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Ylide-Metal Complexes. XIII.[1] An X-Ray Photoelectron Spectroscopic Study of Bis(dimethylsulfoxonium methylide)gold Chloride

Hidetaka Konno[†] and Yoshihisa Yamamoto*
Faculty of Pharmaceutical Sciences, Higashi Nippon Gakuen University,
Ishikari-Tobetsu, Hokkaido 061-02
[†]Faculty of Engineering, Hokkaido University, Sapporo 060

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Bis(dimethylsulfoxonium methylide)gold chloride, $[(CH_3)_2S(O)CH_2AuCH_2S(O)(CH_3)_2]Cl$, has been studied by X-ray photoelectron spectroscopy. The C 1s spectrum was separated into two peaks at E_B=284.0 and 285.1 eV in a ratio of 1:2. The peak at 285.1 eV corresponds to the methyl carbons, and that at 284.0 eV is assigned to the electron-rich methylene carbon (or carbanion). The E_B of Cl $2p_{3/2}$ agreed with that for chlorobis(triphenylphosphine)gold(I) and chlorobis(triphenylmethylenephosphorane)gold(I). The E_B of Au $4f_{7/2}$ was 84.4 eV, suggesting the oxidation number +1. These results indicate that the structure of the title complex is $(CH_3)_2S(O)CH_2Au(Cl)CH_2S(O)(CH_3)_2$, and different from that reported previously.

A previous paper[2] in this series reported an X-ray photoelectron spectroscopic study of methylenetriphenylphosphorane, $(C_6H_5)_3P{=}CH_2$, chlorobis(methylenetriphenylphosphorane)gold(I), $(C_6H_5)_3PCH_2Au(Cl)CH_2P(C_6H_5)_3$, and the corresponding copper(I) complex. However, the separation and assignment of the carbanion peak and the normal carbon peak for the bonded ylide in the complexes have been difficult, because the carbon ratio is 1:18. Only few XPS studies of ylide-metal complexes have been reported, and the separation and assignment of the carbanion and normal carbons remain uncertain. We surveyed ylides from the sulfonium, phosphonium, and arsonium ylides for XPS measurements, and found a dimethylsulfoxonium methylide to be suitable for the assignment, since the carbanion to the normal carbon ratio is 1:2. This paper deals with the XPS measurements and the structure of bis(dimethylsulfoxonium methylide)gold(I) chloride, $[(CH_3)_2S(O)CH_2AuCH_2S(O)(CH_3)_2]Cl$; the results are compared with those[2] from the chlorobis(methylenetriphenylphosphorane)gold(I) previously reported.

Experimental

Preparation of bis(dimethylsulfoxonium methylide)gold(I) chloride, $[(CH_3)_2S(O)CH_2]_2AuCl$ (**1**), was done as reported previously.[1] Sample handling was always carried out in a 99.9995% pure nitrogen atmosphere to prevent possible decomposition. The instrument was a VG ESCA 3 electron spectrometer.

For the XPS measurements, samples were placed on a nickel mesh holder and introduced into the spectrometer in a 99.9995% pure nitrogen atmosphere. After evacuating to a vacuum better than 2.7×10^{-5} Pa (2×10^{-7} Torr), the sample was cooled to 180—200 K, and irradiated with Mg *Kα* X-ray (50—120 W). The analyzer energy was set to give a half width at half maximum [FWHM] of the Au $4f_{7/2}$ peak of 1.18 eV (high resolution) or 1.80 eV (low resolution) for vacuum evaporated gold on a smooth nickel plate. Peak separation of the spectra was made by the Gauss-Newton least-squares method, where a mixed Gaussian-Lorentzian curve shape was utilized. The electron binding energies, E_B, were calibrated by assigning 284.8 eV to the C 1s peak of the contamination from the spectrometer, 285.0 eV to the C 1s peak of the normal phenyl carbons, and 67.5 eV to the Br 3d peak of the bromide in $[(C_6H_5)_3PCH_3]Br$ and $[(C_6H_5)_3AsCH_3]Br$. This calibration is self-consistent (as shown in the results section).

