[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Trimethylgold[1a]

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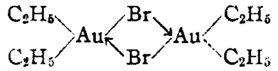
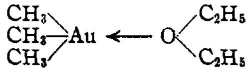
The extensive and elegant studies by Gibson and co-workers[2] on organogold compounds have shown that all of the trivalent gold compounds which they investigated were four-covalent. For example, diethylgold bromide was assigned the following structure



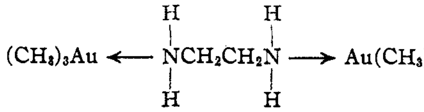
They expressed the view "of the impossibility of existence of compounds having the empirical R_3Au (R = alkyl)."[3] In support of this generalization were the numerous attempts[4] to prepare an R_3Au compound by the Grignard reagent, and by other indirect procedures, under various experimental conditions and with a series of radicals.

We have succeeded in preparing trimethylgold in ether solution by the reaction of methyllithium with gold tribromide or dimethylgold bromide at −65°. The free trimethylgold, however, was highly unstable and began to decompose at about −40 to −35°. The products of this thermal decomposition were gold, methane, and ethane. No molecular weight was determined for the trimethylgold, but it is possible that there is a coördination in ether[5] and that Gibson's postulate of trivalent gold compounds being four-covalent is valid with our compound.



Also it is understandable why the Grignard reagent did not give the R_3Au type, for the R_2AuX type was probably formed in the early stages and this would go more effectively to the R_3Au type with a more reactive organometallic compound like methyllithium and at low temperatures.

The trimethylgold can be stabilized by adding ethylenediamine, 2-aminopyridine, or benzylamine. The resulting coördination compounds may provisionally be represented by structures of which the following is typical



$$(CH_3)_3Au \longleftarrow \overset{H}{\underset{H}{N}}CH_2CH_2\overset{H}{\underset{H}{N}} \longrightarrow Au(CH_3)_3$$

By analogy with triethylgallium, it might be expected that the coördination compound of trimethylgold with amines would be more stable than the coördination compound with ether; for the simple triethylgallium reacts violently with water, the etherate $[(C_2H_5)_3Ga{\cdot}(C_2H_5)_2O]$ vigorously, and the ammine $[(C_2H_5)_3Ga{\cdot}NH_3]$ only very slowly.[6] Some other amines appeared not to form stable coördination compounds with trimethylgold. Also, an orienting experiment indicated that ethylenediamine did not stabilize the homologous triethylgold. This observation was not surprising, for other studies[7] have shown that the ethyl derivatives of copper, thallium and other metals appear to be significantly less stable than the corresponding methyl derivatives.

On the basis of some theoretical considerations it appeared that if the radical attached to gold were neopentyl instead of methyl the organogold compounds might be more stable. This found some qualitative support on the basis of the rates of deposition of gold from the organogold compounds; however, it is doubtful whether the stability could be increased sufficiently to make possible the isolation of the free trineopentylgold.

Cleavage Reactions.—Hydrogen chloride readily cleaved trimethylgold, and also its coördination compound with ethylenediamine, to form dimethylgold chloride and methane.

$$(CH_3)_3Au + HCl \longrightarrow (CH_3)_2AuCl + CH_4$$

In the presence of bromide ion, dimethylgold bromide was formed in preference to the chloride even though an excess of hydrochloric acid was present.

Inasmuch as trialkylgold compounds are readily prepared from alkyllithium compounds and gold tribromide, their cleavage by hydrogen chloride at −65° offers a method of choice for the preparation of dialkylgold halides.

Although trimethylgold was not cleaved by phenol or trichloroacetic acid[8] at −65°, it was readily cleaved by thiophenol or thioglycolic acid to form dimethylgold thiophenate and dimethyl-

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[1] (a) Paper LXIV in the series: "The Relative Reactivities of Organometallic Compounds." The preceding paper is with Tolman, THIS JOURNAL, 68, 522 (1946). (b) Present address: Medical School, U. of Michigan, Ann Arbor, Michigan.

