Halogenocarbonyl Complexes of Gold†

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Carbonyl gold(I) bromide [AuBr(CO)] was obtained in solutions of halogenated hydrocarbons by (*a*) absorption of CO by [Au_2Br_6] in the presence of cyclohexene as a halogen abstractor, (*b*) carbonylation of [Au_2Br_6]; (*c*) carbonylation of AuBr. The compound has been studied by spectroscopic methods in solution, including NMR measurements at variable temperature. Both [AuCl(CO)] and [AuBr(CO)] undergo a rapid exchange process with dissolved CO. The low stability of [AuBr(CO)] with respect to its decomposition to AuBr(s) prevents the isolation of the carbonyl bromide of gold(I). The present findings confirm the trend to lower stability in the sequence Cl > Br > I already established for the carbonylhalogeno derivatives of palladium(II) and platinum(II).

Earlier studies have indicated that the stability of halogenocarbonyl complexes of palladium(II) and platinum(II) decreases along the sequence Cl > Br > I, as suggested by spectroscopic evidence in solution for platinum(II)[1] and by the decreased tendency of palladium(II) halides to bind carbon monoxide on going from $PdCl_2$ to $PdBr_2$. Thus, isolated [$Pd_2Br_4(CO)_2$] always contains $PdBr_2$ impurities, although about 10^{-2} mol dm^{-3} solutions of the carbonyl derivative can be obtained by operating under carbon monoxide.[2]

With gold(I) only the chloride ligand appears to be compatible with the existence of a stable Au–CO bond in species such as [AuCl(CO)][3] and [$Au_2Cl_4(CO)$],[4] although, while this work was in progress, a fluorosulphonate carbonyl derivative of gold(I), [$Au(OSO_2F)(CO)$], has been reported.[5]

We were primarily interested in extending the range of ligands for gold which may give a stable combination with CO: particularly we wanted to prepare the still unknown bromo derivative [AuBr(CO)]. Furthermore, since the fluorosulphonate group is probably electronically not largely different from $AuCl_4$, both being strongly electron-withdrawing, we thought that the already reported mixed-valence carbonyl derivative [$Au_2Cl_4(CO)$],[4] see below, deserved further attention, especially in connection with our earlier proposal about the predominant σ contribution to the M–CO bond in this area of the Periodic Table.[6]

This paper reports the preparation in solution of [AuBr(CO)], new preparative routes to AuX (X = Cl or Br), as precursors to the corresponding carbonyl complexes and to [$Au_2Cl_4(CO)$] and some new ^{13}C NMR data on the carbonyl species.

Experimental

The IR spectra were measured with a Perkin-Elmer model 283 instrument equipped with a grating, each spectrum being calibrated with either a polyethylene film (between 4000 and 600 cm^{-1}), indene (between 600 and 200 cm^{-1}) or CO in the 2200–1800 cm^{-1} region: the accuracy in the latter instance is believed to be ± 1 cm^{-1}. Elemental (C,H) analyses were performed with a Carlo Erba model 1106 analyser. Gold analyses were carried out by calcination of the samples. The ^{13}C NMR spectra were measured with a Bruker AC 200 instrument operating at 50.33 MHz, mass spectra on a VG MM 16 F instrument operating at 70 eV (*ca.* 1.12×10^{-17} J) with a direct sample inlet, at a source temperature of 70 °C. Unless otherwise stated, all the preparative procedures were carried out under an atmosphere of prepurified dry nitrogen with pre-dried solvents. Anhydrous gold(III) chloride[3a] and gold(I) iodide[7] were prepared as reported previously.

Preparations.—AuCl. In a flask (100 cm^3) containing CH_2Cl_2 (25 cm^3), [Au_2Cl_6] (1.296 g, 2.14 mmol) was treated with cyclohexene (4.35 mmol) at room temperature. After 1 h stirring the yellow AuCl was collected by filtration and dried *in vacuo* (83% yield): it gave the expected elemental (Au) analysis.

