Note

Methyl dithiocarbamate gold(I) and gold(III) complexes. Synthesis and reactivity with amines

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Abstract

The reaction of several methyl dithiocarbamates {S(MeS)CNHR} (R = p-MeC$_6$H$_4$, o-MeC$_6$H$_4$, p-MeOC$_6$H$_4$ and 3,5-Me$_2$C$_6$H$_3$) with Au(C$_6$F$_5$)(tht) and Au(C$_6$F$_5$)$_3$(OEt$_2$) gives the suitable complexes containing S-bonded ligands. Thioacylation of primary amines is reported, through a reaction in the coordinated ligands; the new ligands hold the coordination to the gold atom.

Key words: Gold complexes; Dithiocarbamate complexes

Introduction

Dithiocarbamate complexes have been extensively studied due to their applications as vulcanization accelerators, flotation agents, fungicides and pesticides [1, 2]; their antimicrobial activity has also been reported [3, 4]. Usually, dithiocarbamates act as bidentate ligands, but a few gold compounds containing monodentate dithiocarbamate have been reported [5–8]. In this paper we describe the synthesis of gold complexes with methyl dithiocarbamate as ligands. The presence of a methyl group bonded to one of the sulfur atoms favours a monodentate coordination.

Moreover it is known [9] that nucleophilic attack takes place at the positively charged carbon atom of a thiocarbonyl group in analogy to the carbonyl system; indeed dithiocarboxylic acids and their derivatives have been widely used as thioacylating agents. We describe here not only new gold(I) and gold(III) compounds with these ligands but their reactivity at coordinated ligands with amines.

Experimental

The starting products Au(C$_6$F$_5$)(tht) [10], Au(C$_6$F$_5$)$_3$(OEt$_2$) [11] and the methyl dithiocarbamate ligands [12] were prepared by previously published methods.

IR spectra were recorded on a Perkin-Elmer 559 or 883 spectrophotometer, over the range 4000–200 cm^{-1}, using Nujol mulls between polyethylene sheets. ^{1}H and ^{19}F NMR spectra were obtained on a Varian XL-200 instrument in CDCl$_3$ solution; chemical shifts are quoted relative to SiMe$_4$ (^{1}H) and CFCl$_3$ (external; ^{19}F). C, H and N analyses were performed with a Perkin-Elmer 240B microanalyser; Au analyses by ashing in a crucible with aqueous hydrazine. Conductivities were measured in acetone solution with a Philips PW 9509 apparatus. Melting points were determined in a Buchi apparatus and are uncorrected. The yields, melting points, C, H, N and Au analyses, and conductivities are listed in Table 1. Characteristic IR absorptions and ^{1}H NMR data are given in Table 2. ^{19}F NMR data are given below.

Preparation of the complexes

[Au(C$_6$F$_5$){S(MeS)CNHR}] (R = p-MeC$_6$H$_4$ (I), o-MeC$_6$H$_4$ (II), p-MeOC$_6$H$_4$ (III) and 3,5-Me$_2$C$_6$H$_3$ (IV))

To a solution of Au(C$_6$F$_5$)(tht) (0.180 g, 0.4 mmol) in 30 ml of dichloromethane was added 0.4 mmol of S(MeS)CNHR (0.079 g (R = p-MeC$_6$H$_4$), 0.079 g (R = o-MeC$_6$H$_4$), 0.085 g (R = p-MeOC$_6$H$_4$) and 0.084 g (R = 3,5-Me$_2$C$_6$H$_3$)). After stirring for 30 min, the solution was vacuum evaporated to *c.* 5 ml and hexane (15 ml) was added. The white solid was filtered off. ^{19}F NMR: **I**: −117.0 (m, o-F), −159.2 (m, p-F), −162.7 (m, m-F); **II**: −116.9 (m, o-F), −159.2 (m, p-F), −162.8 (m, m-F); **III**: −116.9 (m, o-F), −159.2 (m, p-F), −162.7 (m, m-F); **IV**: −116.9 (m, o-F), −159.2 (m, p-F), −162.8 (m, m-F). Other ^{1}H NMR data (not included in Table 2): **I**: 7.2 (m, 4H). **II**: 7.31 (m, 4H); **III**: 7.27 (m, 4H); **IV**: 7.08 (s, 1H, p-H), 6.96 (s, 2H, o-H).

