

Tris(pentafluorophenyl)gold(III) Complexes with O-, N- or S-donor Ligands

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Abstract

$\text{Au}(\text{C}_6\text{F}_5)_3(\text{OEt}_2)$ is a better intermediate complex than $\text{Au}(\text{C}_6\text{F}_5)_3\cdot\text{tht}$ (tht = tetrahydrothiophen). The former compound can be prepared from $(\text{NBu}_4)[\text{Au}(\text{C}_6\text{F}_5)_3\text{Br}]$ and AgClO_4 in diethylether and the ether ligand can be easily displaced by neutral ligands [$\text{L} = \text{THF}$, OCMe_2 , diox, EtOH , SPPH_3 , SPPH_2Me , OPPH_3 , OAsPh_3 , NCMe , NCPh , NCPH , $\text{NCCH}=\text{CH}_2$, $o\text{-(NC)}_2\text{C}_6\text{H}_4$] as well as cationic ones $[(\text{X})\text{PPh}_2\text{CH}_2\text{-PPh}_2\text{R}]^+$ [$\text{X} = \text{S}$, $\text{R} = \text{Me}$, $\text{CH}_2\text{C}_6\text{F}_5$, COOMe , CH_2Ph ; $\text{X} = \text{O}$, $\text{R} = \text{CH}_2\text{Ph}$] to give the corresponding neutral or cationic tris(pentafluorophenyl)gold(III) complexes most of which were hitherto inaccessible.

Introduction

Gold(I) or gold(III) complexes containing thioether ligands R_2S are useful preparative intermediates since R_2S is easily displaced by other good ligands for gold(I). In particular, we have used $\text{C}_6\text{F}_5\text{Au}(\text{tht})$ (tht = tetrahydrothiophen) where tht can readily be displaced by a variety of ligands both neutral or anionic [1–3]. In the gold(III) complex $\text{Au}(\text{C}_6\text{F}_5)_3\text{-(tht)}$ the Au–S bond is stronger: though tht can be displaced by NH_3 , NC_5H_5 or phosphines [4], other $\text{O}(\text{OPR}_3)$, $\text{S}(\text{SPR}_3)$ or $\text{N}(\text{NC-R})$ donors are unable to do so. Thus, tht is a good ligand for Au(III) and we need to search for others strong enough to stabilize the AuR_3 moiety, however, weak enough to be readily displaced by almost any one we choose. The candidate to perform this role is $\text{Au}(\text{C}_6\text{F}_5)_3(\text{OEt}_2)$ whose preparation and reactivity against neutral or cationic O, S and N-donors is discussed in the following.

Experimental

Instrumentation and general experimental techniques were as described earlier [4]. Nuclear magnetic resonance spectra were recorded on a Varian XL 200 spectrometer in CDCl_3 . Chemical shifts are quoted relative to SiMe_4 (^1H), 85% H_3PO_4 (external, ^{31}P) and

CFCl_3 (external, ^{19}F). The yields, C, H, N and Au analyses and molecular weights of the novel complexes are listed in Table 1.

Preparation of the Complexes

$\text{Au}(\text{C}_6\text{F}_5)_3(\text{OEt}_2)$ (1)

To a solution of $(\text{NBu}_4)[\text{Au}(\text{C}_6\text{F}_5)_3\text{Br}]$ [1] (1.021 g, 1 mmol) in 50 ml of diethyl ether was added AgClO_4 (0.207 g, 1 mmol) and the mixture was stirred for 1.5 h at room temperature. The precipitated AgBr and $(\text{NBu}_4)\text{ClO}_4$ were filtered off and the solution was concentrated to c. 2 ml. Addition of n-hexane (15 ml) precipitated 1 as a white solid. ^1H NMR (in CDCl_3) δ 1.43 (t, 6H, CH_3) and 3.98 [q, 4H, CH_2 , $J(\text{H-H})$ 6.99 Hz] ppm.