AuBr. Gold(III) chloride, [Au_2Cl_6] (3.094 g, 5.10 mmol), suspended in CH_2Cl_2 (50 cm^3) was treated with Pr^iBr (3.0 cm^3, 32.0 mmol) at room temperature for about 15 h with magnetic stirring. The resulting suspension of the violet-black [Au_2Br_6] thus obtained[7] was treated at about −15 °C with cyclohexene (9.87 mmol). After 2 h of stirring at that temperature the yellow suspension of the resulting AuBr was filtered and dried *in vacuo* (82% yield). A correct elemental (Au) analysis was obtained. The IR spectrum showed an intense band at 233 cm^{-1} attributed to the Au–Br stretching vibration.[8]

[AuBr(CO)] *in solution.* (*a*) *From the* [Au_2Br_6]–*cyclohexene*–CO *system.* Operating under an atmosphere of CO, [Au_2Br_6] (0.521 g, 0.60 mmol), suspended in 1,2-dibromoethane (15 cm^3), was stirred for about 8 h at room temperature: an IR spectrum of the supernatant solution showed a band at 2153 cm^{-1} (A = 0.23, cell path = 0.1 mm) due to [AuBr(CO)]. To this mixture, a solution of cyclohexene (1.18 mmol) in 1,2-dibromoethane (30 cm^3) was added dropwise. Slow absorption of gas was observed, the solution became colourless and the IR spectrum showed that the band at 2153 cm^{-1} had increased its intensity.‡ By addition of heptane (50 cm^3) and cooling at about 2 °C, a brown precipitate was obtained which consisted mainly of AuBr.

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‡ The molar absorption coefficient ε of [AuBr(CO)] was estimated to be 970 dm^3 mol^{-1} cm^{-1} in 1,2-dibromoethane, *cf.* 980 dm^3 mol^{-1} cm^{-1} reported[3b] for [AuCl(CO)] in benzene.

(*b*) *Reaction between* $[Au_2Br_6]$ *and* CO. Anhydrous gold(III) bromide, $[Au_2Br_6]$ (0.49 g, 0.56 mmol), was suspended in dibromomethane (15 cm^3) and stirred for 24 h under an atmosphere of CO. A violet-black solid and a violet supernatant solution were obtained. The IR spectrum of the solution had a band at 2156 cm^{-1} (A = 0.29, cell path = 0.10 mm), corresponding to a conversion of about 40% into [AuBr(CO)]. By addition of more solvent (20 cm^3) and after 4 h of stirring under the same conditions, the band did not change in intensity to any appreciable extent (A = 0.29; about 93% conversion) while the amount of the starting $[Au_2Br_6]$ (the suspended violet solid) had decreased considerably.

(*c*) *From* AuBr *and* CO. In gas-volumetric equipment thermostatted at 17.0 ± 0.1 °C, a sample of AuBr (0.222 g, 0.80 mmol) was treated with CO at atmospheric pressure in dibromomethane as reaction medium. After about 30 min of stirring the absorption of CO corresponded to 0.79 mmol, *i.e.* about 99% of the expected amount for the formation of [AuBr(CO)].

In separate experiments, attempts were made to isolate the bromocarbonyl derivative. Gold(I) bromide (3.94 g, 14.2 mmol) was suspended in CH_2Cl_2 (50 cm^3) and treated with CO at atmospheric pressure at about −30 °C. After 3 h of stirring the system consisted of a crystalline colourless solid and a brown supernatant solution. After addition of heptane (50 cm^3) to decrease the solubility of [AuBr(CO)], the colourless solid was filtered at −30 °C and briefly dried *in vacuo*. During the drying procedure the solid became progressively light grey and then grey-green (3.24 g, 82% yield based on the gold content). The elemental (Au) analysis was 71.0% [expected values for [AuBr(CO)] and AuBr: 64.6 and 71.1%, respectively]. The mass spectrum of the solid showed peaks due to Br_2^+, HBr^+ and Br^+;* chlorine-containing fragments were absent.

