A New Route for the Synthesis of Gold(I) and Gold(III) Pentafluorophenyl(Ylide) Complexes

R. USÓN, A. LAGUNA, M. LAGUNA and A. USÓN

Department of Inorganic Chemistry, University of Saragossa, Saragossa, Spain

Received December 17, 1982

The reaction between $Au(C_6F_5)_n$tht (n = 1 or 3; tht = tetrahydrothiophen) and $[RCH_2EPh_3]X$ (E = P or As; R = H, Me, Et or Ph; X = Cl, Br or I) leads to $[RCH_2EPh_3][Au(C_6F_5)_nX]$, and the resulting organoaurate(I) and (III) react with NaH or TlC_5H_5 to give the new ylide derivatives $Au(C_6F_5)_n[CH(R)EPh_3]$.

Introduction

During the last few years [1–4] a large number of ylide complexes of gold in oxidation states (I), (II) or (III) have been described, though there are only a few types of compounds in which a single ylide ligand is attached to the central atom, *i.e.* $[Au(ylide)(PR_3)]Cl$ [5, 6], AuR(ylide) (R = Me or Me_3SiCH_2) [6], $AuMe_2$(ylide)Cl [7], $[AuMe_2(ylide)(PMe_3)]Cl$ [7] and $AuMe_3$(ylide) [3, 7], and no complex is known (besides the ylide ligand) which contains one or more aryl groups.

Ylide complexes have generally been prepared by reacting a gold derivative with free ylide [1]. In the present paper we describe a new route for the synthesis of $Au(C_6F_5)_n[CH(R)EPh_3]$ (n = 1 or 3; E = P; R = H, Me, Et or Ph; E = As; R = H) based on the treatment of the anionic derivatives $[RCH_2EPh_3][Au(C_6F_5)_nX]$ (X = Cl, Br or I) with NaH or TlC_5H_5.

Experimental

IR spectra were recorded over the range 4000–200 cm^{-1} on a Perkin-Elmer 599 spectrophotometer using Nujol mulls between polyethylene sheets; conductivities were measured in 5×10^{-4} *M* acetone solution with a Philips 9501/01 conductimeter. Analyses of C and H were carried out with a Perkin-Elmer 240 microanalyzer; Au was determined by ashing the samples with an aqueous solution of hydrazine.

The yields, analytical results, melting points and conductivities of the novel complexes are collected in Table I.

All the reactions were carried out under nitrogen, and anhydrous and deoxygenated solvents were used.

Preparation of the Complexes

$[RCH_2EPh_3][Au(C_6F_5)X]$ (E = P or As; R = H, Me, Et or Ph; X = Cl, Br or I)

To a solution of $Au(C_6F_5)$tht [8] (0.226 g, 0.5 mmol) in 10 ml of ethanol was added QX (0.5 mmol) ($[CH_3PPh_3]Br$ (0.179 g); $[MeCH_2PPh_3]Br$ (0.185 g); $[EtCH_2PPh_3]Br$ (0.193 g); $[PhCH_2PPh_3]Cl$ (0.194 g) or $[CH_3AsPh_3]I$ (0.224 g)) and the resultant mixture was stirred for 15 min. After evaporation to dryness, the residue was recrystallized from dichloromethane–hexane to give crystals of (*1*)–(*5*).

$[RCH_2EPh_3][Au(C_6F_5)_3X]$ (E = P or As; R = H, Me or Et; X = Br or I)

To a suspension of $Au(C_6F_5)_3$tht [9, 10] (0.236 g, 0.3 mmol) in 10 ml of ethanol was added QX (0.3 mmol) ($[CH_3PPh_3]Br$ (0.107 g); $[MeCH_2PPh_3]Br$ (0.111 g); $[EtCH_2PPh_3]Br$ (0.116 g) or $[CH_3AsPh_3]I$ (0.134 g)). The resulting solution was stirred for 15 min at room temperature, evaporated to dryness and the residue was recrystallized from dichloromethane–hexane to give crystals of (*6*)–(*9*).

