March, 1987] © 1987 The Chemical Society of Japan NOTES *Bull. Chem. Soc. Jpn.*, **60**, *1189—1191 (1987)* 1189

Ylide-Metal Complexes. XII.[1] The Preparation and Properties of Au, Be, Al, Ga, and In Complexes with Dimethylsulfoxonium Methylide

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(Received August 1, 1986)

Synopsis. The reaction of dimethylsulfoxonium methylide, $(CH_3)_2\overset{+}{S}(O)\text{-}\overset{-}{C}H_2$ (**L**), with (triphenylphosphine)gold chloride, $(C_6H_5)_3PAuCl$, yields a new bis(dimethylsulfoxonium methylide)gold(I) chloride, $[(CH_3)_2S(O)CH_2AuCH_2S(O)(CH_3)_2]Cl$. The reaction of the ylide **L** with $BeCl_2$ yields a new compound of tetrakis(dimethylsulfoxonium methylide)beryllium dichloride, $[(CH_3)_2S(O)CH_2]_4BeCl_2$. The reactions of the ylide **L** with $AlCl_3$, $GaCl_3$, and $InCl_3$ yield new dimeric compounds of μ-chloro-bis[tris(dimethylsulfoxonium methylide)metal] pentachloride, $[\{(CH_3)_2S(O)CH_2\}_3M\text{-}Cl\text{-}M\{CH_2S(O)(CH_3)_2\}_3]Cl_5$ (M: Al, Ga, and In). All complexes are thermally stable.

In this series, we have been concerned with the preparation and properties of the metal complexes[2] with methylenetriphenylphosphorane, $(C_6H_5)_3\overset{+}{P}\text{-}\overset{-}{C}H_2$. For the X-ray photoelectron spectroscopy measurements,[3] the phosphorane was an undesirable ylide, i.e., the separation for the carbanion in the coordinated phosphorane was difficult because the intensity ratio between carbanion and phenyl carbons was 1:18. Therefore, we surveyed sulfonium, phosphonium, and arsonium ylides, and found dimethylsulfoxonium methylide, $(CH_3)_2\overset{+}{S}(O)\text{-}\overset{-}{C}H_2$ as a suitable one for XPS study. The intensity ratio between carbanion and methyl carbons is 1:2, and the metal complex with the sulfonium ylide has been reported only for a few compounds.[4] Thus, the present paper deals with the preparation and properties of bis(dimethylsulfoxonium methylide)gold(I) chloride, $[(CH_3)_2S(O)CH_2AuCH_2S(O)(CH_3)_2]Cl$, tetrakis(dimethylsulfoxonium methylide)beryllium dichloride, $[(CH_3)_2S(O)CH_2]_4BeCl_2$, and μ-chloro-bis[tris(dimethylsulfoxonium methylide)metal] pentachloride, $[\{(CH_3)_2S(O)CH_2\}_3M\text{-}Cl\text{-}M\{CH_2S(O)(CH_3)_2\}_3]Cl_5$ (M: Al, Ga, In).

Experimental

Measurements. The ^1H NMR spectra were measured with R-40 (Hitachi) and XL-200 (Varian) NMR spectrometers. The electric conductivities of solutions were determined using a conductometric meter, CM-30 (Shimadzu).

Preparation of Ylide-Metal Complexes. Bis(dimethylsulfoxonium methylide)gold(I) Chloride (1): Dimethylsulfoxonium methylide[5] (**L**) was prepared by refluxing a mixture of trimethylsulfoxonium bromide (0.73 g, 4.22 mmol) and sodium hydride (0.11 g, 4.58 mmol) in dry tetrahydrofuran (20 cm³) under nitrogen until the evolution of hydrogen ceased. The product was cooled and filtered under nitrogen. To the resulting solution was added triphenylphosphine gold chloride (0.93 g, 1.88 mmol); the mixture was then stirred for 3 h at room temperature. The precipitated yellow complex was filtered, washed with dry pentane and dried under vacuum. Yield: 0.67 g (85.5%). Decomp: 165 °C. Found: C, 16.99; H, 3.70%. Calcd for $C_6H_{16}O_2S_2AuCl$ (MW 416.79) C, 17.29; H, 3.87%. Λ=100 S cm² mol⁻¹ in dry methanol at 20 °C. Λ=113 S cm² mol⁻¹ in water at 4 °C.

Tetrakis(dimethylsulfoxonium methylide)beryllium Dichloride (2): The tetrahydrofuran solution of the ylide was prepared from the mixture of trimethylsulfoxonium bromide (0.80 g, 4.62 mmol) and sodium hydride (0.12 g, 5.00 mmol) in dry tetrahydrofuran (20 cm³). To this solution was added beryllium dichloride (0.08 g, 1.00 mmol). The mixture was stirred for 5 d at room temperature. The precipitated white complex was filtered, washed with pentane and dried under vacuum. Yield: 0.45 g (88.8%). Decomp: 151 °C. Found: C, 31.85; H, 7.20%. Calcd for $C_{12}H_{32}O_4S_4BeCl_2$ (MW 448.59) C, 32.13; H, 7.19%. Λ=71 S cm² mol⁻¹ in dry methanol at −50 °C.