[Au(C$_6$F$_5$)$_3${S(MeS)CNHR}] (R = p-MeC$_6$H$_4$ (V), o-MeC$_6$H$_4$ (VI), p-MeOC$_6$H$_4$ (VII) and 3,5-Me$_2$C$_6$H$_3$ (VIII))

To a solution of Au(C$_6$F$_5$)$_3$(OEt$_2$) (0.156 g, 0.2 mmol) in 20 ml of dichloromethane was added 0.2 mmol of

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TABLE 1. Analytical data of complexes **I**–**XII**

Complex	Yield (%)	Analysis found (calc.) (%)				Λ_M[a]	M.p. (°C)
		C	H	N	Au		
Au(C$_6$F$_5$){S(MeS)CNH(*p*-MeC$_6$H$_4$)} (**I**)	90	32.2 (32.1)	2.45 (1.95)	2.6 (2.5)	34.5 (35.1)	7	116
Au(C$_6$F$_5$){S(MeS)CNH(*o*-MeC$_6$H$_4$)} (**II**)	65	32.25 (32.1)	2.05 (1.95)	2.35 (2.5)	35.2 (35.1)	5	98
Au(C$_6$F$_5$){S(MeS)CNH(*p*-MeOC$_6$H$_4$)} (**III**)	87	31.35 (31.2)	2.0 (1.9)	2.75 (2.45)	34.15 (34.1)	5	100
Au(C$_6$F$_5$){S(MeS)CNH(3,5-Me$_2$C$_6$H$_3$)} (**IV**)	70	33.2 (33.4)	2.35 (2.3)	2.45 (2.45)	34.3 (34.25)	6	124
Au(C$_6$F$_5$)$_3${S(MeS)CNH(*p*-MeC$_6$H$_4$)} (**V**)	65	36.55 (36.2)	0.95 (1.25)	1.45 (1.55)	21.5 (22.0)	27	131
Au(C$_6$F$_5$)$_3${S(MeS)CNH(*o*-MeC$_6$H$_4$)} (**VI**)	64	36.8 (36.2)	1.15 (1.25)	1.5 (1.55)	22.0 (22.0)	7	159
Au(C$_6$F$_5$)$_3${S(MeS)CNH(*p*-MeOC$_6$H$_4$)} (**VII**)	60	35.15 (35.55)	1.35 (1.2)	1.45 (1.55)	21.5 (21.6)	12	127
Au(C$_6$F$_5$)$_3${S(MeS)CNH(3,5-Me$_2$C$_6$H$_3$)} (**VIII**)	85	36.45 (36.95)	1.45 (1.45)	1.05 (1.55)	21.2 (21.65)	11	141
Au(C$_6$F$_5$){S(^{n}BuHN)CNH(*p*-MeC$_6$H$_4$)} (**IX**)	30	37.2 (36.85)	3.2 (3.1)	4.85 (4.75)	34.2 (33.6)	16	80
Au(C$_6$F$_5$){S(CyHN)CNH(*p*-MeC$_6$H$_4$)} (**X**)	38	37.95 (39.2)	3.1 (3.3)	3.9 (4.55)	32.5 (32.15)	13	124
Au(C$_6$F$_5$){S(C$_6$H$_5$CH$_2$CH$_2$HN)CNH(*p*-MeC$_6$H$_4$)} (**XI**)	33	41.7 (41.65)	3.05 (2.85)	4.1 (4.4)	31.5 (31.05)	11	108
Au(C$_6$F$_5$){S(^{n}BuHN)CNH(*p*-MeOC$_6$H$_4$)} (**XII**)	27	36.0 (35.9)	3.05 (3.0)	4.1 (4.65)	32.4 (32.7)	11	88

[a] In acetone, Ω^{-1} cm^2 mol^{-1}.

