^{197}Au Mössbauer Spectroscopy Studies of Some Cyclometalated Gold Dimers

Suresh K. Bhargava,* Fabian Mohr, Masashi Takahashi,† and Masuo Takeda†

Department of Applied Chemistry, RMIT University, GPO Box 2476V, Melbourne, 3001, Victoria, Australia

†Department of Chemistry, Faculty of Science, Toho University, Chiba 274-8510

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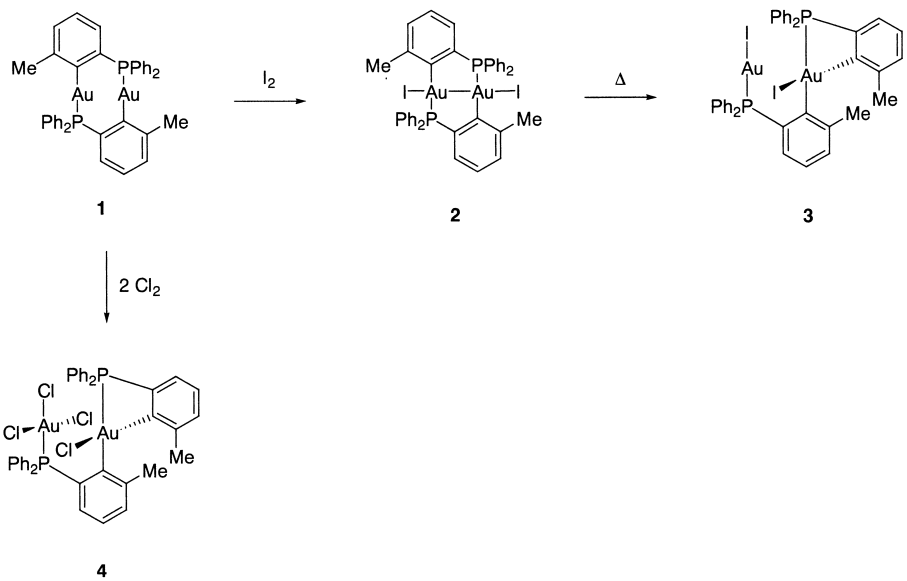
The oxidation states and structures of a series of cyclometalated gold complexes derived from oxidative addition reactions of the digold(I) complex [$Au_2(\mu$-C_6H_3-2-PPh_2-6-Me)$_2$] have been determined by ^{197}Au Mössbauer spectroscopy. The spectra for the binuclear gold(I)/gold(I) and gold(II)/gold(II) complexes indicate the presence of equivalent gold atoms, whereas the gold(I)/gold(III) and gold(III)/gold(III) spectra show signals due to two inequivalent metal centers. The coordination spheres of metal centers in the complexes have been determined from isomer shift and quadrupole splitting data.

Gold-197 Mössbauer spectroscopy has been used to determine structure and bonding in a variety of inorganic gold compounds.[1] In the last 25 years, several extensive studies of binuclear gold complexes containing bidentate donor ligands, phosphorus ylide ligands and cyclometalated ligands have been undertaken; however, very few of these compounds were studied by ^{197}Au Mössbauer spectroscopy.[2,3] More recently, ^{197}Au Mössbauer spectroscopy has been successfully used in the structure elucidation of binuclear cyclometalated gold compounds, where the presence of a true d^9–d^9 gold(II)/gold(II) oxidation state was confirmed.[4] This work illustrates the use of ^{197}Au Mössbauer spectroscopy in determining oxidation states of gold and structural information in a series of binuclear cyclometalated gold complexes with different oxidation states (Scheme 1).

Results and Discussion

Oxidative addition of I_2 to a colorless solution of **1** at −70 °C affords the dark red digold(II) compound **2**, which in solution spontaneously isomerizes to the colorless heterovalent compound **3** above ca. −20 °C. Treatment of **1** with two equivalents of Cl_2 at room temperature affords the bright yellow, highly insoluble compound **4**. All compounds have been fully characterized by NMR (^{31}P and ^{1}H), elemental analysis, X-ray diffraction (**1** and **3**), and X-ray photoelectron spectroscopy (XPS).[5,6] The Mössbauer spectra of compounds **1**–**4** are shown in Fig. 1 and the Mössbauer parameters in Table 1.

The spectra for compounds **1** and **2** consist of a well-resolved quadrupole doublet, as expected for two equivalent metal centers. The isomer shift (IS) and quadrupole splitting



Scheme 1. Oxidative addition reactions of binuclear gold complexes.