$\text{Au}(\text{C}_6\text{F}_5)_3(\text{S})$ [$\text{S} = \text{THF}$ (2), OCMe_2 (3), diox (4) or EtOH (5)]

Complex 1 (0.773 g, 1 mmol) was dissolved in tetrahydrofuran (THF), acetone, 1,4-dioxan (diox) or ethanol (15 ml) and the mixture was stirred for 30 min at room temperature. The solution was concentrated to c. 2 ml and n-hexane (10 ml) was added. By cooling to -20°C complexes 2–5 were obtained as white crystals. ^1H NMR (in CDCl_3) δ 2: 4.00(m) and 2.00(m) ppm; 3: 2.59(s) ppm; 4: 3.68(s) ppm; 5: 0.99 (t, 3H, CH_3 , $J(\text{H-H})$ 6.9 Hz) and 1.49 (m, 2H, CH_2) ppm.

$\text{Au}(\text{C}_6\text{F}_5)_3\text{L}$ [$\text{L} = \text{SPPH}_3$ (6), SPPH_2Me (7), OPPH_3 (8) or OAsPh_3 (9)]

To a solution of complex 1 (0.773 g, 1 mmol) in dichloromethane (20 ml) was added L [$\text{L} = \text{SPPH}_3$ (0.294 g, 1 mmol), SPPH_2Me (0.232 g, 1 mmol), OPPH_3 (0.278 g, 1 mmol), OAsPh_3 (0.322 g, 1 mmol)] and the mixture was stirred for 1 h at room temperature. The solution was concentrated to c. 2 ml and addition of n-hexane (20 ml) gave complexes 6–9. 6: melting point (m.p.) 162°C , ^{31}P NMR (in CDCl_3) δ 44.66(s) ppm, 7: m.p. 196°C , ^{31}P NMR (in CDCl_3) δ 42.23(s) ppm, 8: m.p. 159°C , 9: m.p. 157°C .