Characterization of [AuBr(CO)] *by* IR *and* ^{13}C *NMR Spectra.*—(*a*) IR. Infrared spectra of [AuBr(CO)] were measured on solutions of the compound prepared by treating $[Au_2Br_6]$ or AuBr with CO in different solvents (C_6H_6, CH_2Cl_2, CH_2Br_2, 1,2-dibromoethane); the results are in Table 1.

(*b*) ^{13}C NMR. A solution of both [AuCl(CO)] and [AuBr(CO)] in CD_2Cl_2 was prepared by treating AuBr suspended in a solution of [AuCl(CO)] with 90%-enriched ^{13}CO at about 30 °C. The isotopic exchange was independently found to occur very readily with [AuCl(CO)] at that temperature. From the moles of gold employed and from the free volume of the system, it was estimated that the gold carbonyls were about 80% enriched at equilibrium. The solution was sealed in a 10 mm NMR tube under N_2 at atmospheric pressure and spectra were measured at several temperatures. The results are in Table 2.

The resonance assignment was based on the ^{13}C NMR spectra of a CD_2Cl_2 solution containing ^{13}CO-enriched [AuCl(CO)] only. The ^{13}C NMR spectra were also measured for ^{13}C-enriched benzene solutions of both [AuCl(CO)] and [AuBr(CO)] prepared under carbon monoxide: at room temperature, only one resonance at δ 172 (br) was observed. $[^2H_6]$Benzene solutions containing the individual compounds, prepared under carbon monoxide, had the following resonances: [AuCl(CO)], δ 170.9; [AuBr(CO)], 173.2. The literature reports a value of δ 170.8 for a benzene solution of [AuCl(CO)].[10]

Attempts to prepare [AuI(CO)].—A solution of [AuCl(CO)] (1.10 g, 4.22 mmol) in CH_2Cl_2 (30 cm^3) was treated with Pr^iI (4.51 mmol) under an atmosphere of carbon monoxide at room temperature. After 16 h of stirring, gold metal was deposited on the walls of the container and the supernatant solution had a band at 2162 cm^{-1} attributed to unreacted [AuCl(CO)], which disappeared after 5 h of stirring. A similar reaction with HI carried out under similar conditions also led to gold metal and iodine.

Isolation of the Mixed-valence Carbonyl Derivative $[Au_2Cl_4(CO)]$.—Anhydrous gold(III) chloride, $[Au_2Cl_6]$ (1.57 g, 2.59 mmol), suspended in thionyl chloride (20 cm^3) was treated with [AuCl(CO)] (1.36 g, 5.22 mmol) at about −33 °C. The mixture was stirred for 6 h after which a deep orange solid was present, together with a supernatant solution of the same colour. The solid was filtered off at about −30 °C and dried *in vacuo* (1.95 g, 67% yield) (Found: C, 2.0; Au, 70.3. Calc. for CAu_2Cl_4O: C, 2.1; Au, 69.9%). Hydrogen was absent. The IR spectrum of a solution of $[Au_2Cl_4(CO)]$ in $SOCl_2$, recorded at room temperature, showed two bands at 2180 and 2163 cm^{-1}, the latter absorption being due to some [AuCl(CO)]. A CD_2Cl_2 solution of the compound showed, in the ^{13}C NMR spectrum, a single resonance ($T \approx -50$ °C) at δ 170.8 (see Table 2 for details of the standard).

Results and Discussion

The gold(I) halides AuCl and AuBr can conveniently be prepared by using cyclohexene as halogen abstractor from the corresponding derivatives of gold(III). In the case of AuBr, the intermediate gold(III) bromide, obtained by the halide-exchange reaction from $[Au_2Cl_6]$ with Pr^iBr,[7] was directly reduced *in situ*. Previously reported preparations of AuCl[11] and AuBr[12] involve thermal decomposition of the gold(III) halides, implying an accurate control of temperature and pressure to avoid extensive decomposition of the products.

