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

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Abstract

$Au(C_6F_5)_3(OEt_2)$ is a better intermediate complex than $Au(C_6F_5)_3 \cdot tht$ (tht = tetrahydrothiophen). The former compound can be prepared from $(NBu_4)[Au(C_6F_5)_3Br]$ and $AgClO_4$ in diethylether and the ether ligand can be easily displaced by neutral ligands [L = THF, $OCMe_2$, diox, EtOH, $SPPh_3$, $SPPh_2Me$, $OPPh_3$, $OAsPh_3$, NCMe, NCPh, NCPr, $NCCH{=}CH_2$, o-$(NC)_2C_6H_4$] as well as cationic ones $[(X)PPh_2CH_2PPh_2R]^+$ [X = S, R = Me, $CH_2C_6F_5$, COOMe, CH_2Ph; X = O, R = CH_2Ph] to give the corresponding neutral or cationic tris(pentafluorophenyl)gold(III) complexes most of which were hitherto unaccessible.

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 $C_6F_5Au(tht)$ (tht = tetrahydrothiophen) where tht can readily be displaced by a variety of ligands both neutral or anionic [1–3]. In the gold(III) complex $Au(C_6F_5)_3(tht)$ the Au–S bond is stronger: though tht can be displaced by NH_3, NC_5H_5 or phosphines [4], other $O(OPR_3)$, $S(SPR_3)$ or N(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 $Au(C_6F_5)_3(OEt_2)$ 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

$Au(C_6F_5)_3(OEt_2)$ (1)

To a solution of $(NBu_4)[Au(C_6F_5)_3Br]$ [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 $(NBu_4)ClO_4$ 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(H–H) 6.99 Hz] ppm.

$Au(C_6F_5)_3(S)$ [S = 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(H–H) 6.9 Hz) and 1.49 (m, 2H, CH_2) ppm.

$Au(C_6F_5)_3L$ [L = $SPPh_3$ (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 [L = $SPPh_3$ (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(d) °C, ^{31}P NMR (in $CDCl_3$) δ 42.23(s) ppm, **8**: m.p. 159 °C. **9**: m.p. 157 °C.

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TABLE 1. Analytical data of complexes

Complex	Yield (%)	Analysis: found (calc.) (%)				Molecular weight: found (calc.)
		C	H	N	Au	
1 $Au(C_6F_5)_3(OEt_2)$	80	33.95	1.15		25.5	772
		(34.3)	(1.3)		(25.15)	(773)
2 $Au(C_6F_5)_3(THF)$	72	34.15	1.05		25.65	713
		(34.3)	(1.05)		(25.55)	(770)
3 $Au(C_6F_5)_3(OCMe_2)$	62	32.95	0.9		26.7	721
		(33.35)	(0.8)		(26.05)	(756)
4 $Au(C_6F_5)_3(diox)$	84	33.85	1.3		25.0	
		(33.6)	(1.05)		(25.05)	
5 $Au(C_6F_5)_3(EtOH)$	67	32.6	0.95		25.75	746
		(32.3)	(0.8)		(26.45)	(744)
6 $Au(C_6F_5)_3(SPPh_3)$	87	43.55	1.6		20.75	927
		(43.55)	(1.5)		(19.85)	(993)
7 $Au(C_6F_5)_3(SPPh_2Me)$	86	40.2	1.45		21.35	871
		(40.0)	(1.4)		(21.15)	(931)
8 $Au(C_6F_5)_3(OPPh_3)$	86	44.65	1.65		20.35	957
		(44.3)	(1.55)		(20.15)	(977)
9 $Au(C_6F_5)_3(OAsPh_3)$	70	42.35	1.5		19.6	913
		(42.4)	(1.5)		(19.3)	(1020)
10 $Au(C_6F_5)_3(NCMe)$	90	32.55	0.55	1.95	26.6	
		(32.5)	(0.4)	(1.9)	(26.65)	
11 $Au(C_6F_5)_3(NCPh)$	85	37.6	0.85	2.05	24.65	680
		(37.5)	(0.65)	(1.75)	(24.6)	(801)
12 $Au(C_6F_5)_3(NCPr)$	88	34.2	0.8	2.0	25.0	724
		(34.15)	(0.9)	(1.85)	(25.65)	(767)
13 $Au(C_6F_5)_3(NCCH{=}CH_2)$	80	33.6	0.4	1.9	24.9	744
		(33.6)	(0.4)	(1.85)	(26.2)	(751)
14 $Au(C_6F_5)_3\{(NC)_2C_6H_4\}$	90	37.75	0.6	3.5	22.9	651
		(37.8)	(0.5)	(3.4)	(23.85)	(826)
15 $[Au(C_6F_5)_3\{(S)PPh_2CH_2PPh_2Me\}]ClO_4$	91	43.8	2.4		15.45	
		(43.0)	(2.05)		(16.05)	
16 $[Au(C_6F_5)_3\{(S)PPh_2CH_2PPh_2(CH_2C_6F_5)\}]ClO_4$	89	42.75	1.7		14.6	
		(43.05)	(1.75)		(14.1)	
17 $[Au(C_6F_5)_3\{(S)PPh_2CH_2PPh_2(CH_2COOMe)\}]ClO_4$	75	42.65	2.4		15.9	
		(42.95)	(2.1)		(15.3)	
18 $[Au(C_6F_5)_3\{(S)PPh_2CH_2PPh_2(CH_2Ph)\}]ClO_4$	87	45.55	2.25		15.9	
		(46.0)	(2.25)		(15.1)	
19 $[Au(C_6F_5)_3\{(O)PPh_2CH_2PPh_2(CH_2Ph)\}]ClO_4$	95	46.75	2.35		14.65	
		(46.6)	(2.25)		(15.3)	

