

CHEMISTRY OF ORGANOGOLD COMPOUNDS

I. SYNTHESSES AND PROPERTIES
OF DIHALOGOLD(III) *N,N*-DIALKYLDITHIOCARBAMATES AND
DIALKYLGOLD(III) *N,N*-DIALKYLDITHIOCARBAMATES

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INTRODUCTION

In contrast with the intensive and successful developments in the chemistry of organometallic compounds of many other transition elements, investigations in the field of organogold chemistry have been rather scarce.

Between 1930 and 1949 Gibson and his collaborators synthesized many mono- and dialkylgold derivatives¹, which were derived from trivalent gold with co-ordination number four. In these compounds the bonds from the central gold atom to the four ligands are directed to the corners of a square. The fourth ligand is bound co-ordinatively, usually by means of an atom with strong electron-donor properties such as nitrogen, sulphur, oxygen or halogen. Similar compounds were studied somewhat less elaborately by Kharasch². More recently a few trimethylgold(III) derivatives have been described by Gilman³ and by Coates⁴.

Organic derivatives of monovalent gold have been investigated by Coates^{5,6}. No other organogold compounds have been described.

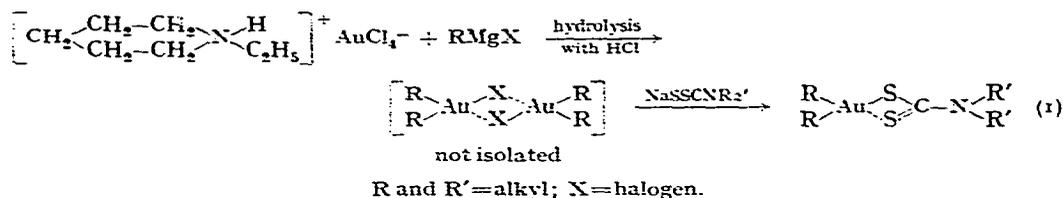
Striking experimental difficulties in the work of Gibson are obvious from the low yields ($\pm 20\%$) obtained in the preparation of dialkylgold(III) derivatives. Clearly these arose because the starting material was insoluble in the solvents used for the alkylations and had to be used in suspension.

For this reason the reaction temperature could not be kept low enough and substantial amounts of metallic gold separated from the reaction mixtures during the isolation of the product, owing to the low stability of the intermediates.

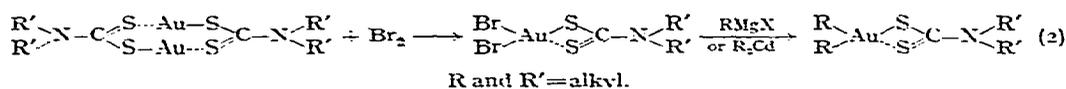
We have developed two improved methods for the preparation of compounds of the Gibson type, by which the yields could be increased to 60–80%. In addition it has been found that the stability of dialkylgold(III) derivatives could be increased by complexing with dithiocarbamate residues.

In the first procedure *N*-ethylpiperidinium tetrachloroaurate $[\text{C}_5\text{H}_{10}\text{NH}-\text{C}_2\text{H}_5]^+\text{AuCl}_4^-$ (hereafter referred to as NEPAuCl₄)⁷ was used as the starting material. Alkylation was performed by the addition of an appropriate alkylmagnesium halide to a solution of the compound in dry methylene chloride⁸ at very low temperatures (–80°). After hydrolysis with dilute acid, an alcoholic solution of a sodium *N,N*-

dialkyldithiocarbamate was added to the organic layer. The dialkylgold(III) *N,N*-dialkyldithiocarbamates formed could be isolated in yields between 60 and 70% (eqn. 1).



In the second method dibromogold(III) *N,N*-dialkyldithiocarbamates, prepared from dimeric gold(I) *N,N*-dialkyldithiocarbamates⁹ and bromine, were converted into the corresponding dialkyl derivatives by treatment with alkylmagnesium halides or dialkylcadmium compounds (eqn. 2).



HALOGOLD(III) *N,N*-DIALKYL DITHIOCARBAMATES

When chlorine is passed into a colourless solution of gold(I) *N,N*-di-*n*-butyldithiocarbamate in chloroform at room temperature, a dark red colour appears immediately which changes gradually into orange or yellow. The colour does not fade entirely before the solution contains two atoms of chlorine per atom of gold. Upon addition of ether, crystalline, yellow dichlorogold(III) *N,N*-di-*n*-butyldithiocarbamate precipitates in 80–90% yield. Thionyl chloride can also be used for chlorination of the monovalent gold compound.

