The *trans* Effect in Gold(III) complexes. Kinetics of Substitution Reactions of the Trichloro(phenyl)aurate(III) Anion in Methanol

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The $[Au(C_6H_5)Cl_3]^-$ ion undergoes reversible solvolysis of the chloride *trans* to $C_6H_5^-$ in methanol solution. The kinetics of the approach to equilibrium on adding excess of LiCl have been followed by stopped-flow spectrophotometry at temperatures below 0 °C and the rate and equilibrium constants determined. In the absence of added Cl^- the complex exists mainly as *trans*-$[Au(C_6H_5)(MeOH)Cl_2]$. The kinetics of the replacement of MeOH by a variety of nucleophiles have been studied. The reactivity follows the sequence $NO_2^- < Cl^- < Br^- < N_3^- \approx I^- < NCS^- <$ thiourea but the nucleophilic discrimination is considerably less than that observed in other gold(III) complexes. The reaction with iodide leads to reduction of the substrate and the formation of I_3^- but the rate-determining step is shown to be a nucleophilic substitution. The kinetics of the reaction $[Au(C_6H_5)Cl_3]^- + nu^- \longrightarrow$ *trans*-$[Au(C_6H_5)Cl_2(nu)]^{x-} + Cl^-$ have been followed in methanol solution by working in the presence of excess of LiCl. Neutral nucleophiles enter by the usual direct associative pathway, the nucleophilicity increasing along the sequence pyridine < Et_2S < thiourea. Nucleophilic discrimination is low. Anionic reagents do not react directly with the anionic $[Au(C_6H_5)Cl_3]^-$ complex but enter by displacing methanol from the solvento species. In this respect $[Au(C_6H_5)Cl_3]^-$ resembles $[Pt(L)Cl_3]^-$, where L is a neutral ligand with a moderate or high σ-donor *trans effect*.

Studies of the effects of charge on the substrate upon nucleophilicity sequences in the reactions of square-planar platinum(II) complexes have indicated that, for anionic species such as $[Pt(L)Cl_3]^-$, the effectiveness of anionic nucleophiles is often reduced to the point where all substitution takes place by way of a rate-determining solvolysis; moreover any dependence of rate upon the concentration of the entering group is seen to be a consequence of competition between the entering and leaving groups for the solvento intermediate.[1] The analogous gold(III) complexes of the type $[AuX_4]^-$ on the other hand exhibit considerable nucleophilic discrimination and the solvolytic path plays only a very minor role in the substitution reactions with anionic nucleophiles.[2–4] The anionic platinum(II) complexes all contain ligands, L, that are moderate-to-strong σ donors and possess significant *trans* effects. It is of some interest to see whether the low reactivity of anionic nucleophiles is due solely to the effect of charge or whether a ligand with a strong σ-donor *trans*-effect ligand is also needed in the complex to reduce the nucleophilic discrimination. Although it has been reported that the chloride *trans* to PPh_3 in $[Au(PPh_3)Cl_3]$ is many orders of magnitude more labile than the chlorides in $[AuCl_4]^-$,[5] no systematic data are available to allow a comparison of the nucleophilic discrimination of gold(III) complexes containing ligands with such a strong *trans* effect. This paper is the first of a series that will examine the way in which the *trans* effect in gold(III) complexes compares with that in other d^8 systems.

Experimental

Preparations and Reagents.—Tetraethylammonium trichloro(phenyl)aurate(III) was a sample prepared for the original publication[6] and recrystallised and reanalysed before use, (Found: C, 32.7; H, 4.95; Cl, 20.7; N, 2.75. $C_{14}H_{25}AuCl_3N$ requires C, 32.9; H, 4.95; Cl, 20.8; N, 2.75%). An attempt was made to determine the crystal structure in order to ascertain the extent of the *trans* influence of the phenyl group but the crystal decomposed in the *X*-ray beam within 12 h.

Other reagents were either of AR grade or else the best quality available; AR methanol was used without further treatment.

