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Displacement of Neutral Nitrogen Donors by Chloride in $AuCl_3$(am) (am = Pyridines and Amines): Kinetics and DFT Calculations Show the Effects of Basicity and π-Acceptor Ability

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The kinetics of the process $AuCl_3(am) + Cl^- \rightarrow AuCl_4^- + am$ (am = sp^2 N-donor isosteric pyridines with different π systems and sp^3 amines; they cover a wide range of basicity) have been studied in methanol at 25 °C. The reactions obey the usual two-term rate law observed in substitutions on square-planar complexes. The second-order rate constants, k_2, are very sensitive to the nature of the leaving group, and plots of $\log k_2$ against the pK_a of the conjugate acids are linear, with the same slope, –0.68, for both "normal" pyridines and pyridines with a more extended π system, such as 4-cyanopyridine, isonicotinic acid, methyl isonicotinate and 4-acetylpyridine. The reactivity of the considered N-donors is different and follows the order sp^3 N-donors > "normal" pyridines > "π-extended" pyridines. This result, with the support of ground-state DFT calculations on the $AuCl_3$(am) derivatives, is explained on the basis of an Au–N bond enforcement due to an increased π-back-donation contribution.

Introduction

The reactivity of gold(III) derivatives with nitrogen-donor bases has been widely studied, mainly involving pyridine and substituted pyridines (am) as entering nucleophiles or leaving groups.[1–3] Substitution reactions of the type (1) take place with an associative mechanism, whose rate constants, in the forward as well as in the reverse reaction, obey the general relationship $k_{obs} = k_1 + k_2$[nucleophile], which is usual for nucleophilic substitutions at planar four-coordinate d^8 metal complexes.[4]

$$AuCl_4^- + am \rightleftarrows AuCl_3(am) + Cl^- \quad (1)$$

The first-order rate constant, k_1, and the second-order rate constant, k_2, refer to the nucleophilic attack on the substrate by, respectively, the solvent and the nucleophile. The second-order rate constants, k_2, are markedly influenced by the nature of am, indicating that the discriminating ability of gold(III) complexes is good. A linear free-energy relationship, $\log k_2 = a pK_a$ + constant, occurs between the rate constant and the basicity of am, measured as the pK_a of its conjugated acid Ham^+. Moreover, steric retardation is observed for pyridines containing one or two *ortho* groups.

Recently, we studied the kinetics of the reverse reaction of process (1) using five-membered N-donor heterocycles (thiazoles, oxazoles, imidazoles and their derivatives) as leaving groups[5] and the results were compared with those in a paper[3] where am = pyridines. It was observed that the reactivity depends not only upon the ligand basicity but also upon the nature of the ligand in the order: pyridines > five-membered heterocycles and this behaviour was attributed to different π interactions in the ground state between the metal centre and the N-donor ligands.

In this work we tried to improve the knowledge about the role of π interactions between N-donors and Au^{III} in the kinetics of displacement by chloride of these ligands from $AuCl_3$(am). As for Pt^{II} substrates,[6] on considering the second-order rate constants k_2, the displaced nitrogen donors can be divided into three groups: (i) "normal" pyridines, (ii) pyridines having a more extended π system and (iii) sp^3 nitrogen-donor bases; and the reactivity towards ligand substitution is in the order: sp^3 nitrogen-donor bases > "normal" pyridines > pyridines with a more extended π system. These differences, which were mainly attributed to a ground-state stabilization due to the π-back-donation from the filled orbitals of the metal to the antibonding orbitals of the pyridine ligands, have been correlated in this paper with the calculated Au–N bond lengths of the $AuCl_3$(am) complexes, obtained by performing ground-state DFT B3PW91 calculations. By plotting the r_{Au-N} values of the $AuCl_3$(am) complexes versus the corresponding pK_a values, linear relationships comparable to those derived from the kinetic measurements were obtained. Furthermore, a

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systematic shortening of the Au–N bond length was observed for pyridines having an extended π system.

