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# Oxidative addition reactions of methyl substituted binuclear gold complexes studied by X-ray photoelectron spectroscopy

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This paper is dedicated to Professor Martin Bennett on the occasion of his retirement for a lifetime contribution to organometallic chemistry.

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**Abstract**

X-ray photoelectron spectra of homovalent binuclear gold complexes with oxidation states of + I, + II, + III as well as heterovalent gold(I)–gold(III) species were obtained. The binding energies for the gold 4f peaks increase as the gold oxidation state increases. Residual gas analysis showed that the gold(I)–gold(III) heterovalent compound is photoreduced to a homovalent gold(I) compound. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* XPS; Binuclear; Gold; Cyclometallated; Heterovalent; Photoreduction

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## 1. Introduction

The technique of X-ray photoelectron spectroscopy (XPS) has been widely used to determine the oxidation state of metals in organometallic and inorganic compounds [1]. The main advantage of XPS over other spectroscopy techniques like NMR and MS, is that solid samples are used, making it ideal for analysis of organometallic compounds that isomerise or decompose in solution, or are too insoluble for solution techniques. Examples include chromium, tungsten and molybdenum nitrosyl complexes [2], Group IV and V phenyl compounds [3] and a variety of gold and platinum complexes [4]. The most common oxidation states of gold are + I and + III, however in recent times, gold oxidation states of − I, + II, + IV and + V have been reported [5]. Due to poor solubility and the non-crystalline nature of many gold compounds, XPS has been the easiest and often only means to determine the oxidation state of this metal.

This work illustrates the use of XPS in determining the oxidation states of gold in a sequence of chlorine oxidative addition (OXAD) reactions forming a variety of complexes with different oxidation states (Scheme 1).

## 2. Results and discussion

Oxidative addition of $Cl_2$ to colourless **1** at − 70° affords the bright yellow gold(II) compound **2**. This compound spontaneously isomerises to the colourless heterovalent compound **3** above about − 20°. Addition of a further equivalent of $Cl_2$ to **3** affords a yellow solution of which yellow **4** precipitates out on standing. All compounds have been fully characterised [6]. The binding energies of the Au $4f_{7/2}$ P 2p and Cl 2p core levels and full width at half maximum values (FWHM) for the four complexes are shown in Table 1.

It can clearly be seen that the Au BE values increase in magnitude as the formal oxidation state of gold increases from + I to + III. The Au 4f BE values are slightly higher than those reported for binuclear ylide complexes of gold(I), gold(II) and gold(III) [7]. Moreover, the BE values are ca. 1 eV lower than those of the analogous binuclear gold compounds without the methyl substituent [8]. The gold $4f_{7/2}$ BE value increases by ca. 1 eV as the oxidation state increases from 0 to

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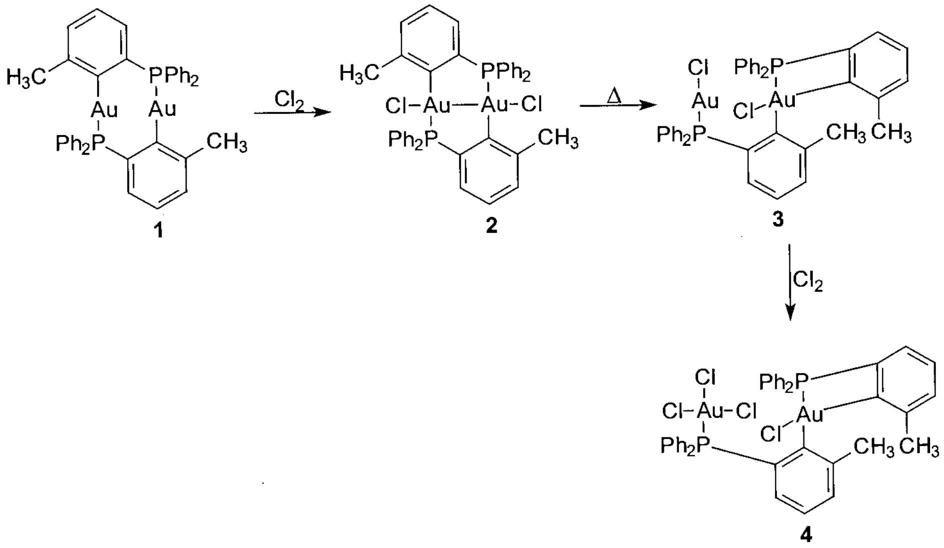

Scheme 1.