Results and Discussion

We have reported[1] that dimethylsulfoxonium methylide, $(CH_3)_2S(O)CH_2$ (**L**),[3–5] in complex **1** was bonded to the metal atom through the carbanion donor atom[6–8] from the result of the ^{1}H NMR measurements. The elemental analysis of **1** and NMR results agreed with the proposed structure $(CH_3)_2S(O)CH_2Au(Cl)CH_2S(O)(CH_3)_2$ (**1a**) or $[(CH_3)_2S(O)CH_2AuCH_2S(O)(CH_3)_2]Cl$ (**1b**). Complex **1** has a free anion[1] judging from the molar conductance (Λ=100 S

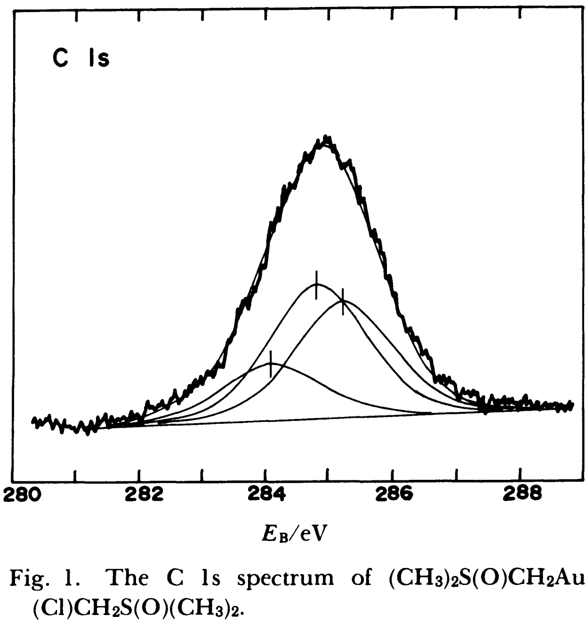


Fig. 1. The C 1s spectrum of $(CH_3)_2S(O)CH_2Au(Cl)CH_2S(O)(CH_3)_2$.

Table 1. Binding Energies for Ylide Metal Complexes and Relative Compounds

	Compound	Binding energies of electrons, E_B/eV											
		C 1s			O	S	N	P	As	Cl	Br	Au	
		(a)	(b)	(c)	1s	2p	1s	2p	3d	$2p_{3/2}$	3d	$4f_{7/2}$	$4f_{5/2}$
1	$[(CH_3)_2S(O)CH_2]_2AuCl$	284.0 (±0.1)	285.1 (±0.2)	284.8[a)]	531.5 (±0.6)	167.7 (±0.2)				197.7 (±0.5)		84.4 (±0.2)	88.1 (±0.1)
2	$[(CH_3)_3S{=}O]Br$		285.4 (±0.2)	284.8[a)]	532.3 (±0.3)	168.4 (±0.4)					67.5[a)]		
3	$[(C_6H_5)_3PCH_2]_2AuCl$	283.8	285.0[a)]					132.4 (±0.4)		197.5 (±0.3)		84.9 (±0.3)	88.6 (±0.1)
	$[(C_6H_5)_3PCH_3]Br$		285.0[a)]					132.6 (±0.4)			67.5[a)]		
	$[(C_6H_5)_3AsCH_3]Br$		285.0[a)]						44.4 (±0.3)		67.5[a)]		
	$[(CH_3)_4N]Cl$		285.4[b)]				402.3			197.1			

Uncertainties shown in parentheses are 90% confidence limits.
a) Reference peaks: E_B[Contamination C 1s]=284.8 eV, E_B[Phenyl C 1s]=285.0 eV, E_B[Br 3d]=67.5 eV. b) E_B of C 1s for methyl carbons was tentatively taken as 285.4 eV.

