Gold-197 Mössbauer Spectra of Some Gold–Ruthenium Cluster Compounds

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The ^{197}Au Mössbauer spectra of nine cluster compounds containing AuL (L = PPh_3 or $\frac{1}{2}Ph_2PCH_2PPh_2$) and $Ru(CO)_3$ groups are reported. In three cases, separate signals are resolved for non-equivalent $Au(PPh_3)$ groups within the cluster. Relative intensities of the two sub-spectra are correlated with estimates of the recoil-free fractions of the two types of atom. For the whole series, the isomer shift and quadrupole splitting become smaller as the number of contacts between the gold atoms and their neighbours increases, and the parameters correlate well with the average Au–Ru bond lengths.

Gold forms a large number of homonuclear cluster compounds, with nuclearities ranging from four to fifty-five,[1,2] and recently a growing number of heteronuclear clusters containing gold and another transition metal have been reported.[2] In general, the metal skeletons of these species are very flexible. The solid-state geometry of the cluster core can sometimes be significantly altered by small changes in the nature of the counter ion and/or the attached phosphine ligand,[2,3] and two examples of skeletal isomerism have recently been reported.[4] In solution, the metal frameworks of many clusters, both homonuclear and heteronuclear, are stereochemically non-rigid.[2,5] When the clusters contain tertiary phosphine ligands, this fluxionality causes the $^{31}P-\{^1H\}$ n.m.r. spectra of solutions to be much simpler than anticipated,[2,5] and correlations with crystallographically determined structures can often be made only by solid-state n.m.r. studies.[6] Indeed, *X*-ray diffraction is normally the only definitive technique for the structural characterization of gold cluster compounds.[2]

Mössbauer spectra, using ^{197}Au, have been recorded for many homonuclear gold clusters.[1,7] Gold atoms bonded to different types of ligand give resolved sub-spectra, but the parameters are relatively insensitive to the number of Au–Au contacts and show only slight variation with the size of the cluster. In a number of compounds, gold atoms bearing the same external ligands occupy geometrically non-equivalent sites within the cluster, but resolved signals have been reported in only one case.†

Prior to our work, no Mössbauer data had been published for heteronuclear gold clusters. However, we anticipated that the more marked differences between the gold sites in these species would make their Mössbauer spectra more sensitive to structural effects. Therefore, we have undertaken the study of a range of gold–ruthenium heteronuclear clusters, including some containing geometrically non-equivalent $Au(PR_3)$ groups (PR_3 = PPh_3 or $\frac{1}{2}Ph_2PCH_2PPh_2$). We now report that separate signals can often be resolved for these atoms, and that the observed isomer shift (i.s.), relative to gold metal, and quadrupole splitting (q.s.) values provide information about the bonding modes of the $Au(PR_3)$ units within the cluster. Data for three of the compounds have been communicated previously.[8]

Experimental

The compounds were prepared by reported methods (see Table 1).[9–16] Mössbauer spectra were recorded as described previously,[17] with the source and sample immersed in liquid helium, using *ca.* 25 mg Au cm^{-2}. Isomer shifts are quoted relative to metallic gold at 4.2 K. In most cases, the spectra were fitted as two unconstrained Lorentzian lines. For spectra which appeared to contain two heavily overlapped doublets, it was necessary to constrain the lines in pairs (equal widths and intensities); attempts at unconstrained two-doublet fits failed to converge.

Results and Discussion

All the compounds studied here have been characterized crystallographically or are closely related to previously structurally characterized compounds (see Table 1). All involve $Au(PPh_3)$ or $Au(\mu-Ph_2PCH_2PPh_2)Au$ and $Ru(CO)_3$ groups together with, in some cases, bridging hydride, acyl, alkynyl, or sulphide ligands.

In the clusters selected, the gold atoms have various patterns of connectivity to neighbouring metal atoms and, in two cases, to hydride ligands: 2Ru, 2Ru + Au, 3Ru + 2Au, 3Ru + Au + H, and 3Ru + 2Au + H. Clusters (**1**)—(**3**) contain only single gold atoms, and the two gold atoms in (**4**) are crystallographically equivalent. All the other clusters have geometrically non-equivalent gold atoms. However, the two gold atoms in (**6**) are rendered non-equivalent only by the position of one of the hydride ligands, and there are only small differences in the Au–Ru bond lengths (Table 1). Although the gold atoms do occupy geometrically distinct sites in the metal core of (**5**), the number and nature of the neighbouring atoms (2Ru + Au) and the mean Au–Ru bond lengths are the same in each case. In all these clusters, the Mössbauer spectra are simple doublets with normal linewidths.

