

¹⁹⁷Au Mössbauer Spectroscopic Studies of Cyclometalated Gold Dimers Containing 2-C₆F₄PPh₂ Ligands

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¹⁹⁷Au Mössbauer spectra have been measured on a series of homovalent and heterovalent dinuclear gold complexes containing the 2-C₆F₄PPh₂ ligand. The correlation plot indicates that the electron densities of the 6s and 6p orbitals of the gold atoms in these complexes are less than those of their protio and 6-methyl analogs, reflecting the electron-withdrawing property of the fluorine substituents.

The Mössbauer spectroscopy of gold was first investigated about forty years ago^{1–3} and has since proved to be a powerful technique for the determination of the structures and bonding in inorganic and organometallic gold compounds in the solid state, particularly for compounds that are either insoluble or unstable in solution.^{4–8} ¹⁹⁷Au Mössbauer spectroscopy has also been successfully used in oxidation state determination and structure elucidation of the dinuclear cyclometalated gold compounds [Au₂(μ-2-C₆H₄PR₂)₂] (R = Et and Ph),⁹ [Au₂(μ-C₆H₃-6-Me-2-PPh₂)₂],¹⁰ and [Au₂(μ-C₆H₃-*n*-Me-2-AsPh₂)₂] (*n* = 5 and 6).¹¹ It was shown that the isomer shift (IS) and quadrupole splitting (QS) values for [Au₂(μ-C₆H₃-6-Me-2-PPh₂)₂] are larger than those reported for the analogous non-methylated protio compound, indicating that electron donation from the methyl substituents increases the 6s electron density of the gold atoms.^{9,10} The Mössbauer parameters reported for the closely related arsenic analogs, [Au₂(μ-C₆H₃-*n*-Me-2-AsPh₂)₂] (*n* = 5 and 6), are smaller than those of the corresponding phosphorus compounds, indicating that the Au–As bond is less covalent than the Au–P bond in these compounds.¹¹ In this work, ¹⁹⁷Au Mössbauer spectroscopy has been applied to confirm the oxidation states of the gold atoms in the homovalent and heterovalent dinuclear complexes containing 2-C₆F₄PPh₂ and to compare the derived parameters with those of the corresponding complexes containing 2-C₆H₄PPh₂ or C₆H₃-6-Me-2-PPh₂.

