GOLD(I) COMPLEXES WITH THIOLATE AND TRIPHENYLPHOSPHINE LIGANDS

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Abstract—The reaction of $[AuCl(PPh_3)]$ with $Pb(SR)_2$ ($R = C_2H_5$, C_6H_5 , $CH_2C_6H_5$, C_6F_5 , $C_6H_2Me_3$ -2,4,6, Pr^i and Bu^i) provides a clean method to obtain complexes of the type $[Au(SR)(PPh_3)]$ in good yields. The new compounds have been characterized by IR, ¹H, ³¹P, ¹⁹F and ³¹C NMR. A study by FAB mass spectrometry indicates that an ion-molecule aggregation process takes place.

Thiolate complexes of gold(I) have been used for many years in the production of decorative elements on ceramics, glass, etc.¹ and more recently as antiarthritic drugs.² Most of the [Au(SR)] compounds are insoluble in common solvents and difficult to characterize. Nevertheless, in recent years X-ray data of some thiolate complexes have been reported.³ Since Coates et al.⁴ described the synthesis of the first triethylphosphine complex of gold(I) thiolate, few of these compounds have been reported.⁵⁻⁸ Related ones such as (2,3,4,6-tetra-O-acetyl-1-thio- β -D-glucopyranosal-S)(triethylphosphine)gold(I), "Auranofin", have been found to be effective anti-arthritic drugs.⁹ In this paper we are mainly concerned with the synthesis and characterization of some new (triphenylphospine) gold thiolates.

EXPERIMENTAL

All the reactions were carried out under nitrogen. Solvents were purified and dried by standard methods. The starting materials, $[AuClPPh_3]^5$ and $[HSC_6H_2Me_3-2,4,6]$,¹⁰ were prepared as described previously, and all other reagents were commercially available.

The Pb(SR)₂ compounds ($R = C_2H_5$, C_6H_5 , $CH_2C_6H_5$, Bu^1 , Pr^i , C_6F_5 and $C_6H_2Me_3$ -2,4,6) were prepared in distilled water from Pb(CH₃COO)₂ and the corresponding thiol.¹¹

IR spectra were recorded as KBr discs with a

Nicolet 5DX-FT IR spectrophotometer. The NMR measurements were taken using Bruker AC-200, Varian–Unity 300 and Bruker WP-200-5X spectrometers. Carbon and hydrogen analyses were carried out on a Perkin–Elmer 2400 CHN analyser and positive FAB mass spectra were recorded with a VG Autospec spectrometer.

Preparation of [Au(SBu^t)(PPh₃)]

[AuCl(PPh₃)] (0.49 g, 1 mmol) was added under nitrogen to a suspension of Pb(SBu¹)₂ (0.19 g, 0.5 mmol) in dry acetone (20 cm³). An immediate change in the colour of the solution indicated that the reaction had taken piace. After 30 min stirring at room temperature the PbCl₂ was filtered off and the solvent removed to dryness *in vacuo*, giving an oily compound. By addition of cold hexane, [Au(SBu^t)(PPh₃)] was obtained as a white powder which was recrystallized from acetone/hexane (10:1 v/v) in the freezer (0.50 g, 92% yield). Found : C, 47.2; H, 4.2. Calc. for C₂₂H₂₄AuPS : C, 48.2; H, 4.4%.

Preparation of $[Au(SR)(PPh_3)]$ compounds $[R = C_2H_5 (II), {}^5 Pr^i (III), CH_2C_6H_5 (IV), {}^5 C_6H_5 (V), {}^5 C_6H_2Me_3-2,4,6 (VI) and C_6F_5 (VII)]$

These complexes were obtained following the above procedure. III: 87% yield. Found: C, 46.9; H, 3.9. Calc. for $C_{21}H_{22}AuPS$: C, 47.2; H, 4.1%. VI: 90% yield. Found: C, 52.8; H, 4.2. Calc. for $C_{27}H_{26}AuPS$: C, 53.1; H, 4.3%. VII: 90% yield.

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Found : C, 43.8 ; H, 2.3. Calc. for $C_{24}H_{15}AuF_5PS$: C, 44.1 ; H, 2.2%.

RESULTS AND DISCUSSION

The thiolate complexes of gold(I) were prepared by reaction of $[AuCl(PPh_3)]$ with $Pb(SR)_2$ compounds under nitrogen using acetone as a solvent

 $Pb(SR)_2 + 2[AuCl(PPh_3)] \longrightarrow$

 $2[Au(SR)(PPh_3)] + PbCl_2$

We consider this as a clean method to obtain this type of compound in a high yield.