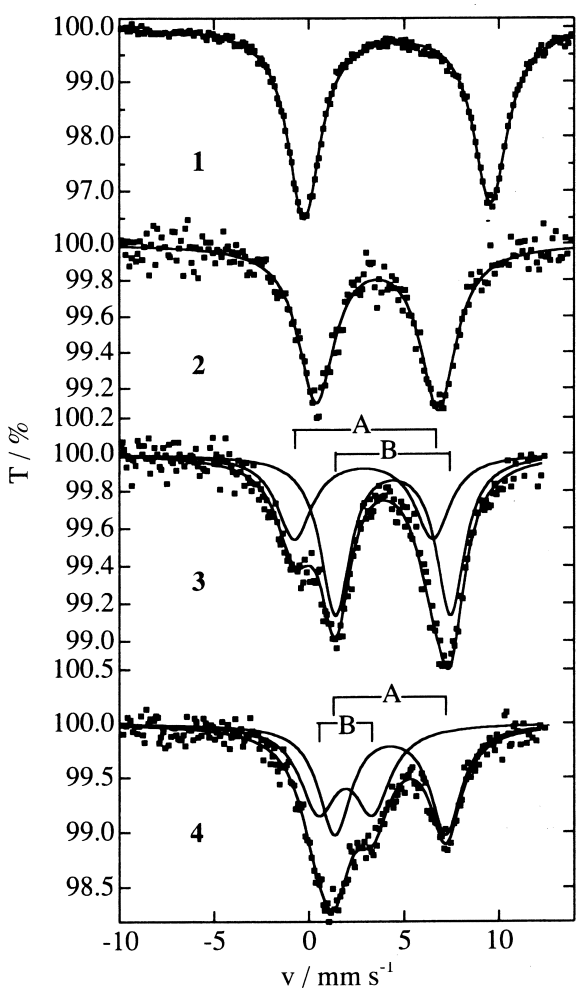


Fig. 1. ^{197}Au Mössbauer spectra for complexes **1–4** at 12 K.

(QS) results for compounds **1** and **2** are very similar to those reported for the analogous non-methylated diethylphosphine compounds, while the IS values are ca. 0.14 mm s^{-1}, larger than those reported for the non-methylated analogues.[4] This arises from an increase in 6s electron density resulting from electron donation by the methyl-substituted phosphine ligand into the sp hybrid orbitals of the C–Au–P unit, since the nuclear radius parameter ($\Delta R/R$) is positive for ^{197}Au.

The IS and QS values for **2** are much lower than those of **1**, being consistent with that observed in other binuclear gold compounds: as the gold oxidation state is increased from +1 to +2 both the IS and QS values decrease.[3,4,7] The results observed for **2** clearly indicate the presence of homovalent gold(II)/gold(II) (d^9–d^9) centers and not heterovalent gold(I)/gold(III) (d^8–d^{10}) oxidation states as found in **3**.

Heterovalent binuclear gold compounds are quite rare, especially those containing four-membered Au–P–C–C rings. A compound similar to **3** is formed in the reaction of nitromethane with a binuclear gold(I) ylide compound, to give a heterovalent gold(I)/gold(III) species containing a four-membered Au–P–C–C ring;[8] however, no ^{197}Au Mössbauer parameters were reported. The spectrum of **3** shows two quadrupole doublets, clearly showing the presence of two inequivalent gold centers. The oxidation state of compound **3** has been determined by XPS; however, the small difference in binding energies of the two oxidation states together with the occurrence of photoreduction has not allowed the structure to be unambiguously confirmed by this technique.[6] However, the proposed structure can be confirmed by using the well-known IS–QS relationship.[1b,7] Figure 2 shows the plot of QS against IS for the binuclear complexes including those of the non-methylated an-

