A HIGH YIELD SYNTHESIS OF DIMETHYLSULFIDE-$\underline{d}_6$, AND PREPARATION OF CHLORO(DIMETHYLSULFIDE-$\underline{d}_6$)GOLD(I) AND TRICHLORO(DIMETHYLSULFIDE-$\underline{d}_6$)GOLD(III)

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SUMMARY

Dimethylsulfide-$\underline{d}_6$ has been prepared in higher yield than reported previously by an improved method involving the reduction of dimethylsulfoxide-$\underline{d}_6$ with triphenylphosphine in a solvent mixture of carbon tetrachloride and 2,2-dimethoxydiethyl ether at 0°C. The high isotopic purity of the compound was demonstrated by its gas phase infrared and mass spectra. Its utility as a ligand in coordination chemistry was then shown by the synthesis of two typical gold complexes, <u>viz</u>., chloro(dimethylsulfide-$\underline{d}_6$)gold(I) and trichloro(dimethylsulfide-$\underline{d}_6$)gold(III).

Key words: Dimethylsulfide, Dimethylsulfoxide, Gold Complexes

INTRODUCTION

As the use of isotopically substituted ligands in metal complexes increases among both spectroscopists and inorganic chemists, high yield syntheses of common ligands and efficient means of introducing them into coordination compounds are necessary. We report here an improved, high yield synthesis of dimethylsulfide-$\underline{d}_6$ and more efficient reactions, based on the sulfide, for the preparation of gold halide complexes.

Dimethylsulfide can be prepared by the reduction of dimethylsulfoxide with a variety of reagents.[1-3] Both dimethylsulfate-$\underline{d}_6$ and dimethylsulfoxide-$\underline{d}_6$

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are commercially available, but the latter is economically preferable as a starting material.

The reduction of dimethylsulfoxide to dimethylsulfide by triphenylphosphine in carbon tetrachloride has been demonstrated by trapping the sulfide as a mercuric chloride complex. Trapping is necessary to avoid a tedious separation of the $(CH_3)_2S$ from a large excess of CCl_4. Thus this method is not really suitable for the isolation and subsequent use of $(CD_3)_2S$. For this reason, Tranquille et al.[3] prepared $(CD_3)_2S$ by the disproportionation of $(CD_3)_2SO$ using aqueous NH_4Br to catalyze the reaction. The yield was 45% based on the $(CD_3)_2SO$ starting material. Moreover, since the reaction uses $(CD_3)_2SO$ as the reductant, this yield can never exceed 50%.

We have adapted the reduction of $(CD_3)_2SO$ by triphenylphosphine in carbon tetrachloride to obtain 70-75% yields of $(CD_3)_2S$ by using the nonvolatile solvent 2,2-dimethoxydiethyl ether (diglyme). The CCl_4 and $(CD_3)_2S$ are readily removed from the bulk in vacuo and the sulfide product is finally purified by fractional distillation.

The syntheses of $(CD_3)_2SAuCl$ and $(CD_3)_2SAuCl_3$ are based on the methods of Teresa.[4-6] A stoichiometric quantity of dimethylsulfide reacts with the tetrachloroaurate anion to form $(CH_3)_2SAuCl_3$; an excess of the sulfide leads to the formation of $(CH_3)_2SAuCl$:

$$(CH_3)_2S + HAuCl_4 \longrightarrow (CH_3)_2SAuCl_3 + HCl$$

$$2(CH_3)_2S + HAuCl_4 + H_2O \longrightarrow (CH_3)_2SAuCl + 3HCl + (CH_3)_2SO$$

Since the latter reaction proceeds by the formation of the gold(III) complex and its subsequent slow reduction to gold(I), the yield of deuterated gold(I) complex, based on the $(CD_3)_2S$ reagent, may be doubled by using a noncoordinating reducing agent such as SO_2:

$$(CD_3)_2S + HAuCl_4 \longrightarrow (CD_3)_2SAuCl_3 + HCl$$

$$(CD_3)_2SAuCl_3 + SO_2 + 2H_2O \longrightarrow (CD_3)_2SAuCl + H_2SO_4 + 2HCl$$

EXPERIMENTAL

Infrared spectra of $(CD_3)_2S$ were recorded on a Beckman IR-12 spectrometer using a 10-cm gas cell fitted with NaCl windows; its mass spectrum was measured on a Hitachi RMU-6E mass spectrometer. Gold analyses were performed by dissolving accurately weighed samples of the complex (ca. 10 mg) in hot aqua regia and then diluting these solutions to 100 ml after complete dissolution. The gold concentrations in these dilutions were determined on a Perkin Elmer 360 atomic absorption spectrometer which had been calibrated with serial dilutions of commercially available standards.