Chlorination of other gold(I) *N,N*-dialkyldithiocarbamates can be performed similarly; for the lower homologues (methyl, ethyl and *n*-propyl), which are insoluble or only sparingly soluble in chloroform, a suspension in chloroform is used. In these cases the dichlorogold(III) *N,N*-dialkyldithiocarbamates precipitate immediately and can be crystallized from solvents such as dimethylformamide or acetonitrile.

Dichlorogold(III) *N,N*-dimethyldithiocarbamate can also be prepared in 68% yield from pyridinotrichlorogold¹⁰ ($\text{AuCl}_3 \cdot \text{Py}$) in dimethylformamide by addition of an equivalent amount of sodium *N,N*-dimethyldithiocarbamate¹¹.

By addition of bromine dissolved in carbon tetrachloride to a solution of gold(I) *N,N*-di-*n*-butyldithiocarbamate, the corresponding dibromogold(III) *N,N*-di-*n*-butyldithiocarbamate is obtained. The transient coloration of the solution is dark violet in this case and vanishes more quickly; the product is red instead of yellow.

Bromination can also be accomplished with *N*-bromosuccinimide or *N*-bromophthalimide in practically quantitative yields but the isolation and purification of the product is more difficult. Reaction temperatures between 30° and 50° are suitable.

Iodine reacts differently with monovalent gold *N,N*-di-*n*-butyldithiocarbamate. From equimolecular amounts a rather unstable violet product is formed, which decomposes in chloroform solution to a yellow crystalline compound, leaving a violet

solution. From the results of micro-analyses, the crystalline product appears to be a monoiodogold dithiocarbamate $[\text{IAuSSCN}(n\text{-C}_4\text{H}_9)_2]$. The same product is formed immediately in high yield from 0.5 mole of iodine and 1 mole of gold(I) *N,N*-di-*n*-butyldithiocarbamate.

Similar apparently bivalent gold derivatives of bromine or chlorine are obtained by carefully adding exactly 0.5 mole of these halogens to a solution of 1 mole of gold *N,N*-di-*n*-butyldithiocarbamate. Their melting points are higher than those of the corresponding dihalogold derivatives (Table 1).

TABLE I
MELTING POINTS OF $\text{X}_n\text{AuSSCN}(n\text{-C}_4\text{H}_9)_2$ ($^{\circ}\text{C}$)

	X		
	Cl	Br	I
$\text{X}_2\text{AuSSCN}(n\text{-C}_4\text{H}_9)_2$	120.5-122	109-109.5	106-108.5
$\text{XAuSSCN}(n\text{-C}_4\text{H}_9)_2$	128.5-129	143-144	134.5-135.5
$\text{AuSSCN}(n\text{-C}_4\text{H}_9)_2$		160.5	

Structures for these monohalogold derivatives involving the hitherto unknown bivalent gold are improbable because of the absence of paramagnetic character. Determinations of molecular weights in nitrobenzene solutions indicated a monomeric structure for the compounds $\text{XAuSSCN}(n\text{-C}_4\text{H}_9)_2$ in this solvent; the solutions do not show increased conductivity, which excludes the presence of ions.

Corresponding behaviour (diamagnetic, monomeric, non-conductive) has been found by Brain and Gibson for dichlorogold-dibenzylsulphide²² which on X-ray analysis appeared to be a molecular compound formed from a monochlorogold(I) and a trichlorogold(III) derivative, and which dissociates in solution into its components.

A similar explanation for the structure of our monohalogold derivatives is corroborated by two chemical arguments. Firstly, monobromogold *N,N*-di-*n*-butyldithiocarbamate can be converted into a mixture of about equal amounts of gold(I) and dimethylgold(III) *N,N*-di-*n*-butyldithiocarbamate (35% and 39% respectively) by treatment with dimethylcadmium. Secondly, the monobromogold derivative can also be obtained in 75% yield by simply mixing equivalent amounts of gold(I) and dibromogold(III) *N,N*-di-*n*-butyldithiocarbamate in chloroform followed by addition of carbon disulphide to precipitate the compound. Unlike the gold(I) and dibromogold(III) *N,N*-di-*n*-butyldithiocarbamates the solubility in carbon disulphide of the monobromogold dithiocarbamate is very low.

