Reductive Carbonylation of Gold(III) Chloride

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The reaction of anhydrous $AuCl_3$ with CO in thionyl chloride gives [Au(CO)Cl] in substantially quantitative yields. The reaction takes place *via* the intermediate formation of a soluble carbonyl species which has been characterised spectroscopically and is believed to be a mixed-valence carbonyl complex of formula $[Au_2(CO)Cl_4]$. Under nitrogen or argon, $AuCl_3$ and [Au(CO)Cl] give an insoluble microcrystalline substance of analytical formula $AuCl_2$, which further reacts with CO to yield [Au(CO)Cl].

WE recently reported [1] that anhydrous gold(III) chloride, prepared *in situ* from hydrated tetrachloroauric(III) acid is reduced to [Au(CO)Cl] in thionyl chloride [equation (1)]. We now report some new observations on the

$$Au_2Cl_6 + 4\,CO \longrightarrow 2\,COCl_2 + 2[Au(CO)Cl] \qquad (1)$$

reductive carbonylation (1) which have led to the isolation of what are believed to be intermediates of the reaction. The results are also relevant to the general problem of metal halide carbonylations.[2]

RESULTS AND DISCUSSION

Reaction (1), at atmospheric pressure of carbon monoxide and room temperature, usually results in substantially quantitative yields of the carbonylchloro-derivative of Au^I. When the atmosphere of carbon monoxide was constantly maintained, no products other than [Au(CO)Cl] were observed. However, if for some reason (*e.g.* small free volume of the reaction flask or failure to supply the reaction flask with fresh carbon monoxide) the amount of CO present is well below that required by stoicheiometry (1), the formation of a black solid was observed. Further treatment with carbon monoxide eventually resulted in the formation of [Au(CO)Cl] in excellent yield. The possibility therefore exists that the black precipitate could be due to a reaction between unchanged gold(III) chloride and [Au(CO)Cl]. It was therefore decided to run a series of reactions between Au_2Cl_6 and [Au(CO)Cl] under an inert atmosphere (nitrogen or argon) at different molar ratios and concentrations in $SOCl_2$, CH_2Cl_2, and CCl_4. The results (see also Table) have shown conclusively the following facts.

Reactions between $AuCl_3$ and [Au(CO)Cl] [a]

Run	Amount of $AuCl_3$ (mmol)	Amount of [Au(CO)Cl] (mmol)	Solvent volume (cm^3)	Reaction time (h)	Yield of black solid (%) [b]
1	0.92	0.80	$SOCl_2$ (25)	48	*c*
2	3.43	3.65	(20)	3	24
3	8.67	8.27	(10)	4	49
4	1.12	1.09	CCl_4 (20)	120	*c*
5	5.08	5.26	CH_2Cl_2 (20)	1.5	42
6	1.58	1.61	$SOCl_2$ (40)	0.5	*d*
7	7.42	2.54	(30)	28	77 [e]

[a] At room temperature under nitrogen or argon. [b] Yield of black solid analysing for $AuCl_2$ based on the total moles of gold used in the reaction. [c] Followed gas-volumetrically without noting any significant volume change. [d] Not determined. The i.r. spectrum of the resulting solution showed a new band at 2 180 cm^{-1} in addition to that due to [Au(CO)Cl] (see also Figure 1). [e] Molar ratio Au^{III} : Au^I = 2.92 : 1.

(*a*) The slightly soluble $AuCl_3$ promptly dissolved in $SOCl_2$ in the presence of [Au(CO)Cl] (total gold concentration 0.08 mol dm^{-3}, see Table, run 6). (*b*) The yellow-orange solution resulting from (*a*) showed an i.r. carbonyl band at *ca.* 2 180 cm^{-1}, clearly distinct (see Figure 1) from that due to [Au(CO)Cl] in the same solvent (2 162 cm^{-1}). In the i.r. cell the new carbonyl species rapidly decomposed presumably due to irradiation by the visible region of the light beam and/or contact with the KBr of the cell windows. Over long reaction times the new carbonyl species was converted into AuCl ($COCl_2$ was observed spectroscopically and no CO was evolved). (*c*) When $AuCl_3$, suspended in a small volume of $SOCl_2$ (see Table), was treated with a concentrated solution of [Au(CO)Cl] {molar ratio $AuCl_3$: [Au(CO)Cl] = 3 : 1} a *ca.* 80% yield of a black substance of analytical formula $AuCl_2$ (hereinafter indicated as '$AuCl_2$') was obtained (see Table, run 7). (*d*) The i.r. spectrum of the solution from (*c*) showed the carbonyl-stretching band of $COCl_2$ at 1 805 cm^{-1}. (*e*) In no case did the treatment of $AuCl_3$ with [Au(CO)Cl] under an inert atmosphere (nitrogen) result in significant volume changes, as monitored by gas-volumetric determinations (see Table, runs 1 and 4).