Result and Discussion

When a methanolic solution of the neutral $AuCl_3$(am) substrate is allowed to react with an appropriate excess of chloride, repetitive scanning of the spectrum in the region 240–360 nm shows that the reaction evolves in a first-order fashion leading to the substitution of the neutral base with a chloride ion. The presence of well-maintained isosbestic points, whose positions depend only upon the spectrum of the starting compound, and the comparison of the final spectrum with that of original samples of the substituted products at the same concentration, clearly indicate a single reaction stage. The addition of $LiClO_4$ indicates that primary salt effects are absent and secondary effects are negligible, thus no further attempt has been made to maintain constant ionic strength. The reactions have been studied in the presence of 0.1 mol dm^{-3} CH_3SO_3H. Preliminary experiments have shown that, at constant chloride concentration, the rate of reaction is independent of the concentration of acid over the range 0.02–0.2 mol dm^{-3}. The acid simply serves to protonate the released N-donor ligand, thus preventing the reverse reaction and forcing the reaction to completion. Moreover, the presence of acid helps to avoid a slow reduction of the gold(III) derivatives of the most basic amines. The rate constants have been determined in the usual way from the change in absorbance as a function of time at convenient wavelength. All the reactions have been studied in the presence of a sufficient excess of chloride over the substrate to provide pseudo-first-order conditions and the observed rate constants, k_{obs}, collected in Table 1, obey the general relationship $k_{obs} = k_1 + k_2[Cl^-]$, which is usual for nucleophilic substitutions on gold(III) complexes.

The k_1 terms, referring to the pathway in which the rate-determining step is the nucleophilic attack of the solvent, followed by the rapid entry of chloride into the solvento complex,[7] are quite small and thus this reaction pathway makes a small contribution to the whole process. The k_2 terms are the second-order rate constants for the direct at-

Table 1. First-order rate constant, k_{obs}, for the reaction $AuCl_3$(am) + $Cl^- \rightarrow AuCl_4^-$ + am in methanol at 25 °C (0.1 mol dm^{-3} CH_3SO_3H).

am	[Cl$^-$] /mol dm^{-3}	10^3k_{obs}/s^{-1}	am	[Cl$^-$] /mol dm^{-3}	10^3k_{obs}/s^{-1}
4-Methoxypyridine	0.01	0.69 ± 0.01	pyridine	0.01	4.17 ± 0.02
	0.02	1.27 ± 0.01		0.02	7.54 ± 0.01
	0.03	1.78 ± 0.01		0.03	10.7 ± 0.04
	0.04	2.40 ± 0.02		0.04	13.9 ± 0.03
	0.05	2.95 ± 0.01		0.05	18.1 ± 0.02
Methyl isonicotinate	0.001	9.6 ± 0.1	4-cyanopyridine	0.0005	48.0 ± 0.1
	0.002	12.2 ± 0.1		0.0010	62.7 ± 0.7
	0.003	14.3 ± 0.1		0.0015	71.0 ± 0.1
	0.004	18.0 ± 0.2		0.0020	83.6 ± 0.3
	0.005	20.2 ± 0.1		0.0025	93.0 ± 0.2
4-Acetylpyridine	0.001	4.0 ± 0.2	3,5-dimethylpyridine	0.01	0.76 ± 0.01
	0.002	5.6 ± 0.1		0.02	1.58 ± 0.02
	0.003	7.1 ± 0.1		0.03	2.21 ± 0.03
	0.004	9.0 ± 0.2		0.04	3.11 ± 0.07
	0.005	10.3 ± 0.1		0.05	3.84 ± 0.03
4-Chloropyridine	0.001	7.58 ± 0.01	piperidine	0.1	0.15 ± 0.01
	0.002	10.16 ± 0.02		0.2	0.29 ± 0.01
	0.003	12.63 ± 0.01		0.3	0.41 ± 0.02
	0.004	15.80 ± 0.02		0.4	0.53 ± 0.01
	0.005	18.38 ± 0.01		0.5	0.64 ± 0.01
4-Methylpyridine	0.01	1.38 ± 0.01	isonicotinic acid	0.001	2.51 ± 0.06
	0.02	2.48 ± 0.02		0.002	5.01 ± 0.06
	0.03	3.44 ± 0.03		0.003	7.71 ± 0.07
	0.04	4.48 ± 0.03		0.004	9.93 ± 0.06
	0.05	5.51 ± 0.01		0.005	12.61 ± 0.03
4-Aminopyridine	0.02	0.016 ± 0.001	4-bromopyridine	0.0005	5.29 ± 0.04
	0.04	0.03 ± 0.02		0.0010	6.44 ± 0.03
	0.07	0.05 ± 0.01		0.0015	7.78 ± 0.04
	0.10	0.07 ± 0.01		0.0020	8.98 ± 0.02
	0.15	0.10 ± 0.01		0.0025	10.02 ± 0.03
4-(Dimethylamino)pyridine	0.1	0.05 ± 0.01	cyclohexylamine	0.1	1.2 ± 0.1
	0.2	0.10 ± 0.02		0.2	1.9 ± 0.2
	0.3	0.16 ± 0.01		0.3	3.0 ± 0.2
	0.4	0.21 ± 0.01		0.4	4.0 ± 0.3
	0.5	0.26 ± 0.02		0.5	4.9 ± 0.1
Morpholine	0.002	0.04 ± 0.01			
	0.01	0.14 ± 0.03			
	0.02	0.28 ± 0.01			
	0.03	0.38 ± 0.06			
	0.04	0.51 ± 0.09			