Kinetics.—The kinetics was studied by the stopped-flow technique using a HiTech stopped-flow spectrophotometer, the solutions being brought to the reaction temperature in narrow-bore poly(tetrafluoroethylene) (ptfe) spiral heat exchangers in a 1,2-dihydroxyethane–water thermostat; the latter is electrically heated internally and cooled by liquid nitrogen externally, the whole unit being kept in a large Dewar vessel. Care was taken to ensure that the volume of solution used in a single run was considerably less than the capacity of the heat exchanger and that sufficient time elapsed between runs to allow thermal equilibration to occur. The temperature probe, which also served as thermoregulator, was placed as close as possible to the heat exchangers and mixer. The equipment and details of the technique used to monitor the reaction have been reported elsewhere.[7] The first-order rate constants were determined by a non-linear least-squares regression of the curve of photomultiplier voltage *versus* time. The software provides a graphic display of the residuals, which had to be small and randomly distributed about the calculated curve before the rate constant could be accepted but there was no provision for a statistical analysis of the fit. Rate constants quoted are the average of at least five concordant separate determinations, together with their standard deviations. The concentrations of the solutions of the complexes were held low enough for the change in absorbance to be proportional to the change in % transmission, and hence to the photomultiplier voltage. Experiments using a more elaborate and time-consuming data-processing program which converted the photomultiplier voltage into absorbance gave identical results.

Table 1. First-order rate constants for approach to equilibrium in the reaction,* $[Au(C_6H_5)Cl_3]^- + MeOH \rightleftharpoons$ *trans*-$[Au(C_6H_5)Cl_2(MeOH)] + Cl^-$

$10^3[LiCl]/mol\ dm^{-3}$	$T/°C$	$k_{obs.}/s^{-1}$
0.50	−30.0	5.74 ± 0.43
1.0		8.72 ± 0.26
5.0		22.1 ± 0.80
10.0		42.4 ± 2.1
0.50	−20.0	10.6 ± 0.2
1.0		14.8 ± 0.4
5.0		46.0 ± 0.2
10.0		82.5 ± 0.9
0.50	−10.0	21.2 ± 0.4
1.0		30.1 ± 0.4
5.0		90.7 ± 0.8
10.0		157 ± 0.8
0.50	0.0	41.5 ± 1.1
1.0		58.6 ± 0.5
5.0		179 ± 5
10.0		306 ± 5

$T/°C$	$Intercept/s^{-1}$	10^{-3} Slope/ $dm^3\ mol^{-1}\ s^{-1}$	$K/dm^3\ mol^{-1}$
−30.0	4.1 ± 0.7	3.79 ± 0.12	920
−20.0	7.3 ± 0.6	7.57 ± 0.10	1 040
−10.0	15.9 ± 2.1	14.3 ± 0.4	900
0.0	31.7 ± 5.6	27.7 ± 1.0	870

$\Delta H^‡_s = 36.0 \pm 2.2\ kJ\ mol^{-1}$, $\Delta H^‡_{Cl} = 34.3 \pm 0.7\ kJ\ mol^{-1}$, $\Delta S^‡_s = -84 \pm 9\ J\ K^{-1}\ mol^{-1}$, $\Delta S^‡_{Cl} = -34 \pm 3\ J\ K^{-1}\ mol^{-1}$.

* In methanol. $[complex] = 1.0 \times 10^{-4}\ mol\ dm^{-3}$

Preliminary studies of the spectra before and after mixing the reagents were made with a Perkin-Elmer Lambda 5 spectrophotometer, the optimum wavelengths for the stopped-flow study being deduced from the spectral changes. The second stage of the reaction with thiocyanate is too fast to permit an estimation of the spectral properties of the first product and the optimum wavelength for the study was found by trial and error.

No attempt was made to maintain constant ionic strength because preliminary studies showed that the only processes which contribute to the reaction involve a neutral species interacting with an ionic species; such processes are not subject to primary salt effects. Unnecessary complication of the system by adding lithium perchlorate was therefore avoided.

Results

(1) *Reversible Solvolysis of* $[Au(C_6H_5)Cl_3]^-$ *in Methanol.*—The u.v. spectrum of a solution of $[NEt_4][Au(C_6H_5)Cl_3]$ in methanol changes rapidly when LiCl is added and, in the presence of sufficient chloride, becomes virtually identical to that of the same complex in dichloromethane. These changes are consistent with a reversible solvolysis of the type (1). The

$$[Au(C_6H_5)Cl_3]^- + MeOH \rightleftharpoons \textit{trans}\text{-}[Au(C_6H_5)(MeOH)Cl_2] + Cl^- \quad (1)$$

change is fast, but could be followed by stopped-flow spectrophotometry at reduced temperatures. The rate of approach to equilibrium, in the presence of a sufficient excess of LiCl, is first order and the rate constants, collected in Table 1, $k_{obs.}$, obey the relationship, $k_{obs.} = k_s + k_{Cl}[Cl^-]$.