In clusters (**7**)—(**9**), the differences between the distinct gold sites are much more marked than in (**5**) and (**6**), and the non-equivalent gold atoms have different connectivities. The Mössbauer spectra show considerable broadening or even resolved splitting of the high-velocity components, indicating

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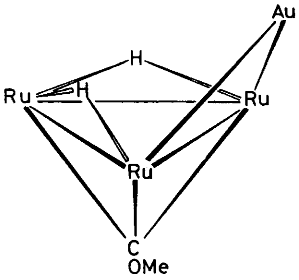
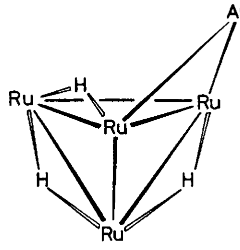
† The published spectrum of $[Au_7(PPh_3)_7]OH$ (J. W. A. van der Velden, P. T. Buerskens, J. J. Bour, W. P. Bosman, J. H. Noordik, M. Kolenbrander, and J. A. K. M. Buskes, *Inorg. Chem.*, 1984, **23**, 146) shows two doublets thought to correspond to the axial and equatorial atoms of a pentagonal-bipyramidal cluster. However, the area ratio of the two sub-spectra is *ca.* 1.4:1 instead of the expected 0.4:1; the discrepancy is due to a very large linewidth for the less intense doublet (3.8 mm s^{-1}). The treatment given later in the present paper suggests that the recoil-free fraction would be greater for the axial atoms (0.086) than the equatorial atoms (0.077), but this effect increases the expected ratio only to 0.48:1.

Table 1. The metal frameworks of the gold–ruthenium cluster compounds (with all terminal ligands omitted), and important bond distances (pm)



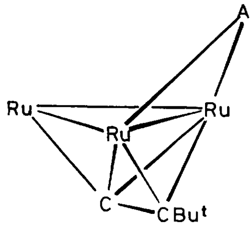
$\bar{d}$(Au–Ru)	274.5
d(Au–P)	230.8
Ref. 9	

(**1**) $(Ph_3PAu)[Ru(CO)_3]_3(\mu\text{-}H)_2(\mu_3\text{-}COMe)$



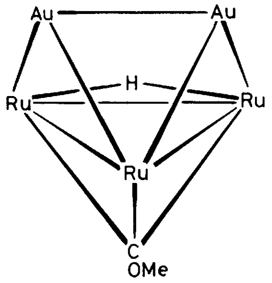
No *X*-ray diffraction study has been performed on this cluster.
Ref. 10

(**2**) $(Ph_3PAu)[Ru(CO)_3]_4(\mu\text{-}H)_3$



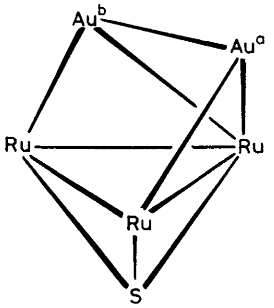
$\bar{d}$(Au–Ru)	276.0
d(Au–P)	227.6
Ref.11	

(**3**) $(Ph_3PAu)[Ru(CO)_3]_3(C_2Bu^t)$



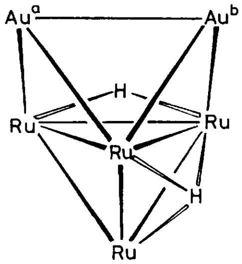
$\bar{d}$(Au–Ru)	274.6
$\bar{d}$(Au–P)	231.6
d(Au–Au)	317.6
Ref. 12	

(**4**) $(Ph_3PAu)_2[Ru(CO)_3]_3(\mu\text{-}H)(\mu_3\text{-}COMe)$



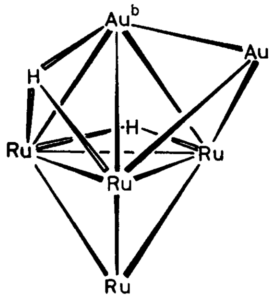
$\bar{d}$(Au^a–Ru)	278.9
$\bar{d}$(Au^b–Ru)	278.9
d(Au^a–P)	230.7
d(Au^b–P)	231.5
d(Au–Au)	280.2
Ref. 13	