Results and Discussion

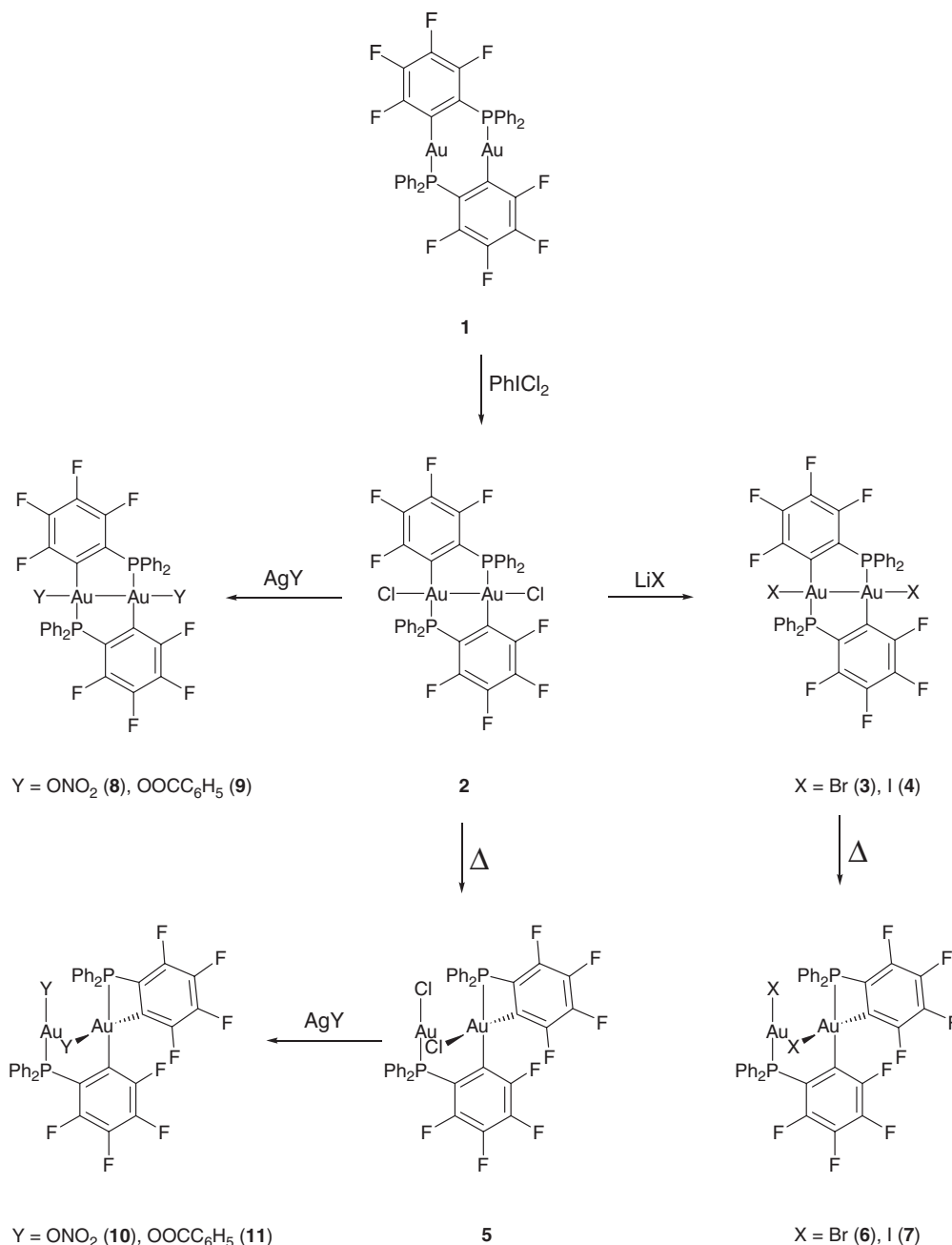
As described elsewhere,¹² the dinuclear digold(I) **1** and dihalodigold(II) complexes **2–4**, containing μ-2-C₆F₄PPh₂, shown in Scheme 1, are made similarly and are structurally similar to their μ-2-C₆H₄PPh₂ counterparts, although the fluorine substituents cause small contractions in the Au...Au separations. Complexes **2–4** rearrange in toluene solution at 70 °C to heterovalent, gold(I)–gold(III) compounds [XAu(μ-2-

C₆F₄PPh₂)(κ²-2-C₆F₄PPh₂)AuX] [X = Cl (**5**), Br (**6**), and I (**7**)]; this behavior resembles that of the dihalodigold(II) compounds of C₆H₃-6-Me-2-PPh₂,¹³ but differs from that of the dihalodigold(II) compounds of 2-C₆H₄PPh₂, which undergo reductive coupling of the aryl groups to give digold(I) complexes [XAu(μ-2,2'-Ph₂PC₆H₄C₆H₄PPh₂)AuX].^{14,15} Treatment of [Au₂Cl₂(μ-2-C₆F₄PPh₂)₂] (**2**) or [ClAu(μ-2-C₆F₄PPh₂)(κ²-2-C₆F₄PPh₂)AuCl] (**5**) with silver nitrate or benzoate gives the corresponding disubstituted oxanion complexes [Au₂Y₂(μ-2-C₆F₄PPh₂)₂] [Y = ONO₂ (**8**) and OOCCH₃ (**9**)] or [YAu(μ-2-C₆F₄PPh₂)(κ²-2-C₆F₄PPh₂)AuY] [Y = ONO₂ (**10**) and OOCCH₃ (**11**)], respectively (Scheme 1).

Complexes **1–11** were analyzed by Mössbauer spectroscopy; the spectra and parameters are shown in Figure 1 and Table 1, respectively.