tack of Cl^- at the substrate and are summarized in Table 2. For a better comparison of the different reactivity of the groups of amines, we have again examined some of the reactions in ref.[3], in the same experimental conditions, increasing both the number of pyridines and the pK_a range.

Table 2. Second-order rate constants, k_2,[a] and pK_a of Ham^+ for the reaction $AuCl_3(am) + Cl^- \rightarrow AuCl_4^- + am$ in methanol at 25 °C (0.1 mol dm^{-3}, CH_3SO_3H).

am	k_2/dm^3 mol s^{-1}	pK_a of Ham^+[b]
4-Methoxypyridine	0.0565 ± 0.0008	6.47
Methyl isonicotinate	2.7 ± 0.1	3.26
4-Acetylpyridine	1.60 ± 0.04	3.52
4-Chloropyridine	2.73 ± 0.06	3.84
4-Methylpyridine	0.103 ± 0.001	6.02
4-Aminopyridine	0.00065 ± 0.00001	9.12
4-Bromopyridine	2.40 ± 0.06	3.84
Pyridine	0.34 ± 0.01	5.25
4-Cyanopyridine	22 ± 1	1.90
3,5-Dimethylpyridine	0.078 ± 0.002	6.34
Piperidine	0.00122 ± 0.00003	11.1
Isonicotinic acid	2.51 ± 0.04	3.26
4-(Dimethylamino)pyridine	0.000537 ± 0.000007	9.37
Morpholine	0.0122 ± 0.0003	8.33
Cyclohexylamine	0.0095 ± 0.0003	10.66

[a] Determined by linear regression of k_{obs} values vs. chloride concentration. [b] pK_a values were taken from ref.[8]

The reacting species can be divided into three groups, as depicted in the plot of $\log k_2$ versus pK_a of Ham^+ (Figure 1):

i: "normal" pyridines;
ii: pyridines with a more extended π system;
iii: sp^3 nitrogen-donor bases.