These observations can be rationalised as follows. The complex [Au(CO)Cl] reacts with $AuCl_3$ giving a soluble 1 : 1 adduct which is responsible for the carbonyl absorption at *ca.* 2 180 cm^{-1} [equation (2)]. The shift to

$$AuCl_3 + [Au(CO)Cl] \longrightarrow [Au_2(CO)Cl_4] \qquad (2)$$

higher wavenumber of the carbonyl-stretching vibration, as compared to [Au(CO)Cl], is consistent with bonding of the gold(I) centre to Au^{III}, *i.e.* with the increase of the average oxidation state from I to II for the soluble carbonyl species. It is also to be noted that complexes

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[1] D. Belli Dell'Amico and F. Calderazzo, *Gazzetta*, 1973, **103**, 1099.

[2] M. I. Bruce and F. G. A. Stone, *J.C.S. Dalton*, 1973, 1238 and refs. therein.

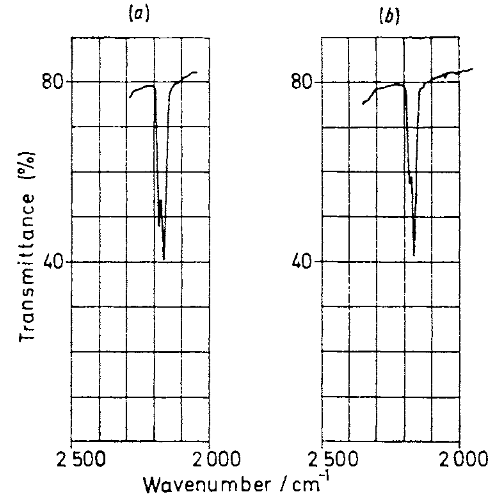
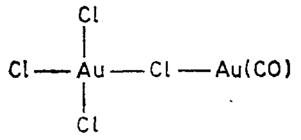


FIGURE 1 Reaction between $AuCl_3$ and [Au(CO)Cl] (run 6 of the Table) in $SOCl_2$ as solvent in a 0.1 mm KBr cell. I.r. spectra measured (*a*) immediately after filling the cell; (*b*) after *ca.* 15 min

of general formula [Au_2Cl_4·olefin] have been obtained by Hüttel and his co-workers [3] treating olefins and cyclooctatetraene [4] with $AuCl_3$. Although we could not determine the molecular complexity of the adduct, we tentatively suggest that the carbonyl complex is binuclear with the mixed-valence structure (I). Structure (I) is strongly supported by the observation of the carbonyl-stretching band at *ca.* 2 180 cm^{-1} indicative of a terminal carbonyl group. The structure, which is consistent with the general rule that in carbonylhalogeno-derivatives [5] formation of dimers or polynuclear species occurs *via* halogen rather than carbonyl bridges, is believed to be very similar to adducts between Lewis acids and carbonyl halides of Fe^{II}, Mn^{II}, and Ni^{II}.[6] These halogen-bridged adducts show an increase in the carbonyl-stretching vibrations by *ca.* 20 cm^{-1}, in good agreement with our findings. The alternative possibility of a carbonyl-bridged dimer, [$Cl_3Au(CO)AuCl$], containing the Au^{III}–OC–Au^{I} sequence is much less probable in view of the low basicity of the carbonyl oxygen in this case and the fact that such bonding should lead to a decrease in the carbonyl-stretching vibration, as has been found in the case of addition of Lewis acids to terminal carbonyl groups.[7]



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

(I)

Further confirmation of the existence of mixed-valence complexes of type (I) comes from the isolation of a similar complex containing pyridine, which of course has no possibility of functioning as a bridging ligand. A complex of formula [Au_2Cl_4(py)] had been mentioned earlier but was not isolated.[3] Its preparation has now become possible by treating [AuCl(py)], prepared *in situ* from [Au(CO)Cl] and pyridine, with $AuCl_3$.