The Mössbauer spectra of **1–4**, **8**, and **9** (Figure 1) each consist of the expected well resolved quadrupole doublet, showing that the two gold atoms in these complexes are equivalent. In contrast, complexes **5–7**, **10**, and **11** each show a pair of quadrupole doublets, confirming the presence of two inequivalent gold centers. It is worth noting that the IS and QS values for the dihalodigold(II) complexes **2–4**, **8**, and **9** are much smaller than those of the digold(I) complex **1**, consistent with the formation of higher oxidation states.^{5,9–11}

The isomer shift and quadrupole splitting values for the dinuclear gold(I) complex **1** are less than those of its protio and 6-methyl analogs {[Au₂(μ-2-C₆H₄PPh₂)₂] (**12**)⁹ and [Au₂(μ-C₆H₃-6-Me-2-PPh₂)₂] (**13**)¹⁰ respectively (Table 1)}, and decrease in the order **1** < **12** < **13**. This decrease can be attributed to the electron-withdrawing nature of the fluorine substituents compared to hydrogen and methyl groups, which affects the population of the 6s and 6p orbitals in the gold atoms, resulting in smaller IS and QS values, respectively. The electronic effect of fluorine is also evident from the smaller IS and QS values for [Au₂Br₂(μ-2-C₆F₄PPh₂)₂] (**3**) compared to



Scheme 1. Oxidative addition reaction of dinuclear gold(I) complex, rearrangement of dinuclear gold(II) complexes, and preparation of digold(II) and digold(I,III) oxanion complexes.

those reported for its protio analog $[\text{Au}_2\text{Br}_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)_2]$ (**18**). The same trend has also been observed in the digold(I,III) complex **7** and its 6-methyl analog **15**; the IS and QS values for $[\text{IAu}(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)(\kappa^2\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)\text{AuI}]$ (**7**) are smaller than those found in the 6-methyl analog. A decrease in the QS value (6.50 mm s^{-1}) is also observed for the complex $[\text{Au}_2\text{I}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$ (**4**) compared to that of 6.54 mm s^{-1} in the protio analog $[\text{Au}_2\text{I}_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)_2]$ (**17**), whereas surprisingly the IS value has not changed. The correlation plot for complexes **1–11** is shown in Figure 2. Additional data, summarized in Table 1, are taken from Refs. 9–11.

The correlation plot shows three distinct regions, corresponding to Au^{I} , Au^{II} , and Au^{III} oxidation states. The oxidation

states of the gold atoms in complexes **1–11** lie close to similar oxidation states within the expected regions: +1 in **1**, +2 in **2–4**, **8**, and **9**, and mixed-valence state $\text{Au}^{\text{I}}\text{–Au}^{\text{III}}$ in **5–7**, **10**, and **11**.

The Au^{I} atoms in the mixed-valence $\text{Au}^{\text{I}}\text{–Au}^{\text{III}}$ compounds **5–7**, **10**, and **11** are located in the low IS and QS region in the expected Au^{I} area of the plot, indicating the different chemical environment compared to the symmetric gold(I) dimers. There is no clear trend in the ordering of the IS and QS values for complexes **5–7**, **10**, and **11** that can be correlated to the hardness of the coordinated ligands. This is in contrast to that observed in the Au^{II} complexes (see later).

