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^{197}Au Mössbauer Spectroscopic Study of Binuclear Cycloaurated Complexes Containing Bridging (2-Diphenylarsino-*n*-methyl)phenyl ($n = 5$ and 6)

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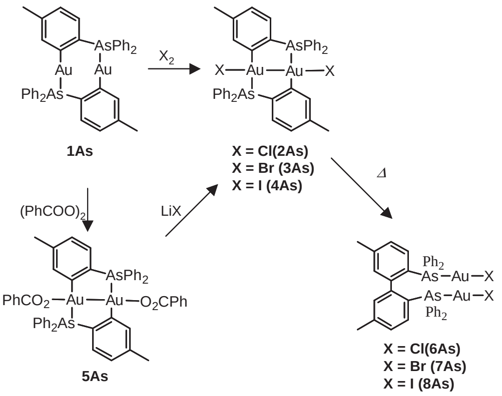
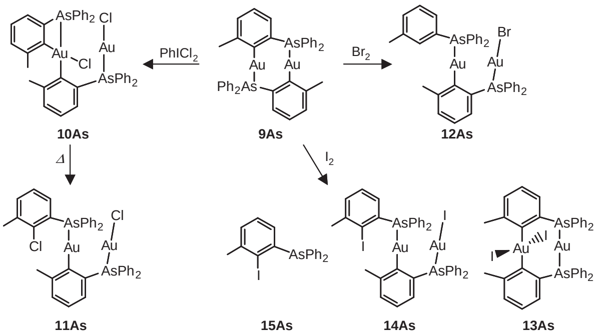
^{197}Au Mössbauer spectra have been measured on a series of binuclear gold complexes containing a bridging As–C ligand. The plot of quadrupole splitting (*Q.S.*) against isomer shift (*I.S.*) indicates that the gold–arsenic bond in these complexes is less covalent than the gold–phosphorus bond in analogous P–C complexes.

^{197}Au Mössbauer spectroscopy is a powerful technique to determine oxidation states and to elucidate the structure and bonding of inorganic and organometallic gold compounds,[1] though it has some disadvantages such as the short half-life (18.3 h) of the source nuclide, ^{197}Pt, and the high γ-ray energy leading to low recoil-free fractions. The preparation, structure, and reactivity of a wide variety of binuclear gold complexes bridged by bidentate ligands such as bis(diphenylphosphino)methane,[2] dithiocarbamate,[3] phosphorus bis(ylides),[4] and methylenethiophosphinate[5] have been investigated. Schmidbaur et al. have applied ^{197}Au Mössbauer spectroscopy to bi- and tri-nuclear gold complexes containing phosphorus bis(ylides) $CH_2PR_2CH_2$ ($R = $ Me, Et, and Ph) and di(tertiary)-phosphines $Ph_2PCR_2PPh_2$ ($R = $ H and Me), and have discussed the problem of absorption intensities arising from inequivalent gold centres.[6] Moore et al.[7] also have studied the ^{197}Au Mössbauer spectra of acyclic binuclear gold complexes, $[R(X)Au(Ph_2PNHPPh_2)Au(X)R]$ ($X = $ Cl, Br, and I; $R = C_6F_5$ and C_6Cl_5).

Recently, we have reported Mössbauer spectroscopic studies of the binuclear cyclometallated gold complexes $[Au_2(\mu\text{-}C_6H_4PR_2)_2]$ ($R = $ Et and Ph) and $[Au_2(\mu\text{-}C_6H_3\text{-}2\text{-}PPh_2\text{-}n\text{-}Me)_2]$ ($n = 5$ and 6),[8] and have shown that the 6s electron density of the gold atoms is increased by electron donation from the methyl substituents. This study also showed the utility of ^{197}Au Mössbauer spectroscopy for studying compounds that are either insoluble or unstable in solution.



Scheme 1. Reactivity of 5-methyl-substituted gold complex.



Scheme 2. Reactivity of 6-methyl-substituted gold complex.