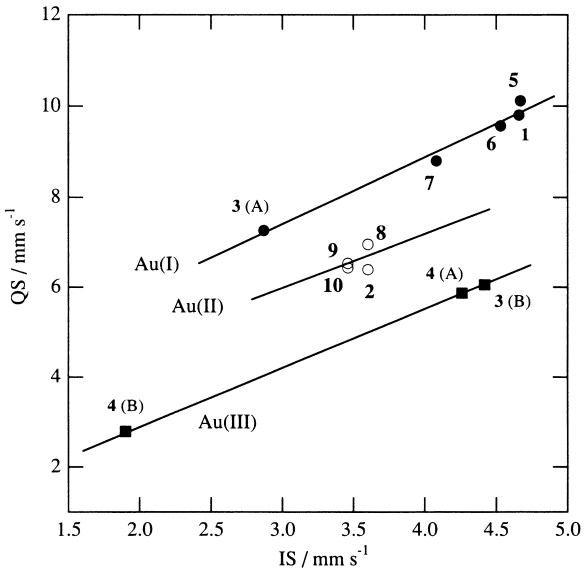


Fig. 2. Plot of Qs against IS for a series of binuclear gold complexes. Data for compounds **5–10** are from reference 4.
5 $Au_2(\mu\text{-}C_6H_4\text{-}2\text{-}PEt_2)_2$, **6** $Au_2(\mu\text{-}C_6H_4\text{-}2\text{-}PPh_2)_2$, **7** $Au_2(\mu\text{-}C_6H_4\text{-}2\text{-}AsPh_2)_2$, **8** $Au_2(\mu\text{-}C_6H_4\text{-}2\text{-}PEt_2)_2I_2$, **9** $Au_2(\mu\text{-}C_6H_4\text{-}2\text{-}PPh_2)_2I_2$, **10** $Au_2(\mu\text{-}C_6H_4\text{-}2\text{-}PPh_2)_2Br_2$.

Table 1. ^{197}Au Mössbauer Parameters for Compounds **1–4** at 12 K

Compound	Oxidation state	IS/mm s^{-1} a) (± 0.10)	QS/mm s^{-1} (± 0.10)	Γ_1/mm s^{-1} (± 0.10)	Γ_2/mm s^{-1} (± 0.10)	A (%)[b]
1	Au(I)	4.67	9.81	2.14	2.05	100
2	Au(II)	3.60	6.39	2.25	2.40	100
3 site A	Au(I)	2.87	7.26	2.27	2.27	40
site B	Au(III)	4.42	6.06	1.85	1.85	60
4 site A	Au(III)	4.26	5.87	2.24	2.24	48
site B	Au(III)	1.90	2.79	2.19	2.19	52

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

alogues.[4] The two gold sites (A and B) of **3** appear at distinctly different positions; i.e. site A lies in the region of Au(I) parameters and site B in that of Au(III) parameters. The IS and QS values for site A are smaller than those usually observed for an Au(I) site due to the coordination of the harder iodide ligand to the gold(I) center. Conversely, the parameters for site B are considerably larger, suggesting coordination by a softer ligand. The small relative absorption area for site A is also consistent with Au(I) in class I heterovalent compounds.[1b,9]

Solid state techniques such as XPS and Mössbauer spectroscopy are often the only available techniques in the structure elucidation of highly insoluble compounds, compound **4** being a good example of this. This compound is insoluble in common organic solvents and dissolves only with difficulty in *aqua regia* with decomposition, which has made characterization by techniques such as NMR, mass spectroscopy, and X-ray crystallography impossible. XPS of **4** indicates the presence of only gold(III) centers, but the technique could not determine if a homo- or heterovalent gold(III) compound was present.[6] The ^{197}Au Mössbauer spectrum, however, clearly shows the presence of two different gold(III) sites, which can be assigned to the terminal-$PAuCl_3$ site and the gold(III) site contained within the four-membered ring. Both sites (A and B) lie in the region expected for Au(III) compouds. In addition, the parameters for site A of **4** closely match those for the Au(III) site of **3**. Furthermore, the IS and QS values for site B are fairly small, which indicates that site A is coordinated to a soft ligand (phosphine) and site B to a hard ligand (chloride), consistent with the proposed structure.

The structures and oxidation states of a series of binuclear cyclometalated organogold complexes were unambiguously determined by ^{197}Au Mössbauer spectroscopy. In this work we have shown that ^{197}Au Mössbauer spectroscopy is a very powerful technique in structural and valence state investigations of gold compounds, particularly for compounds that are insoluble or unstable in solution and hence cannot be analyzed by more conventional spectroscopic techniques such as NMR and mass spectroscopies. The combination of IS and QS data can be used to identify gold oxidation states of +1, +2, and +3 in both homo- and heterovalent systems. The technique also allows two inequivalent gold centers of the same oxidation state to be distinguished.

Experimental

Compounds **1**–**4** were prepared following a literature procedure.[5] Gold-197 Mössbauer spectra were obtained on a Wissel Mössbauer spectrometer system consisting of a MDU-1200 function generator, DFG-1200 driving unit, MVT-100 velocity transducer and MVC-1200 laser calibrator. Both the Mössbauer source and the absorber were kept at 12 K in a cryostat incorporating a closed cycle refrigerator, and the γ-rays were counted with a pure Ge solid state detector.[10] The source (360 MBq) was made by neutron irradiation of a 100 mg disc of enriched metallic ^{196}Pt in the JRR-4 reactor of JAERI. The absorber thickness was 50–130 mg Au cm^{-2}. The data were analyzed by the usual least squares method. The isomer shift is given relative to ^{197}Pt/Pt source at 12 K.

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