[2] Some recent references are Gibson and Weller, *J. Chem. Soc.*, 102 (1941), and Ewens and Gibson, *ibid.*, 109 (1941).

[3] Burawoy, Gibson and Holt, *ibid.*, 1024 (1935). See, also, Gibson, *Brit. Assoc. Advancement Sci. Rept.*, 35 (1938) [*C. A.*, 33, 2838 (1939)]; Gibson and Colles, *J. Chem. Soc.*, 2409 (1931); and Gibson, "*Troisième Conseil de Chimie Solvay:* Rapports et Discussions," 422 (1928).

[4] Kharasch and Isbell, THIS JOURNAL, 53, 2701 (1931).

[5] Gilman and Jones, *ibid.*, 62, 1243 (1940). If the trimethylgold is associated there might be the possibility of structures formed as a consequence of an attachment of carbon atoms of another $(CH_3)_3$-Au group through and between the hydrogen atoms to an incompleted valence shell of gold. See, Pitzer and Gutowsky, *ibid.*, 68, 2204 (1946), on the structure of trimethylaluminum. Also, particularly, Rundle and Sturdivant, *ibid.*, 69, 1561 (1947), for the possibility of a structure related to tetramethylplatinum where a methyl group is bonded to more than one other atom.

[6] Dennis and Patnode, *ibid.*, 54, 182 (1932). See, also, pp. 556–557 in Gilman, "Organic Chemistry," John Wiley and Sons, N. Y. (1943).

[7] By R. G. Jones and L. A. Woods.

[8] Trichloroacetic acid has been used by W. E. Catlin to measure the rates of cleavage of relatively unreactive organolead and organotin compounds.

gold carboxymethylmercaptide, respectively.

$$(CH_3)_3Au + HSR \longrightarrow (CH_3)_2AuSR + CH_4$$

The ability of RSH compounds to cleave triethylbismuth and tetraethyllead at a much more rapid rate than some phenols and carboxylic acids has been reported.[9]

Trimethylgold did not react with benzoyl chloride at temperatures up to −20°, whereas, under essentially the same conditions, methylcopper reacted with benzoyl chloride to form acetophenone.[10] This lower reactivity of trimethylgold toward some functional groups might have been predicted on the basis of the generalization that in any group or sub-group the higher the ionization potential of a metal the less reactive will be its organometallic compounds.[11a]

Disproportionation and Thermal Decomposition.—When an ether suspension of gold tribromide is added to an ether solution of trimethylgold at −75°, then stirred for two hours and allowed to come to room temperature, dimethylgold bromide is one of the products. This indicates that the following reaction occurred

$$2(CH_3)_3Au + AuBr_3 \rightleftarrows 3(CH_3)_2AuBr \quad [I]$$

A reaction of this type is rather general with organometallic compounds and a related equilibrium has been reported with organoberyllium compounds[11b]

$$2RBeX \rightleftarrows R_2Be + BeX_2$$

In the disproportionation or redistribution reaction[11c] [I], one might expect to find some methylgold dibromide. This appears to be the case when dimethylgold bromide is refluxed in ether solution. Incidental to the thermal decomposition of methylgold compounds, it should be mentioned that the solid bis-(trimethylgold)-ethylenediamine explodes violently when heated in an open crucible.

Experimental

Trimethylgold.—A suspension of 8.74 g. (0.02 mole) of gold tribromide[12] in 60 cc. of ether was cooled to −65° and stirred while a solution of 0.06 mole of methyllithium in 50 cc. of ether was added over a period of three hours. The mixture gave a negative color test I.[13] The suspension was allowed to warm up slowly to room temperature. At about −40 to −35° a gold mirror began to form on the walls of the flask. The mixture was gently refluxed for two hours and the evolved gas was collected and analyzed. The gas consisted of 0.023 mole (76.8% yield) of ethane, and 0.011 mole (18.4% yield) of methane.