+ I and + II. The increase in BE value, as the oxidation state is increased from + II to + III is only about 0.5 eV. The change in BE values is however sufficient to allow identification of the oxidation state of gold in the system with some confidence. The BE values for P 2p and Cl 2p do not change significantly as the gold oxidation state is increased, illustrating that the gold centre undergoes greater changes both in terms of co-ordination number and co-ordination geometry, which changes from linear gold(I) to square planar gold(III) as the oxidation state is increased. The only exception is the P 2p BE value for **4**, which is 0.4 eV higher that in the other three complexes. This suggests that the four chlorine atoms remove some electron density from phosphorus through the gold atoms.

Gold(II) compounds used to be considered rare but, with recent work on binuclear compounds, gold(II) is now considered a fairly common oxidation state of the metal [9]. Early work suggesting the presence of gold(II) often proved to be heterovalent + I and + III states which gave an average oxidation state of + II. The study of non-methylated cyclometallated gold(II) analogues of **2** by $^{197}$Au Mössbauer spectroscopy has shown that each gold atom is present in an identical $d^9$ state [10]. Our XPS results confirm the presence of only one gold oxidation state in **2**, thus confirm the presence of a gold(II)–gold(II) centre. The BE values are in good agreement with those reported for non-methylated analogues [8].

Heterovalent binuclear gold compounds are relatively rare, especially those containing Au–P–C rings like compound **3**. A similar compound to **3** is formed during the OXAD reaction with nitromethane, to give a binuclear gold(II) ylide compound [11], however no XPS measurements have been reported on this compound. The Au 4f core level spectrum of **3** (Fig. 1) shows considerable broadening of the Au 4f doublet. Curve fitting of the data results in two distinct peaks, whose BE values indicate the presence of both gold(I) and gold(III). $^{197}$Au Mössbauer spectroscopy of **3** has confirmed the presence of both gold(I) and gold(II) [12]. During our XPS measurements it was observed that the gold 4f peak slowly changed over time from the mixed gold(I), gold(III) state to a predominantly gold(I) state. Fig. 2 shows the change occurring in the Au 4f doublet over a period of 40 min. At the same time an increase in the analysis chamber pressure was observed. This suggested photo stimulated reduction of the compound. Such photoreduction occurring during XPS measurements have been observed in the study of

Table 1
BE and FWHM values (eV) for complexes **1**–**4** (all data ± 0.05)

| Compound | Au oxidation state | Au $4f_{7/2}$ | FWHM | P 2p | Cl 2p |
|---|---|---|---|---|---|
| Au metal | 0 | 84.0 | 1.1 | | |
| **1** | +I | 85.1 | 1.7 | 132.1 | |
| **2** | +II | 86.5 | 1.9 | 132.1 | 198.7 |
| **3** | +I, +III | 85.2, 86.7 | 1.7, 1.9 | 132.1 | 198.9 |
| **4** | +III | 86.9 | 1.9 | 132.5 | 198.7 |

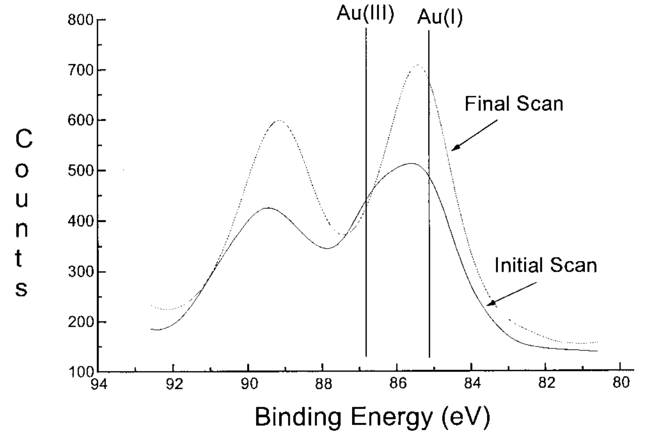

Fig. 1. Au $4f_{7/2}$ core level spectra of complex **3** showing photoreduction over time.