(2) *Displacement of Co-ordinated Methanol from* trans-$[Au(C_6H_5)(MeOH)Cl_2]$ *by Nucleophiles.*—Dilute solutions of the trichloro substrate in methanol (2×10^{-5} mol dm^{-3}) are virtually completely (98%) solvolysed to the *trans* species. When nucleophiles are added there is an extremely rapid change in spectrum, even at the lowest temperatures, followed by a slow change that can be followed by repetitive scan spectrophotometry at room temperature. It is assumed that the fast change is the displacement of the co-ordinated methanol *trans* to the phenyl group, followed by a slow displacement of the *cis* chloride ions. The fast first stage can be studied by stopped-flow spectrophotometry and the reactions, carried out in the presence of at least a 20-fold excess of nucleophile, follow pseudo-first-order kinetics. The observed rate constants are collected in Table 2.

(3) *Displacement of Co-ordinated Chloride from* $[Au(C_6H_5)Cl_3]$.—Addition of LiCl at the minimum concentration used (5×10^{-3} mol dm^{-3}) to a solution of $[Au(C_6H_5)Cl_3]^-$ in methanol (1×10^{-4} mol dm^{-3}) ensures that the bulk of the substrate (83%) is in the form of the trichloro complex, (the rapid two-fold dilution on mixing the reagents takes place under non-equilibrium conditions). At higher chloride concentrations the amount of solvolysis is correspondingly less but a compromise has to be made between maximum conversion and minimum interference with the irreversibility of the substitution being studied. Preliminary observations of the spectral changes involved, making use of relatively slow scans at room temperature, showed that the spectrum measured as soon as possible after mixing was independent of the amount of nucleophile added and the same as that observed when there was no added chloride. The subsequent changes were the same whether or not LiCl had been added.

The first stage of the reaction was followed at the optimum wavelength under pseudo-first-order conditions and the rate constants are collected in Table 3. Runs were carried out over a range of chloride-ion concentrations and temperatures. Except in the cases with the lowest nucleophile concentrations and the highest chloride concentrations, the reactions appeared to go to completion and the precision of the kinetic data was such that a more elaborate treatment of the data obtained under reversible conditions was not worthwhile.

The subsequent reactions were noted but not studied in detail and the kinetic data are not reported here.

(4) *The Reaction with Iodide.*—When LiI was added to a solution containing $[Au(C_6H_5)Cl_3]^-$, whether or not excess of LiCl had been added, the spectrum rapidly changed to that of the I_3^- ion with peaks at 366 and 458 nm and a shoulder at 293 nm. The yellow colour slowly faded and, after 30 min, there was no significant absorption at wavelengths longer than 260 nm. The formation of I_3^- is typical of the behaviour of gold(III) complexes[8] [equation (2)] and its subsequent consumption is

$$Au^{III} + 3I^- \longrightarrow Au^I + I_3^- \quad (2)$$

presumably through reaction between σ-bound C_6H_5 and I_2 [equation (3)] a typical case of cleavage of a metal–carbon

$$[Au(C_6H_5)I]^- + I_3^- \longrightarrow [AuI_2]^- + C_6H_5I + I^- \quad (3)$$

bond. It has been reported that $[\{Au(C_6F_5)\}_2(dppe)]$ [dppe = 1,2-bis(diphenylphosphino)ethane] reacts with I_2 in dichloromethane to give $[(IAu)_2(dppe)]$ and presumably C_6F_5I.[9]

Discussion

Because of the overall lability of the system we were unable to isolate and characterise independently the reaction products and so the conclusion that the changes that are being observed are due to the replacement of the ligand *trans* to the phenyl group rests on the following evidence.

Table 2. First-order rate constants for the reaction,* *trans*-$[Au(C_6H_5)(MeOH)Cl_2]^-$ + nu^{x-} $\longrightarrow$ *trans*-$[Au(C_6H_5)(nu)Cl_2]^{x-}$ + MeOH

