A New Synthesis of Dimethylgold(III) Chloride Using Tetramethyltin

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The reaction of $HAuCl_4$ or $AuCl_3$ with $Sn(CH_3)_4$ in methanol at low temperatures gives $[(CH_3)_2AuCl]_2$ in yields from 40 to 45%.

Gold is widely used for the interconnection of components in integrated circuits and microwave devices. As the dimensions of the components are reduced further and further, vapour phase deposition techniques are gaining importance, and for this reason volatile gold compounds have recently received considerable attention for use in laser-controlled deposition of high purity gold. To date only a limited number of suitable compounds has been published [1–5], the most promising ones being dimethyl(2,4-pentanedionato)gold(III) and its fluorinated analogues. These compounds have a high vapour pressure, which increases with the number of fluorine substituents, and undergo decomposition readily at relatively low temperatures [6–18]. This unusual volatility has also been noted for pentanedionate complexes of other metals [19].

Most synthetic pathways to dimethyl (2,4-pentanedionato)gold and its fluorinated derivatives rely on an efficient preparation of dimethylgold(III) halides, which can be reacted with thallium(I) acetylacetonate, 1,1,1-trifluoroacetylacetonate or 1,1,1,5,5,5-hexafluoroacetylacetonate to give the desired products (eq. (1)) [20, 21, 28a].

In the recent literature only one other method has been described, which uses neutral acetylacetone or one of its derivatives for the reaction with $(CH_3)_3Au$ (eq. (2)) [22, 23]. Since the preparation of $(CH_3)_3Au$ offers no advantage over the synthesis of $(CH_3)_2AuX$ compounds, because of the comparable low yields and expensive reagents, this is still not a really satisfactory alternative.

The traditional syntheses of dimethylgold(III) chloride, bromide or iodide are mainly derived from the method of Brain and Gibson [20]. In these processes $AuCl_3$, $AuBr_3$ or their donor complexes are methylated by Grignard reagents or methyllithium [24–27, 28b]. As the starting materials are only sparingly soluble in the solvents used for the alkylation, the reactions are largely heterogeneous. This complication, and the strong reducing effect of these alkylating agents, lead to a reduction of the yields below 30 to 35%. Large quantities of metallic gold are obtained in the process, which are quite tedious to recover.

Results

We now report an improved and convenient synthesis of $[(CH_3)_2AuCl]_2$ using $Sn(CH_3)_4$ as the alkylating agent (eq. (3)). Unlike CH_3Li or Grignard reagents, tetramethyltin is not hydrolyzed by water, and therefore protic solvents like methanol can be used, which allow the reaction to be carried out homogeneously.

Both $AuCl_3$ and $HAuCl_4$, and even the commercial hydrate $HAuCl_4 \cdot aq$ (50% Au [w/w]) can be employed as the gold-containing reaction component.

The reaction is best carried out at −50 °C. While at room temperature only metallic gold, $(CH_3)_3SnCl$, $(CH_3)_2SnCl_2$ and alkanes are the reaction products to be isolated [29], at temperatures below −50 °C acceptable yields of dimethylgold(III) chloride are obtained reproducibly. After the initial reaction period, hydrochloric acid can be added to convert all $Au(CH_3)_3$, also formed in

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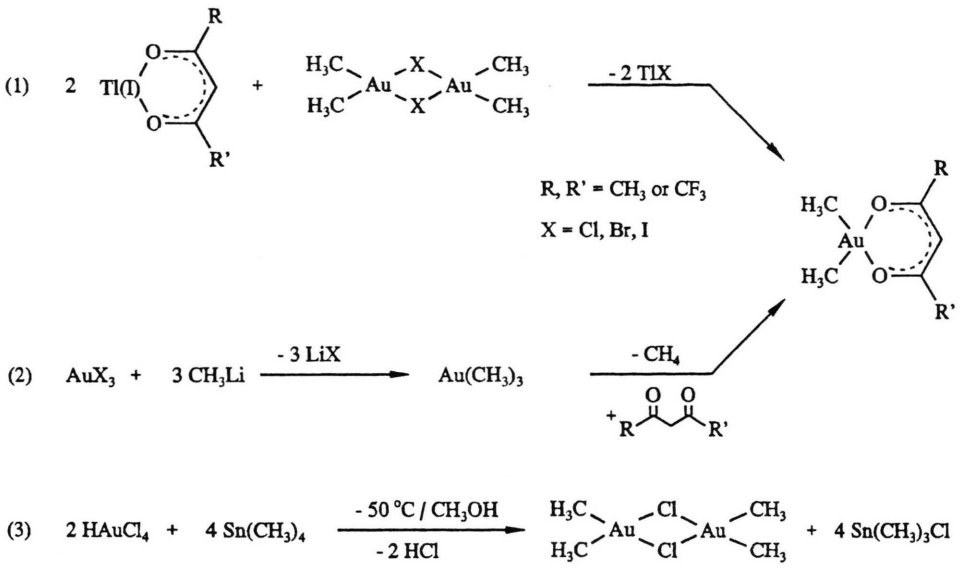

the process, into $[(CH_3)_2AuCl]_2$. Very pure product is obtained in 40 to 45% yield upon crystallization of the residue left from the organic phase after removal of all insoluble material by filtration and of all volatiles by evaporation.

GC–MS analysis of the reaction mixtures shows that the methyltin chlorides $(CH_3)_nSnCl_{4-n}$ are present as the by-products, which have an equilibrium distribution depending on the solvent, the concentration and the temperature. $(CH_3)_3SnCl$ is always found as the major component.

This procedure offers several advantages with respect to the syntheses described in the literature:

1) The starting materials are relatively inexpensive and can be used as purchased.

2) The reaction does not have to be carried out under inert gas atmosphere and in carefully dried solvents.

3) The product is obtained very pure after a simple aqueous work up procedure, without any further purification.

4) The yields exceed those of the literature procedures by about 10%.

Experimental

A solution of $Sn(CH_3)_4$ (1.2 ml, 8.66 mmol) in 10 ml of methanol is cooled to −78 °C and added rapidly to a solution of $HAuCl_4 \cdot aq$ (50% Au [w/w]), (1.055 g, 2.67 mmol) in 10 ml of methanol kept at −50 °C. After 20 h of stirring at −50 °C a colourless solution with a minor precipitate of metallic gold is obtained. 1.5 ml of concentrated aqueous hydrochloric acid in 10 ml of methanol is added dropwise, while keeping the temperature below −40 °C. The reaction mixture is allowed to warm to room temperature within 2 h. All volatile compounds are removed *in vacuo* at room temperature, and the residue, containing metallic gold and the product, is extracted three times with 10 ml of dry pentane. When pentane is removed from the extract after filtration, a highly pure colourless product is obtained.

Yield 311 mg (44%), m.p. 73 °C (Lit. [28b]: 71–73 °C), ^1H NMR (C_6D_6): δ = 1.05 ppm, s.

Note added in proof (22.4.1994): Experiments with gold(III) bromide, as obtained from the gold recovery process applied to electronic waste, have shown similar results. Dimethylgold bromide is obtained in 40–50% yield under similar reaction conditions as employed for dimethylgold chloride (above).

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