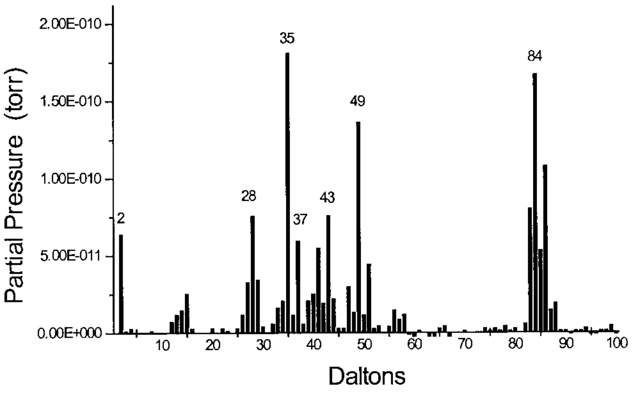

Fig. 2. Mass spectrum of residual chamber gas analysed during irradiation of **3**.

some platinum compounds [13]. This photoreduction of **3** could be accelerated by irradiating the sample with a 10 keV electron beam for a short period of time. Examination of the gold 4f doublet during irradiation showed that after only 60 s of exposure the peak curve fitted to give 54% gold(I) and after ca. 10 min of irradiation this had further reduced with ca. 66% being present as gold(I). Mass spectra of the residual chamber gas were recorded for compound **3**, both before and during X-ray irradiation. Fig. 2 shows the mass spectrum of the residual chamber gas obtained after irradiation.

The majority of the peaks can be assigned to decomposition products of the organic moieties of the compound, including various alkyl and aryl fragments. Due to the limited mass range of the instruments no phosphine fragments could be observed. The two major peaks at 35 and 37 Da with the isotopic ratio of 3:1 can be assigned to loss of chlorine. This seems to indicate that the radiation causes reduction to a gold(I) species accompanied by the loss of chlorine and decomposition of the compound. These observations of reduction of **3** in the solid state are consistent with reduction experiments carried out with **3** in solution. Observation of photoreduction and identifying chamber gas components can provide additional structural information, akin to observing both molecular ion and fragment peaks in mass spectroscopy. Refluxing **3** in a high boiling solvent for a prolonged period of time causes reduction to **1** as well as the formation of several other products. However treating **3** with reducing agents such as Cu or Zn powder only leads to the precipitation of elemental gold. Photoreduction is a common occurrence in gold compounds, especially gold(I) compounds such as Au(CO)Cl which are easily photoreduced to metallic gold in light at room temperature [14].

## 3. Conclusions

In this work we have shown that XPS is an important additional technique in structure determination of gold compounds, particularly for compounds that are insoluble or unstable in solution and hence cannot be fully characterised by other spectroscopic techniques. The change in BE values of the Au 4f doublets can be used to identify gold oxidation states of + I, + II, + III in both homo- and heterovalent systems. The BE values of co-ordinated ligands are not significantly affected by changes in the gold oxidation state. Photoreduction by the X-ray beam combined with residual gas analysis by mass spectroscopy can be utilised as a further tool in the structural elucidation of gold species.

## 4. Experimental

The gold compounds **1**–**4** were prepared according to a modified literature procedure [15]. XPS was performed on a VG Microlab 310F with an Al anode unmonochromated X-ray source operated at a power of 300 W and 15 kV excitation voltage.

The energy of the Al–$K_\alpha$ line was taken to be 1486.6 eV. The sample was tilted such that escaping electrons were collected by the electron analyser normal to the sample surface unless otherwise stated. The circular area of the sample from which escaping electrons were detected was ca. 2 mm in diameter. All survey spectra were performed in Constant Analyser Energy (CAE) mode at a pass energy of 100 eV at 1 eV steps between data points. All single element scans were performed in CAE mode at a pass energy of 20 and 0.1 eV steps. The spectrometer was calibrated with a sputtered copper (99.999%) sample and deposited gold on silicon sample giving Cu $2p_{3/2}$, Cu (KLL), Au $4f_{7/2}$ binding energies of 932.60, 334.8 eV (KE) and 84.00 eV, respectively. All samples for analysis in the Microlab were mounted on aluminium stubs using double sided adhesive conducting carbon tape. The base pressure of the analysis chamber was $6 \times 10^{-11}$ torr before samples were introduced. Charge correction was with respect to the low binding energy C 1s component taken to be 285.0 eV. The Au metal standard was prepared by vacuum depositing Au onto an aluminium stub. The four Au complexes (**1**–**4**) were analysed as powders on double sided carbon tape. Residual Gas Analysis was performed using a Dycor Quadrupole Gas Analyser Model M100 with a resolution of 0.5 amu at 10% height over a range from 1 to 100 Da.

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