In all reactions involving organolithium compounds a nitrogen atmosphere and dry reagents were used.

bis-(Trimethylgold)-ethylenediamine.—A solution of 1.54 g. (0.005 mole) of dimethylgold bromide in 60 cc. of ether was cooled to −65°, and 0.0065 mole of methyllithium in 25 cc. of ether was added with stirring during fifteen minutes. The resulting clear solution was stirred for one-half hour, and then 1.5 cc. of 95% ethylenediamine was added. The milky solution was stirred for one hour at −65° before it was allowed to warm up to room temperature. No precipitate of metallic gold appeared. The ether solution was washed with 25-cc. portions of water and evaporated. The crystalline residue was dissolved in 10 cc. of ether, and then 15 cc. of petroleum ether (b. p. 28–38°) was added. On slow evaporation of the solution in a refrigerator, colorless crystals were formed and these were dried in a desiccator over phosphorus pentoxide in the dark. The yield was 1.2 g. (88%) of compound free of halogen, soluble in ether, insoluble in ethanol or petroleum ether (b. p., 28–38°), and very sensitive to light. The compound decomposed in a melting point capillary over the range 94–98°.

Anal. Calcd. for $C_4H_{13}NAu$: N, 5.14; Au, 72.40. Found: N, 5.21, 5.15 and 5.4; Au, 72.2 and 71.9.

When 0.2 g. of the complex was warmed in an open porcelain crucible preparatory to analysis, it exploded violently and pulverized the crucible. A drop of concentrated nitric acid added to the dry powder also detonates it. When moistened carefully and treated with dilute acids it precipitates gold. This indicates that the complex may be decomposed to trimethylgold and ethylenediamine and that the trimethylgold then breaks down promptly to gold and the hydrocarbons.

Trimethylgold α-Aminopyridine.—This compound was prepared from 0.005 mole of trimethylgold and 0.0075 mole of α-aminopyridine in ether at −65°. After washing the ether solution with water and then removing the ether by evaporation, the oil was dried over phosphorus pentoxide to give 1.1 g. (65.5%) of compound which gave a negative bromine test, and was partially soluble in petroleum ether (b. p. 60–68°) or benzene. From these solutions, metallic gold precipitated in a short time.

Anal. Calcd. for $C_8H_{15}N_2Au$: N, 8.32; Au, 58.62. Found: N, 8.24; Au, 58.46.

Trimethylgold Benzylamine.—This compound, prepared from 0.005 mole of trimethylgold and 0.0075 mole of benzylamine, was purified with some difficulty by crystallizing several times from petroleum ether (b. p. 28–38°) to give white needles melting at 51.5–53°. The yield was 1.0 g. (57.3%).

Anal. Calcd. for $C_{10}H_{18}NAu$: N, 4.01; Au, 56.40. Found: N, 4.30; Au, 56.75.

Attempts to stabilize trimethylgold with the following nitrogen compounds were unsuccessful: aniline, dimethylaniline, *p*-phenylenediamine, piperidine, ethylamine, dimethylamine and glyoxime.

Cleavage of bis-(Trimethylgold)-ethylenediamine with Hydrogen Chloride.—To a solution of 1.36 g. (0.005 mole) of bis-(trimethylgold)-ethylenediamine in 25 cc. of ether cooled to −65° was added, with stirring and over a twenty-minute period, 0.01 mole of hydrogen chloride in 85 cc. of ether. A white precipitate formed, and after the mixture had warmed up to room temperature it was stirred for one-half hour and then refluxed for five minutes. The evolved gas was collected and found to consist of 0.0049 mole (98% yield) of methane.

The ether solution was washed with 25 cc. of water, and the crude dimethylgold chloride remaining after evaporation of the solvent was purified by recrystallization from petroleum ether (b. p. 28–38°) to yield 1.2 g. (91.6%). The dimethylgold chloride, as well as a mixture with an authentic specimen, melted at 71–72°.

Cleavage of Trimethylgold and Triethylgold with Hydrogen Chloride.—A solution of 0.01 mole of trimethylgold, prepared from dimethylgold bromide and methyllithium in 80 cc. of ether at −65°, was treated with 0.01 mole of hydrogen chloride in 35 cc. of ether. The yield of methane was 0.0088 mole (88%); and the yield of dimethylgold bromide was 2.7 g. (88%) (melting point and also mixed m. p. with an authentic specimen was 67–68°).