TABLE 1. Analytical data of complexes

Complex	Yield (%)	Analysis: found (calc.) (%)				Molecular weight: found (calc.)
		C	H	N	Au	
1 $\text{Au}(\text{C}_6\text{F}_5)_3(\text{OEt}_2)$	80	33.95 (34.3)	1.15 (1.3)		25.5 (25.15)	772 (773)
2 $\text{Au}(\text{C}_6\text{F}_5)_3(\text{THF})$	72	34.15 (34.3)	1.05 (1.05)		25.65 (25.55)	713 (770)
3 $\text{Au}(\text{C}_6\text{F}_5)_3(\text{OCMe}_2)$	62	32.95 (33.35)	0.9 (0.8)		26.7 (26.05)	721 (756)
4 $\text{Au}(\text{C}_6\text{F}_5)_3(\text{diox})$	84	33.85 (33.6)	1.3 (1.05)		25.0 (25.05)	
5 $\text{Au}(\text{C}_6\text{F}_5)_3(\text{EtOH})$	67	32.6 (32.3)	0.95 (0.8)		25.75 (26.45)	746 (744)
6 $\text{Au}(\text{C}_6\text{F}_5)_3(\text{SPh}_3)$	87	43.55 (43.55)	1.6 (1.5)		20.75 (19.85)	927 (993)
7 $\text{Au}(\text{C}_6\text{F}_5)_3(\text{SPh}_2\text{Me})$	86	40.2 (40.0)	1.45 (1.4)		21.35 (21.15)	871 (931)
8 $\text{Au}(\text{C}_6\text{F}_5)_3(\text{OPPh}_3)$	86	44.65 (44.3)	1.65 (1.55)		20.35 (20.15)	957 (977)
9 $\text{Au}(\text{C}_6\text{F}_5)_3(\text{OAsPh}_3)$	70	42.35 (42.4)	1.5 (1.5)		19.6 (19.3)	913 (1020)
10 $\text{Au}(\text{C}_6\text{F}_5)_3(\text{NCMe})$	90	32.55 (32.5)	0.55 (0.4)	1.95 (1.9)	26.6 (26.65)	
11 $\text{Au}(\text{C}_6\text{F}_5)_3(\text{NCPh})$	85	37.6 (37.5)	0.85 (0.65)	2.05 (1.75)	24.65 (24.6)	680 (801)
12 $\text{Au}(\text{C}_6\text{F}_5)_3(\text{NCPr})$	88	34.2 (34.15)	0.8 (0.9)	2.0 (1.85)	25.0 (25.65)	724 (767)
13 $\text{Au}(\text{C}_6\text{F}_5)_3(\text{NCCH}=\text{CH}_2)$	80	33.6 (33.6)	0.4 (0.4)	1.9 (1.85)	24.9 (26.2)	744 (751)
14 $\text{Au}(\text{C}_6\text{F}_5)_3\{(\text{NC})_2\text{C}_6\text{H}_4\}$	90	37.75 (37.8)	0.6 (0.5)	3.5 (3.4)	22.9 (23.85)	651 (826)
15 $[\text{Au}(\text{C}_6\text{F}_5)_3\{(\text{S})\text{PPh}_2\text{CH}_2\text{PPh}_2\text{Me}\}]\text{ClO}_4$	91	43.8 (43.0)	2.4 (2.05)		15.45 (16.05)	
16 $[\text{Au}(\text{C}_6\text{F}_5)_3\{(\text{S})\text{PPh}_2\text{CH}_2\text{PPh}_2(\text{CH}_2\text{C}_6\text{F}_5)\}]\text{ClO}_4$	89	42.75 (43.05)	1.7 (1.75)		14.6 (14.1)	
17 $[\text{Au}(\text{C}_6\text{F}_5)_3\{(\text{S})\text{PPh}_2\text{CH}_2\text{PPh}_2(\text{CH}_2\text{COOMe})\}]\text{ClO}_4$	75	42.65 (42.95)	2.4 (2.1)		15.9 (15.3)	
18 $[\text{Au}(\text{C}_6\text{F}_5)_3\{(\text{S})\text{PPh}_2\text{CH}_2\text{PPh}_2(\text{CH}_2\text{Ph})\}]\text{ClO}_4$	87	45.55 (46.0)	2.25 (2.25)		15.9 (15.1)	
19 $[\text{Au}(\text{C}_6\text{F}_5)_3\{(\text{O})\text{PPh}_2\text{CH}_2\text{PPh}_2(\text{CH}_2\text{Ph})\}]\text{ClO}_4$	95	46.75 (46.6)	2.35 (2.25)		14.65 (15.3)	

$\text{Au}(\text{C}_6\text{F}_5)_3\text{NCR}$ [$R = \text{Me}$ (10), Ph (11), Pr (12), $\text{CH}=\text{CH}_2$ (13) or $o\text{-(NC)}\text{C}_6\text{H}_4$ (14)]

To a suspension of 1 (0.154 g, 0.2 mmol) in n-hexane (20 ml) was added NCR [$R = \text{Me}$ (0.3 ml, 6 mmol), Ph (0.3 ml, 3 mmol), Pr (0.3 ml, 3.5 mmol), $\text{CH}=\text{CH}_2$ (0.3 ml, 4.5 mmol), $o\text{-(NC)}\text{C}_6\text{H}_4$ (0.026 g, 0.2 mmol)]. The mixture was stirred for 1 h at room temperature. The white complexes 10–14 were filtered off and washed with n-hexane (2×5 ml).

10: ^1H NMR (in CDCl_3) δ 2.52(s) ppm. 11: ^1H NMR (in CDCl_3) δ 7.50(m) ppm; ^{19}F NMR (in CDCl_3) δ -122.78 (m, $o\text{-F}$ C_6F_5 *trans* to NCR), -124.11 (m, $o\text{-F}$ C_6F_5 *cis*), -156.47 (t, $p\text{-F}$ C_6F_5 *cis*), -156.63 (t, $p\text{-F}$ C_6F_5 *trans*), -161.62 (m, $m\text{-F}$ C_6F_5 *trans*) and -162.15 (m, $m\text{-F}$ C_6F_5 *cis*). 12: ^1H NMR (in CDCl_3) δ 1.05 [t, CH_3 $J(\text{H-H})$ 7.3 Hz], 1.84 (m, $-\text{CH}_2-$) and 2.75 [t, $\text{NC}-\text{CH}_2$, $J(\text{H-H})$ 7.0 Hz] ppm. 13: ^1H NMR (in CDCl_3) AMX system $J(\text{AM})$ 0,