μ-Chloro-bis[tris(dimethylsulfoxonium methylide)aluminium] Pentachloride (3): The tetrahydrofuran solution of the ylide was prepared from the mixture of trimethylsulfoxonium bromide (0.78 g, 4.51 mmol) and sodium hydride (0.13 g, 5.42 mmol) in dry tetrahydrofuran (15 cm³) under nitrogen. Aluminium trichloride (0.15 g, 1.12 mmol) was added to the solution. The mixture was stirred for 3 d at room temperature. The precipitated white complex was filtered under nitrogen, washed with pentane and dried under vacuum. Yield: 0.68 g (61.5%). Decomp: 142 °C. Found: C, 26.11; H, 6.28%. Calcd for $C_{18}H_{48}O_6S_6Al_2Cl_6$ (MW 819.68) C, 26.38; H, 5.90%. Λ=608 S cm² mol⁻¹ in water at 5 °C. Λ=130 S cm² mol⁻¹ in dry methanol at −50 °C.

μ-Chloro-bis[tris(dimethylsulfoxonium methylide)gallium] Pentachloride (4): Gallium trichloride (0.20 g, 1.13 mmol) was added to the tetrahydrofuran solution of the ylide which was prepared from the mixture of trimethylsulfoxonium bromide of 0.78 g (4.51 mmol) and sodium hydride (0.13 g, 5.42 mmol) in dry tetrahydrofuran (15 cm³) under nitrogen. The mixture was stirred for 1 d at room temperature. The precipitated white complex was filtered, washed with pentane under nitrogen, and dried under vacuum. Yield: 0.71 g (57.4%). Decomp: 138 °C. Found: C, 23.68; H, 5.47%. Calcd for $C_{18}H_{48}O_6S_6Ga_2Cl_6$ (MW 905.16) C, 23.89; H, 5.35%. Λ=135 S cm² mol⁻¹ in dry methanol at −50 °C.

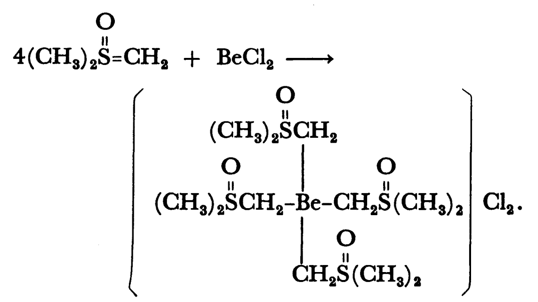
μ-Chloro-bis[tris(dimethylsulfoxonium methylide)indium] Pentachloride (5): Complex **5** was prepared from a reaction mixture of indium trichloride (0.16 g, 0.72 mmol) and a tetrahydrofuran solution of the ylide which was prepared from the mixture of trimethylsulfoxonium bromide (0.50 g, 2.89 mmol) and sodium hydride (0.08 g, 3.33 mmol) in dry tetrahydrofuran (15 cm³) under nitrogen. After 3 d at room temperature, the precipitated white complex was filtered, washed with pentane, and dried. Yield: 0.62 g (72.5%). Decomp: 160 °C. Found: C, 21.65; H, 4.86%. Calcd for $C_{18}H_{48}O_6S_6In_2Cl_6$ (MW 995.32) C, 21.72; H, 4.86%. Λ=100 S cm² mol⁻¹ in dry methanol at −50 °C.

Results and Discussion

Gold Complex. Bis(dimethylsulfoxonium methylide)gold(I) chloride (**1**) was prepared from the reaction of dimethylsulfoxonium methylide (**L**) and (triphenylphosphine)gold chloride, $(C_6H_5)_3PAuCl$. Complex **1** is slightly soluble in alcohols, DMSO, and water, but insoluble in common organic solvents such as acetone, benzene, and ether.

The ^1H NMR spectrum of **1** showed a singlet signal for the methylene group at 3.03 ppm and a singlet signal for methyl groups at 3.52 ppm in a ratio of 2:6 in CD_3OD as is shown in Table 1. The chemical shift of the methylene group is at a lower field than that of **L** (Table 1). This property is similar to those of metal complexes[2] with methylenetriphenylphosphorane, e.g. $[(C_6H_5)_3PCH_2\text{-}M\text{-}CH_2P(C_6H_5)_3]Cl_2$, M: IIB group metals.[2c] Thus, the ylide in complex is bonded to the gold atom through the carbanion donor atom.[6] Complex **1** has a free anion according to the molar conductance (cf. Experimental section). Then, the compound is a $[(CH_3)_2S(O)CH_2AuCH_2S(O)(CH_3)_2]Cl$, in which the cation has a linear configuration. The elemental analysis of **1** agreed with the proposed structure.