Properties

Dichlorogold(III) *N,N*-dialkyldithiocarbamates are yellow, the dibromo derivatives red, crystalline and monomeric compounds. In general, they are more soluble in organic solvents than the corresponding gold(I) dithiocarbamates. Solubility increases with the length of the alkyl chain in the dithiocarbamate residue. Thus the *N,N*-dimethyl compounds are only soluble in warm dimethylformamide or dimethylsulphoxide, whereas the dibutyl compounds dissolve satisfactorily in chlorinated

hydrocarbons and in acetone, tetrahydrofuran, pyridine and acetonitrile. All compounds are insoluble or nearly so in water, ligroin and ether.

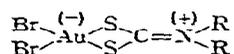
They are stable towards dilute strong acids but not towards basic reagents. Dichloro- and dibromogold(III) *N,N*-di-*n*-butyldithiocarbamate can even be crystallized from glacial acetic acid.

TABLE 2
PROPERTIES OF GOLD DITHIOCARBAMATES

Compound	R	M.p. (°C)	C-N stretching frequency (cm ⁻¹) (KBr-disc)
[AuSSCN ₂] ₂	CH ₃	> 300	1506
	C ₂ H ₅	~ 230	1496
	<i>n</i> -C ₃ H ₇	213	1490
	<i>n</i> -C ₄ H ₉	160.5	1488
	<i>n</i> -C ₉ H ₁₉	136.5-138	1487
Br ₂ AuSSCN ₂	CH ₃	331-333	1592
	C ₂ H ₅	270-277.5	1577
	<i>n</i> -C ₃ H ₇	183.5-185	1567
	<i>n</i> -C ₄ H ₉	109-109.5	1565
	<i>n</i> -C ₉ H ₁₉	114	1572
(CH ₃) ₂ AuSSCN ₂	CH ₃	168	1553
	C ₂ H ₅	~ 90 (decomp.)	1538
	<i>n</i> -C ₃ H ₇	47.5	1527
	<i>n</i> -C ₄ H ₉	41	1522
	<i>n</i> -C ₉ H ₁₉	54-57	1534

The C-N absorption bands in the infrared are above 1565 cm⁻¹. The pronounced shift relative to the corresponding frequency of gold(I) *N,N*-dialkyldithiocarbamates (1487-1506 cm⁻¹, see Table 2) indicates a strong C-N double bond character¹³.

It may be assumed therefore that the canonical formula



plays an important role in describing the structure or state of these compounds.

DIALKYL GOLD(III) *N,N*-DIALKYLDITHIOCARBAMATES

As outlined in the introduction dialkylgold(III) *N,N*-dialkyldithiocarbamates were obtained in two ways:

a) Dibromogold(III) *N,N*-dialkyldithiocarbamates dissolved or suspended in dry methylene chloride, when reacted at low temperature (-80°) with alkylmagnesium halides, give rise to dialkylgold(III) *N,N*-dialkyldithiocarbamates in 80% yield (eqn. 2). These products are colourless oils or low melting crystalline compounds which can be distilled or sublimed *in vacuo*.

Alkylation can also be brought about by pure dialkylcadmium compounds, which have been described by Krause¹⁴. It is essential to raise the reaction temperature to

about 0° in this case. Especially with dimethylcadmium (b.p. 105.5°) high yields (80–90 %) of the dimethylgold(III) *N,N*-dialkyldithiocarbamates were obtained.

Dialkylmercury compounds¹⁵ do not react with the bromo derivatives at low temperature. At room temperature substantial amounts of gold separate, leaving a solution which sometimes contains a small amount of the dialkylgold(III) dithiocarbamate.

Attempts to introduce phenyl, allyl or cyclopentadienyl residues with the aid of diphenylcadmium, phenylmagnesium bromide, allylmagnesium bromide or cyclopentadienylsodium, respectively, were unsuccessful. In all cases only gold(I) dialkyldithiocarbamates were formed.

b) The reagent NEPAuCl_4 (NEP = *N*-ethylpiperidinium) was prepared according to Dennstedt⁷ from HAuCl_4 and a hydrochloric acid solution of *N*-ethylpiperidine. When dissolved in methylene chloride NEPAuCl_4 reacts with alkylmagnesium halides at -80° , and at this temperature no metallic gold separates from the solution. The reaction mixture is then shaken with dilute hydrochloric acid at the lowest possible temperature. Magnesium halide and *N*-ethylpiperidinium hydrochloride are extracted into the water-layer and the dialkylgold(III) halide remains in the methylene chloride. The organic layer is kept as cold as possible, dried with anhydrous sodium sulphate and converted immediately into the corresponding dialkylgold(III) *N,N*-dialkyldithiocarbamate by adding an alcoholic solution of the appropriate sodium dialkyldithiocarbamate¹⁶. Yields vary for the various homologues (25–70 %) and are lower than those obtained by the previous method. Dimethylcadmium can be used to introduce methyl groups in NEPAuCl_4 by the same procedure, but with diethylcadmium no diethylgold(III) *N,N*-dialkyldithiocarbamate is obtained.