The bromocarbonyl compound [AuBr(CO)] could be prepared in solution by one of routes (1)–(3). Reaction (2) requires

$$\tfrac{1}{2}Au_2Br_6 + CO + C_6H_{10} \longrightarrow [AuBr(CO)] + C_6H_{10}Br_2 \quad (1)$$

$$\tfrac{1}{2}Au_2Br_6 + CO \longrightarrow [AuBr(CO)] + Br_2 \quad (2)$$

$$AuBr + CO \longrightarrow [AuBr(CO)] \quad (3)$$

some comments. It is actually the sum of two reactions (2a) and (2b), the latter representing the equilibrium of carbonyl bromide

$$\tfrac{1}{2}Au_2Br_6 + 2CO \longrightarrow AuBr(CO) + COBr_2 \quad (2a)$$

$$COBr_2 \rightleftharpoons CO + Br_2 \quad (2b)$$

to CO and Br_2.[13a] Since the species COX_2 with X = Br is thermodynamically less favoured than carbonyl chloride $COCl_2$,[13b] reaction (2) is not the best suited for preparing solutions of the carbonylgold bromide. Also, since we start from the sparingly solubly gold(III) bromide at atmospheric pressure of CO, *i.e.* under conditions of constant concentrations of both reagents, the concentration of [AuBr(CO)] is constant as long as solid $[Au_2Br_6]$ is present. At atmospheric pressure of CO, the maximum concentration of [AuBr(CO)] which could be obtained was 3.0×10^{-2} mol dm^{-3} in CH_2Br_2 as solvent. Subtraction of Br_2 with cyclohexene, see equation (1), leads to a substantially quantitative conversion of $[Au_2Br_6]$ into [AuBr(CO)].

Attempts to isolate [AuBr(CO)] by low-temperature filtration of the colourless crystalline solid failed, probably due an intrinsic low stability of the solid under reduced pressure of CO [equation (4)]. Presumably, the enthalpy and entropy

$$[AuBr(CO)](s) \longrightarrow CO + AuBr(s) \quad (4)$$

changes involved in the transformation of solid [AuBr(CO)] to solid AuBr represent a very delicate balance and a reduction in the CO pressure is sufficient to destabilize the system (K_4 =

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* A sample of [AuCl(CO)] showed the following mass fragmentation pattern (*m/z*, relative intensity, assignment): 260, 24, $[AuCl(CO)]^+$; 232, 10, $[AuCl]^+$; 225, 9, $[Au(CO)]^+$; 36, 100, HCl^+; and 35, 8, Cl^+.

Table 1 Infrared CO stretching vibrations of [AuBr(CO)] and [AuCl(CO)] in different solvents*

	$\tilde{\nu}_{CO}$/cm^{-1}	
Solvent	[AuBr(CO)]	[AuCl(CO)]
C_6H_6	2151	2153
CH_2Cl_2	2159	2162
CH_2Br_2	2156	2158
1,2-$C_2H_4Br_2$	2153	2156

* Solutions containing both [AuBr(CO)] and [AuCl(CO)] gave a unique band at a wavenumber intermediate between those of the individual compounds, due to low resolution in those solvents.

Table 2 Carbon-13 NMR chemical shifts of gold(I) carbonyl complexes as a function of temperature

	δ[a]	
T/°C	[AuCl(CO)][b]	[AuBr(CO)]
21[c]	—	—
0	172.3	174.4
−30	172.0	174.3
−50	171.8	174.1
−70	171.5	173.8

[a] Measured on CD_2Cl_2 solutions containing both [AuCl(CO)] and [AuBr(CO)], about 80% ^{13}C-enriched. The solutions were transferred to the NMR tube under nitrogen. The concentration of CO is estimated to be about one order of magnitude lower than that of each of the gold compounds. Chemical shifts are from $SiMe_4$ using the resonance of CD_2Cl_2 (δ 53.8) as reference. A third resonance due to dissolved CO was also present: δ 184.4 (0), 184.3 (−30), 184.2 (−50) and 184.0 (−70 °C). A value of δ 181.3 for gaseous CO has been reported.[9] [b] The resonance of [AuCl(CO)] was established for solutions containing this compound only, under the same conditions. [c] At room temperature, only one resonance at δ 172.6 was observed.

p_{CO}). Also, it is interesting that probably no important kinetic barriers have to be overcome to convert [AuBr(CO)](s) into AuBr(s), as the solid-state structure of [AuBr(CO)] can be assumed to be similar to that of [AuCl(CO)].[14]

In spite of the unsuccessful attempts to isolate the compound, the presence of [AuBr(CO)] in solution has been established conclusively by spectroscopic measurements and by the observed 1:1 (Au:CO) molar ratio in the course of gas-volumetric measurements of the CO absorbed by AuBr in dibromomethane.