Beryllium Complex. Tetrakis(dimethylsulfoxonium methylide)beryllium dichloride (**2**) was prepared from a reaction mixture of dimethylsulfoxonium methylide (**L**) and $BeCl_2$. Complex **2** is soluble in methanol and slightly soluble in ethanol, but insoluble in chloroform, dichloromethane, DMSO, DMF, and water. The ylide is bonded to the beryllium atom through the carbanionic donor atom judging from the NMR spectral results (Table 1). Two coordination geometries for the compound are considered to be possible: a tetrahedral configuration of monomeric,[7] dimeric,[8] or polymeric[9] or a trigonal bipyramidal configuration of monomeric,[10] dimeric,[11] or trimeric.[12] The elemental analysis for **2** agreed with the composition of L_4MCl_2, i.e., the structure can not be a tetrahedral of dimeric or polymeric and a trigonal configuration. Complex **2** has free anions according to molar conductance. Thus, we suggest that the structure of **2** is a monomeric tetrahedron:



$$4(CH_3)_2\overset{\overset{O}{\|}}{S}{=}CH_2 + BeCl_2 \longrightarrow \left[Be\left(CH_2\overset{\overset{O}{\|}}{S}(CH_3)_2\right)_4\right]Cl_2$$

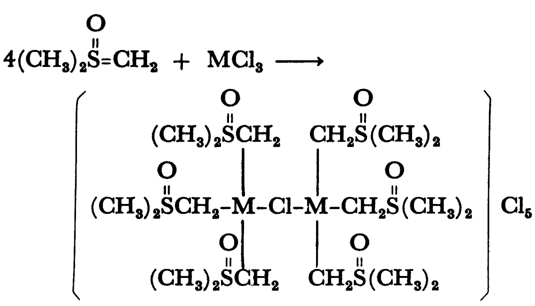
2

Aluminium, Gallium, and Indium Complexes. μ-Chloro-bis(dimethylsulfoxonium methylide)metal(Al (**3**), Ga (**4**), In (**5**)) pentachloride were prepared from a reaction mixture of dimethylsulfoxonium methylide (**L**) and MCl_3 (M: Al, Ga, In), respectively. Complexes **3**—**5** are slightly soluble in DMSO, DMF, methanol and water, but insoluble in chloroform, dichloromethane, and ether. Gallium complex **4** and indium complex **5** are unstable in water at 5 °C, giving the corresponding salt, $[(CH_3)_3S{=}O]Cl$ (**6**). The ylide is bonded to the metal atoms, judging from the NMR spectral results (Table 1). The elemental analysis of **3**—**5** agreed with the composition of L_3MCl_3. From the elemental analysis, four structures for the complexes are considered to be possible: a trigonal planar configuration of monomeric, $[L_3M]Cl_3$, a trigonal bipyramidal configuration of monomeric, $[L_3MCl_2]Cl$, a tetrahedral configuration of monomeric, $[L_3MCl]Cl_2$ and a tetrahedral configuration of dimeric, $[L_6M_2Cl]Cl_5$. The structure of $AlCl_3$, $GaCl_3$ and $InCl_3$ is known to be the bridge structure[13] by chlorines. In addition, the organoaluminium chlorides, bromides and iodides are generally dimeric. The most significant feature of the structure of methylaluminium dichloride, which has been determined by X-ray crystallography,[14] is that the dimer is held together through bridging atoms. Complexes **3**—**5** have free anions according to the molar conductance. Thus, we suggest that the structure of **3**—**5** comprises dimers bridged by chlorine and a metal with a tetrahedral coordination.

Table 1. ^1H NMR Spectra of Complexes, Ylide, and Salt

Complex No.	CH_2 δ/ppm	CH_3 δ/ppm	Solvent	Standard (δ=0)	Temp °C
1	3.08 s (2H)	3.59 s (6H)	D_2O	DSS	5
	3.03 s (2H)	3.52 s (6H)	CD_3OD	TMS	r. t.
2	2.69 s	3.30 s [a]	CD_3OD	TMS	−50
3	2.71 s (2H)	3.83 s (6H)	D_2O	DSS	5
	2.65 s	3.32 s [a]	CD_3OD	TMS	−50
4	2.60 s	3.31 s [a]	CD_3OD	TMS	−50
5	2.63 s	3.28 s [a]	CD_3OD	TMS	−50
6'		3.83 s	D_2O	DSS	r. t.
L[b]	1.92 s (2H)	2.95 s (6H)	C_6D_6	TMS	35

6': $[(CH_3)_3S{=}O]Br$. **L**: $(CH_3)_2S(O){=}CH_2$. a) This signal is overlapped with solvent. b) Ref. 4.



M	Al	Ga	In
No.	**3**	**4**	**5**

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