The $[Au(SR)(PPh_3)]$ complexes $(R = C_2H_5, C_6H_5 \text{ and } CH_2C_6H_5)$ were first prepared in 1965 by Kowala *et al.* following the reaction between chloro(triphenylphosphine)gold(I) and the appropriate thiol in the presence of one equivalent of NaOH, using aqueous ethanol as a solvent.⁵ The characterization data reported by these authors were concerned only with the microanalysis and molecular weight determination. Therefore, we have considered it to be of interest to complete the characterization using NMR spectroscopy and FAB mass spectrometry. All of these compounds are very soluble in most common solvents and were characterized by spectroscopy data and microanalyses.

The IR spectra of the gold thiolates showed typical bands of the triphenyl phosphine¹² and pentafluorophenyl group.¹¹ The strong band corresponding to v(Au-Cl) in the [AuCl(PPh₃)] compound is completely absent in the spectra of the new compounds, and a weak band which appears in the 290–320 cm⁻¹ region may be due to v(Au–S). Analogous data have been reported for related compounds.⁷ The ³¹P NMR spectra of the [Au(SR)(PPh₃)] complexes recorded in CDCl₃ showed a unique signal in the range 36.4–39.0 ppm (Table 1), as expected for the two-coordinate monophosphine derivatives of gold(I).^{13,14 31}P NMR measurements of these compounds after maintaining the solution at room temperature for 10 days did not show any resonance due to the free phosphine, in contrast to results of Kowala et al.⁵ regarding the instability of these types of compounds in solution. ¹H and ¹³C NMR data of these [Au(SR)PPh₃)] compounds are collected in Tables 1 and 2. At room temperature the ${}^{13}C{}^{1}H$ NMR spectra showed doublets for all the phosphine carbon atoms due to coupling with the phosphorus

Compound	'H NMR	³¹ P NMR	¹⁹ F NMR
[Au(SEt)(PPh ₃)]	3.07 q CH ₂ 1.45 t CH ₃ 7.45 m PPh ₃	36.4 s	
[Au(SBu ^t)(PPh ₃)]	1.50 s CH ₃ 7.41 m PPh ₃	39.0 s	
[Au(SPr ⁱ)(PPh ₃)]	1.46 d CH ₃ 3.67 m CH 7.48 m PPh ₃	38.6 s	
$[Au(SCH_2C_6H_5)(PPh_3)]$	4.19 s CH ₂ 7.12 m C ₆ H ₅ 7.41 m PPh ₃	37.0 s	
$[Au(SC_6H_5)(PPh_3)]$	7.13 m C_6H_5 7.48 m PPh ₃	36.4 s	
$[Au(SC_6H_2Me_3-2,4,6)(PPh_3)]$	2.26 s <i>p</i> -CH ₃ 2.66 s <i>o</i> -CH ₃ 6.91 s C ₆ H ₂ Me ₃ 7.44 m PPh ₃	36.5 s	
$[Au(SC_6F_5)(PPh_3)]$	7.48 m P <i>Ph</i> ₃	37.1 s	$-132.7 \text{ dd } o-C_6F_5$ -163.1 tt $p-C_6F_5$ -164.7 td $m-C_6F_5$

Table 1. ¹H, ³¹P and ¹⁹F NMR data for the complexes

¹H δ values in ppm from TMS, ³¹P δ values in ppm from H₃PO₄ and ¹⁹F δ values in ppm from CFCl₃; CDCl₃ solvent, room temperature.