Preparation of Dimethylsulfide-d_6. Diglyme (25 ml) and triphenylphosphine (19.67 g, 0.075 mole) were degassed on a vacumm line in a 100-ml flask fitted with a dropping funnel and a thermometer. Carbon tetrachloride (4.0 ml) was added through the dropping funnel. The mixture was cooled to 0°C and dimethylsulfoxide-d_6 (4.0 ml, 0.051 mole) was added slowly. After stirring for 3½-4 hr, the ice-bath was allowed to warm to room temperature. Caution: If the ice-bath is removed too soon, a vigorous exothermic reaction may blow off the dropping funnel and thermometer. Premature removal also results in discoloration and poor yields. The volatile components were collected in a liquid nitrogen trap until approximately 10 ml had been transferred. This mixture was distilled through a 15-cm Vigereaux column, collecting the fraction boiling up to 38°C. The yield of $(CD_3)_2S$ was 73% (2.74 g) and from its mass spectrum the isotopic purity was greater than 99.9%. Its authenticity was also clearly established by its gas phase infrared spectrum, the major peaks occurring at 2255sh, 2245sh, 2238sh, 2235sh, 2151sh, 2142sh, 2136sh, 2102m, 2030w, 2020w, 1070s, 1057s, 1052s, 1025w, 1014w, 1005w, 830w, 656m, and 636m cm^{-1}.[3]

Preparation of Chloro(dimethylsulfide-d_6)gold(I). Dimethylsulfide-d_6 (0.2 ml) was added to a solution of $HAuCl_4 \cdot H_2O$ (0.20 g, 5.3 mmole) dissolved in absolute ethanol (5 ml), followed immediately by addition of 6% sulfurous acid (0.6 ml). After the entire solution had decolorized, the shiny white precipitate was filtered off, recrystallized from chloroform, and dried *in vacuo* (mp 115-120°C dec.)

Anal. Calcd for C_2D_6AuClS: C, 7.97; D, 3.98; Au, 65.5. Found: C, 7.94; D, 3.97; Au, 67.0.

Preparation of Trichloro(dimethylsulfide-d_6)gold(III). Dimethylsulfide-d_6 (0.5 ml) was syringed into a solution of $HAuCl_4 \cdot H_2O$ (2.0 g) dissolved in absolute ethanol (15 ml). The yellow precipitate which formed was collected by filtration, recrystallized from chloroform, and dried over P_2O_5 in a desiccator. Anal. Calcd for $C_2D_6AuCl_3S$: C, 6.47; D, 3.25. Found: C, 6.52; D, 3.30.

RESULTS AND DISCUSSION

The yield of $(CD_3)_2S$ obtained by the method described above represents a significant improvement over that obtained by Tranquille et al.[3] (73 vs. 45%) based on the amount of dimethylsulfoxide-d_6 used. A careful yield optimization was carried out using varying amounts of triphenylphosphine and carbon tetrachloride. Reducing the amount of triphenylphosphine below that reported here results in low yields of $(CD_3)_2S$. Increasing the amount of carbon tetrachloride gives an apparent increase in the yield of the desired product, but gas chromatography indicates that this is an artifact due to increased CCl_4 contamination of the product. Thus the yield of $(CD_3)_2S$ is insensitive to the CCl_4 concentration, consistent with its expected catalytic role:[1]

$$(CD_3)_2SO + (C_6H_5)_3P \xrightarrow[\text{diglyme}]{CCl_4} (CD_3)_2S + (C_6H_5)_3PO$$

The isolation of triphenylphosphine oxide as a product was verified by infrared analysis of the insoluble pot residue and its melting point.

The retention of isotopic purity in the formation of the gold complexes was demonstrated by the infrared and Raman spectra of the solid complexes. Details of these spectra, as well as complete normal coordinate analyses of the vibrational data, will be reported elsewhere.[7]

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