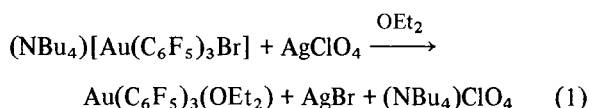
δ 6.00 [dd, H_X , $J(AX)$ 18.1, $J(MX)$ 12.4 Hz] and 6.74 (m, H_A and H_M) ppm. 14: 1H NMR (in $CDCl_3$) δ 8.0(m) ppm; ^{19}F NMR (in $CDCl_3$) δ -122.69 and -124.07 (m, *o*-F C_6F_5 *trans* and *cis* respectively), -156.30 and -156.40 (t, *p*-F C_6F_5 *cis* and *trans* respectively) and -161.50 and -162.01 (m, *m*-F C_6F_5 *trans* and *cis*, respectively) ppm.

$[Au(C_6F_5)_3\{(X)PPh_2CH_2PPh_2R\}]ClO_4$ [$X = S$, $R = Me$ (15), $CH_2C_6F_5$ (16), CH_2COOMe (17) or CH_2Ph (18); $X = O$, $R = CH_2Ph$ (19)]

To a solution of complex 1 (0.773 g, 1 mmol) in dichloromethane (20 ml) was added $[(X)PPh_2CH_2PPh_2R]ClO_4$ [1 mmol; $X = S$, $R = Me$ (0.531 g), $CH_2C_6F_5$ (0.697 g), CH_2COOMe (0.589 g) or CH_2Ph (0.607 g); $X = O$, $R = CH_2Ph$ (0.591 g)]. The mixture was stirred for 1 h at room temperature and the solution was concentrated to *c.* 2 ml. Addition of *n*-hexane (20 ml) precipitated complexes 15–19 as white solids. 15: m.p. 138 °C, Λ_M 141 $\Omega^{-1} cm^2 mol^{-1}$. 16: m.p. 125 °C, Λ_M 148 $\Omega^{-1} cm^2 mol^{-1}$. 17: m.p. 145 °C, Λ_M 115 $\Omega^{-1} cm^2 mol^{-1}$. 18: m.p. 195(d) °C, Λ_M 140 $\Omega^{-1} cm^2 mol^{-1}$. 19: m.p. 106(d) °C, Λ_M 140 $\Omega^{-1} cm^2 mol^{-1}$.

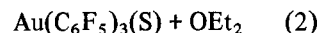
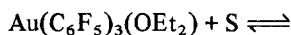
Results and Discussion

Addition of an equimolecular amount of solid $AgClO_4$ to a diethylether solution of $(NBu_4)[Au(C_6F_5)_3Br]$ (eqn. (1)) gives a precipitate of $AgBr$ and $(NBu_4)ClO_4$. From the filtrate $Au(C_6F_5)_3(OEt_2)$ (1) can easily be isolated.



The white complex 1 is unstable at room temperature, metallic gold being formed within 60 min, but can safely be stocked for 2–3 weeks at -20 °C. It is possible, however, to take its IR spectrum, where two bands at 820(s) and 800(s,br) cm^{-1} , characteristic for tris(pentafluorophenyl) complexes [4], are detected. It is non-conducting in acetone solution, the solute probably being $[Au(C_6F_5)_3(OCMe_2)]$ (see below).