nu	T/°C	10^3[nu]/mol dm^{-3}	$k_{obs.}$/s^{-1}
Br^-	−30.0	1.00	12.9 ± 0.1
		2.50	28 ± 1
		5.0	42 ± 2
		10.0	88 ± 0.4
	−20.0	1.00	20 ± 0.2
		2.50	43 ± 0.5
		5.0	77 ± 0.2
		10.0	103 ± 2.5
	−10.0	0.50	24 ± 0.6
		1.00	40 ± 0.7
		2.50	83 ± 1.2
		5.0	149 ± 7
	0.0	0.50	45 ± 1
		1.00	78 ± 3
		2.50	162 ± 11
I^-		5.0	276 ± 8
	−30.0	5.0	189 ± 12
		10.0	302 ± 13
	−20.0	5.0	287 ± 7
		10.0	427 ± 5
NO_2^-	−30.0	5.0	18 ± 1
		10.0	35 ± 0.1
		15.0	47 ± 0.6
		20.0	66 ± 0.2
	−20.0	5.0	31 ± 0.8
		10.0	64 ± 2
		15.0	85 ± 0.7
		20.0	141 ± 6
N_3^-	−30.0	2.5	75 ± 0.7
		5.0	126 ± 4.5
		7.5	173 ± 2.5
		10.0	210 ± 4.4
NCS^-	−30.0	0.320	23 ± 1.4
		0.640	42 ± 0.8
		0.96	53 ± 3.4
		1.28	72 ± 3.7
		1.79	102 ± 3.1
		2.56	144 ± 3.8
Thiourea	−30.0	1.00	63 ± 2.2
		2.00	131 ± 7
		5.0	380 ± 10

* In methanol with no added chloride. [complex] = 5×10^{-5} mol dm^{-3}

(*i*) The change in the electronic spectrum on adding LiCl to a solution of $[NEt_4][Au(C_6H_5)Cl_3]$ in methanol is reversible and the limiting spectrum in the presence of a sufficient excess of chloride is the same as that of the complex alone in the non-co-ordinating solvent, CH_2Cl_2. (*ii*) Provided a sufficient excess of nucleophile has been added to overcome competition between Cl^- and the nucleophile for a place in the co-ordination sphere of Au^{III}, the spectrum of the product at the end of the first fast stage of reaction is the same, irrespective of whether the reactions are studied in the presence or absence of added LiCl. (*iii*) In all cases the first changes are fast (but still measurable) and they are followed by slow changes which, except in the case of the reaction with iodide, do not involve the reduction of Au^{III} to Au^{I}; from the general form of the spectral change and reactivity these can be identified as being a consequence of the displacement of the two *cis* chlorides.

The electronic spectrum of the first product of the reaction with LiI is dominated by the peaks of I_3^-. It is presumed that the Au^{III} is reduced in this reaction and that $[Au(C_6H_5)I]^-$, or some other gold(I) species which retains the Au–C bond, is formed. The reduction obeys the same rate law as associative ligand substitution and the kinetics alone do not allow a distinction to be drawn between a rate-limiting ligand substitution followed by a rapid reduction either internally or externally, and a direct inner-sphere two-electron transfer through a chloride bridge.

The changes that follow the addition of LiCl to a methanolic solution of $[Au(C_6H_5)Cl_3]^-$ are consistent with an assumption that what is being studied is the reversible solvolysis/complexation process *trans* to the phenyl group [reaction (1)]. The rate equation, studied under pseudo-first-order conditions is $k_{obs.} = k_s + k_{Cl}[Cl^-]$ where k_s and k_{Cl} are the rate constants for the solvolysis of the chloro complex and the chloride complexation of the methanol complex, respectively. The solvolytic equilibrium constant, $K_s = k_s/k_{Cl}$, can be calculated from these data, the values being collected in Table 1. The errors involved in this determination are of a similar magnitude to the variation of the equilibrium constant with temperature, the enthalpy change of complexation being not much greater than 2–3 kJ mol^{-1}.

In the absence of added chloride, the substrate in methanol exists mainly as *trans*-$[Au(C_6H_5)(MeOH)Cl_2]$ and the displacement of methanol by the nucleophile (nu) can be studied under fast reaction conditions at temperatures $\leqslant 0$ °C. All the reactions obey the rate equation $k_{obs.} = k_1 + k_2[nu]$, but, as has been pointed out for the analogous reactions of $[Pt(dien)(H_2O)]^{2+}$ (dien = diethylenetriamine) with weak nucleophiles,[10] this is indicative of the reversibility of the complexation reaction, equation (4),

$$trans\text{-}[Au(C_6H_5)(MeOH)Cl_2] + nu \rightleftharpoons trans\text{-}[Au(C_6H_5)(nu)Cl_2] + MeOH \quad (4)$$

with the [nu]-independent rate constant, k_1, being identified with that for the reverse solvolytic process, and k_2 with that for the complexation reaction. The rate constants, so derived, are collected in Table 4. The data indicate a nucleophilicity sequence $NO_2^- < Cl^- < Br^- < N_3^- \approx I^- < SCN^- <$ thiourea. There is a suggestion from the analysis of the reaction of the complex with Et_2S (see below) that this nucleophile is unable to compete with chloride for the methanol complex but, with this exception, the sequence is not much different from that found for $[AuCl_4]^-$.[11]

