Inorganica Chimica Acta, 114 (1986) 91–94

Synthesis of Halo(ylide)gold(I) Complexes

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Received October 10, 1985

Abstract

Reactions of $[Au(C_6F_5)(ylide)]$ (ylide = CH_2PPh_3, CH_2PPh_2Me, CH_2PPhMe_2, $CH(Me)PPh_3$, $CH(Ph)PPh_3$) with HCl or HBr in diethyl ether lead to $[AuX(ylide)]$ (X = Cl, Br). The use of acids with weakly coordinating anions (X = ClO_4, BF_4) affords cationic bis(ylide) of the type $[Au(ylide)_2]X$.

Introduction

The chemistry of gold(I)–ylide compounds has developed fairly well [1] and numerous examples of different stoichiometries [2] $[Au(ylide)(PR_3)]X$ (X = Cl, NO_3), $[Au(ylide)_2]X$ (X = Cl, Br, $AuCl_4$, ClO_4), $[AuR(ylide)]$ (R = Me, CH_2SiMe_3, C_6F_5 [3]), $[Au_2\{(CH_2)_2PR_2\}_2]$, $[Au_2\{(CH_2)_2PR_2\}\{(PPh_2)_2CH\}]$ or $[Au(SPPh_2CH_2]_2$ [4] have been reported. It is noteworthy, however, that very few halo- or pseudohalo gold(I)–ylide compounds have so far been reported. Very recently the neutral $[AuCl\{C(PPh_3)_2\}]$ [5], $[Au(CN)(CH_2PPh_3)]$ [6] and the carbonyl stabilized $[AuCl\{CH(PPh_3)COOR\}$ (R = Me, Et) [7] have been described. Surprisingly, $[Au(CN)(CH_2PPh_3)]$ does not react [6] with dry HCl in $CHCl_3$, despite the fact that the Au–C bond is readily cleaved by HCl both in alkyl [8] and in pentafluoroaryl [9] gold(I) derivatives.

In the present paper, we report a general method for the preparation of neutral AuX(ylide) (X = Cl, Br) based on the reaction between AuR(ylide) (R = C_6F_5) and diethyl ether solutions of dry HCl or HBr.

Experimental

IR spectra were recorded over the range 4000–200 cm^{-1} on a Perkin-Elmer 599 Spectrophotometer using Nujol mulls between polyethylene sheeets; conductivities were measured in 5×10^{-4} M acetone solution with a Philips 9501/01 conductimeter; molecular weights were determined in approximately 10^{-2} M solution in $CHCl_3$ using the isopiestic method on a Knauer vapor pressure osmometer model 1100. ^1H NMR were recorded in a Varian XL-200 in $CDCl_3$ solution using TMS as internal reference. C, H and N analyses were carried out with a Perkin-Elmer 240 microanalyzer; Au was determined by ashing the samples with an aqueous solution of hydrazine.

Preparation of the Starting $[Au(C_6F_5)(CH_2PPh_nMe_{3-n})]$ (n = 1, 2) Complexes

To a (30 ml) diethyl ether suspension of $[CH_3PPh_nMe_{3-n}]ClO_4$ (0.3 mmol, 0.076 g for $n = 1$ or 0.3 mmol, 0.094 g for $n = 2$) 0.3 mmol of n-BuLi (0.4 ml of a 0.75 M hexane solution) were added under dry N_2. $Au(C_6F_5)(tht)$ [10] (0.3 mmol, 0.136 g) was added to the resulting clear solution and the mixture was magnetically stirred for 30 min. Thereafter, the solution was dry-evaporated, washed with 2 X 5 ml of H_2O, and 20 ml of dichloromethane was added to the residue. The solution obtained was dried with anhydrous $MgSO_4$, filtered and vacuum-concentrated to ~5 ml. Addition of n-hexane (20 ml) precipitated the following products.

$[Au(C_6F_5)(CH_2PPh_2Me)]$

Yield, 82%, *Anal.* Calc. for $C_{20}H_{15}AuF_5P$: C, 41.55; H, 2.6; Au, 34.1%: (Molecular weight 578). Found: C, 41.55; H, 2.7; Au, 34.5%; (Molecular weight 634). Melting point 118 °C; $\Lambda_M = 6$ ohm^{-1} cm^2 mol^{-1}; ν(Au–C) = 576(m) cm^{-1}; ^1H NMR (ppm): 1.57(d, ^2J(P–H) = 13.2 Hz, 2H, $-CH_2-$), 2.28(d, ^2J(P–H) = 13.0 Hz, 3H, P–$\underline{Me}$).