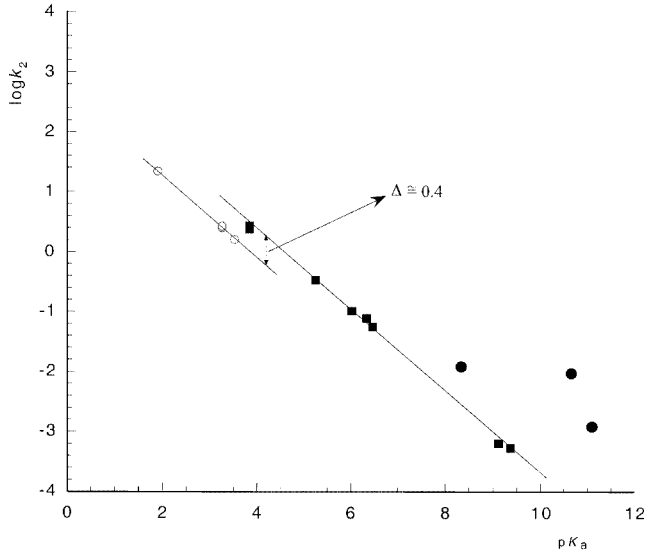

Figure 1. Plots of $\log k_2$ for the reaction $AuCl_3(am) + Cl^- \rightarrow AuCl_4^- + am$ against pK_a of Ham^+: (■) pyridine, 4-chloropyridine, 4-methoxypyridine, 4-methylpyridine, 4-bromopyridine, 3,5-dimethylpyridine, 4-aminopyridine, 4-(dimethylamino)pyridine; (○) 4-cyanopyridine, 4-acetylpyridine, methyl isonicotinate, isonicotinic acid; (●) morpholine, cyclohexylamine, piperidine.

The first group includes the complexes with pyridine: 4-bromopyridine, 4-chloropyridine, 4-methylpyridine, 4-methoxypyridine, 4-aminopyridine, 4-(dimethylamino)pyridine and 3,5-dimethylpyridine, while the second group includes the derivatives of 4-cyanopyridine: isonicotinic acid, methyl isonicotinate and 4-acetylpyridine. The lability of pyridines is considerably lower than that of the third group of derivatives, that is, the complexes of the sp^3-ligands piperidine, cyclohexylamine and morpholine. Unfortunately, the different steric hindrance around the N atom of these sp^3 N-donors avoids a direct relationship between $\log k_2$ and the corresponding pK_a values.

Both "normal" (■ in Figure 1) and "π extended" (○ in Figure 1) pyridines obey the linear relationship $\log k_2 = \alpha pK_a$ + constant, with $\alpha = -0.68$. For the entry of pyridines on $AuCl_4^-$ in the same experimental conditions, a similar free-energy relationship was found,[1] with $\alpha = 0.16$. The parameter α is a measure of the ability of a substrate to discriminate among isosteric nitrogen donors and can be assumed to be a relative measure of its electrophilicity. The asynchronous substitution, characteristic of planar-tetracoordinate gold(III) complexes, offers the opportunity to describe separately the energetic contributions of bond formation and bond rupture to the free energy of activation.[7] The relatively low discrimination among nitrogen donors in the entry reaction ($\alpha = 0.16$), together with the relatively high dependence of reactivity upon the basicity of the leaving nitrogen bases in the reverse processes ($\alpha = -0.68$, this work), strongly suggests a transition state for all these substitutions in which the Au–N bond is only partially formed in the rate-determining transition state, whereas the Au–Cl bond is practically formed to the same extent in the ground and transition states.

The lower lability of pyridine ligands, as compared with the sp^3 N-donors, allows the assumption that the Au–N bond in the case of pyridine derivatives may be reinforced by π bonding, that is, by the π-back-donation from the filled orbitals of the metal to the antibonding orbitals of the ligand, leading to a relative stabilization of the corresponding ground state. Moreover, π interactions of this type can also be invoked to explain the small but significant difference between the reactivity of "normal" and "π-extended" pyridines, which is $\Delta\log k_2 \approx 0.4$ (Δ in Figure 1), corresponding to about 2.3 kJ mol^{-1}. To support this hypothesis, ground-state DFT calculations on the $AuCl_3(am)$ (am = pyridines) have been performed and the r_{Au-N} bond lengths, collected in Table 3, have been measured.