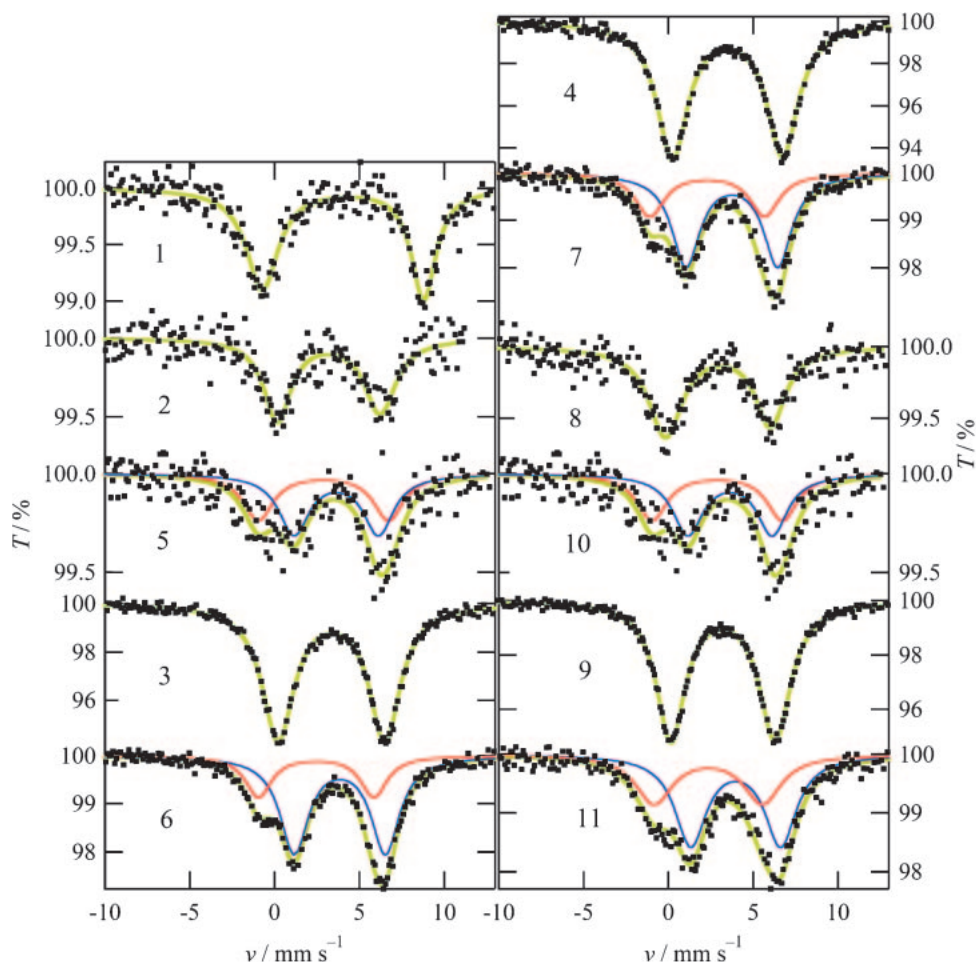


Figure 1. ^{197}Au Mössbauer spectra for complexes 1–11 at 12 K.

Experimentally, the plot of QS against IS for the digold(II) complexes falls in the intermediate region between those obtained for the gold(I) and gold(III) plots. The gold atoms containing the four-membered ring unit (complexes 5–7, 10, and 11) lie in the Au^{III} region of the plot, close to the gold(III) atoms containing similar chemical environments, and away from the gold(III) atom containing the P-Au-X_3 unit.

Among the gold(II)–gold(II) complexes 2–4, 8, and 9, the values of IS increase in the order $\text{ONO}_2 < \text{Cl} < \text{OOCCH}_3 < \text{Br} < \text{I}$, which is in agreement with the expectation based on the softness of the ligand. This result is in contrast to the observations for the dinuclear biphenyldiyl complexes $[\text{Au}_2\text{X}_2(2,2'\text{-Ph}_2\text{As-5-MeC}_6\text{H}_3\text{C}_6\text{H}_3\text{-5-Me-AsPh}_2)]$ ($\text{X} = \text{Cl, Br, and I}$) and also for the mononuclear organogold complexes $[\text{AuX}(\text{PPh}_3)]$ ($\text{X} = \text{I, Br, Cl, OCOCH}_3, \text{N}_3, \text{CN, and CH}_3$), in which the values of IS increase as the ligands become harder.^{3,11}

Experimental

Complexes 1–11 were prepared following a literature procedure.¹² Gold-197 Mössbauer spectra were acquired at Toho University, Japan, 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. The γ -ray source (210 MBq) was prepared by neutron irradiation of a 40 mg disc of enriched metallic ^{196}Pt in the JRR-4 reactor at

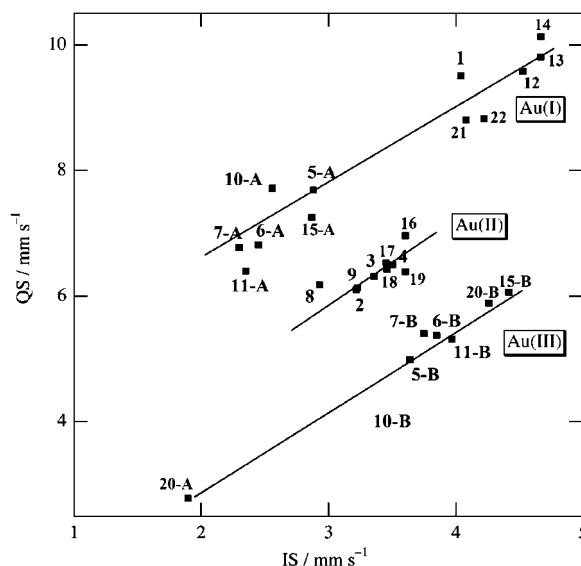


Figure 2. Plot of QS against IS for dinuclear gold complexes.