In view of the isolation of the practically insoluble '$AuCl_2$' in moderate yields (runs 2, 3, and 5 of the Table) when $AuCl_3$ was treated in the molar ratio 1 : 1 with relatively concentrated solutions of [Au(CO)Cl], the system $AuCl_3$–[Au(CO)Cl] may be represented by reaction (2) competing with (3). Over long reaction times '$AuCl_2$'

$$[\mathrm{Au_2(CO)Cl_4}] + 2\,\mathrm{AuCl_3} \longrightarrow 4\,\text{'}\mathrm{AuCl_2}\text{'} + \mathrm{COCl_2} \quad (3)$$

can further react with the excess of [Au(CO)Cl] in solution according to the stoicheiometry (4). This accounts

$$2\,\text{'}\mathrm{AuCl_2}\text{'} + [\mathrm{Au(CO)Cl}] \longrightarrow \mathrm{COCl_2} + 3\,\mathrm{AuCl} \quad (4)$$

for the observed formation of the insoluble AuCl over long reaction times, for the spectroscopically detected $COCl_2$, and for the failure to detect CO evolution. Confirmation of this reaction scheme comes from the fact that, as indicated in (*c*), the yields of '$AuCl_2$' were optimised by treating $AuCl_3$ with [Au(CO)Cl] in a 3 : 1 molar ratio. The stoicheiometry (3) is supported by the satisfactory analytical results obtained for the solid product ('$AuCl_2$') and by the spectroscopically detected $COCl_2$, whose increasing concentration was found to parallel the decrease in concentration of [Au(CO)Cl].

In view of the considerable amount of literature data concerning the non-existence [8] of compounds of composition $AuCl_2$, it was very surprising that such a solid could be obtained under our experimental conditions. As far as the nature of the product analysing for $AuCl_2$ is concerned, the following facts have been established. The substance does not contain carbon monoxide, as shown by the analytical results and by the absence of carbonyl-stretching vibrations (Nujol mull). It is diamagnetic at room temperature, and it absorbs carbon monoxide very rapidly even in the solid state at room temperature, the final product of the reaction being [Au(CO)Cl]. *X*-Ray analysis has shown that the product of reaction (3) has a powder diagram different from that of the starting $AuCl_3$ and from that reported for AuCl.[9] The *X*-ray powder data in Figure 2 definitely show that '$AuCl_2$', as obtained under our experimental conditions, is a new substance. Attempts are now being made to grow single crystals of it and we hope to report its molecular structure.

Under carbon monoxide, [Au(CO)Cl] was the only observed reaction product. Under these conditions, a reaction scheme similar to (2)—(4) also applies, except

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[3] R. Hüttel, H. Reinheimer, and K. Nowak, *Chem. Ber.*, 1968, **101**, 3761.

[4] P. Tauchner and R. Hüttel, *Chem. Ber.*, 1974, **107**, 3761.

[5] F. Calderazzo, in 'Halogen Chemistry,' ed. V. Gutmann, Academic Press, vol. 3, p. 383.

[6] M. Pankowski, B. Demerseman, G. Bouquet, and M. Bigorgne, *J. Organometallic Chem.*, 1972, **35**, 155.

[7] D. F. Shriver and A. Alich, *Inorg. Chem.*, 1972, **11**, 2984.

[8] J. D. Corbett and L. F. Bruding, *J. Inorg. Nuclear Chem.*, 1959, **11**, 20 and refs. therein.

[9] E. M. W. Janssen, J. C. W. Folmer, and G. A. Wiegers, *J. Less-Common Metals*, 1974, **38**, 71.

that the reaction does not stop with formation of 'AuCl$_2$', but further reduction to Au^I takes place. A species which is believed to play an important role in the reduction of gold is [Au$_2$(CO)Cl$_4$], *i.e.* the mixed-valence carbonyl derivative. The reduction is believed to occur *via* COCl$_2$ elimination, followed by addition of CO from the solution to the co-ordinatively unsaturated 'AuCl'.

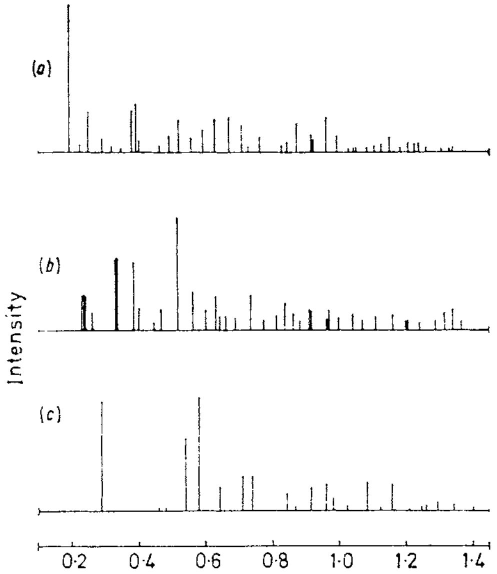

FIGURE 2 *X*-Ray powder patterns for AuCl$_3$ obtained (*a*) from hydrated tetrachloroauric(III) acid and SOCl$_2$, (*b*) from AuCl$_2$, and (*c*) from AuCl.[8] The results for AuCl$_3$ are in satisfactory agreement with those reported in ref. 7 for AuCl$_3$ obtained from gold metal and chlorine