Properties

Dialkylgold(III) *N,N*-dialkyldithiocarbamates are insoluble in water, but easily soluble in most organic solvents. They do not decompose in dilute acids or bases and are stable towards mild reducing agents. With bromine they react violently forming dibromogold(III) dithiocarbamates and, presumably, alkyl bromides. The diisopropylgold compounds are less stable; especially under the influence of light they gradually turn yellow and gold(I) *N,N*-dialkyldithiocarbamate is formed.

Dialkylgold(III) dithiocarbamates are monomeric in benzene like the dibromo- and dichlorogold(III) dithiocarbamates. From the infra-red absorption spectra it appears that the double-bond character of the C–N group is less pronounced than in the halo compounds described in the previous section. The C–N stretching frequencies (1522–1553 cm^{-1}) are intermediate between those of the gold(I) and dihalogold(III) *N,N*-dialkyldithiocarbamates (Table 2).

The infra-red absorption spectrum of dimethylgold(III) *N,N*-dimethyldithiocarbamate has been determined also in the long wavelength region. There is a strong absorption band at 554 cm^{-1} (nujol mull), probably due to an Au–C stretching vibration in accordance with the findings of Coates⁶. Two intensive bands at 1184 and 1210 cm^{-1} (KBr-disc), which are absent in the spectrum of $\text{AuSSCN}(\text{CH}_3)_2$, may be due to symmetrical deformation of the methyl groups bound to the gold atom⁴.

EXPERIMENTAL

Part of the experimental work was carried out with technical assistance of Miss J. VAN ECK. Microanalyses were performed mainly by Mr. J. DIERSMAN. Melting points were measured with the Leitz Mikroskopheiztisch 350 and are uncorrected.

Gold(I) N,N-dialkyldithiocarbamates

These compounds were prepared as described by Åkerström⁹. HAuCl_4 was dissolved in a saturated sodium chloride solution, cooled to 0° , and reduced with sodium sulphite. Addition of a sodium *N,N*-dialkyldithiocarbamate afforded the required product.

The lower homologues (methyl, ethyl and propyl) were isolated by filtration of the yellow precipitate followed by several washings with water, alcohol and ether and drying *in vacuo*. They were used without further purification (for melting points see Table 2). The higher homologues were extracted from the reaction mixture with chloroform. The organic layer was dried over sodium sulphate, the solvent evaporated *in vacuo* and the residue crystallized from a suitable solvent, after treatment with activated carbon where necessary.

$\text{AuSSCN}(n\text{-C}_3\text{H}_7)_2$, yellow to orange needles from 1,2-dichloroethane; m.p. 160.5° , yield 95%. (Reported⁹ m.p. $154.5\text{--}157.5^\circ$, yield 60%.)

$\text{AuSSCN}(n\text{-C}_9\text{H}_{19})_2$, white plates from acetone, m.p. $136.5\text{--}138^\circ$. (Found: S, 11.86; N, 2.71. $\text{C}_{19}\text{H}_{38}\text{AuNS}_2$ calcd.: S, 11.84; N, 2.59%.)

Dichlorogold(III) N,N-dialkyldithiocarbamates

a) Chlorine gas was passed into a solution of gold(I) *N,N*-di-*n*-butyldithiocarbamate in warm chloroform until the temporary red coloration changed into dark yellow. The solution was concentrated by evaporation *in vacuo* and ether was added until no more precipitate was formed. The product, dichlorogold(III) *N,N*-di-*n*-butyldithiocarbamate, was crystallized quickly from ethyl alcohol. Yellow needles; m.p. $120.5\text{--}122^\circ$, yield 85%. (Found: Au, 41.74; N, 3.03; S, 13.69. $\text{C}_9\text{H}_{18}\text{AuCl}_2\text{NS}_2$ calcd.: Au, 41.71; N, 2.97; S, 13.58%.) The analogous dimethyl derivative was obtained by a similar procedure.