$Au(C_6F_5)_3NCR$ [R = Me (10), Ph (11), Pr (12), $CH{=}CH_2$ (13) or o-$(NC)C_6H_4$ (14)]

To a suspension of **1** (0.154 g, 0.2 mmol) in n-hexane (20 ml) was added NCR [R = Me (0.3 ml, 6 mmol), Ph (0.3 ml, 3 mmol), Pr (0.3 ml, 3.5 mmol), $CH{=}CH_2$ (0.3 ml, 4.5 mmol), *o*-$(NC)C_6H_4$ (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**: ^{1}H NMR (in $CDCl_3$) δ 2.52(s) ppm. **11**: ^{1}H NMR (in $CDCl_3$) δ 7.50(m) ppm; ^{19}F NMR (in $CDCl_3$) δ −122.78 (m, *o*-F C_6F_5 *trans* to NCR), −124.11 (m, *o*-F C_6F_5 *cis*), −156.47 (t, *p*-F C_6F_5 *cis*), −156.63 (t, *p*-F C_6F_5 *trans*), −161.62 (m, *m*-F C_6F_5 *trans*) and −162.15 (m, *m*-F C_6F_5 *cis*). **12**: ^{1}H NMR (in $CDCl_3$) δ 1.05 [t, CH_3 *J*(H–H) 7.3 Hz], 1.84 (m, $-CH_2-$) and 2.75 [t, $NC-CH_2$, *J*(H–H) 7.0 Hz] ppm. **13**: ^{1}H NMR (in $CDCl_3$) AMX system *J*(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(C₆F₅)₃{(X)PPh₂CH₂PPh₂R}]ClO₄ [X = S, R = Me (15), CH₂C₆F₅ (16), CH₂COOMe (17) or CH₂Ph (18); X = O, R = CH₂Ph (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 ohm^{-1} cm^2 mol^{-1}. **16**: m.p. 125 °C, Λ_M 148 ohm^{-1} cm^2 mol^{-1}. **17**: m.p. 145 °C, Λ_M 115 ohm^{-1} cm^2 mol^{-1}. **18**: m.p. 195(d) °C, Λ_M 140 ohm^{-1} cm^2 mol^{-1}. **19**: m.p. 106(d) °C, Λ_M 140 ohm^{-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.

$$(NBu_4)[Au(C_6F_5)_3Br] + AgClO_4 \xrightarrow{OEt_2} Au(C_6F_5)_3(OEt_2) + AgBr + (NBu_4)ClO_4 \quad (1)$$

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).

$$Au(C_6F_5)_3(OEt_2) + S \rightleftharpoons Au(C_6F_5)_3(S) + OEt_2 \quad (2)$$

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 ν(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 = $SPPh_3$ (**6**), $SPPh_2Me$ (**7**), $OPPh_3$ (**8**), $OAsPh_3$ (**9**), NCMe (**10**), NCPh (**11**), NCPr (**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 ν(P–O), ν(P–S) or ν(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 ν(C≡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 Λ_M = 115–140 ohm^{-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 ν(P–S) vibration appears at *c.* 590 cm^{-1} in complexes **15–18** and ν(P–O) at 1198 cm^{-1} in **19**.

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