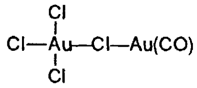
The CO stretching vibration is a few wavenumbers lower than that of the corresponding chloro-derivative (see Table 1); thus, IR spectroscopy was not in this case particularly useful in distinguishing between [AuCl(CO)] and [AuBr(CO)] in solution. Carbon-13 NMR spectra were used instead. However, it was soon realized that, in order to obtain reliable data, the spectra had to be run at low temperature since, at room temperature, a rapid exchange was observed between co-ordinated and dissolved carbon monoxide. As is shown in Table 2, only one resonance was observed at room temperature for a solution containing both ^{13}C-enriched [AuCl(CO)] and [AuBr(CO)] in the presence of dissolved carbon monoxide. After the ^{13}C chemical shift of [AuCl(CO)] has been established independently for a CD_2Cl_2 solution containing only this compound, it was readily found that [AuBr(CO)] absorbs about 2 ppm downfield with respect to [AuCl(CO)]. This downfield shift is consistent with all earlier NMR findings for platinum(II) carbonyl species as a function of the bonded halide.[1]

This paper has thus definitely established the existence of [AuBr(CO)] and has, at the same, pointed out that, in the series of halogenocarbonyl complexes of gold(I), the stability with respect to the corresponding AuX(s) systems decreases drastically in the sequence Cl > Br. Again this is consistent with our earlier findings with palladium(II) complexes.[2] Accordingly, a solution of [AuCl(CO)] in CH_2Cl_2 was treated with Pr^{i}I and found to produce gold and iodine, presumably according the stoichiometry (5). The observed products suggest [AuI(CO)],

$$[AuCl(CO)] + RI \longrightarrow CO + Au + RCl + \tfrac{1}{2}I_2 \quad (5)$$

which might be formed *in situ*, undergoes a reductive elimination of iodine with evolution of CO. Moreover, a suspension of AuI obtained by treating $[Au_2Cl_6]$ with Pr^{i}I in CH_2Cl_2 as medium, although perfectly stable in the absence of CO, undergoes decomposition to gold metal and I_2 in the presence of CO. This again implies the transient formation of the unstable [AuI(CO)]. It is interesting that similar results were obtained with Au(SR), produced *in situ*[15] by treating [AuCl(CO)] with RSH under CO.

The mixed-valence compound $[Au_2Cl_4(CO)]$ could be obtained by treating $[Au_2Cl_6]$ with [AuCl(CO)] at low temperature (about −33 °C). This compound had been identified earlier in solution,[3b] but its isolation had not been achieved until now. The CO stretching vibration of this product has been observed at 2180 cm^{-1} in $SOCl_2$, which represents an about 20 cm^{-1} increase with respect to [AuCl(CO)]. This value should be compared with the CO stretching vibration reported[5] at 2198 cm^{-1} for $[Au(OSO_2F)(CO)]$.



$$\mathrm{Cl{-}\underset{Cl}{\overset{Cl}{Au}}{-}Cl{-}Au(CO)}$$

However, while the latter compound was reported to be thermally stable up to 190 °C, $[Au_2Cl_4(CO)]$ is unstable at room temperature, an easy decomposition pathway being available for cleavage of the Au^{III}–Cl_b (Cl_b = bridging chloride) bond to give [AuCl(CO)] or chlorine elimination to AuCl and $COCl_2$. In connection with our earlier proposal about the predominant σ contribution to the Au–CO bond, it is significant that isolation of carbonyl derivatives of gold(I) has been successful in systems containing strongly electron-withdrawing groups such as $AuCl_4$ and OSO_2F.[5]

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