(**5**) $\{(\mu\text{-}Ph_2PCH_2PPh_2)Au_2\}[Ru(CO)_3]_3(\mu_3\text{-}S)$



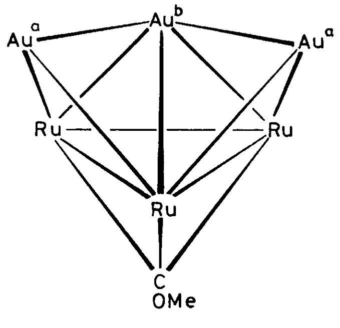
$\bar{d}$(Au^a–Ru)	277.5
$\bar{d}$(Au^b–Ru)	281.5
d(Au^a–P)	230.4
d(Au^b–P)	230.9
d(Au–Au)	282.3
Ref. 14	

(**6**) $\{(\mu\text{-}Ph_2PCH_2PPh_2)Au_2\}[Ru(CO)_3]_4(\mu\text{-}H)(\mu_3\text{-}H)$



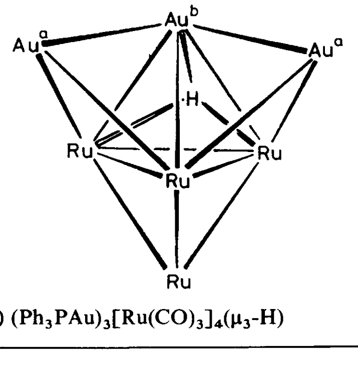
$\bar{d}$(Au^a–Ru)	284.2
$\bar{d}$(Au^b–Ru)	296.6
d(Au^a–P)	229.6
d(Au^b–P)	227.5
d(Au–Au)	279.1
Ref. 15	

(**7**) $(Ph_3PAu)_2[Ru(CO)_3]_4(\mu\text{-}H)(\mu_3\text{-}H)$



$\bar{d}$(Au^a–Ru)	282.0
$\bar{d}$(Au^b–Ru)	287.7
$\bar{d}$(Au^a–P)	231.2
d(Au^b–P)	230.4
$\bar{d}$(Au–Au)	297.0
Ref. 9	

(**8**) $(Ph_3PAu)_3[Ru(CO)_3]_3(\mu_3\text{-}COMe)$



$\bar{d}$(Au^a–Ru)	283.7	283.4
$\bar{d}$(Au^b–Ru)	293.9	293.5
$\bar{d}$(Au^a–P)	229.7	228.4
d(Au^b–P)	228.8	227.6
$\bar{d}$(Au–Au)	283.7	283.0
Ref. 16		

(**9**) $(Ph_3PAu)_3[Ru(CO)_3]_4(\mu_3\text{-}H)$

Table 2. ^{197}Au Mössbauer data for clusters giving two resolvable doublets

		I.s.	Q.s.	Linewidth			
Cluster	Co-ordination		mm s^{-1}		Area ratio, a:b	χ^{2a}	Ref.
(7a)	$AuRu_2P$	3.0	7.5	2.0	1.1	1.40	8
(7b)	$AuRu_3HP$	2.3	5.4				
(7a′)	$AuRu_2P$	3.0	7.5	1.8	0.8	1.39	*b*
(7b′)	$AuRu_3HP$	2.3	5.6	2.2			
(8a)	$AuRu_2P$	2.7	7.0	2.5	1.6	1.13	8
(8b)	Au_2Ru_3P	2.4	5.2				
(8a′)	$AuRu_2P$	2.8	7.4	2.0	1.2	1.13	*b*
(8b′)	Au_2Ru_3P	2.5	5.2	2.2			
(9a)	$AuRu_2P$	3.0	7.4	2.0	1.3	1.19	8
(9b)	Au_2Ru_3HP	2.0	4.9				
(9a′)	$AuRu_2P$	2.9	7.4	2.2	1.5	1.20	*b*
(9b′)	Au_2Ru_3HP	1.9	4.9	1.9			

^{a} Per degree of freedom. ^{b} This work.
Estimated error limits are ±0.1 mm s^{-1} for i.s. and q.s., ±0.2 mm s^{-1} for the linewidths, and *ca.* ±0.3 for the area ratios.