$Au(C_6F_5)[CH(R)PPh_3]$ (R = H, Me, Et or Ph)

The preparation was carried out by two methods:

a) To a suspension of NaH (0.8 g, 33.3 mmol) in 20 ml of diethyl ether was added the organoaurate(I) ((*1*) (0.216 g, 0.3 mmol), (*2*) (0.220 g, 0.3 mmol); (*3*) (0.157 g; 0.25 mmol) or (*4*) (0.188 g, 0.25 mmol)). After 1 h stirring at room temperature the excess of NaH was removed by filtration through Al_2O_3 (1 cm). Evaporation to dryness of the colourless filtrate led to the formation of white crystals of (*10*)–(*13*), which were recrystallized from dichloromethane–hexane.

b) To a suspension of TlC_5H_5 (0.269 g, 1 mmol) in 15 ml of dichloromethane was added the organoaurate(I) ((*1*) 0.361 g; 0.5 mmol); (*2*) (0.368 g, 0.5 mmol) or (*4*) (0.376 g, 0.5 mmol)). After 2 h stirring at room temperature the excess of TlC_5H_5, along

0020/1693/83/$3.00

TABLE I. Analytical Data for Complexes.

Complex	Yield (%)	Analysis found (Calcd.) (%)			Λ_M[c]	Mol. wt.[d] Found (Calcd.)	M.p. (°C)	ν(Au–C) (cm^{-1})
		C	H	Au				
1 $[CH_3PPh_3][Au(C_6F_5)Br]$	90	41.7 (41.6)	2.8 (2.5)	26.8 (27.3)	137		111	
2 $[MeCH_2PPh_3][Au(C_6F_5)Br]$	90	43.0 (42.5)	2.9 (2.7)	26.4 (26.8)	138		86	
3 $[EtCH_2PPh_3][Au(C_6F_5)Br]$	83	43.6 (43.3)	2.9 (3.0)	26.2 (26.3)	134		86	
4 $[PhCH_2PPh_3][Au(C_6F_5)Cl]$	84	50.1 (49.5)	3.1 (3.0)	25.2 (26.2)	110		144(d)	
5 $[CH_3AsPh_3][Au(C_6F_5)I]$	86	37.3 (37.0)	2.4 (2.2)	25.2 (24.3)	134		83	
6 $[CH_3PPh_3][Au(C_6F_5)_3Br]$	90	42.7 (42.1)	1.8 (1.7)	18.5 (18.7)	110		117	
7 $[MeCH_2PPh_3][Au(C_6F_5)_3Br]$	90	43.3 (42.7)	2.1 (1.9)	18.6 (18.4)	101		96	
8 $[EtCH_2PPh_3][Au(C_6F_5)_3Br]$	95	43.6 (43.2)	2.4 (2.1)	18.0 (18.2)	100		113	
9 $[CH_3AsPPh_3][Au(C_6F_5)_3I]$	88	38.8 (38.8)	1.6 (1.6)	16.6 (17.2)	102		84	
10 $Au(C_6F_5)(CH_2PPh_3)$	68[a] 50[b]	47.0 (46.9)	2.6 (2.7)	31.4 (30.8)	1	681 (640)	157	575
11 $Au(C_6F_5)[CH(Me)PPh_3]$	50[a] 35[b]	48.2 (47.7)	2.9 (2.9)	29.2 (30.1)	7	715 (654)	134	572
12 $Au(C_6F_5)[CH(Et)PPh_3]$	40[a]	48.6 (48.5)	3.3 (3.2)	29.6 (29.5)	4	670 (668)	106	560
13 $Au(C_6F_5)[CH(Ph)PPh_3]$	72[a] 70[b]	51.9 (52.0)	3.1 (3.0)	26.8 (27.5)	0	761 (716)	159	
14 $Au(C_6F_5)(CH_2AsPh_3)$	51[a]	43.9 (43.9)	2.6 (2.5)	29.3 (28.8)	1	703 (684)	144	550
15 $Au(C_6F_5)_3(CH_2PPh_3)$	52[a]	46.2 (45.6)	2.1 (1.8)	19.4 (20.2)	1	1008 (974)	252	588
16 $Au(C_6F_5)_3(CH_2AsPh_3)$	20[a]	44.1 (43.6)	1.9 (1.7)	18.8 (19.3)	3	967 (1018)	231	530

[a] Reaction with NaH. [b] With Tlcp. [c] In acetone, $ohm^{-1}\ cm^2\ mol^{-1}$. [d] In chloroform.

with the precipitated TlCl, was filtered off and the filtrate was evaporated to dryness. The residue was recrystallized from ether–hexane to give (*10*), (*11*) and (*13*).