Table 2. ¹³C NMR data for the complexes

Compound	RS moieties	PPh ₃			
[Au(SEt)(PPh ₃)]	23.3 s CH ₂ 23.8 s CH ₃	130.0 <i>i</i> - C_6H_5 (54) 133.6 <i>o</i> - C_6H_5 (14) 129.1 <i>m</i> - C_6H_5 (11) 131.5 <i>p</i> - C_6H_5 (2)			
[Au(SBu ^t)(PPh ₃)]	39.6 s CH ₃ 46.0 s C	129.4 <i>i</i> - C_6H_5 (56) 134.1 <i>o</i> - C_6H_5 (14) 129.2 <i>m</i> - C_6H_5 (11) 131.6 <i>p</i> - C_6H_5 (2)			
[Au(SPr ⁱ)(PPh ₃)]	32.2 s CH ₃ 35.0 s CH	129.4 <i>i</i> - C_6H_5 (56) 134.1 <i>o</i> - C_6H_5 (13) 129.1 <i>m</i> - C_6H_5 (11) 131.6 <i>p</i> - C_6H_5 (0)			
$[Au(SCH_2C_6H_5)(PPh_3)]$	32.8 s CH ₂ , 147.6 <i>i</i> -C ₆ H ₅ 128.3 o-C ₆ H ₅ , 128.5 <i>m</i> -C ₆ H ₅ 131.9 p-C ₆ H ₅	129.8 <i>i</i> -C ₆ H ₅ (55) 134.1 <i>o</i> -C ₆ H ₅ (14) 129.0 <i>m</i> -C ₆ H ₅ (11) 131.4 <i>p</i> -C ₆ H ₅ (2)			
[Au(SC ₆ H ₅)(PPh ₃)]	141.4 <i>i</i> -C ₆ H ₅ , 128.0 <i>o</i> -C ₆ H ₅ 128.4 <i>m</i> -C ₆ H ₅ , 132.5 <i>p</i> -C ₆ H ₅	129.0 <i>i</i> -C ₆ H ₅ (60) 134.2 <i>o</i> -C ₆ H ₅ (14) 129.2 <i>m</i> -C ₆ H ₅ (11) 131.8 <i>p</i> -C ₆ H ₅ (2)			
$[Au(SC_6H_2Me_3-2,4,6)(PPh_3)]$	20.7 <i>p</i> - <i>C</i> H ₃ , 24.5 <i>o</i> -CH ₃ 128.0 <i>i</i> - <i>C</i> ₆ H ₂ , 132.0 <i>m</i> - <i>C</i> ₆ H ₂ 133.3 <i>p</i> - <i>C</i> ₆ H ₂ , 140.8 <i>o</i> - <i>C</i> ₆ H ₂	129.6 <i>i</i> - C_6H_5 (57) 134.1 <i>o</i> - C_6H_5 (14) 129.6 <i>m</i> - C_6H_5 (11) 131.6 <i>p</i> - C_6H_5 (2)			

¹³C δ values in ppm from TMS. Splitting due to carbon-phosphorus coupling in Hz in parentheses. Solvent CDCl₃, room temperature.

atom. The coordination of the phosphine ligand to the AuSR fragment is clearly indicated by the different values in chemical shifts and coupling constants with respect to the free phosphine.¹⁴ The ¹H and ¹³C resonances for the different R groups bonded to the sulphur atom were consistent with those expected for this type of complex.

The chemical shifts in the ¹⁹F NMR spectrum of $[Au(SC_6F_5)(PPh_3)]$ were similar to those reported for the C_6F_5 group in other perfluorophenyl derivatives.^{11,15} The *ortho*- and *meta*- fluorine resonances appeared as doublets of doublets and triplets respectively, and the *para*-fluorine signal as a triplet of triplets.

The positive FAB mass spectra of $[Au(SR)PPh_3]$ (Table 3) were recorded using 3-nitrobenzyl alcohol as a matrix and acetone as a solvent. The $[Au(SCH_2C_6H_5)(PPh_3)]$ and $[Au(SBu^t)(PPh_3)]$ compounds did not show an $[M]^+$ peak, but a fragmentation pattern formed by the loss of C_6X_5 (X = H or F), PPh₃ or SR groups from the molecular ion appeared in all of the spectra. [Au (PPh₃)]⁺ was the base peak in most of the complexes and mass peaks higher than $[M]^+$, such as $[Au_2$ (SR)(PPh₃)₂], were observed in some cases. The former indicated that an ion-molecule aggregation process took place.¹⁶ The presence of peaks corresponding to $[AuO(PPh_3)_n]$ (n = 1,2) fragments in

Ion	R =	Et	$\mathbf{B}\mathbf{u}^{t}$	\mathbf{Pr}^{i}	$CH_2C_6H_5$	C_6H_5	$C_6H_2Me_3$	C_6F_5
Au ₂ (SR)(PI	$(h_{3})_{2}$		1007;100		1041; <2			1117; 29.5
Au(SR)(PP	h ₃)	520; <2		534; 5.9		568;15.0	610;74.5	658; 20.1
Au(SR)(PP	h_2)			457;6.8				
$Au(PPh_3)_2$			721; 31.0		721;72.8			721;24.7
Au(PPh ₃)		459;100	459;40.6	459;100	459;100	459;100	459;100	459;100
AuO(PPh ₃)	2							737; 2.3
AuO(PPh ₃)		475; 3.4		475;4.1				475; 3.1
RSSR	*	122; 5.7	178; 3.5	150;8.7	•			
HSR				76;40.0			152;15.1	152; 8.4
SR					123;95.8	109; 5.0		
PPh ₃		262;5.8	262; 3.9		262;7.3	262;7.3		

Table 3. FAB mass spectra (positive ion; m/z and relative intensities) of [Au(SR)(PPh₃)]

Matrix : 3-nitrobenzyl alcohol.

some spectra suggests that an oxidation process occurred during the ionization. Recently, similar data have been reported for $[Au(C_2Ph)(PPh_3)]$.¹⁷

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