In the presence of sufficient LiCl to convert the major part of the substrate into the trichloro complex the observed behaviour depends upon whether or not the entering nucleophile is charged. For pyridine, diethyl sulphide, and thiourea, a plot of $k_{obs.}$ against the concentration of nucleophile is linear with a slope that depends upon the nature of the entering species. The reaction with thiourea (tu) follows the classical rate equation $k_{obs.} = k_1 + k_2[tu]$ and the values of k_1, agree, within experimental error, with those for the solvolysis of $[Au(C_6H_5)Cl_3]^-$, k_s, in methanol at the same temperature; however, the reaction with diethyl sulphide obeys the simpler relationship $k_{obs.} = k_2[Et_2S]$. This suggests that, under the conditions of the experiment, Et_2S is unable to compete with Cl^- for the consumption of the solvento species, *trans*-$[Au(C_6H_5)(MeOH)Cl_2]$, and the solvolytic pathway does not lead to the formation of product.

The reactions with anionic reagents obey a more complicated rate equation (5), which is consistent with chloride mass-law

$$k_{obs.} = k_s k_x[X^-]/(k_{Cl}[Cl^-] + k_x[X^-]) \quad (5)$$

Table 3. First-order rate constants for the reaction[a] $[Au(C_6H_5)Cl_3]^- + nu^{x-} \longrightarrow trans\text{-}[Au(C_6H_5)(nu)Cl_2]^{x-} + Cl^-$