We have recently extended this work to binuclear gold(I) complexes having 2-diphenylarsino-*n*-methylphenyl as bridging ligands.[9] The reactivity of 5- and 6-methyl-substituted cyclometallated gold complexes is summarized in Schemes 1 and 2, respectively. The complexes have been characterized by ^{1}H NMR, positive-ion FAB-MS, and elemental analysis. The molecular structures of **2As**–**4As** and **6As**–**15As** have been determined by X-ray crystallography. Oxidative addition of a 5-methyl-substituted cyclometallated gold(I) complex (**1As**) with halogens at -78 °C gave the gold(II) complexes (**2As**–**4As**). The reaction of **1As** with dibenzoyl peroxide at room temperature gave a gold(II) complex (**5As**), which reacted with lithium halides to give **2As**–**4As** in high yield. Whereas the bis(benzoato) complex is stable in toluene, the halide complexes undergo rearrangement to give digold(I) complexes (**6As**–**8As**) containing a biphenyl framework as a result of C–C coupling. Similar behavior is observed in the phosphorus analogues.[10]

The oxidative addition reactions of the 6-methyl-substituted digold(I) complex (**9As**) depend significantly on the halogens. The reaction of **9As** with $PhICl_2$ at room temperature gives a heterovalent, gold(I)–gold(III) complex (**10As**), which contains a four-membered As–Au^{III}–C–C ring. The latter is cleaved when **10As** is heated in toluene at 70 °C to give the digold(I) complex (**11As**). The reaction of **9As** with bromine at 50 °C gives a digold(I) complex (**12As**) in which, unexpectedly, one bromine atom has been lost and the gold atoms are inequivalent. The reaction of **9As** with iodine gives a mixture

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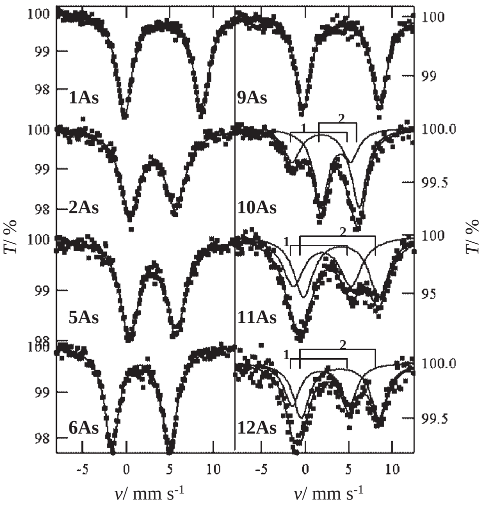

Fig. 1. ^{197}Au Mössbauer spectra for **1As**, **2As**, **5As**, **6As**, and **9As**–**12As**.

of **13As** and **14As**, the diiodo analogues of **10As** and **11As**, together with the iodinated ligand **15As**. The phosphorus analogues of **11As**, **12As**, **13As**, and **14As** were not detected in the corresponding reactions of $Au_2(\mu\text{-}C_6H_3\text{-}2\text{-}PPh_2\text{-}6\text{-}Me)_2$ (**9P**), showing that, in the sterically crowded 6-methyl-substituted systems, replacement of phosphorus by arsenic increases the lability of the initially formed oxidative addition products, possibly because of weaker Au–As bonding.

In this paper, we describe the ^{197}Au Mössbauer spectra of binuclear homo and hetero gold(I)–gold(I), homo gold(II)–gold(II), and mixed valent gold(I)–gold(III) complexes having As–Au–C bonds.

Experimental

The preparation of **1As**–**15As** is described elsewhere.[9] ^{197}Au Mössbauer spectra were measured at 12 K as described previously.[8] The ^{197}Pt/Pt Mössbauer source was prepared by neutron irradiation of a 100 mg disc of enriched metallic ^{196}Pt in the JRR-4 reactor of JAERI. The Mössbauer spectra were measured at Toho University using a Mössbauer spectrometer from Wissel (MDU-1200 function generator, DFG-1200 driving unit, MVT-100 velocity transducer and MVC-1200 laser calibrator). The isomer shift is given relative to the ^{197}Pt/Pt source at 12 K.

