Preparation and Properties of Stable Salts Containing Mono- or Bis-(pentafluorophenyl)aurate(I) and Mono-, Tris-, or Tetrakis-(pentafluorophenyl)aurate(III) Ions

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Summary Tetrahydrothiophen (tht) and/or chloride may readily be displaced from [ClAu(tht)] or [Cl_3Au(tht)] with LiC_6F_5 to give novel organometallic anionic complexes of gold(I) or gold(III).

The only hitherto described[1] anionic aryl-gold complexes are of the type $[RAuX_3]^-$ (X = Cl, Br, or I; R = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4, *p*-BrC_6H_4, or *p*-$O_2NC_6H_4$).

We now report the preparation (see Scheme) of novel anionic gold-containing aryl complexes of the types $[(C_6F_5)_2Au]^-$ and $[(C_6F_5)AuX]^-$ (X = Cl or Br), and $[(C_6F_5)_4Au]^-$, $[(C_6F_5)_3AuBr]^-$, and $[(C_6F_5)AuBr_3]^-$.

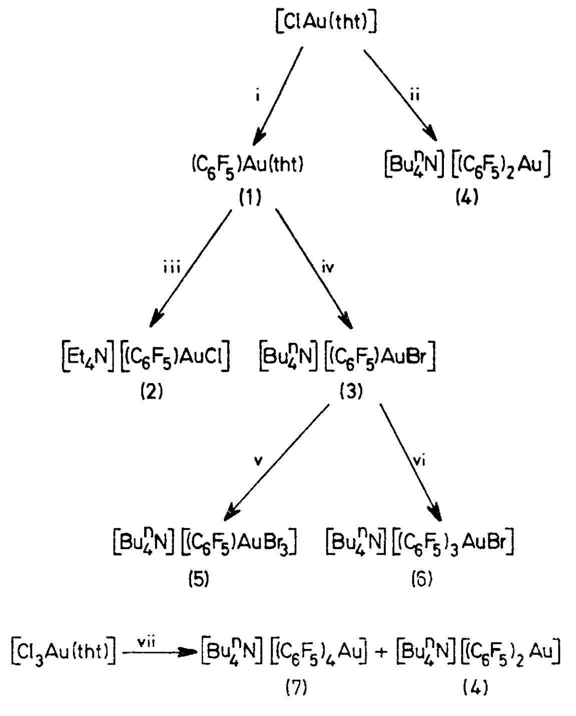
Table. Properties of the aurate(I) and aurate(III) complexes

Compound	M.p./°C	$\Lambda_M{}^a/\Omega^{-1}$ cm^{-2} mol^{-1}	ν(Au–X)/cm^{-1}
(**1**)	109 (decomp.)	11	—
(**2**)	91	147	318
(**3**)	70	133	230
(**4**)	110	116	—
(**5**)	70	105	260,230
(**6**)	60	125	—
(**7**)	240	102	—

[a] In acetone; conc. *ca.* 5 × 10^{-4} M.

The reaction (1:1) of [ClAu(tht)][2] (tht = tetrahydrothiophen) with LiC_6F_5 in diethyl ether at −78 °C (slowly allowed to warm to room temperature) leads to the synthesis (84% yield) of the white microcrystalline compound (**1**) which, to the best of our knowledge, is the first reported organogold(I) complex containing an S-donor ligand. The tht ligand is readily displaced from (**1**) not only by other neutral ligands[3], but also by anionic ones. Thus, the addition of $Bu^n{}_4NBr$ or Et_4NCl to complex (**1**) (in acetone solution, at room temperature, in presence of HBr or HCl, respectively) affords the complexes (**2**) (73% yield) and (**3**) (53%), respectively.

The reaction of [ClAu(tht)] with an excess (4:1) of LiC_6F_5 gives rise to the displacement of both ligands and to the formation of bis(pentafluorophenyl)aurate(I), which is isolated (60% yield) as complex (**4**) $[Bu^n{}_4N][(C_6F_5)_2Au]$.



Scheme. *Reagents:* i, LiC_6F_5; ii, $Bu^n{}_4NBr$, $2LiC_6F_5$; iii, Et_4NCl, HCl; iv, $Bu^n{}_4NBr$, HBr; v, Br_2; vi, $(C_6F_5)_2TlBr$; vii, $4LiC_6F_5$, $Bu^n{}_4NBr$.

Neutral gold(I) complexes can be oxidized[4] with halogens or with bis(pentafluorophenyl)thallium(III) bromide. Similarly, the anionic complex (**3**) undergoes oxidative addition with, *e.g.*, bromine to give (65% yield) complex (**5**) or with the organothallium compound to afford (90%) complex (**6**).

Anionic gold(III) complexes may, nevertheless, also be obtained by direct treatment of $[Cl_3Au(tht)]$[2] or $K[AuCl_4]$ with an excess (5:1) of LiC_6F_5. After hydrolysing the excess of LiC_6F_5 and addition of $[Bu^n_4N]Br$, the anionic complex (**7**) precipitates (47% yield), though always in a mixture with the gold(I) complex (**4**) (30%). Since (**7**) is less soluble in dichloromethane the mixture can be separated easily.

All the complexes gave satisfactory elemental (C, H, N, and Au) analyses. The Λ_M and ν(Au–X) values are listed in the Table. Their conductivities are as expected: *i.e.* (**1**) is non-conducting, whereas (**2**)—(**7**) behave as 1:1 electrolytes.

The i.r. absorptions in the 400—200 cm^{-1} region of the digonal gold(I) complexes (**2**) and (**3**) and square-planar gold(III) complexes (**5**) and (**6**) are in accordance with those expected for the respective symmetry. The sole ν(Au–Br) vibration for complex (**6**) and the lowest of the three absorptions expected for complex (**5**) are doubtlessly below the range of our instrument[1b] (4000—200 cm^{-1}).

All the complexes melt without decomposition (see Table) and their m.p.s. are reproducible, even after heating the molten compounds to 200 °C. They are stable even when exposed to daylight and atmospheric moisture. The stability of the complexes, especially of (**4**) and (**7**) is noteworthy, since the only hitherto known compounds of the general formula $[R^1R^2Au]^-$ ($R^1 = R^2 = HC{\equiv}C-$ or $PhC{\equiv}C-$) are quite unstable[5] or have not been isolated ($R^1 = Me$; $R^2 = Me, Et, Bu^t, Bu^tCH_2$, or Ph) and were therefore only studied in solution.[6] Furthermore, the only hitherto reported complex of the type $[R_4Au]^-$ (R = Me) has not been isolated, and its solutions seem not to be stable in the presence of air.[7]

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