If the same reaction (eqn. (1)) is carried out in other solvents [tetrahydrofuran (THF), acetone $OCMe_2$, ethanol EtOH, or dioxane (diox)], only $AgBr$ precipitates and evaporation to dryness of the filtrated solution affords mixtures of $Au(C_6F_5)_3$ -(solvent) and $(NBu_4)ClO_4$. Extraction with diethyl ether and evaporation of the filtrate affords complex 1. In the corresponding solvent, by addition of *n*-hexane and cooling to -20 °C, the complexes 2–5 can be isolated (by displacing the equilibrium (eqn. (2)) to the right).



where S = THF (2), $OCMe_2$ (3), dioxane (4), EtOH (5).

Complexes 2–5 are white stable solids at -20 °C but unstable at room temperature. They are monomeric (chloroform) and non-conducting (acetone). Complex 4 is too unstable in $CHCl_3$ solution and its molecular weight could not be measured. In the IR spectra of complexes 2–5 (Nujol mulls) the $\nu(C-O)$ vibration of the S ligands appears at 1010(m), 1650(s), 1100(s) and 1042(m) cm^{-1} , i.e. at lower frequencies than in the free ligand (1076, 1710, 1120 and 1080 cm^{-1} , respectively [5]).

It is possible to take advantage of the easy displacement of OEt_2 in complex 1 to prepare a variety of complexes which cannot be synthesised starting from $Au(C_6F_5)_3(tht)$ owing to the poor donor characteristics of some ligands. For instance, addition of L [$L = SPh_3$ (6), SPh_2Me (7), $OPPh_3$ (8), $OAsPh_3$ (9), $NCMe$ (10), NPh (11), NPr (12), $NC(CH=CH_2)$ (13) or *o*-(NC) $_2C_6H_4$ (14)] gives complexes $Au(C_6F_5)_3L$ (6–14) as white solids, some of them (6–9) stable, others (10–14) unstable at room temperature, though all of them can be stocked at -20 °C. Complexes 6–14 are non-conducting in acetone. Molecular weights (in chloroform solution) of the stable ones at room temperature (6–9) are in agreement with the monomeric nature of the solutes whilst the others give lower molecular weights probably due to partial dissociation of the L ligand [4]. Their IR spectra show two bands at 820(s) and 800(s,br) cm^{-1} , which are characteristic for trifluorophenylgold(III) complexes [4].

Moreover, the attachment of the neutral ligand L shifts the $\nu(P-O)$, $\nu(P-S)$ or $\nu(As-S)$ frequencies towards lower energies: 6, 590(vs) (620, free ligand); 7, 750(vs) (680); 8, 1145(s) (1195); 9, 860(vs) (880) cm^{-1} . On the contrary $\nu(C\equiv N)$ is shifted towards higher energies in the nitrile complexes: 10, 2315(s) and 2335(m) (2220 and 2270, free ligand); 11, 2290(s) (2240); 12, 2320(s) (2220); 13, 2292(s) (2240); 14, 2290(s) (2170) cm^{-1} [6].

Finally, even cationic ligands of the type $[(X)PPh_2CH_2PPh_2R]^+$ with $X = S$ or O, displace the OEt_2 molecule in complex 1 to give cationic complexes $[Au(C_6F_5)_3\{(X)PPh_2CH_2PPh_2R\}]ClO_4$ [$X = S$, $R = Me$ (15), $CH_2C_6F_5$ (16), CH_2COOMe (17) or $CH_2C_6H_5$ (18); $X = O$, $R = CH_2C_6H_5$ (19)] which are air and moisture stable white solids at room temperature. Their acetone solutions are conducting with $\Lambda_M = 115$ –140 $\Omega^{-1} cm^2 mol^{-1}$ as expected for 1:1 electrolytes. Their IR spectra show the two absorptions characteristic for tris(pentafluorophenyl)gold(III) complexes and two bands at 1100(s,br) and

625(m) cm^{-1} due to the ClO_4^- anion [7]. The $\nu(\text{P}-\text{S})$ vibration appears at *c.* 590 cm^{-1} in complexes 15–18 and $\nu(\text{P}-\text{O})$ at 1198 cm^{-1} in 19.

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