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NOVEL ANIONIC GOLD(I) AND GOLD(III) ORGANOCOMPLEXES

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Summary

Tetrahydrothiophen (tht) and/or chloride may readily be displaced from ClAu(tht) with perhaloaryl lithium to give anionic complexes of the $[R_2Au]^-$ or $[RAuX]^-$ type ($R = C_6F_5$ or C_6Cl_5; X = Cl or Br).

Anionic gold(III) complexes can be prepared both by the reaction of Cl_3Au-(tht) or $K[AuCl_4]$ with LiC_6F_5 or by the oxidative addition of halogens or $(C_6F_5)_2TlBr$ to gold(I) complexes.

Introduction

Studies of anionic arylgold complexes have been limited to those of the type $[RAuX_3]^-$ (X = Cl or Br; $R = C_6H_5$ or p-YC_6H_4; Y being Me, Cl, Br or NO_2) obtained by two routes (a) by a method [1] starting from $[RAuCl_2]_2$, for which details have not been reported, and (b) by reactions [2] of the type

$$2[AuX_4]^- + YC_6H_4NHNH_2 \cdot HX \rightarrow [AuX_2]^- + [(YC_6H_4)AuX_3]^- + N_2 + 4\ HX$$

in which theoretical yields cannot surpass 50% but in which observed yields are 16—30%.

Furthermore, the preparation of solutions of the anionic complexes $[(CH_3)_2Au]^-$ and $[(CH_3)_4Au]^-$ has been described [3,4]. They are not stable when exposed to air and atmospheric moisture, and all attempts to isolate the compounds proved unsuccessful.

We report below the preparation of a series of novel anionic organo-gold(I) and -gold(III) compounds which were obtained in satisfactory yields. Those of the $[R_2Au]^-$ and $[R_4Au]^-$ type have no ancillary ligand attached to the gold atom.

Some of the results were the subject of a preliminary communication [5].

Results and discussion

(a) Gold(I) complexes

Chlorotetrahydrothiophen gold(I) (ClAu(tht)) may easily be prepared by adding an excess of the neutral ligand to an ethanol solution of $HAuCl_4$. The product is not very stable at room temperature, and its reaction with C_6F_5MgBr leads to metallic gold. The more reactive LiC_6F_5, however, reacts at low temperature according to eqn. 1 and leads to the air- and thermally-stable $C_6F_5Au(tht)$,

$$ClAu(tht) + LiC_6F_5 \xrightarrow[85\%\ yield]{-40^{\circ}C} LiCl + C_6F_5Au(tht) \tag{1}$$

which is the first reported organogold(I) complex containing an S-donor ligand.

$C_6F_5Au(tht)$ is of synthetic interest since the (tht) ligand is readily replaced by other neutral ligands, and because of the high yield of reaction 1 and the low cost of (tht).

Of greater relevance is, however, the fact that the ligand also be readily replaced by aryl groups or by halide ions. Thus anionic complexes of hitherto unknown types are obtained according to eqns. 2 and 3.

$$C_6F_5Au(tht) + LiC_6F_5 \xrightarrow{n\text{-}Bu_4NBr} [n\text{-}Bu_4N][(C_6F_5)_2Au] + LiBr \tag{2}$$

$$C_6F_5Au(tht) + [R_4N]X \xrightarrow{HX} [R_4N][C_6F_5AuX] \tag{3}$$

Reactions 1 and 2 may be combined in a single process. Thus, the reaction of $ClAu(tht)$ with an excess of LiC_6F_5 leads directly to $[(C_6F_5)_2Au]^-$, which was precipitated as the corresponding tetraalkylammonium salt.

$[R_4N][(C_6Cl_5)_2Au]$ was prepared similarly. It was not possible to obtain $C_6Cl_5Au(tht)$ by reaction 2, since the $C_6Cl_5Au(tht)$ produced according to eqn. 1 could not be separated from the other products.

In process 3, which leads to salts with the anion $[C_6F_5AuX]^-$ (X = Cl or Br), the replacement of the weak base (tht) is facilitated by the presence of the acid. The reaction takes place both with $[n\text{-}Bu_4N]Br$ and with $[Et_4N]Cl$. That with $[n\text{-}Bu_4N]I$ leads to the cleavage of the Au—C bond and to the formation of $[n\text{-}Bu_4N][AuI_2]$.

(b) Gold(III) complexes

They were prepared by two different routes:

(1) By arylation of gold(III) complexes, such as $Cl_3Au(tht)$ or $K[AuCl_4]$ with LiC_6F_5:

$$Cl_3Au(tht) + LiC_6F_5 \xrightarrow{n\text{-}Bu_4NBr} [n\text{-}Bu_4N][(C_6F_5)_4Au] + [n\text{-}Bu_4N][(C_6F_5)_2Au] \tag{4}$$

The resulting mixture can easily be resolved by washing with CH_2Cl_2, in which the gold(I) complex is far more soluble.