$Au(C_6F_5)(CH_2AsPh_3)$

To a suspension of NaH (0.8 g, 33.3 mmol) in 20 ml of tetrahydrofuran was added (*5*) (0.122 g, 0.15 mmol). After 2 1/2 h refluxing the excess of NaH was filtered off and the filtrate was evaporated to dryness. The residue was washed with 3 X 5 ml of water, dissolved in dichloromethane and dried with anhydrous $MgSO_4$. Evaporation to dryness and recrystallization from ether–hexane led to white crystals of (*14*).

$Au(C_6F_5)_3(CH_2PPh_3)$

To a suspension of NaH (0.8 g, 33.3 mmol) in 20 ml of ether was added (*6*) (0.317 g, 0.3 mmol), and the mixture was stirred for 24 h at room temperature. The excess of NaH was filtered off and the filtrate was evaporated to dryness to give the white solid (*15*), which was recrystallized from dichloromethane–hexane.

$Au(C_6F_5)_3(CH_2AsPh_3)$

To a suspension of NaH (0.8 g, 33.3 mmol) in 20 ml of tetrahydrofuran was added (*9*) (0.344 g, 0.3 mmol). After 2 h refluxing the solution was filtered and the filtrate was evaporated to dryness. The residue was washed with 3 X 5 ml of water, dissolved in dichloromethane, and dried with anhydrous $MgSO_4$. Evaporation to dryness and recrystallization from ether–hexane yielded white crystals of (*16*).

Results and Discussion

Halo-organoaurate(I) and -(III) were prepared according to eqn. (1) by starting from $Au(C_6F_5)_n$-(tht) (n = 1 or 3; tht = tetrahydrothiophen) as has been described elsewhere [9, 11]:

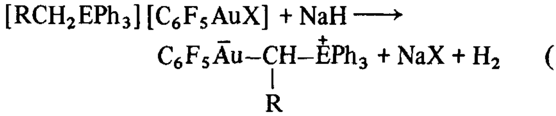
$$Au(C_6F_5)_n tht + QX \longrightarrow Q[Au(C_6F_5)_nX] + tht \quad (1)$$

$Q = CH_3PPh_3$, $MeCH_2PPh_3$, $EtCH_2PPh_3$, $PhCH_2PPh_3$ or CH_3AsPh_3

n = 1 or 3; X = Cl, Br or I

The white or yellow (X = I) air- and moisture-stable solids produced showed conductivities expected for 1:1 electrolytes (see Table I).

The complexes (*1*)–(*9*) can be used as precursors for the synthesis of gold–ylide derivatives, *via* deprotonization of the RCH_2 group of the cation and elimination of the halide attached to the metal centre. Thus, the reaction of the gold(I) derivatives with NaH proceeds with evolution of hydrogen and precipitation of sodium halide, as represented in eqn. 2



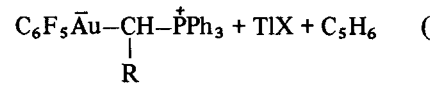
$$[RCH_2EPh_3][C_6F_5AuX] + NaH \longrightarrow C_6F_5\bar{A}u-\underset{\displaystyle R}{\underset{|}{C}}H-\overset{+}{E}Ph_3 + NaX + H_2 \quad (2)$$

E = P, R = H(*10*), Me(*11*), Et(*12*), Ph(*13*); E = As, R = H(*14*)

The reaction readily takes place at room temperature (1 h), except for E = As and R = H which requires refluxing of the tetrahydrofuran solution.

The organoaurate(III) $[RCH_2EPh_3][(C_6F_5)_3AuX]$ are less reactive, *i.e.* formation of the ylide derivative has only been observed for E = P and R = H(*15*), after 24 h stirring at room temperature, and for E = As and R = H(*16*) which requires refluxing of the tetrahydrofuran solution. Moreover, the last reaction gives rise to partial decomposition to metallic gold and therefore renders lower yields than those obtained for the corresponding gold(I) derivative. For E = P and R = Me or Et the unchanged anionic complexes were recovered.