$[Au(C_6F_5)(CH_2PPhMe_2)]$

Yield, 71% *Anal.* Calc. for $C_{15}H_{13}AuF_5P$: C, 34.9; H, 2.5; Au 38.2%. (molecular weight 516) Found: C, 34.8; H, 2.4; Au, 38.3%. (molecular weight 531). Melting point 132 °C (decomposition); Λ_M = 4 ohm^{-1} cm^2 mol^{-1}; ν(Au–C) = 562(m) cm^{-1}; ^1H NMR (ppm): 1.37(d, ^2J(P–H) = 13.4 Hz, 2 H, $-\underline{CH_2}-$), 2.00 (d, ^2J(P–H) = 13.05 Hz, 6 H, P–$\underline{Me}$).

Compounds $[Au(C_6F_5)(ylide)]$ have previously been described [3] and were prepared by the publish-

0020-1693/86/$3.50

TABLE I. Analytical Data for Complexes

	Yield (%)	*Anal.* Found (calc.)			Λ_M[a]	Molecular weight[b]	Melting point (°C)
		C	H	Au			
1 $[AuBr(CH_2PPh_3)]$	82	41.15 (41.25)	3.1 (3.1)	35.5 (35.6)	2	563 (553)	164(d)
2 $[AuBr(CH_2PPh_2Me)]$	82	34.05 (34.25)	2.85 (3.1)	39.9 (40.1)	4	518 (491)	135(d)
3 $[AuBr(CH_2PPhMe_2)]$	84	25.5 (25.2)	2.9 (3.05)	46.05 (45.9)	5	456 (429)	153(d)
4 $[AuBr(CH(Me)PPh_3)]$	82	42.35 (42.35)	3.3 (3.35)	35.2 (34.7)	2	562 (567)	163(d)
5 $[AuBr(CH(Ph)PPh_3)]$	83	47.25 (47.7)	3.2 (3.35)	30.95 (31.3)	2	631 (629)	192(d)
6 $[AuCl(CH_2PPh_3)]$	93	44.65 (44.85)	3.25 (3.35)	38.7 (38.7)	2	505 (509)	200(d)
7 $[AuCl(CH_2PPh_2Me)]$	81	37.25 (37.65)	3.3 (3.4)	43.65 (44.1)	3	487 (447)	148(d)
8 $[AuCl(CH_2PPhMe_2)]$	88	28.0 (28.1)	3.0 (3.4)	51.4 (51.2)	1	407 (385)	182(d)
9 $[AuCl(CH(Me)PPh_3)]$	82	45.6 (45.95)	3.6 (3.65)	37.35 (37.65)	0	495 (523)	158(d)
10 $[AuCl(CH(Ph)PPh_3)]$	85	51.0 (51.35)	3.5 (3.6)	34.0 (33.65)	3	575 (585)	181(d)
11 $[Au(CH_2PPh_3)_2]ClO_4$	88	53.8 (53.75)	4.0 (4.05)	23.55 (23.2)	130	–	208(d)
12 $[Au(CH_2PPh_3)_2]BF_4$	50	54.1 (54.55)	4.05 (4.05)	23.9 (23.55)	137	–	214(d)

[a]In acetone ohm^{-1} cm^2 mol^{-1}. [b]In chloroform.

ed method; (ylide) = CH_2PPh_3, $CH(Me)PPh_3$, $CH(Ph)PPh_3$.

Preparation of [AuX(CHRPR'₃)] (Complexes 1–10)

Diethyl ether solutions (30 ml) were prepared containing 0.2 mmol of each of the following precursors: $[Au(C_6F_5)(CH_2PPh_3)]$ [3] (0.128 g); $[Au(C_6F_5)(CH_2PPh_2Me)]$ (0.116 g); $[Au(C_6F_5)(CH_2PPhMe_2)]$ (0.103 g); $[Au(C_6F_5)(CH(Me)PPh_3)]$ [3] (0.131 g); or $[Au(C_6F_5)(CH(Ph)PPh_3)]$ [3] (0.143 g). Then 0.6 mmol of a diethyl ether solution of dry HX (6 ml of 0.1 M HCl or HBr) was added to each solution. The mixtures were magnetically stirred for two hours to allow for the slow precipitation of complexes (**1–10**), which thereafter were filtered and washed with diethyl ether (2 × 5 ml). For yields, see Table I.