A solution of trimethylgold, prepared from 8.74 g.

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[9] Gilman and Nelson, This Journal, **59**, 935 (1937).

[10] Gilman and Woods, *ibid.*, **65**, 435 (1943).

[11] (a) Gilman and Jones, *ibid.*, **62**, 2353 (1940); (b) Gilman and Schulze, *ibid.*, **49**, 2904 (1927); (c) Calingaert and Beatty in Chap. 24 of Gilman, "Organic Chemistry," John Wiley and Sons, New York, N. Y., 1943.

[12] Prepared in accordance with the directions of Gibson and Colles, *J. Chem. Soc.*, 2407 (1931).

[13] Gilman and Schulze, This Journal, **47**, 2002 (1925).

(0.02 mole) of gold tribromide and 0.074 mole of methyllithium in ether at −65°, was cleaved with 0.04 mole of hydrogen chloride in 50 cc. of ether. The yields of dimethylgold bromide varied from 3.07 to 3.98 g. (50–65%).

By a similar procedure, diethylgold bromide (m. p. 56.5–58°) was prepared in a yield of 57.5%.

Dineopentylgold Bromide.—A suspension of 8.74 g. (0.02 mole) of gold tribromide in 60 cc. of ether was cooled to −65° and rapidly stirred while 0.06 mole of neopentylmagnesium chloride[14] in 125 cc. of ether was added over a period of seventy-five minutes. The mixture was stirred for an additional two hours after which it gave a negative color test I.[13] Then a solution of 0.023 mole of hydrogen chloride in 35 cc. of ether was added during twenty minutes, and after two hours the mixture was allowed to warm up to −15° and then treated with 15 cc. of water. The ether solution was separated and the solvent removed under reduced pressure to leave a crystalline residue. This was extracted with 100 cc. of petroleum ether (b. p. 28–38°), the solution was washed with a little water, dried over sodium sulfate, and allowed to evaporate spontaneously in a refrigerator. The yield of product melting at 121.5–123° was 1.0 g. (11.9%).

Anal. Calcd. for $C_{10}H_{22}BrAu$: Au, 47.02. Found: Au, 46.80.

Cleavage of Trimethylgold with Thioglycolic Acid and with Thiophenol.—A solution of 0.0093 mole of methyllithium in 25 cc. of ether was added to a stirred suspension of 1.54 g. (0.005 mole) of dimethylgold bromide in 60 cc. of ether at −65°. After one-half hour, 0.84 g. (0.0093 mole) of thioglycolic acid in 20 cc. of ether was added slowly. Then, after two hours, the mixture was allowed to warm up to room temperature, poured into 20 cc. of water, and the ether removed by evaporation. The aqueous suspension was treated with 10% hydrochloric acid until precipitation was complete. Crystallization from ethanol yielded 1.5 g. (94%) of crystalline dimethylgold carboxymethylmercaptide.

Anal. Calcd. for $C_4H_9O_2SAu$: Au, 61.94. Found: Au, 62.40.

The cleavage with thiophenol was carried out under the same conditions and concentrations as with thioglycolic acid. After extraction of the product with 2 cc. of 10% potassium hydroxide in 10.0 cc. of water, the residue was dissolved in 80 cc. of warm ether and then 15 cc. of methanol was added. From the resulting solution, by spontaneous evaporation, was obtained 1.49 g. (88.5%) of pale-yellow crystals of dimethylgold thiophenate melting at 132–133° and decomposing above 138°.

Anal. Calcd. for $C_8H_{11}SAu$: Au, 58.62. Found: Au, 58.52 and 58.62.

Phenol and trichloroacetic acid did not react with trimethylgold in ether at −65°.