Results and Discussion

The ^{197}Au Mössbauer spectra are shown in Fig. 1 and the parameters are summarized in Table 1. The spectra for all of the 5-methyl-substituted complexes and **9As** show a well resolved quadrupole doublet, showing that the two gold atoms in these complexes are equivalent. The spectra of **10As**–**12As** show two quadrupole doublets, clearly showing the presence of two inequivalent gold centers. In ^{197}Au Mössbauer spectroscopy, the oxidation state of gold atoms is easily determined by the relation between quadrupole splitting (*Q.S.*) and isomer shift (*I.S.*) (Fig. 2). Data for $Au_2(\mu\text{-}C_6H_4\text{-}2\text{-}PPh_2\text{-}6\text{-}Me)_2$ (**9P**), $Au_2I_2(\mu\text{-}C_6H_4\text{-}2\text{-}PPh_2\text{-}6\text{-}Me)_2$ (**4P**), $Au_2(\mu\text{-}C_6H_4\text{-}2\text{-}PEt_2)_2$ (**16P**), $Au_2(\mu\text{-}C_6H_4\text{-}2\text{-}PPh_2)_2$ (**17P**), $Au_2(\mu\text{-}C_6H_4\text{-}2\text{-}AsPh_2)_2$ (**17As**), $Au_2I_2(\mu\text{-}C_6H_4\text{-}2\text{-}PEt_2)_2$ (**18P**), $Au_2I_2(\mu\text{-}C_6H_4\text{-}2\text{-}PPh_2)_2$ (**19P**), $Au_2Br_2(\mu\text{-}C_6H_4\text{-}2\text{-}PPh_2)_2$ (**20P**), $IAu(\mu\text{-}2\text{-}Ph_2PC_6H_3\text{-}6\text{-}Me)AuI\{\eta^2\text{-}(6\text{-}MeC_6H_3PPh_2)\}$ (**21P**), $Cl_3Au(\mu\text{-}2\text{-}Ph_2PC_6H_3\text{-}6\text{-}Me)AuCl\{\eta^2\text{-}(6\text{-}MeC_6H_3PPh_2)\}$ (**22P**) are from Ref. 8.

Table 1. ^{197}Au Mössbauer Parameters for **1As**–**12As**, **9P**,[8] **17P**,[8] and **17As**[8] at 12 K

	Oxidation state	*I.S.*/mm s^{-1} a) (±0.10)	*Q.S.*/mm s^{-1} (±0.10)	*A* /%b)
1As	Au(I)	4.22	8.82	100
2As	Au(II)	3.04	5.20	100
3As	Au(II)	3.09	5.21	100
4As	Au(II)	3.05	5.50	100
5As	Au(II)	3.05	5.36	100
6As	Au(I)	1.67	6.60	100
7As	Au(I)	1.57	6.37	100
8As	Au(I)	1.53	6.44	100
9As	Au(I)	4.16	8.79	100
10As	Au(I)	1.87	6.66	34
	Au(III)	4.02	4.38	66
11As	Au(I)	1.95	6.61	47
	Au(I)	4.15	8.66	53
12As	Au(I)	1.77	6.54	43
	Au(I)	4.03	8.92	57
9Pc)	Au(I)	4.67	9.81	100
17Pd)	Au(I)	4.53	9.58	100
17Asd)	Au(I)	4.08	8.80	100

a) Relative to ^{197}Pt/Pt source at 12 K. b) Relative absorption area. c) Ref. 8b. d) Ref. 8a.

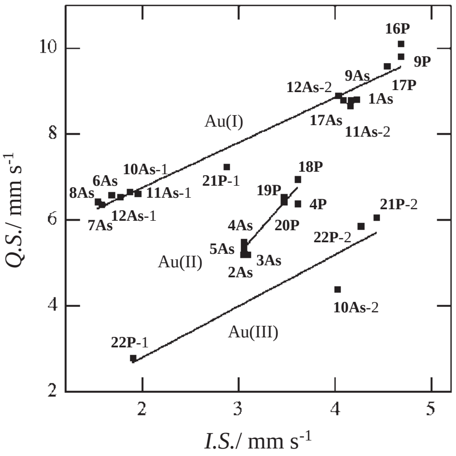

Fig. 2. Plot of *Q.S.* against *I.S.* for a series of binuclear gold complexes.