nu	T/°C	10^3[nu]/mol dm^{-3}	$k_{obs.}$/s^{-1}	$k_{calc.}$[b]/s^{-1}
$(NH_2)_2CS$	−30.0	5.0	5.8 ± 0.2	
		10.0	14.8 ± 0.8	
		25.0	28.9 ± 1.3	
		50.0	62.3 ± 2.1	
		100.0	97.6 ± 4.9	
	−20.0	5.0	19.6 ± 0.7	
		10.0	27.6 ± 1.2	
		25.0	45.6 ± 2.1	
		50.0	83.2 ± 4.0	
		100.0	146 ± 7	
	−10.0	5.0	27.6 ± 1.1	
		10.0	40.0 ± 1.8	
		25.0	80.2 ± 3.3	
		50.0	133 ± 6	
		100.0	243 ± 9	
	0.0	5.0	47.6 ± 1.9	
		10.0	66.4 ± 2.8	
		25.0	125 ± 5	
		50.0	213 ± 8	
Et_2S	0.0	10.0	2.46 ± 0.01[d]	
		20.0	4.93 ± 0.07[d]	
		35.0	8.40 ± 0.04[d]	
		50.0	11.5 ± 0.02[d]	
py	0.0	5.0	23.0 ± 0.2	
		5.0	23.7 ± 0.3[e]	
		5.0	23.4 ± 0.2[f]	
		10.0	25.5 ± 0.3	
		10.0	25.5 ± 0.2[e]	
		10.0	25.7 ± 0.2[f]	
		50.0	37.4 ± 0.5	
		50.0	38.2 ± 0.5[e]	
		50.0	38.7 ± 0.4[f]	
		100.0	51.5 ± 0.5	
		100.0	52.1 ± 0.6[e]	
		100.0	52.3 ± 0.7[f]	
I^-	−20.0	5.0	5.85 ± 0.7	
	−10.0	5.0	14.2 ± 0.1	14.0
		10.0	14.7 ± 0.1	14.9
		20.0	15.2 ± 0.1	15.4
		50.0	15.9 ± 0.1	15.7
	0.0	5.0	27.6 ± 0.03	27.5
		10.0	28.8 ± 0.08	29.3
		20.0	30.8 ± 0.2	30.3
		35.0	31.0 ± 0.2	30.8
		50.0	30.6 ± 0.2	31.0
	10.0	5.0	57.3 ± 0.1	57.3
		10.0	58.4 ± 0.5	58.6
		20.0	59.9 ± 0.8	59.3
		35.0	59.5 ± 0.5	59.6
		50.0	59.3 ± 0.2	59.7
NO_2^-	−20.0	5.0	3.70 ± 0.07	
		10.0	4.38 ± 0.05	
		15.0	5.94 ± 0.25	
		20.0	6.40 ± 0.05	
	−10.0	5.0	8.74 ± 0.11	8.55
		10.0	10.7 ± 0.1	10.7
		15.0	11.6 ± 0.1	11.7
		20.0	12.1 ± 0.1	12.3
		30.0	12.3 ± 0.1	12.9
		40.0	13.3 ± 0.1	13.3
		50.0	13.8 ± 0.1	13.5
		60.0	13.9 ± 0.3	13.6
	0.0	5.0	20.0 ± 0.1	20.4
		10.0	24.2 ± 0.1	24.4
		15.0	26.0 ± 0.1	26.2
		15.0	21.0 ± 0.1[c]	20.4
		20.0	27.4 ± 0.3	27.2
		20.0	22.1 ± 0.1[c]	22.2
	10.0	5.0	41.5 ± 0.1	41.4
		10.0	48.9 ± 0.2	49.1
		15.0	51.9 ± 0.1	52.3
		20.0	54.5 ± 0.5	54.0
N_3^-	−30.0	2.50	1.88 ± 0.04[d]	
		5.0	1.89 ± 0.03[d]	
		7.5	1.82 ± 0.03[d]	
		10.0	2.09 ± 0.07[d]	
	−20.0	2.50	5.3 ± 0.3[d]	5.5
		5.0	7.2 ± 0.3[d]	6.9
		7.5	7.4 ± 0.2[d]	7.5
		10.0	7.9 ± 0.2[d]	7.9
	−10.0	2.50	11.4 ± 0.1[d]	10.8
		5.0	12.2 ± 0.1[d]	12.6
		7.5	12.9 ± 0.1[d]	13.3
		10.0	13.1 ± 0.1[d]	13.7
		20.0	14.5 ± 0.1[d]	14.4
		30.0	14.7 ± 0.2[d]	14.6
		40.0	14.8 ± 0.2[d]	14.7
		50.0	14.8 ± 0.2[d]	14.8
		60.0	15.2 ± 0.1[d]	14.8
	0.0	2.50	23.7 ± 0.2[d]	24.8
		5.0	26.0 ± 0.6	24.8
		5.0	26.7 ± 0.3[d]	28.0
		7.5	27.8 ± 0.3[d]	29.2
		7.5	28.0 ± 0.4	26.8
		10.0	29.2 ± 0.2[d]	29.9
		10.0	28.8 ± 0.6	28.0
		20.0	30.8 ± 0.2[d]	30.8
		50.0	32.8 ± 0.3[d]	31.3
	10.0	2.50	49.9 ± 1.0[d]	48.8
		5.0	53.8 ± 0.3[d]	54.8
		10.0	56.5 ± 0.4[d]	58.3
		20.0	60.7 ± 0.1[d]	60.3
		50.0	62.8 ± 0.5[d]	61.5
NCS^-	−10.0	0.64	8.5 ± 0.3	8.5
		0.64	6.6 ± 0.1[e]	6.2
		1.28	8.3 ± 0.1[e]	8.5
		6.4	12.9 ± 0.1	12.6
		6.4	11.0 ± 0.2	11.9
		64	13.2 ± 0.4	13.2
		64	13.2 ± 0.1[e]	13.2

[a] In methanol. [complex] = 5×10^{-5}, [LiCl] = 5.0×10^{-3} mol dm^{-3}, except where otherwise stated. [b] $k_{calc.}$ values are obtained from equation (5) using the optimised values for k_1 and k_{-1}/k_x given in Table 6. [c] [LiCl] = 15.0×10^{-3} mol dm^{-3}. [d] [LiCl] = 2.5×10^{-3} mol dm^{-3}. [e] [LiCl] = 10.0×10^{-3} mol dm^{-3}. [f] [LiCl] = 50.0×10^{-3} mol dm^{-3}.

retardation of a substitution that goes by way of rate-determining solvolysis [reaction (1), with rate constants as defined] followed by a non-reversible reaction (4) with rate constant k_x defining k_{nu} for nucleophile X. There is no detectable contribution from any other [X$^-$]-dependent term. Analysis of the kinetic data by a non-linear regression gave values for k_s and k_{Cl}/k_x. Where the data are good enough to analyse these are collected in Table 6 and the calculated rate constants, $k_{calc.}$,

Table 4. Derived rate constants, k_{nu}/dm^3 mol^{-1} s^{-1}, for the reaction *trans*-$[Au(C_6H_5)(MeOH)Cl_2] + nu^{n-} \longrightarrow$ *trans*-$[Au(C_6H_5)nu)Cl_2]^{n-}$ + MeOH and a comparison with those for the corresponding reaction between $[AuCl_4]^-$ in methanol at 25.0 °C *

	Nucleophile						
T/°C	NO_2^-	Cl^-	Br^-	N_3^-	I^-	NCS^-	tu
−30.0	3 120	3 800	8 300	18 100	22 600	54 100	80 000
−20.0	7 020	7 600	14 200		28 000		
−10.0		14 300	27 600				
0.0		27 700	51 000				
25.0*	0.028		0.14	0.35	84	7.4	400

* Data from ref. 11.