TABLE 2. Characteristic IR and ^{1}H NMR spectra for complexes **I**–**XII**

Complex	ν(N–H) (cm^{-1})	^{1}H NMR[a] (δ)		
		N–H	S–Me	Me[b]
Au(C$_6$F$_5$){S(MeS)CNH(*p*-MeC$_6$H$_4$)} (**I**)	3252(m)	10.45(s)	2.73(s)	2.41(s)
Au(C$_6$F$_5$){S(MeS)CNH(*o*-MeC$_6$H$_4$)} (**II**)	3233(m)	10.39(s)	2.72(s)	2.35(s)
Au(C$_6$F$_5$){S(MeS)CNH(*p*-MeOC$_6$H$_4$)} (**III**)	3280(m)	10.46(s)	2.73(s)	3.85(s)
Au(C$_6$F$_5$){S(MeS)CNH(3,5-Me$_2$C$_6$H$_3$)} (**IV**)	3240(m)	10.49(s)	2.72(s)	2.35(s)
Au(C$_6$F$_5$)$_3${S(MeS)CNH(*p*-MeC$_6$H$_4$)} (**V**)	3360(m)	9.64(s)	2.67(s)	2.44(s)
Au(C$_6$F$_5$)$_3${S(MeS)CNH(*o*-MeC$_6$H$_4$)} (**VI**)	3340(m)	9.53(s)	2.66(s)	2.21(s)
Au(C$_6$F$_5$)$_3${S(MeS)CNH(*p*-MeOC$_6$H$_4$)} (**VII**)	3340(m)	9.57(s)	2.66(s)	3.87(s)
Au(C$_6$F$_5$)$_3${S(MeS)CNH(3,5-Me$_2$C$_6$H$_3$)} (**VIII**)	3320(m)	9.61(s)	2.67(s)	2.38(s)
Au(C$_6$F$_5$){S(^{n}BuHN)CNH(*p*-MeC$_6$H$_4$)} (**IX**)	3393(m), 3302(m)	8.7(s), 6.0(s)		2.41(s)
Au(C$_6$F$_5$){S(CyHN)CNH(*p*-MeC$_6$H$_4$)} (**X**)	3369(m), 3291(m)	8.75(s), 5.87(s,br)		2.41(s)
Au(C$_6$F$_5$){S(C$_6$H$_5$CH$_2$CH$_2$HN)CNH(*p*-MeC$_6$H$_4$)} (**XI**)	3369(m), 3304(m)	8.75(s), 5.95(s)		2.37(s)
Au(C$_6$F$_5$){S(^{n}BuHN)CNH(*p*-MeOC$_6$H$_4$)} (**XII**)	3287(s)	8.7(s), 5.9(s)		3.85(s)

[a] Recorded in CDCl$_3$ at 200 MHz referred to internal TMS. [b] Methyl bonded to the phenyl of dithiocarbamate.

S(MeS)CNHR (0.039 g (R = *p*-MeC$_6$H$_4$), 0.039 g (R = *o*-MeC$_6$H$_4$), 0.043 g (R = *p*-MeOC$_6$H$_4$) and 0.042 g (R = 3,5-Me$_2$C$_6$H$_3$)). The colourless solution was stirred for 45 min. The solvent was vacuum evaporated to *c.* 5 ml and hexane (15 ml) was added. Later evaporation to *c.* 5 ml and addition of cool hexane (10 ml) afforded a white solid which was filtered off. ^{19}F NMR: V: −122.0 (m, *o*-F, *cis* to dithiocarbamate), −122.8 (m, *o*-F, *trans* to dithiocarbamate), −156.5 (m, *p*-F, *cis*), −156.8 (m, *p*-F, *trans*), −160.8 (m, *m*-F, *cis*), −161.3 (m, *m*-F, *trans*); **VI**: −122.0 (m, *o*-F, *cis*), −122.7 (m, *o*-F, *trans*), −156.3 (m, *p*-F, *cis*), −156.7 (m, *p*-F, *trans*), −160.7 (m, *m*-F, *cis*), −161.2 (m, *m*-F, *trans*); **VII**: −122.2 (m, *o*-F, *cis*), −122.7 (m, *o*-F, *trans*), −156.4 (m, *p*-F, *cis*), −156.7 (m, *p*-F, *trans*), −160.7 (m, *m*-F, *cis*), −161.2 (m, *m*-F, *trans*); **VIII**: −121.9 (m, *o*-F, *cis*), −122.7 (m, *o*-F, *trans*), −156.6 (m, *p*-F, *cis*), −156.8 (*m*, *p*-F, *trans*), −160.9 (m, *m*-F, *cis*), −161.3 (m, *m*-F, *trans*). Other ^1H NMR data (not included in Table 2): **V**: 7.2 (m, 4H); **VI**: 7.3 (m, 4H). **VII**: 7.1 (m, 4H); **VIII**: 7.1 (s, 1H, *p*-H), 6.7 (s, 2H, *o*-H).