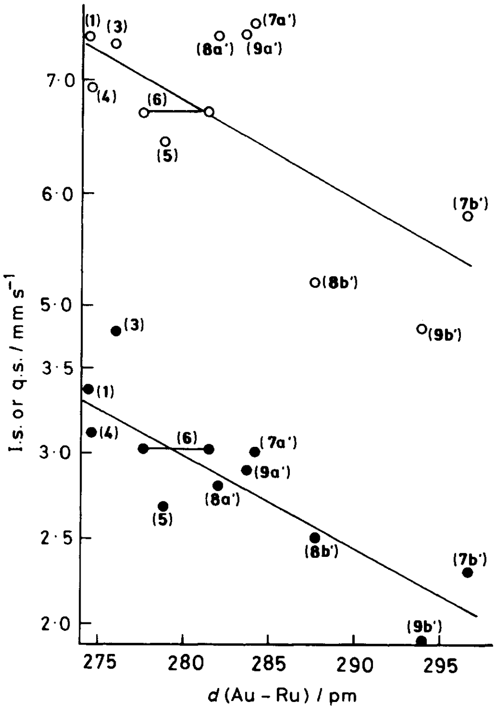


Figure. Correlation of i.s. ● and q.s. ○ with average Au–Ru bond length. The cluster numbering is as in Table 1. Cluster (**6**) gives an unresolved Mössbauer spectrum although the crystal structure reveals slightly different bond lengths; both bond lengths are shown; (**7**)—(**9**) have resolved spectra corresponding to the two different observed bond lengths, and both sets of parameters are shown. The regression lines are q.s./mm s^{-1} = (32.7 ± 7.9) − (0.0923 ± 0.0278) *d*/pm and i.s./mm s^{-1} = (18.3 ± 2.7) − (0.0547 ± 0.0096) *d*/pm

the presence of two overlapping doublets (see ref. 8 for reproductions of the spectra).

In conventional compounds of the type $(R_3P)AuX$, the i.s. and q.s. are well correlated, with the latter increasing about twice as fast as the former as the ligands X are changed.[18,19] This means that the lower-velocity lines of doublet spectra always occur at about the same position (*ca.* −0.5 mm s^{-1}) and only the higher-velocity line shows marked changes of position. When more than one doublet occurs in the spectrum, the lower-velocity lines therefore overlap more closely than those at higher velocity, giving an asymmetric broadening of the spectrum when the doublets are not resolved.[20] Satisfactory computer fitting is difficult to achieve under these conditions, when the differences in line position are less than the linewidth, and some constraints usually have to be applied. For our preliminary report,[8] we had constrained all four peaks to be equal in width; these data are included in Table 2, together with those for a fit in which the widths have been constrained in pairs. In each case, the two peaks of each doublet were constrained to have the same intensity. The four lines can be paired in two possible ways: nested or overlapped. The i.s.–q.s. correlation suggests the former, and we have adopted this; within the rather large error limits suggested, the parameters are indistinguishable for either fitting.

In clusters (**8**) and (**9**), the two types of gold atom are present in a ratio of 2:1, so that the intensities can be used as a guide to assignment. In both cases, the outer doublet is clearly the more intense, and the parameters of these doublets are very similar. The gold atoms to which they correspond have the same connectivity (2Ru + Au). This unit is also found in (**7**), and the outer doublet of this spectrum has parameters similar to those of (**8**) and (**9**). The remaining gold atoms have different environments in each of the clusters, and this is reflected in significant differences in their Mössbauer parameters. There appears to be a correlation between the parameters and the connectivity of the gold atoms to their neighbours: as the connectivity decreases, the i.s. increases, and this trend can be extrapolated to the value for the $Au(PPh_3)$ unit common to the three clusters.

The data for all the compounds fall in the same region as for the homonuclear gold clusters,[1,7,19] but there is a considerably wider range of values. If the data for all the gold–ruthenium clusters are arranged in order of decreasing i.s. (Table 3), clear correlations are seen. Not only is the normal correlation between decreasing i.s. and decreasing q.s. evident, but both parameters decrease systematically as the number of adjacent metal atoms increases from two [(**1**)—(**3**)] to three [(**4**)—(**9a′**)] to four or five [(**7b′**)—(**9b′**)]. There is a range of values within each group, which must reflect changes in electron density. Although the local environment of the gold atom is apparently very similar in each case, there are significant variations in the bond lengths, and the Mössbauer parameters correlate well with the average bond lengths. Since in homonuclear clusters the connectivity seems to have very little influence on the Mössbauer parameters,[1,19] it seems reasonable to use only the Au–Ru bond lengths for this correlation. As the Figure shows, decreasing i.s. is strongly correlated with increasing bond length (r^2 = 0.76); the q.s. shows a similar but slightly less well defined

Table 3. ^{197}Au Mössbauer data for gold sites in Au–Ru clusters, in order of decreasing i.s.