Ylide complexes can also be obtained by using TlC_5H_5 (eqn. 3)



$$[RCH_2PPh_3][C_6F_5AuX] + TlC_5H_5 \longrightarrow C_6F_5\bar{A}u-\underset{\displaystyle R}{\underset{|}{C}}H-\overset{+}{P}Ph_3 + TlX + C_5H_6 \quad (3)$$

R = H, Me, Ph

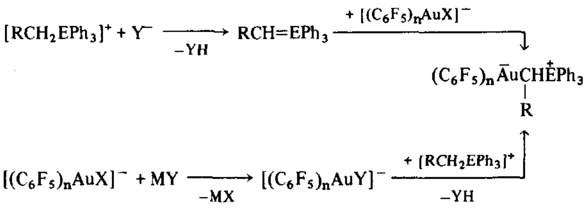
though its usefulness is more limited than that of NaH, *i.e.* it did not react with the organoaurate(III) ((*6*)–(*9*)) or with complex (*5*), and the unchanged starting compounds were recovered in each case.

In relation to processes (2) and (3) the following observations have been made:

a) In the reactions with NaH (process 2) the presence of a yellow colour, characteristic of the free ylide $RCH{=}PPh_3$, can only be perceived in the case of (*4*) (R = Ph), whilst in all the other cases, even where no reaction takes place, no change in colour has been observed.

b) The presence of the free ylide cannot be perceived in the reaction with TlC_5H_5 (process 3). In these cases, except for (*4*), a slight decomposition to metallic gold and formation of a small amount of $[Au(C_6F_5)_2]^-$ can be detected by IR spectroscopy of the crude product, which, however, disappears upon recrystallization from ether–hexane.

Two possible mechanisms are to be considered: 1) Attack upon the cation under formation of ylide and subsequent substitution of the halide linked to the gold atom, or 2), substitution of the halogen of the organoaurate and subsequent interaction with the cation, under hydrogen abstraction and formation of the gold-ylide derivative (Scheme 1).



MY = NaH or TlC_5H_5

Scheme 1

The first mechanism seems to be significant only in the reaction of (*4*) with NaH, whereas the second one should be preferred in all the other cases, and would also account for the presence of other gold derivatives among the products of the reaction with TlC_5H_5.

The new complexes (*10*)–(*16*) are white air- and moisture-stable solids, which are monomeric and nonconducting in solution (Table I). The IR spectra of the ylides show a distinctive band at 580–530 cm^{-1}, assignable to the ν(Au–C) vibration [5, 6], which is not present in the spectra of the organoaurate precursors. The gold(I) complexes also exhibit a band characteristic of the C_6F_5 group [11] at ~795 cm^{-1}, whilst the gold(III) complexes show two absorptions [9, 10] at 805(s) and 795(s, br) cm^{-1}.

References

1 H. Schmidbaur 'Organogold Compounds'. Gmelin Handbuch der Anorganischen Chemie. Springer Verlag. Berlin (1980), p. 29, 39, 40, 77, 95, 101 and 257.

2 N. Holy, V. Deshler and H. Schmidbaur, *Chem. Ber., 115,* 1379 (1982).

3 J. Stein, J. P. Fackler, C. Paparizos and H. W. Chen, *J. Am. Chem. Soc., 103,* 2192 (1981).

4 Y. Yamamoto, *Chem. Lett.*, 311 (1980).

5 H. Schmidbaur and R. Franke, *Angew. Chem., 85,* 449 (1973).

6 H. Schmidbaur and R. Franke, *Chem. Ber., 108,* 1321 (1975).

7 H. Schmidbaur and R. Franke, *Inorg. Chim. Acta, 13,* 79 (1975).

8 R. Usón, A. Laguna and J. Vicente, *J. Organometal. Chem., 131,* 471 (1977).

9 R. Usón, A. Laguna, M. Laguna and E. Fernandez, *Inorg. Chim. Acta, 45,* L177 (1980).

10 R. Usón, A. Laguna, M. Laguna and E. Fernandez, *J. Chem. Soc., Dalton,* 1971 (1982).

11 R. Usón, A. Laguna, J. Garciá and M. Laguna, *Inorg. Chim. Acta, 37,* 201 (1979).