Table 5. Derived rate constants, k_{nu}/dm^3 mol^{-1} s^{-1}, for the reaction *trans*-$[Au(C_6H_5)Cl_3]^- + nu \longrightarrow$ *trans*-$[Au(C_6H_5)(nu)Cl_2] + Cl^-$ and a comparison with those for the corresponding reaction of $[AuCl_4]^-$ in methanol at 25.0 °C^a

	Nucleophile			
T/°C	MeOH^b	py	Et_2S	tu
−30.0	0.16 (0.20 ± 0.15)			960 ± 80
−20.0	0.28 (0.53 ± 0.05)			1 330 ± 26
−10.0	0.61 (0.7 ± 0.09)			2 250 ± 45
0.0	1.22 (1.2 ± 0.1)	157	225	3 681 ± 80
25.0^a	0.000 019	1.6		400

^{a} Data from ref. 11. ^{b} k_s/[MeOH]; no correction has been made for the change in the density of methanol with temperature (values in parentheses are from the analysis of the kinetics of the reaction with thiourea).

Table 6. Rate constants derived from the analysis of the $[Cl^-]$ mass-law retardation of entry of X^- into $[Au(C_6H_5)Cl_3]^-$

X	T/°C	k_s/s^{-1}	k_{Cl}/k_x	k_{Cl}/k_x from Table 4*
NO_2^-	−10.0	14.4	0.682	1.22
	0.0	30.5	0.499	
	10.0	60.1	0.452	
I^-	−10.0	15.9	0.131	0.163
	0.0	31.4	0.144	
	10.0	60.0	0.046	
N_3^-	−10.0	15.1	0.397	0.210
	0.0	33.1	0.320	
	10.0	62.4	0.278	
NCS^-	−10.0	13.3	0.073	0.070

* Calculated from the rate constants at −30 °C.

compared with the experimental data in Table 3. The values of k_s compare well with those determined from the reversible solvolysis of the trichloro species and the ratios k_{Cl}/k_x agree as well as can be expected with those determined directly from the reactions of the solvolysed species. In the cases not listed the analysis does not converge satisfactorily.

It must be concluded, therefore, that the anionic species $[Au(C_6H_5)Cl_3]^-$ does not react directly with any of the anionic nucleophiles investigated and that all of the substitution takes place through a rate-determining solvolysis followed by substitution into the neutral methanol complex. There is no evidence for an additional non-retarded first-order dependence on the concentration of thiocyanate, the strongest anionic nucleophile studied, nor is there any additional contribution that can be ascribed to direct reaction of the trichloro substrate with iodide. Anionic gold(III) complexes that do not contain strong *trans*-effect groups, *e.g.* $[AuCl_4]^-$,[11] $[AuBr_4]^-$ and *trans*-$[Au(CN)_2X_2]^-$,[4] all react directly with anionic nucleophiles and show great nucleophilic discrimination. In methanol the solvolytic path makes only a minor contribution to the rate of reaction. Therefore charge effects alone are not sufficient to repress the direct reaction between anionic species; the diminution of the nucleophilic discrimination that arises from a strong *trans*-influence (ground-state weakening) ligand is also required. In this way, Au^{III} appears to behave like the analogous platinum(II) species, $[(Pt(L)Cl_3]^-$, where L is a neutral ligand which has a moderate-to-large *trans* effect, *e.g.* Me_2S, Et_2S, Me_2SO, PMe_3, PEt_3, PPh_3, $P(OMe)_3$, and $AsEt_3$.[1] Little has been done with anionic platinum(II) complexes which contain only weak *trans*-influence ligands and so it is not possible to say whether the direct entry of nucleophiles can be observed in the absence of a *trans*-effect.