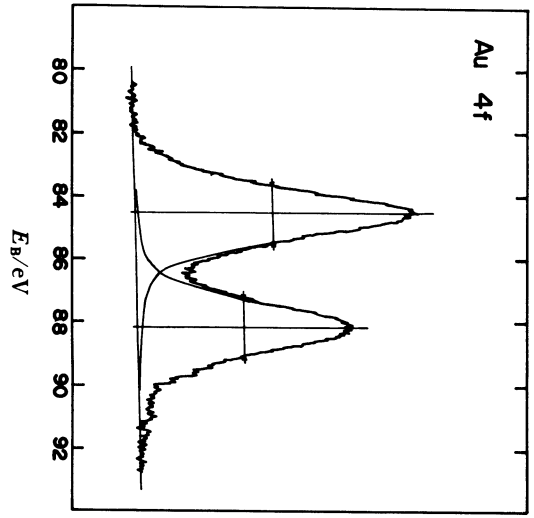


Fig. 2. The Au 4f spectrum of $(CH_3)_2S(O)CH_2Au(Cl)CH_2S(O)(CH_3)_2$ (this spectrum was measured together with the C 1s spectrum in Fig. 1).

cm^2 mol^{-1}) in dry methanol. Thus, we suggested that the structure of **1** is $[(CH_3)_2S(O)CH_2AuCH_2S(O)(CH_3)_2]Cl$ (**1b**).[1)]

With the XPS, the C 1s peak of **1** can be separated into three peaks having an intensity ratio of 1:x:2 (Fig. 1). The peak separation was carried out under only two limiting conditions: One that the peak intensity ratio between methylene carbons, methyl carbons, and carbonaceous contamination from the spectrometer is 1:2:x, and the other that the three peaks have the same FWHM. After the separation, the peak with an intensity x changed slightly in each measurement and could be assigned as a contamination carbon peak at 284.8±0.2 eV (with our instrument). The reproducibility of the E_B for carbonaceous contamination, when no other organic materials contaminate the sample surface, has been established by data accumulated over the 10-year operation of the instrument. The peak at 285.1 eV (C 1s (b) in Table 1) is assigned to methyl carbon and the peak at 284.0 eV to methylene carbon (C 1s (a)). The spectrum in Fig. 1 was taken in the high-resolution mode; the FWHM of the separated carbon peaks was 1.85 eV. The FWHM of the Au $4f_{7/2}$ peak for **1** taken under the same conditions was 1.81 eV (Fig. 2). Fig. 2 also indicates that there were no distortions of the spectra due to the charge-up effect. It should be noted that the symmetric peak shape for the contamination peak is a first approximation. Usually, the contamination peak shows a slight tailing at the higher E_B side: The degree of asymmetry is about 12:13 in a half width at half maximum. The asymmetric peak shape can be expressed by the superposition of a few symmetric peaks; but this introduces more parameters for the peak separation, leading to the arbitrary convergence in the calculation. The above approximation may not

Table 2. Relative Peak Intensities of XPS

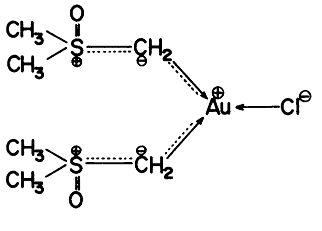
	Compound		Au 4f / S 2p	C 1s / S 2p		O 1s / S 2p	Cl 2p / S 2p	C 1s / Br 3d
				(a)	(b)			
1	$[(CH_3)_2S(O)CH_2]_2AuCl$	Atomic ratio	0.5	1	2	1	0.5	
		Intensity ratio	5.72	0.78	1.57	2.25	0.74	
			(±0.76)	(±0.03)	(±0.06)	(±0.20)	(±0.07)	
2	$[(CH_3)_3S{=}O]Br$	Atomic ratio			3	1		3
		Intensity ratio			2.23	2.24		1.42
					(±0.28)	(±0.62)		(±0.18)
					[0.74]			[0.47]
	$[(C_6H_5)_3PCH_3]Br$ $[(C_6H_5)_3AsCH_3]Br$	Atomic ratio						19
		Intensity ratio						9.59[a]
								(±1.76)
								[0.50]