[Au(C₆F₅){S(R′HN)CNHR}] (R=p-MeC₆H₄ and R′=n-Bu (IX), Cy (X), CH₂CH₂C₆H₅, (XI); R=p-MeOC₆H₄ and R′=n-Bu (XII))

To a solution of **I** (0.112 g, 0.2 mmol) in 20 ml of chloroform was added a small excess of amine (22 μl, 0.25 mmol ($NH_2{}^nBu$); 30 μl, 0.25 mmol (NH_2Cy) or 30 μl, 0.25 mmol ($NH_2(CH_2)_2C_6H_5$)). After stirring and refluxing for about 30 min, an unknown blue solid appeared that was filtered off. Evaporation under vacuum to *c.* 5 ml and addition of hexane (15 ml) afforded complexes **IX–XI** as white solids which were filtered off.

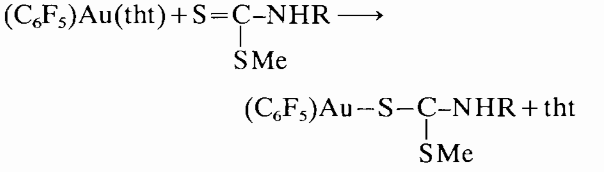
The same procedure but starting with **III** (0.115 g, 0.2 mmol) and $NH_2{}^nBu$ (22 μl, 0.25 mmol) let to **XII**.

^{19}F NMR: **IX**: −116.9 (m, *o*-F), −159.9 (m, *p*-F), −163.0 (m, *m*-F); **X**: −116.9 (m, *o*-F), −160.0 (m, *p*-F), −163.1 (m, *m*-F); **XI**: −116.9 (m, *o*-F), −159.9 (m, *p*-F), −163.0 (m, *m*-F); **XII**: −116.8 (m, *o*-F), −159.9 (m, *p*-F), −163.1 (m, *m*-F). Other ^1H NMR data (not included in Table 2): **IX**. 7.2 (m, 4H), 3.57 (m, 2H), 1.56 (m, 2H), 1.34 (m, 2H), 0.94 (t, 3H); **X**: 7.26 (m, 4H), 4.0 (m), 2.0 (m), 1.67 (m), 1.39 (m), 1.12 (m), **XI**: 7.1 (m, 9H), 3.83 (m, 2H), 2.95 (t, 2H); **XII**. 7.12 (m, 4H), 3.56 (m, 2H), 1.56 (m, 2H), 1.33 (m, 2H), 0.93 (t, 3H)

Results and discussion

Synthesis of gold(I) complexes

Methyl dithiocarbamates react with $Au(C_6F_5)(tht)$ (tht = tetrahydrothiophene) by displacement of tht, leading to the neutral complexes **I–IV** (eqn. (1))



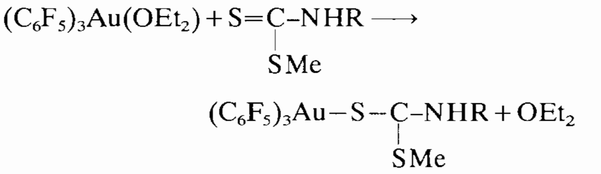
$$(C_6F_5)Au(tht) + S{=}\underset{\displaystyle SMe}{\underset{|}{C}}{-}NHR \longrightarrow (C_6F_5)Au{-}S{-}\underset{\displaystyle SMe}{\underset{|}{C}}{-}NHR + tht \qquad (1)$$

R=*p*-MeC₆H₄ (**I**), *o*-MeC₆H₄ (**II**), *p*-MeOC₆H₄ (**III**) or 3,5-Me₂C₆H₃ (**IV**)

Complexes **I–IV** are white solids, stable to air and moisture at room temperature. They are soluble in dichloromethane, acetone, chloroform and diethyl ether; they are insoluble in hexane. Their C, H, N and Au analyses and conductivities (Table 1) confirm the nature of these compounds. The ^{19}F NMR spectra show a typical C_6F_5 pattern. The ^1H NMR spectra show that the tht disappears and the methyl dithiocarbamate is occupying its place (characteristic ^1H data are given in Table 2; other in 'Experimental'). *Para*-substituted phenyls in these ligands show an AA′BB′ system, which is overlapped with the $CHCl_3$ signal. The N–H absorption can be seen in the IR spectra (see Table 2).

