might indicate that the gold atoms are sensitive to the Au–Au interactions as well as to the Au–Fe bond.[2] On the basis of model (**IV**), the low i.s. would be attributed to the three-centre two-electron bond of the Au_3 unit giving a low (Au)6*s* population, further diminished by donation to the iron atom. The ^{197}Au data thus support model (**IV**).

The ^{57}Fe data (see Table) show a pronounced quadrupole splitting, consistent with the substituted iron pentacarbonyl model, (**IV**). Both parameters are in the range observed for equatorially substituted $Fe(CO)_4$–alkene complexes;[14] an analogous structure is possible for the trigold complex, but seems unlikely on steric grounds, and is not supported by the i.r. data. If the structure is more akin to an axially substituted trigonal bipyramid, the relatively small value of the q.s. suggests a strong σ-interaction, comparable to that by a hydride ligand, as is also indicated by the ^{197}Au data. However, the i.s.$_{\text{Fe}}$ is considerably higher than for $[Fe(CO)_4H]^-$, which may indicate a degree of π involvement ($d_\pi \rightarrow e'$).

Conclusions

The ^{57}Fe and ^{197}Au Mössbauer data for $[Fe(CO)_4\{Au[P(C_6H_{11})_3]\}_2]$ are consistent with the presence of two localised Fe–Au bonds in a conventional *cis*-$[Fe(CO)_4X_2]$ structure. For $[Fe(CO)_4\{Au[P(C_6H_{11})_3]\}_3]^+$, the data suggest a tetrahedral $FeAu_3$ cluster structure with delocalised bonding.

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