(2) By oxidative addition of halogens or $(C_6F_5)_2TlBr$ to anionic gold(I) complexes:

$$[(C_6Cl_5)_2Au]^- + I_2 \rightarrow [(C_6Cl_5)_2AuI_2]^- \tag{5}$$

$$[(C_6F_5)AuBr]^- + Br_2 \rightarrow [(C_6F_5)AuBr_3]^- \tag{6}$$

$$[(C_6F_5)AuBr]^- + (C_6F_5)_2TlBr \rightarrow [(C_6F_5)_3AuBr]^- \tag{7}$$

Anionic organogold(III) complexes of the general formula $[R_nAuX_{4-n}]^-$ ($n = 1$, 2, 3 or 4) may be obtained by processes (4—7).

TABLE 1

ANALYTICAL DATA FOR COMPOUNDS I—IX

Complex		Analysis found (calcd.) (%)				Λ_M (ohm^{-1} cm^2 mol^{-1})	M.p. (°C)
		C	H	N	Au		
I	$C_6F_5Au(tht)$	26.29	1.65	—	41.67	11	109(dec.)
		(26.56)	(1.78)		(43.56)		
II	$[n\text{-}Bu_4N][(C_6F_5)_2Au]$	42.61	4.44	1.73	25.53	116	110
		(43.48)	(4.69)	(1.81)	(25.46)		
III	$[n\text{-}Bu_4N][(C_6Cl_5)_2Au]$	35.89	3.53	1.49	21.75	106	181
		(35.85)	(3.87)	(1.49)	(21.00)		
IV	$[Et_4N][(C_6F_5)AuCl]$	31.89	3.91	2.65	37.40	147	91
		(31.74)	(3.80)	(2.64)	(37.18)		
V	$[n\text{-}Bu_4N][(C_6F_5)AuBr]$	38.86	5.37	2.14	27.39	133	70
		(38.50)	(5.29)	(2.04)	(28.69)		
VI	$[n\text{-}Bu_4N][(C_6F_5)_4Au]$	44.37	3.10	1.22	17.88	102	240
		(43.37)	(3.28)	(1.26)	(17.78)		
VII	$[n\text{-}Bu_4N][(C_6F_5)_3AuBr]$	39.26	3.79	1.46	18.50	125	60
		(40.01)	(3.55)	(1.37)	(19.30)		
VIII	$[n\text{-}Bu_4N][(C_6F_5)AuBr_3]$	31.08	4.30	1.59	22.95	105	70
		(31.22)	(4.29)	(1.65)	(23.27)		
IX	$[n\text{-}Bu_4N][(C_6Cl_5)_2AuI_2]$	28.58	2.84	1.15	17.67	101	209(dec.)
		(28.21)	(3.04)	(1.17)	(16.52)		

Attempted oxidative addition of $HgCl_2$, $ClCOCH_3$ MeI were unsatisfactory. Thus the reactions of $[(C_6F_5)_2Au]^-$ with $HgCl_2$ or $ClCOCH_3$ lead to the substitution products $[(C_6F_5)AuCl]^-$ and $[AuCl_2]^-$, respectively. MeI gives a mixture of products whose main components are (according to C, H, N analyses and IR spectra) $[n\text{-}Bu_4N][AuI_2]$ and $[n\text{-}Bu_4N][C_6F_5AuI]$.

All the isolated complexes have been characterized by elemental analyses (C, H, N, Au), melting points, conductivities (cf. Table 1) and IR spectra. The great thermal stability of the anionic complexes is noteworthy, all of them may be heated to over 200°C without decomposition. $[n\text{-}Bu_4N][(C_6F_5)_4Au]$ (m.p. 240°C) is stable towards $HgCl_2$ and Cl_2.

The IR spectra of these novel complexes show, along with the characteristic vibrations of the C_6F_5 [6] or C_6Cl_5 groups [7,8], bands due to ν(Au—X) (X = Cl or Br). In the gold(I) complexes the latter give two strong bands at 318 (X = Cl) and 230 (X = Br) cm^{-1}. For $[(C_6F_5)AuBr_3]^-$ two bands are observed at 260 and 230 cm^{-1}, assignable to ν_{asym} and ν_{sym} (Br—Au—Br), respectively. The bands expected for ν(Au—Br) *trans* to C_6F_5, as well as the single band expected for $[(C_6F_5)_3AuBr]^-$ would probably be found at lower energies [2] beyond the range of our spectrophotometer (4000—200 cm^{-1}).

Experimental

I. $C_6F_5Au(tht)$

To a solution of 10 mmol of LiC_6F_5 in 60 ml of ether at —78°C was added the equimolecular amount of ClAu(tht), prepared by addition of an excess of (tht) to an ethanol solution of $HAuCl_4$. The mixture was allowed to warm to room temperature during 30 min with magnetic stirring. It was treated with a few drops of water and filtered through anhydrous $MgSO_4$. Concentration of the filtrate to ca. 5 ml led to crystallization of I. Another fraction of I was obtained after addition of 5 ml of hexane and subsequent evaporation (84% yield). I is soluble in ether, dichloromethane and acetone.

II. [n-Bu_4N][(C_6F_5)$_2$Au]

The reaction was carried out as for I but with a 4 : 1 excess of LiC_6F_5. After hydrolysis, the calculated amount of [n-Bu_4N]Br was added to precipitate II. The complex was filtered off and washed with water and ethanol (60% yield). II is soluble in dichloromethane and acetone, and slightly soluble in ether and benzene.