$[Au(CH_2PPh_3)_2]X$ ($X = ClO_4$ (11), BF_4 (12))

To a diethyl ether solution (30 ml) containing 0.2 mmol (0.128 g) of $[Au(C_6F_5)(CH_2PPh_3)]$ was added 0.1 mmol of acid (0.1 ml of an aqueous 1 M $HClO_4$ solution or 1.25 ml of a diethyl ether 0.08 M, HBF_4 solution). A white precipitate of **11** or **12** was instantaneously formed, and was filtered and washed with diethyl ether (2 × 5 ml).

Addition of 0.1 mmol of PPh_3 (0.026 g) to the filtrate of **11** gave a clear solution which was magnetically stirred for 10 min. Thereafter, the solution was vacuum-concentrated to ~5 ml. Addition of ethanol (10 ml) precipitated 0.053 g of $[Au(C_6F_5)(PPh_3)]$ [11] (84% yield).

Reaction of $[AuCl(CH_2PPh_3)]$ with $[Au(C_6F_5)(CH_2PPh_3)]$

To a diethyl ether solution (20 ml) containing 0.2 mmol of $[Au(C_6F_5)(CH_2PPh_3)]$ (0.128 g) was added 0.2 mmol of $[AuCl(CH_2PPh_3)]$ (0.102 g). The mixture was magnetically stirred for 24 h. Thereafter, the starting materials were recovered.

When 0.2 mmol of $AgClO_4$ (0.041 g) was added to the above mixture, a precipitate was formed. After filtration the solid was dissolved in CH_2Cl_2 (20 ml) and the AgCl produced was removed by filtration. The filtrate was vacuum-concentrated to ~5 ml. Upon addition of diethyl ether (20 ml), 0.119 g of $[Au(CH_2PPh_3)_2]ClO_4$ (**11**) (71% yield) was obtained.

Results and Discussion

Some plausible reactions which lead to halo gold(I)–ylide compounds have proved unsatisfactory or

TABLE II. ^{1}H NMR Data and Some Significant IR Bands

	$-CH_2-$ or $-CH-$ (ppm) [^2J(P–H) (Hz)]	P-$\underline{Me}$ (ppm) [^2J(P–H) (Hz)]	CH–$\underline{Me}$ (ppm) [^3J(P–H) (Hz)]	ν(Au–C)	ν(Au–X)
1 $[AuBr(CH_2PPh_3)]$	2.08(d) [12.0]	–	–	597	223
2 $[AuBr(CH_2PPh_2Me)]$	1.83(d) [12.2]	2.27(d) [13.0]	–	589	218
3 $[AuBr(CH_2PPhMe_2)]$	1.65(d) [12.5]	2.00(d) [13.4]	–	588	217
4 $[AuBr(CH(Me)PPh_3)]$	2.74(dq) [11.2] [^3J(H–H), 7.1]	–	1.64(dd) [22.4]	580	215
5 $[AuBr(CH(Ph)PPh_3)]$	4.15(d) [12.9]	–	–	589	216
6 $[AuCl(CH_2PPh_3)]$	2.10(d) [12.1]	–	–	601	330
7 $[AuCl(CH_2PPh_2Me)]$	1.85(d) [12.4]	2.26(d) [13.1]	–	594	315
8 $[AuCl(CH_2PPhMe_2)]$	1.67(d) [13.0]	2.00(d) [13.1]	–	589	313
9 $[AuCl(CH(Me)PPh_3)]$	2.76(dq) [11.4] [^3J(H–H), 7.2]	–	1.62(dd) [22.3]	583	323
10 $[AuCl(CH(Ph)PPh_3)]$	3.99(d) [13.0]	–	–	592	323
11 $[Au(CH_2PPh_3)_2]ClO_4$	1.66(d) [12.5]	–	–	562	–
12 $[Au(CH_2PPh_3)_2]BF_4$	1.67(d) [12.7]	–	–	563	–

unsuccessful. For instance, H abstraction with NaH from a phosphonium dibromo-aurate (an extension of the method used [3] to prepare $[Au(C_6F_5)(ylide)]$) in THF where the dibromoaurate is more soluble (eqn. (1)) only proceeds for R = H, R′ = Ph,