Cluster	Co-ordination	I.s.	Q.s.	Linewidth		χ^2
		mm s^{-1}				
(**3**)	Ru_2P	3.51	7.33	2.13	1.97	1.14
(**1**)	Ru_2P	3.38	7.38	1.99	2.05	1.01
(**2**)	Ru_2P	3.22	7.39	2.21	1.85	1.19
(**4**)	$AuRu_2P$	3.11	6.93	1.92	2.27	1.02
(**6**)	$AuRu_2P$	3.02	6.71	1.90	1.98	1.05
(**7a**′)	$AuRu_2P$	3.0	7.5	1.8		1.39
(**9a**′)	$AuRu_2P$	2.9	7.4	2.2		1.20
(**8a**′)	$AuRu_2P$	2.8	7.4	2.0		1.13
(**5**)	$AuRu_2P$	2.68	6.45	2.03	2.22	0.96
(**8b**′)	Au_2Ru_3P	2.5	5.2	2.2		1.13
(**7b**′)	$AuRu_3HP$	2.3	5.6	2.2		1.39
(**9b**′)	Au_2Ru_3HP	1.9	4.9	1.9		1.20

correlation ($r^2 = 0.52$). It has been shown previously that ligation by carbonyl groups increases the effective electronegativity (Lewis acidity) of a metal atom,[21] so that the $Ru(CO)_3$ groups are appreciably more electronegative than $Au(PR_3)$. Increase in the Ru–Au bond length therefore results in withdrawal of electron density from the gold atom, as the decrease in Mössbauer parameters clearly shows.

It is also noticeable that, for clusters (**8**) and (**9**), the ratio of the areas of the two subspectra (*ca.* 1.4:1) is considerably less than that expected from the stoicheiometry (2:1). Even if the large uncertainties in the observed ratios are taken into account, it is evident that they are significantly less than the expected value, and fittings in which the intensities were constrained in the ratio 2:1 were obviously unsatisfactory. This observation presumably means that the inequivalent gold atoms have different recoil-free fractions.* Two major factors affect the recoil-free fraction, the strength of binding of the gold atom to its neighbours, and the effective mass of the recoiling unit. The strength of binding should be related to the electron density in the bonds and (inversely) to the bond lengths. On this basis the atoms with the larger parameters [(**8a**′), (**9a**′), with $AuRu_2P$ co-ordination] should give the relatively more intense signal, but the opposite effect is observed: the signals for these atoms show only 70% of the intensity associated with those with Au_2Ru_3P or Au_2Ru_3HP co-ordination [(**8b**′), (**9b**′)]. The experimental ratios can be satisfactorily explained, however, in terms of the masses of the units. As the number of neighbours of any gold atom increases, so does the effective mass, which thus increases the recoil-free fraction. To a first approximation, the recoiling unit could be taken as the gold atom together with its immediate neighbours, the phosphorus atom and the adjoining metal atoms. Thus, the unit common to both clusters is PAu_2Ru_2 (mass, M 627) which in (**8**) and (**9**) is paired with PAu_3Ru_3 (M 925) or PAu_3Ru_3H (M 926). The data previously collected for gold(I) compounds[19] give the relationship $\ln f = -2.2 - 550/M$, from which the two recoil-free factors (f) may be calculated as 0.045 and 0.060. [It is reasonable to use the gold(I) data since the Mössbauer parameters of the clusters fall in the same range as those for gold(I) complexes.] Since there are two atoms of the former type and one of the second, the intensity ratio would be expected to be about 1.5:1, which is very close to that observed. For cluster (**7**) the observed area ratio is not significantly different from the expected 1.0:1. The corresponding recoiling units are PAu_2Ru_2 (M 627) and PAu_2Ru_3H (M 729), from which the calculated ratio of recoil-free fractions is 0.88:1, in satisfactory agreement with experiment.

Conclusions

The ^{197}Au Mössbauer parameters are strongly correlated with the structural features of the gold–ruthenium clusters, showing marked decreases as the connectivity of the gold atoms increases and the average bond length increases. It is likely that similar trends will be found for other heteronuclear clusters. It should therefore become possible to make estimates of the likely environments of gold atoms in new clusters without recourse to *X*-ray crystallography. In cases where there is more than one environment for the gold atoms, the intensity ratios reflect the effective masses of the gold atoms together with their immediate neighbours.

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