III. [n-Bu_4N][(C_6Cl_5)$_2$Au]

To a solution of 12 mmol of LiC_6Cl_5 in 60 ml of ether at −60°C was added 4 mmol of ClAu(tht). The solution was stirred for 30 min; solid CO_2 and then 4 mmol of [n-Bu_4N]Br were added. After addition of 30 ml of acetone the suspension was filtered and the filtrate was evaporated to dryness. The residue was extracted with 10 ml of dichloromethane and the addition of 50 ml of ether caused crystallization of some III. On evaporation of the filtrate to dryness another portion of III was obtained mixed with HC_6Cl_5. The latter was removed by washing with hot benzene, and the III was recrystallized from dichloromethane/ethanol (1 : 1) (62% yield). III is soluble in acetone and dichloromethane and insoluble in ethanol and n-hexane.

IV. [Et_4N][(C_6F_5)AuCl]

To a solution of I (1 mmol) and [Et_4N]Cl · $5H_2O$ (1 mmol) in 20 ml of ethanol was added 1 mmol of conc. HCl. The mixture was stirred for 8 h at room temperature. A small amount of gold was filtered off and the filtrate evaporated to dryness. The residue was washed with ether and extracted with 2 ml of dichloromethane, in which [Et_4N]Cl is insoluble. IV was crystallized by addition of ether and successive refrigeration (53% yield). IV is soluble in dichloromethane, acetone and ethanol, slightly soluble in ether, and insoluble in n-hexane.

V. [n-Bu_4N][(C_6F_5)AuBr]

To a solution of I (1 mmol) and [n-Bu_4N]Br (1 mmol) in 5 ml of acetone was added 1 mmol of conc. HCl. The mixture was stirred for 2 h at room temperature and then concentrated to 1 ml. Addition of ether to the vigorously stirred solution caused separation of V (73% yield). V is soluble in dichloromethane, acetone, ethanol and benzene, slightly soluble in ether, and insoluble in n-hexane.

VI. [n-Bu_4N][(C_6F_5)$_4$Au]

(a) From K[$AuCl_4$]. To a solution of LiC_6F_5 (10 mmol) in 80 ml of ether at −78°C was added K[$AuCl_4$] (2.5 mmol). The stirred solution was allowed to warm to room temperature during 1 h, then treated with a few drops of water. [n-Bu_4N]Br (2.5 mmol) was added, and the precipitate of impure VI was recrystallized from dichloromethane/ether (1 : 1) (12% yield). Evaporation of the filtrate gave complex II (44% yield). VI is soluble in acetone and slightly soluble in ethanol and ether.

(b) From $Cl_3Au(tht)$. To a solution of LiC_6F_5 (10.4 mmol) in 50 ml of ether at −78°C was added $Cl_3Au(tht)$ (1.3 mmol), prepared by addition of the calculated amount of (tht) to an ethanol solution of $HAuCl_4$. The mixture was allowed to warm to room temperature and stirred for 10 min. It was hydrolyzed with a few drops of water and $[n\text{-}Bu_4N]Br$ (1.3 mmol) was added. After 30 min stirring the mixture was filtered and the filtrate was washed with water and with ether. The residue (a mixture of II and VI) was extracted with dichloromethane to remove the soluble II (30% yield). The remaining solid was recrystallized from acetone/benzene (47% yield).

VII. $[n\text{-}Bu_4N][(C_6F_5)_3AuBr]$

To a solution of V (0.3 mmol) in 10 ml of benzene was added $(C_6F_5)_2TlBr$ (0.3 mmol). The mixture was stirred for 5 h. The black precipitate (TlBr + Au) was filtered off, and the filtrate was evaporated to dryness. Addition of n-pentane to the oily residue with vigorous stirring gave a precipitate which was extracted with ether. After slow evaporation, VII crystallized out (90% yield). VII is soluble in dichloromethane, acetone and ether, and insoluble in n-pentane and n-hexane.

VIII. $[n\text{-}Bu_4N][(C_6F_5)AuBr_3]$

To a dichloromethane (2 ml) solution of V (0.3 mmol) was added Br_2 (0.3 mmol) in the same solvent. The mixture was stirred for 14 h. Upon addition of ether (3 ml) a small amount of $[n\text{-}Bu_4N][AuBr_4]$ separated. Evaporation of the filtrate to dryness gave a yellowish-red precipitate of VIII, which was washed with n-pentane (65% yield). VIII is soluble in dichloromethane, acetone and ether; and insoluble in n-pentane and n-hexane.

IX. $[n\text{-}Bu_4N][(C_6Cl_5)_2AuI_2]$

To a dichloromethane solution of III (0.3 mmol) was added I_2 (0.3 mmol). The mixture was stirred for 5 h. The yellow complex IX separated and additional amounts of IX were obtained by adding ether to the filtrate (50% yield). IX is soluble in dichloromethane and acetone, slightly soluble in ether, and insoluble in n-hexane.

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