the Japan Atomic Energy Agency (JAEA). The absorber thickness was $50\text{--}130 \text{ mg Au cm}^{-2}$. Both the Mössbauer source and the absorber were cooled to a temperature of 12 K in a cryostat

Table 1. ^{197}Au Mössbauer Parameters for Dinuclear Gold Complexes

Compound	Au oxidation state	IS/mm s $^{-1}$	QS/mm s $^{-1}$
$[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$ (1)	I	4.04	9.51
$[\text{Au}_2\text{Cl}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$ (2)	II	3.22	6.10
$[\text{Au}_2\text{Br}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$ (3)	II	3.36	6.30
$[\text{Au}_2\text{I}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$ (4)	II	3.45	6.50
$[\text{Au}_2(\text{ONO}_2)_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$ (8)	II	2.93	6.18
$[\text{Au}_2(\text{OOCCH}_3)_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$ (9)	II	3.23	6.14
$[\text{ClAu}(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)(\kappa^2\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)\text{AuCl}]$ (5)	I (site A)	2.88	7.69
	III (site B)	3.64	4.98
$[\text{BrAu}(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)(\kappa^2\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)\text{AuBr}]$ (6)	I (site A)	2.45	6.81
	III (site B)	3.85	5.37
$[\text{IAu}(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)(\kappa^2\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)\text{AuI}]$ (7)	I (site A)	2.29	6.77
	III (site B)	3.75	5.41
$[(\text{O}_2\text{NO})\text{Au}(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)(\kappa^2\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)\text{Au}(\text{ONO}_2)]$ (10)	I (site A)	2.56	7.71
	III (site B)	3.51	4.23
$[(\text{C}_6\text{H}_5\text{COO})\text{Au}(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)(\kappa^2\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)\text{Au}(\text{OOCCH}_3)]$ (11)	I (site A)	2.35	6.40
	III (site B)	3.97	5.31
$[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)_2]$ (12) ^a	I	4.53	9.58
$[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{H}_3\text{-}6\text{-Me-}2\text{-PPh}_2)_2]$ (13) ^b	I	4.67	9.81
$[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PEt}_2)_2]$ (14) ^a	I	4.67	10.12
$[\text{IAu}(\mu\text{-}2\text{-C}_6\text{H}_3\text{-}6\text{-Me-}2\text{-PPh}_2)(\kappa^2\text{-}2\text{-C}_6\text{H}_3\text{-}6\text{-Me-}2\text{-PPh}_2)\text{AuI}]$ (15) ^b	I (site A)	2.87	7.26
	III (site B)	4.42	6.06
$[\text{Au}_2\text{I}_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PEt}_2)_2]$ (16) ^a	II	3.60	6.96
$[\text{Au}_2\text{I}_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)_2]$ (17) ^a	II	3.46	6.54
$[\text{Au}_2\text{Br}_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)_2]$ (18) ^a	II	3.46	6.44
$[\text{Au}_2\text{I}_2(\mu\text{-}2\text{-C}_6\text{H}_3\text{-}6\text{-Me-}2\text{-PPh}_2)_2]$ (19) ^b	II	3.60	6.39
$[\text{Cl}_3\text{Au}(\mu\text{-}2\text{-C}_6\text{H}_3\text{-}6\text{-Me-}2\text{-PPh}_2)(\kappa^2\text{-}2\text{-C}_6\text{H}_3\text{-}6\text{-Me-}2\text{-PPh}_2)\text{AuCl}]$ (20) ^b	III (site A)	4.26	5.87
	III (site B)	1.90	2.79
$[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{AsPh}_2)_2]$ (21) ^a	I	4.08	8.80
$[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{H}_3\text{-}5\text{-Me-}2\text{-AsPh}_2)_2]$ (22) ^c	I	4.22	8.82

a) Ref. 9. b) Ref. 10. c) Ref. 11.

incorporating a closed cycle refrigerator, and a pure Ge solid state detector was used for counting the γ -rays.¹⁶ The data were analyzed by least-squares methods and the isomer shifts are given relative to the $^{197}\text{Pt}/\text{Pt}$ source at 12 K.

This work was the result of a collaboration between RMIT University, Australia and Toho University, Japan, and was supported in part by the Inter-University Program for the Joint Use of JAEA Facilities.

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