Synthesis of gold(III) complexes

Methyl dithiocarbamates react with $Au(C_6F_5)_3(OEt_2)$ by displacement of diethyl ether, leading to the neutral complexes **V–VIII** (eqn. (2)).



$$(C_6F_5)_3Au(OEt_2) + S{=}\underset{\displaystyle SMe}{\underset{|}{C}}{-}NHR \longrightarrow (C_6F_5)_3Au{-}S{-}\underset{\displaystyle SMe}{\underset{|}{C}}{-}NHR + OEt_2 \qquad (2)$$

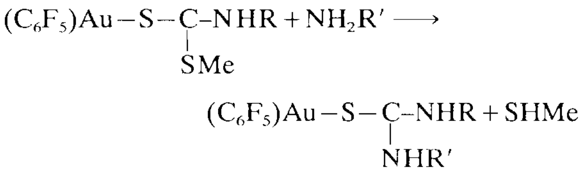
R=*p*-MeC₆H₄ (**V**), *o*-MeC₆H₄ (**VI**), *p*-MeOC₆H₄ (**VII**) or 3,5-Me₂C₆H₃ (**VIII**)

Complexes **V–VIII** are white solids, stable to air and moisture at room temperature They are soluble in dichloromethane, acetone (their solutions are non-conducting), chloroform and diethyl ether; they are insoluble in hexane The ^{19}F NMR spectra show two types of C_6F_5 in a 2:1 ratio, which are characteristic of $Au(C_6F_5)_3$ compounds [11]. The chemical shifts of the ^1H NMR spectra are almost the same in gold(I) and gold(III) complexes; only N–H resonances are about 0.9 ppm higher in gold(I) than in gold(III) compounds. The ν(N–H) can be seen in the IR spectra (Table 2)

Reactivity of the coordinated methyl dithiocarbamates

It has been shown that a nucleophilic substitution can be obtained through a nucleophilic attack at the carbon atom of a thiocarbonyl group in compounds of type S(X)CR′ (with X=OR, SR,..) continued by mercaptolysis, aminolysis... In this manner amines, alcohols and so on, can be thioacylated [9]. We have studied the reactivity of these complexes with typical nucleophilic agents such as amines.

The reactions of the gold(I) complexes with alkyl primary amines give the neutral complexes **IX–XII**, with low yields, and mercaptane which is observed by its bad smell (eqn. (3)). No reaction has been observed with ammonia.



$$(C_6F_5)Au{-}S{-}\underset{\displaystyle SMe}{C}{-}NHR + NH_2R' \longrightarrow (C_6F_5)Au{-}S{-}\underset{\displaystyle NHR'}{C}{-}NHR + SHMe \qquad (3)$$

R = *p*-MeC_6H_4, R′ = n-Bu (**IX**), Cy (**X**) or $CH_2CH_2C_6H_5$ (**XI**)
R = *p*-$MeOC_6H_4$, R′ = n-Bu (*XII*)

First a blue insoluble precipitate appears, the nature of which we have not determined, although it seems to be gold decomposition or a type of gold cluster (it is insoluble in all solvents and the C, H and N analyses are very low). Complexes **IX–XII** are white solids, stable to air and moisture at room temperature. They are soluble in dichloromethane, acetone, chloroform and diethyl ether and insoluble in hexane They are non-conducting in acetone solutions. The ^1H NMR spectra show that the singlet at δ 2.73 due to the methyl group bonded to the sulfur atom has disappeared and the resonances due to the R′HN group are present. two different NH resonances are noticed in every product: one coming from the starting RNH group (which appears at a similar chemical shift) and the other from the entering amine. The ^{19}F spectra show only a type of C_6F_5 as we expected. The IR spectra have two different N–H absorptions (see Table 2).

We also tried aromatic primary amines (aniline or *p*-nitroaniline) and there was no reaction. On the contrary, the gold complexes decomposed to metallic gold with secondary amines such as $NHMe_2$ or $NHEt_2$.

The reactivity of gold(III) complexes is much more complex because of the superposition of several reactions (substitution of the amine for the methyl dithiocarbamate, the expected thioacylation reaction and decomposition of the complexes, as we have observed from the ^{19}F NMR spectra of the crude reaction) and a mixture of products are obtained.

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