Uncertainties shown in parentheses are 90% confidence limits. Values in brackets are per one carbon atom.
a) The contributions from the contaminated carbons are not excluded.

lead to a serious error in the E_B values of the separated peaks. The validity of the peak separation is supported by the good reproducibility of the relative peak intensities, as shown in Table 2. Further, C 1s/S 2p and O 1s /S 2p relative intensities for **1** agree well with those for trimethylsulfoxonium bromide, $[(CH_3)_3S{=}O]Br$ (**2**), and C 1s/Br 3d relative intensity per carbon atom for **2** (0.47) agrees with the 0.50 for $[(C_6H_5)_3PCH_3]Br$ and $[(C_6H_5)_3AsCH_3]Br$ as well. In Table 2, the intensity due to the contaminated carbons is excluded by the peak separation, except for $[(C_6H_5)_3PCH_3]Br$ and $[(C_6H_5)_3AsCH_3]Br$. For these two compounds, the peak separation could not be performed precisely due to the large number of phenyl carbons. In this case, however, the contribution from the contaminated carbon is negligible compared with the intrinsic intensity. The results imply that the peak separation is correct and that the stability of **1** during the measurements was comparable to that of **2** and the others in Table 2. The E_B[S 2p] for **2** coincides with that for trimethylsulfoxonium iodide, $[(CH_3)_3S{=}O]I$, reported in Ref. 9.

The E_B value of the ylide methylene carbons for chlorobis(methylenetriphenylphosphorane)gold(I),[2] $(C_6H_5)_3PCH_2Au(Cl)CH_2P(C_6H_5)_3$ (**3**), was not very reliable (as mentioned in the introduction). The E_B value for the ylide methylene carbons in **3**, however, is very close to that of ylide methylene carbons in **1** (Table 1). The E_B of the ylide methylene carbon of **3** strongly suggests that the carbon is anionic (or possibly a carbanion).

The E_B[Au $4f_{7/2}$] for **1** is lower than that for **3** or chlorobis(triphenylphosphine)gold(I), $(C_6H_5)_3PAu(Cl)P(C_6H_5)_3$ (**4**),[2,10] but higher than that (E_B=84.2—84.4 eV) for tetraethylammonium dibromoaurate(I), $[(C_2H_5)_4N][Au(I)Br_2]$ (**5**),[10] which leads to the conclusion that the oxidation number of gold in **1** is +1. The E_B[Cl $2p_{3/2}$] for **1** agrees well with those for **3** and **4**,[2,10] and is higher than that for the unbound chloride ion in tetramethylammonium chloride, $[(CH_3)_4N]Cl$, and others.[11] The bond between the chlorine atom and gold atom in **4** has been established by X-ray diffraction.[12] Thus, the chlorine atom in **1** is bonding to the gold atom. Consequently, the structure of **1** must be similar to **3** and **4**, and the trigonal structure as shown in Scheme 1.



Scheme 1.

In the previous paper,[1] the structure of **1** was suggested to be bis(dimethylsulfoxonium methylide)-gold(I) chloride (**1b**) from the results of the electric conductivity (Λ=100 S cm^2 mol^{-1}) in dry methanol. Later, however, it was found that the compound **4** in which chlorine is bonding to gold[12] also shows the electric conductivity in dry methanol and it is 75 S cm^2 mol^{-1} (similar to the value for **1**). This indicates that the chlorine atom in **4** dissociates in the methanol, and so does the one in **1**.

Both E_B[O 1s] and E_B[S 2p] for **1** are lower than those for **2**, indicating that the density of electrons on the S=O group of **1** is higher than that for **2**. As E_B[Au $4f_{7/2}$] for **1** is lower than for **3**, the electrons on the ylide methylene carbons in **1** may be delocalizing over the molecular orbitals of O=S-C-Au-C-S=O as shown in Scheme 1.

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