The absence of data for the entry of anionic reagents into $[Au(C_6H_5)Cl_3]^-$ makes any attempt to compare its nucleophilic discrimination with that of $[AuCl_4]^-$ rather limited but a comparison of the data in Table 5 for three nucleophiles {MeOH, pyridine (py), and thiourea; the reaction between Et_2S and $[AuCl_4]^-$ not having been studied} shows that the presence of the phenyl group, while increasing the lability by some orders of magnitude, reduces the response to the nature of the entering group enormously. The reduction in nucleophilic discrimination is inadequate, in itself, to account for the absence of any pathway for the direct entry of anions into the trichlorophenyl complex because the direct entry of pyridine, which is a much poorer nucleophile than thiocyanate, is observed. There must therefore be a direct suppression of the entry of anionic nucleophiles into the anionic complex. The reactivity of nucleophiles towards *trans*-$[Au(C_6H_5)(MeOH)Cl_2]$ is much better documented than that for the trichloro species but there are no data for the $[Au(MeOH)Cl_3]$ complex with which to make comparison. The reactivity sequence is that of the tetrachloro complex but with a low nucleophilic discrimination.

The possibility that these reactions have a dissociative mechanism cannot be ruled out without further consideration. It is well known that the presence of metal–carbon σ bonds promotes the dissociative mechanism in d^8 systems,[12] even though two such bonds are needed in platinum(II) species for the dissociative mechanism to dominate.[13] Rate equation (5) applies equally well to a dissociative process in which the intermediate is a three-co-ordinate species rather than the solvento complex. Dissociative reactions between the methanol species and the various nucleophiles would give the simple second-order rate law provided methanol was extremely efficient in trapping the three-co-ordinate intermediate. Studies of the exchange of co-ordinated and free methanol would be needed to resolve this unambiguously. Nevertheless, the fact that a weak nucleophile, such as pyridine, enters the trichloro complex following the same rate equation as that for the strong nucleophile thiourea, *i.e.*, $k_{obs.} = k_s + k_2[py]$, indicates that the associative mechanism plays a major part in these reactions and in the absence of evidence to the contrary we see no reason to propose a change in mechanism in the reactions with the anionic ligands.

The rate constants for the reaction between the substrates and I^- follow the same patterns as those for the reactions of the other anionic reagents even though the first observed product of the reaction with iodide suggests a two-electron redox process. The response to *trans* influence and substrate discrimination is much the same as that of the other anionic reagents.

The question as to whether the reaction with I^- is a direct inner-sphere two-electron reduction of the gold(III) substrate as has been assigned to the reaction of $[AuCl_4]^-$ with I^- in water[8] or a rate-determining substitution to generate a more reducible iodo species which is then rapidly reduced by I^- [equation (6)]

$$I^- + I\text{-}Au^{III}\text{-}L \longrightarrow I\text{-}I\text{-}Au^{III}\text{-}L^- \longrightarrow I_2 + Au^I + L^- \quad (6)$$

(an internal redox process is probably less likely) can now be addressed. It seems that the balance between the two pathways is very dependent on external factors. In aqueous solution the rate constant for the reduction of $[AuCl_4]^-$ by iodide is some 1 500 times larger than that for substitution by bromide and it has been concluded that this is inconsistent with the nucleophilicity differences between the two halides and indicates direct inner-sphere reduction.[7] In methanol solution the rate constant for reaction with I^- is only 600 times greater than that with Br^- [8] and no comment was made about the nature of the reaction. In order to assign a direct inner-sphere redox mechanism to the reduction of $[Au(C_6H_5)Cl_3]^-$ by I^- it would be necessary to explain why the high *trans*-labilising effect of the Au–C bond increases the reactivity with respect to an inner-sphere redox process in much the same way as it does towards substitution. In particular, it is not clear why the direct reduction of $[Au(C_6H_5)Cl_3]^-$ by iodide is prevented. For this reason we suggest that the rate-determining step in the reduction of $[Au(C_6H_5)Cl_3]^-$ by I^- is the substitution of the *trans* chloride by MeOH. The replacement of this methanol by I^- is required before reduction takes place. The fact that the ratio of the rate constants for the reaction of *trans*-$[Au(C_6H_5)(MeOH)Cl_2]$ with I^- and Br^- is as little as 2.7:1 is, in part, a reflection of the low nucleophilic discrimination of this substrate, but mainly confirmation of our conclusion that substitution is rate determining. It would suggest that direct reduction of the $[AuCl_4]^-$ anion takes place in methanol as well as in water. Since there is no evidence for the build up of significant concentrations of a gold(III) iodide-containing species, it must be concluded that the presence of the phenyl group has a profound effect on the rate of reduction of the iodo complex.

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