It is well known that both *I.S.* and *Q.S.* values for Au(I) and Au(III) compounds increase as the ligands become softer or more electron-donating, because the s and p electron densities increase. The *Q.S.* values for Au(III) compounds are smaller than those for Au(I) owing to the presence of the non-bonding electron pair in the d_{z^2} orbital, thus enabling Au(I) and Au(III) to be distinguished. In the digold(II) compounds, each gold atom is planar-coordinated, as in gold(III); one of the bonds is to the adjacent gold atom, which acts as a soft ligand. Thus, the *I.S.* and *Q.S.* values for digold(II) are intermediate between those for Au(I) and Au(III).

The oxidation states of the complexes are determined unambiguously from Fig. 1: +1 in **1As**, **6As**–**9As**, +2 in **2As**–**5As**, two Au(I) sites in **11As** and **12As**, and a mixed-valence state

(Au(I) and Au(III)) in **10As**. The absorption intensities corresponding to Au(I) and Au(III) in **10As** are not equal, the latter being about twice as large as the former. A similar disparity was found in the phosphorus analogue **21P** and can be attributed to the difference in the recoil-free fraction arising from different vibrational frequencies associated with the different coordination numbers.

The *I.S.* and *Q.S.* values for **1As** and **9As** are essentially the same: 4.22 and 8.82 mm s^{-1} for **1As** and 4.16 and 8.79 mm s^{-1} for **9As**. This clearly indicates that the electronic environment of the gold atoms is not affected by the position of the methyl group in the bridging ligand. The values of *I.S.* for **1As** and **9As** are, however, larger than that for the non-methyl-substituted complex (4.08 mm s^{-1}), indicating that both the s and p electron densities of the gold atom are increased due to the electron donation by the methyl group. The same trend has also been found in the phosphorus analogues: the *I.S.* (4.67 mm s^{-1}) and *Q.S.* (9.81 mm s^{-1}) values for the 6-methyl-substituted derivatives are, respectively, 0.14 and 0.23 mm s^{-1} larger than those of the unsubstituted complex.[8] The *I.S.* and *Q.S.* values for **9As**, in which the Au–Au distance is 2.9543(10) Å, are similar to those for **11As** and **12As**, whose Au–Au separations are 3.2510(6) and 3.1304(4) Å, respectively. The Mössbauer parameters are clearly insensitive to the intermolecular Au–Au separations in these digold(I) complexes and presumably also to the presence or absence of aurophilic interactions.

Although the oxidation states of the gold atoms in **1As**, **9As**, **11As**-2, **12As**-2 (having As–Au–C bonds) and **6As–8As**, **10As**, **11As**-1, **12As**-1 (having As–Au–X bonds) are +1, there are large differences in the Mössbauer parameters. This indicates that the s electron density of gold atoms coordinated by hard ligands such as halides is smaller than that of gold atoms coordinated by soft ligands containing carbon or arsenic as donor atoms. The Mössbauer parameters are, therefore, a sensitive reflection of the electron-donating ability of the ligand.

Among the biphenylyl complexes, **6As–8As**, the value of the *I.S.* becomes larger in the order $X = I < Br < Cl$, contrary to the expectation from the softness of the ligand. This tendency has been confirmed in the mononuclear organogold complexes, Ph_3PAuX. *I.S.* values increase in the order $X = I < Br < Cl < OCOCH_3$, $N_3 < CN < CH_3$,[11] following the spectrochemical series. The electron distribution around the gold(I) atom in the halide complexes may be determined by a subtle balance of the donation and back-donation. This tendency is, however, not evident in the digold(II) complexes. The adjacent gold(II) atom clearly has considerable influence on the electronic environment of the gold(II) atom to which it is attached.

The *I.S.* and *Q.S.* values for the arsenic complexes are smaller than those for the phosphorus complexes (Fig. 2). This means that both s and p electron densities of the gold atoms in the arsenic complexes are smaller than those in the phosphorus complexes. The Mössbauer parameters clearly show that the Au–As bond is less covalent than the Au–P bond.

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