b) A solution of sodium *N,N*-dimethyldithiocarbamate¹⁶ (0.01 mole) in 15 ml of methyl alcohol was added slowly with stirring to a solution containing 0.01 mole of pyridinotrichlorogold¹⁰ ($\text{AuCl}_3 \cdot \text{Py}$) in 20 ml of dimethylformamide. A yellow precipitate was formed which could be crystallized from dimethylformamide. Reddish needles, decomposing at about 250° without melting, were obtained in 68% yield. (Found: Au, 50.43; N, 3.75; S, 16.39. $\text{C}_3\text{H}_6\text{AuCl}_2\text{NS}_2$ calcd.: Au, 50.75; N, 3.61; S, 16.52%.) Rather low yields were obtained for the di-*n*-butyl derivative¹¹ when this procedure was followed.

Dibromogold(III) N,N-dialkyldithiocarbamates

A gold(I) *N,N*-dialkyldithiocarbamate (0.01 mole) was suspended or dissolved in about 50 ml of chloroform at 30° . Bromine (0.01 mole), dissolved in 15 ml of carbon tetrachloride, was added with stirring over 10 min. The solvent was evaporated *in vacuo* and the residue crystallized from a suitable solvent. The yields varied from 50 to 90%. Details for the purification of the different compounds together with

physical and analytical data are collected in Table 3. For the molecular weight of the dibromogold(III) *N,N*-di-*n*-butyldithiocarbamate values of 503 (in benzene) and 600 (in naphthalene) were found; calcd. for $\text{Br}_2\text{AuSSCN}(\text{C}_4\text{H}_9)_2$ 561.

TABLE 3
DIBROMOGOLD(III) *N,N*-DIALKYL DITHIOCARBAMATES, $\text{Br}_2\text{AuSSCNR}_2$

<i>R</i>	<i>M.p.</i> ($^{\circ}\text{C}$)	% S <i>Found</i> (<i>Calcd.</i>)	% N <i>Found</i> (<i>Calcd.</i>)	
CH_3	331-333	13.54 (13.44)	3.07 (2.94)	Red-orange needles from dimethylformamide. Can be sublimed (250° , 0.2 mm)
C_2H_5	270-277.5	12.69 (12.70)	2.86 (2.77)	Red needles from acetonitrile
<i>n</i> - C_3H_7	183.5-185	12.22 (12.03)	2.69 (2.63)	Red-orange needles by addition of ether to the methylene chloride solution
<i>n</i> - C_4H_9	109-109.5	11.30 (11.43)	2.71 (2.50)	Red-orange needles from carbon tetrachloride or glacial acetic acid
<i>n</i> - C_7H_{15}	114	9.48 (9.14)	2.02 (2.00)	Yellow-orange needles by addition of ether to the chloroform solution

Dialkylgold(III) N,N-dialkyldithiocarbamates

In all reactions involving organomagnesium or organocadmium compounds a nitrogen atmosphere and dry reagents were used.

a) A solution or suspension of 0.005 mole of a dibromogold(III) *N,N*-dialkyldithiocarbamate in 75 ml of methylene chloride was cooled to -80° . A solution of 0.01 mole of the appropriate alkylmagnesium halide in ether, or a corresponding pure dialkylcadmium compound was added with stirring, over a ten-minute period. When a dialkylcadmium compound was added, the reaction temperature was raised to 0° . After fifteen minutes the reaction mixture was poured into 150 ml of dilute hydrochloric acid and shaken. The methylene chloride layer was separated and dried over sodium sulphate. The solvent was evaporated *in vacuo* and the residue eluted through a silica column with ethyl alcohol.

b) An appropriate alkylmagnesium halide (0.01 mole) in about 20 ml of ether was added with stirring to a solution of 0.005 mole of NEPAuCl_4 in 100 ml of methylene chloride at -80° over a ten-minute period. The reaction mixture was stirred for ten minutes and then poured into 150 ml of cold dilute hydrochloric acid. The methylene chloride layer was separated after shaking, filtered, cooled and quickly treated with a solution of about 0.008 mole of a sodium *N,N*-dialkyldithiocarbamate. The solvent was evaporated *in vacuo* and the product purified chromatographically on silica with methyl alcohol and/or crystallized from a suitable solvent. Details are presented in Table 4.