Trimethylgold and Benzoyl Chloride.—A solution of 0.005 mole of trimethylgold in 75 cc. of ether at −65° was stirred while 0.7 g. (0.005 mole) of benzoyl chloride in 25 cc. of ether was added over a period of ten minutes. After two hours the solution was allowed to slowly warm up to room temperature. Gold was precipitated at about −30°, and gas was evolved. The mixture was refluxed briefly and all of the evolved gas was collected. The yield of ethane was 0.0039 mole (52%), and the yield of methane was 0.0011 mole (7.3%). The ether solution was treated with 40 cc. of 10% potassium hydroxide and 20 cc. of methanol, and the mixture was shaken until the odor of benzoyl chloride disappeared. The yield of benzoic acid was 98%, and there was no qualitative test for ketone. This experiment was repeated with the same results.

Reaction of Methyllithium with Methyl Iodide in Presence of a Small Amount of Gold Tribromide.—A solution of 7.1 g. (0.05 mole) of methyl iodide in 15 cc. of ether was added to a suspension of 1.09 g. (5 mole per cent.) of gold tribromide in 15 cc. of ether. To this mixture was added 0.05 mole of methyllithium in 40 cc. of ether over a period of twenty minutes. The suspension refluxed rapidly and gas was evolved. After standing for five hours, the apparatus was swept out with nitrogen. A bluish-purple suspension, probably colloidal gold, was visible throughout the reaction. The yield of ethane was 0.029 mole (58%), and the yield of methane was 0.013 mole (13%). In a duplicate experiment, the same observations were made, and the yield of ethane was 0.026 mole (52%), and the yield of methane was 0.021 mole (21%).

In a control experiment in which the methyl iodide was omitted, there was obtained 0.0025 mole of ethane and 0.0024 mole of methane.

Thermal Decomposition of Dimethylgold Bromide.—A solution of 1.54 g. (0.005 mole) of dimethylgold bromide in 25 cc. of ether was refluxed for forty-eight hours. The solution turned reddish brown after a short time, and metallic gold separated. The gas resulting from the decomposition amounted to 0.00308 mole of ethane (61.5% based on two methyl groups from dimethylgold bromide).

The red solution was filtered and the residue washed with ether until the washings were colorless, to give 0.612 g. (62%) of gold.

From the ether was recovered 0.144 g. (9.4%) of dimethylgold bromide, by extraction of the residue with petroleum ether (b. p., 28–38°); and by extraction of the residue with chloroform (in accordance with a procedure of Brain and Gibson)[15] there was obtained 0.21 g. (11.3%) of what appeared to be methylgold dibromide on the basis of solubilities.

The residue, remaining after the chloroform extraction, was apparently the water-soluble hydrated gold tribromide, as evidenced by physical properties.

Analytical Procedures.—Nitrogen analyses were carried out by a slow and careful combustion in a micro-Dumas apparatus. It was necessary to have the long burner as hot as practicable to ensure the complete combustion of the low molecular weight hydrocarbons resulting from the sudden decomposition of the gold compounds.

For gold analyses, the weighed sample was wrapped in ashless filter paper, placed in a weighed porcelain crucible and moistened with 10% hydrochloric acid. This crucible was placed in a Gooch crucible and slowly warmed on a hot-plate until the gold compound decomposed. The paper was carefully burned off, and the residue heated for one-half hour to one hour over a Meker burner.

The halogen analyses were carried out by decomposing the compound with warm alcoholic potassium hydroxide, filtering off the metallic gold, acidifying the filtrate with nitric acid, and titrating the halogen by the Volhard method.

Summary

Trimethylgold, the first R_3Au type prepared, has been synthesized by the reaction of methyllithium with gold tribromide or dimethylgold bromide at −65°. The compound is highly unstable, and begins to decompose at about −40 to −35° into gold, methane and ethane.

Coördination compounds with amines like ethylenediamine are more stable. These, like the trimethylgold, are cleaved smoothly by hydrogen chloride and RSH compounds to give dimethylgold salts.

As might have been predicted, trimethylgold is of a low order of chemical reactivity toward some functional groups. It does, however, react with gold tribromide to give dimethylgold bromide.

Triethylgold appears to be distinctly less stable than trimethylgold.

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[14] The authors are grateful to Dr. F. C. Whitmore for the neopentylmagnesium chloride.

[15] Brain and Gibson, *J. Chem. Soc.*, 762 (1939).