By plotting the r_{Au-N} values of the $AuCl_3(am)$ complexes versus the corresponding pK_a values, linear relationships comparable to those derived from the kinetic measurements have been obtained, as depicted in Figure 2. "Normal" pyridines (■ in Figure 2) respond to the equation $r_{Au-N} = (-0.0027 \pm 0.0001)pK_a + (2.1119 \pm 0.0005)$, while the equation for "π-extended" pyridines (○ in Figure 2) is $r_{Au-N} = (-0.0027 \pm 0.0001)pK_a + (2.1077 \pm 0.0004)$. The increase of electron density on the N atom, quite well represented by the pK_a values of the free ligands, appears to lead to an enforcement of the Au–N σ bond. The effect of growing

Table 3. Calculated r_{Au-N} bond lengths of $AuCl_3$(am) derivatives (am = pyridines) and pK_a of Ham^+.[a]

am	r_{Au-N} /Å	pK_a of Ham^+
4-Methoxypyridine	2.09397	6.47
Methyl isonicotinate	2.09899	3.26
4-Acetylpyridine	2.09800	3.52
4-Chloropyridine	2.10118	3.84
4-Methylpyridine	2.09490	6.02
4-Aminopyridine	2.08734	9.12
4-Bromopyridine	2.10175	3.84
Pyridine	2.09816	5.25
4-Cyanopyridine	2.10250	1.90
3,5-Dimethylpyridine	2.09429	6.34
Isonicotinic acid	2.09871	3.26
4-(Dimethylamino)pyridine	2.08601	9.37

[a] More details on the geometries and energies of the optimized systems are available in the electronic supporting information.

pK_a on the metal–pyridine bond shortening was, however, already partly observed in a paper regarding Pt^{II}-pyridines derivatives, where it was confirmed on the basis of NMR measurements.[10]

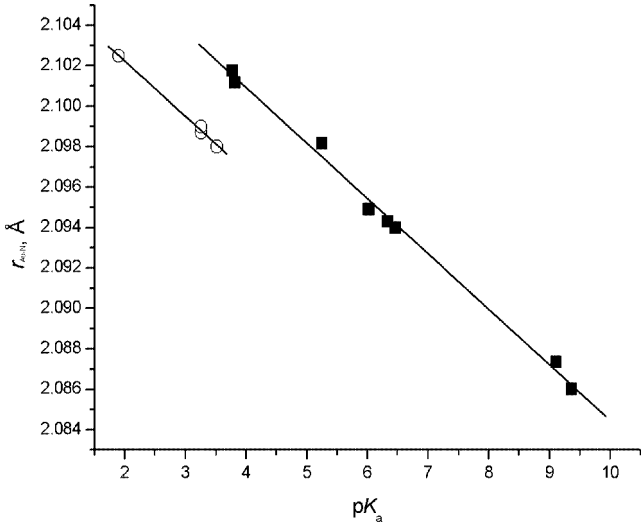

Figure 2. Plots of r_{Au-N} bond lengths against pK_a of Ham^+: (■) pyridine, 4-chloropyridine, 4-methoxypyridine, 4-methylpyridine, 4-bromopyridine, 3,5-dimethylpyridine, 4-aminopyridine, 4-(dimethylamino)pyridine; (○) 4-cyanopyridine, 4-acetylpyridine, methyl isonicotinate, isonicotinic acid.

The small difference between the reactivity of the "normal" and "p-extended" groups of pyridines appears to be correlated to a small difference between the corresponding ground-state r_{Au-N} bond lengths, which is about 0.004 Å. As all the considered pyridines are isosteric, it seems reasonable to conclude that this difference could be ascribed to an enforcement of the Au–N bond because of a greater π-back-donation contribution for the second group of ligands, as supposed from the results of the kinetic measurements.

Conclusion

In summary, the results of kinetic measurements on the process $AuCl_3$(am) + $Cl^- \rightarrow AuCl_4^-$ + am (am = sp^2 N-donor isosteric pyridines with different π systems and sp^3 amines) reported in this paper highlight the role of π-back-donation from the gold centre to the N-donor ligands in the stabilization of the $AuCl_3$(am) complexes and in the reactivity of these species towards substitution reactions. Besides the great difference between sp^2 and sp^3 N-donors, the small but significant difference observed between "normal" and "π-extended" pyridines, which has found a nice correlation with the calculated r_{Au-N} bond lengths, should be noted.