Molecular weight determination for dimethylgold(III) *N,N*-dimethyldithio-

TABLE 4
 DIALKYLGOLD(III) *N,N*-DIALKYLDITHIOCARBAMATES, $R_2AuSSCNR'_2$

<i>R</i>	<i>R'</i>	M.p., °C	% S Found (Calcd.)	% N Found (Calcd.)	Preparative method and yield	Physical and chemical properties
CH ₃	CH ₃	168	18.34 (18.47)	4.14 (4.03)	b) 60% CH ₃ MgI b) 65% (CH ₃) ₂ Cd	White plates from cyclohexane
CH ₃	C ₂ H ₅	90 (decomp.)	16.97 (17.09)	3.79 (3.73)	b) 55% (C ₂ H ₅) ₂ Cd	Light yellow needles from cyclohexane or ether
CH ₃	<i>n</i> -C ₃ H ₇	47.5	15.86 (15.96)	3.47 (3.47)	a) 85% (C ₂ H ₅) ₂ Cd	White plates after sublimation <i>in vacuo</i> ; purified chromatographically on silica in methyl alcohol; after evaporation of solvent crystallized from ethyl alcohol by cooling to -80°
CH ₃	<i>n</i> -C ₄ H ₉	41	14.86 (14.86)	3.29 (3.25)	a) 80% (C ₂ H ₅) ₂ Cd b) 60% (C ₂ H ₅) ₂ Cd	White plates after sublimation <i>in vacuo</i> ; purified chromatographically on silica in methyl alcohol; after evaporation of solvent crystallized from ethyl alcohol by cooling to -80°
CH ₃	<i>n</i> -C ₈ H ₁₇	54-57	11.41 (11.22)	2.40 (2.45)	a) 80% (C ₂ H ₅) ₂ Cd	White plates from ligroin (b.p. 60-80°) at -80°
C ₂ H ₅	CH ₃	59-62	17.21 (17.09)	3.38 (3.73)	b) 30% C ₂ H ₅ MgBr	Colourless oil. Purified chromatographically and distilled in vacuo
C ₂ H ₅	<i>n</i> -C ₃ H ₇	---	14.35 (13.96)	3.02 (3.05)	a) 55% C ₂ H ₅ MgBr a) 70% (C ₂ H ₅) ₂ Cd	White needles from methyl alcohol. Light-sensitive and unstable
iso-C ₃ H ₇	CH ₃	87.5-89	15.93 (15.96)	3.59 (3.47)	b) 25% iso-C ₃ H ₇ MgBr	Light yellow plates from methylene chloride and ether
C ₆ H ₅ CH ₂	CH ₃	109-110	13.30 (12.84)	2.80 (2.86)	b) 20% C ₆ H ₅ (C ₂ H ₅)MgCl	

carbamate: found 330 (in benzene); calcd. for $(\text{CH}_3)_2\text{AuSSCN}(\text{CH}_3)_2$ 347. With the exception of $(\text{CH}_3)_2\text{AuSSCN}(\text{C}_2\text{H}_5)_2$, $(\text{C}_2\text{H}_5)_2\text{AuSSCN}(\text{CH}_3)_2$, $(\text{iso-C}_3\text{H}_7)_2\text{AuSSCN}(\text{CH}_3)_2$ and $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{AuSSCN}(\text{CH}_3)_2$, all compounds could be purified by sublimation or distillation *in vacuo*.

SUMMARY

Monomeric dialkylgold(III) *N,N*-dialkyldithiocarbamates ($\text{R}_2\text{AuSSCNR}'_2$) can be prepared in good yields from monomeric dibromogold(III) *N,N*-dialkyldithiocarbamates ($\text{Br}_2\text{AuSSCNR}'_2$) and alkylmagnesium halides or dialkylcadmium compounds.

In addition *N*-ethylpiperidinium tetrachloroaurate can be converted by treatment with alkylmagnesium halides or dimethylcadmium and with sodium *N,N*-dialkyldithiocarbamates into the corresponding dialkylgold(III) *N,N*-dialkyldithiocarbamates.

The monomeric dihalogold(III) *N,N*-dialkyldithiocarbamates can be prepared from the dimeric gold(I) *N,N*-dialkyldithiocarbamates and equimolecular amounts of bromide or chlorine.

Apparently gold(I) *N,N*-dialkyldithiocarbamates react also with half the amount of chlorine, bromine or iodine, with formation of products which according to analyses seem to be monohalogold derivatives ($\text{X AuSSCNR}'_2$, X = Cl, Br or I). Evidence is given for the absence of a divalent gold atom in these compounds. On the basis of chemical arguments they seem to be molecular compounds of dihalogold(III) and gold(I) derivatives which dissociate in solution.

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