$$[\mathrm{Au_2(CO)Cl_4}] \longrightarrow \mathrm{COCl_2} + 2\,\text{'AuCl'} \qquad (5)$$

$$\text{'AuCl'} + \mathrm{CO} \longrightarrow [\mathrm{Au(CO)Cl}] \qquad (6)$$

EXPERIMENTAL

Solvents were dried and purified by the conventional methods. Anhydrous gold(III) chloride was prepared from the commercially available tetrachloroauric(III) acid and thionyl chloride as previously described.[1] The infrared spectra were recorded on a Perkin-Elmer 337 instrument equipped with a grating. Each spectrum was obtained on the expanded abscissa scale and calibrated with CO; the wavenumbers are believed to be accurate to ±2 cm^{-1}.

Reaction of AuCl$_3$ *with* [Au(CO)Cl].—1 : 1 *Molar ratio* (*run* 6 *of the Table*). Anhydrous gold(III) chloride (0.48 g, 1.58 mmol) was suspended in SOCl$_2$ (40 cm^3) and solid [Au(CO)Cl] (0.42 g, 1.61 mmol) was added by operating under nitrogen. After a few minutes the precipitate of AuCl$_3$ disappeared and an orange solution formed. A small quantity of a yellow precipitate (probably AuCl) appeared after a while. The i.r. spectrum of the solution was recorded and a band at 2 180 cm^{-1} was observed to rapidly decrease in intensity, being finally replaced by the carbonyl absorption of [Au(CO)Cl] at 2 162 cm^{-1}.

In a control gas-volumetric experiment (run 1 of the Table) carried out under nitrogen, AuCl$_3$ (0.28 g, 0.92 mmol) and [Au(CO)Cl] (0.209 g, 0.80 mmol) were mixed together in SOCl$_2$ (25 cm^3) as solvent which had been previously saturated with nitrogen. After 2 d, no significant variation of volume had occurred. The i.r. spectrum of the filtered solution showed only the carbonyl absorption of COCl$_2$ at 1 805 cm^{-1}. Similar results were obtained in CCl$_4$ as solvent.

3 : 1 *Molar ratio* (*run* 7 *of the Table*). Under nitrogen, anhydrous AuCl$_3$ (2.25 g, 7.42 mmol) was suspended in SOCl$_2$ (10 cm^3) and treated dropwise with a solution of [Au(CO)Cl] (0.66 g, 2.54 mmol) dissolved in SOCl$_2$ (20 cm^3). When the addition of [Au(CO)Cl] was complete (in *ca.* 0.5 h), the suspension of AuCl$_3$ began to darken. An i.r. spectrum of the solution measured after 3 h showed the presence of [Au(CO)Cl] (band at 2 162 cm^{-1}; no special precaution was taken to record the spectrum within the time limits of stability of the species characterised by the 2 180 cm^{-1} band). The progress of the reaction was monitored by i.r. spectroscopy: after 5 h a decrease in the intensity at 2 162 cm^{-1} was observed, while the intensity of the COCl$_2$ band at 1 805 cm^{-1} had correspondingly increased. After 20 h, the band at 2 162 cm^{-1} had almost disappeared. The reaction mixture was filtered under argon and the black microcystalline solid was dried *in vacuo* (2.05 g, 77% yield). The solid is very hygroscopic (Found: Au, 73.5, 72.5; Cl, 25.9, 27.1. AuCl$_2$ requires Au, 73.55; Cl, 26.5%). The magnetic susceptibility * (Faraday method), χ_M corr., was -13.5×10^{-6} c.g.s. units at 23 °C.

Preparation of [Au$_2$Cl$_4$(py)].—The complex [Au(CO)Cl] (1.090 g, 4.18 mmol) was dissolved in CH$_2$Cl$_2$ (10 cm^3) and treated dropwise with a solution of pyridine (0.331 g, 4.18 mmol) in CH$_2$Cl$_2$ (10 cm^3). On addition of the pyridine solution, CO evolution was observed. To the resulting colourless solution, AuCl$_3$ (1.234 g, 4.07 mmol) was added. The resulting black-green solid was filtered off and dried *in vacuo* (1.83 g, 73% yield) (Found: C, 10.3; H, 1.1; Au, 63.9. N, 2.0. C$_5$H$_5$Au$_2$Cl$_4$N requires C, 9.75; H, 0.80; Au, 64.05; N, 2.30%). The complex is very sensitive to moisture.

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