$$[CH_2R{\cdot}PR'_3][AuBr_2] + NaH \longrightarrow NaBr + H_2 + [AuBr(CHR{\cdot}PR'_3)] \qquad (1)$$

leading to $[AuBr(CH_2PPh_3)]$ (**1**) in low yield (30%). In all the other cases [R = H, R′ = Ph$_3$, Ph$_2$Me, PhMe$_2$; R = Me, R′ = Ph$_3$; R = Ph, R′ = Ph$_3$], the reactions take place very slowly and decomposition to metallic gold is observed.

A different approach, addition of free ylide to ClAu(tht), leads to intractable mixtures, probably owing to the action of the ylide on both the neutral and the anionic ligand in the precursor, which are both partially displaced.

Finally, the reaction of arylgold(I)–ylides with HCl or HBr in diethyl ether solution leads to the preparation of bromo (**1–5**) and chloroderivatives (**6–10**), according to eqn. (2).

$$Au(C_6F_5)(CHR{-}PR'_3) + HX \longrightarrow C_6F_5H + [AuX(CHR{-}PR'_3)] \qquad (2)$$

X = Br R = H $R'_3 = Ph_3$ (1) X = Cl (6)
R = H $R'_3 = Ph_2Me$ (2) (7)
R = H $R'_3 = PhMe_2$ (3) (8)
R = Me $R'_3 = Ph_3$ (4) (9)
R = Ph $R'_3 = Ph_3$ (5) (10)

All the complexes (**1–10**) are insoluble in diethyl ether and can easily be recovered with yields between 80–93% (see Table I). Since no side-reaction has been observed, the use of an excess (200%) of HX permits both shorter reaction and better yields.

Complexes (**1–10**) are white colored and exist as air-, light- and moisture-stable solids at room temperature. They are monomeric in chloroform solution and non-conducting in acetone solution. Their IR spectra show one single band in the 600–560 cm^{-1} region, assignable to ν(Au–C) [3, 12, 13]. The bromo derivatives (**1–5**) present one band due to ν(Au–Br) [13] at 280 cm^{-1}, and the chloro derivatives (**6–10**) exhibit one band due to ν(Au–Cl) [14] at 320 cm^{-1} (Table II).

Substitution of other acids for HCl or HBr leads to different results. For instance, if HCF_3COO is used a reaction takes place, but the resulting oily residues could not be crystallised. On the other hand, the use of acids whose anions are weakly coordinating ones (HBF_4, $HClO_4$) leads to cationic ylides, according to eqn. (3).

$$2[Au(C_6F_5)(CH_2PPh_3)] + HX \xrightarrow{OEt_2} [Au(CH_2PPh_3)_2]X + \text{‘}Au(C_6F_5)(OEt_2)\text{’} + C_6F_5H \qquad (3)$$

$X = ClO_4$ (11)
BF_4 (12)

Complexes **11** and **12** are only slightly soluble in diethyl ether and can readily be obtained in 88% or 50% yield, respectively. Both give conducting acetone solutions (Λ_M = 130.5 (**11**) and 137.5 (**12**) ohm^{-1} cm^2 mol^{-1}) [15] according to their ionic nature.

The assumed formation of ‘$Au(C_6F_5)(OEt_2)$’ (eqn. (3)) could not be directly proved. The diethyl ether filtrate slowly decomposes under separation of metallic gold, and evaporation only accelerates this decomposition. Addition of PPh_3 to the filtrate stops the decomposition, and upon evaporation and addition of ethanol the stable $(C_6F_5)AuPPh_3$ [11] was obtained.

On the other hand, the reaction (eqn. (4)) does not take place (24 h). Addition of $AgClO_4$ causes

$$AuCl(ylide) + AuC_6F_5(ylide) \xrightarrow{OEt_2} [Au(ylide)_2]Cl + \text{'}Au(C_6F_5)(OEt_2)\text{'} \qquad (4)$$

the precipitation of AgCl and $[Au(ylide)_2]ClO_4$, which can be separated by making use of the solubility of the latter in dichloromethane. Thus, the different results of eqn. (2) and (3) can be explained by the differences in coordinating ability of the halide or the ClO_4^- or BF_4^- anions, respectively.

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