Experimental Section

Materials: The compound $KAuCl_4 \cdot 2H_2O$ was prepared from pure gold foil (99.99%). Pure reagent-grade LiCl, $LiClO_4$ and CH_3SO_3H (Aldrich) were used without further purification. Pyridines and amines were recrystallized or distilled before use when necessary. Anhydrous MeOH was obtained by distillation over Mg wires, but traces of water did not appear to have any appreciable effect upon the reactions. Acetone and dimethylformamide were pure reagent-grade products (Aldrich and BDH).

Instruments: Electronic spectra and kinetic measurements were obtained on a Perkin–Elmer Lambda 15 spectrophotometer. ^1H NMR spectra were taken on Bruker Avance 300 and/or Bruker AC 200 spectrometers at 298 K and are referred to internal tetramethylsilane. The conductivity of 1×10^{-3} mol dm^{-3} solutions of the complexes in dimethylformamide at 25 °C was measured with a Radiometer CDM 83 instrument. Elemental analyses were performed by the Microanalytical Laboratory of the Faculty of Pharmaceutical Sciences of the University of Padua.

Preparation of the Complexes: Trichloro(pyridine)gold(III) was first characterized by Renz,[9] trichloro(3,5-dimethylpyridine)gold(III) and trichloro(4-methylpyridine)gold(III) by Cattalini and Tobe[3] and trichloro(4-cyanopyridine)gold(III) by Cattalini et al.,[1] but the other derivatives of the type $AuCl_3$(am) are described here for the first time. All the complexes were prepared by the following method: $KAuCl_4 \cdot 2H_2O$ (0.415 g, 1.0 mmol) was dissolved in water (20 mL) and a stoichiometric amount of the nitrogen-donor base, dissolved in a small volume of water (2–3 mL), was added dropwise whilst stirring. The yellow precipitate, formed almost immediately, was filtered off, washed three times with water (10 mL) and dried in vacuo. For the most basic ligands, piperidine, cyclohexylamine, 4-aminopyridine, 4-(dimethylamino)pyridine and morpholine, it was necessary to keep them at 0 °C and in the dark to prevent a possible reduction of gold(III). All the complexes were nonconductive in organic solvents. Yields were in any case nearly quantitative (>95%). Analytical and ^1H NMR spectra are collected in Tables 4 and 5, respectively.

Kinetics: The reactions were initiated by adding a 0.015 mol dm^{-3} acetone solution (10–20 μL) of the substrate complex, $AuCl_3$(am), to a methanolic solution of chloride ion, previously brought to the reaction temperature (25 °C) in a thermostatted cell in the spectrophotometer. The concentration of the entering group was always large enough to provide pseudo-first-order conditions. After preliminary repetitive scan experiments in the range 240–360 nm to search for isosbestic points and spectral changes, the kinetics were studied by measuring the changing absorbance at suitable wave-

Table 4. Analytical data for the complexes (calculated values in parentheses).

Complex	Formula	C	H	N	Cl
(pyridine)$AuCl_3$	$C_5H_5AuCl_3N$	15.9 (15.7)	1.67 (1.32)	3.71 (3.66)	27.5 (27.8)
(4-methylpyridine)$AuCl_3$	$C_6H_7AuCl_3N$	18.3 (18.2)	1.65 (1.78)	3.49 (3.53)	26.7 (26.8)
(3,5-dimethylpyridine)$AuCl_3$	$C_7H_9AuCl_3N$	20.4 (20.5)	2.18 (2.21)	3.33 (3.41)	25.7 (25.9)
(4-chloropyridine)$AuCl_3$	$C_5H_4AuCl_4N$	14.2 (14.4)	1.27 (0.97)	3.32 (3.36)	34.1 (34.0)
(4-bromopyridine)$AuCl_3$	$C_5H_4AuBrCl_3N$	12.9 (13.0)	1.04 (0.87)	3.12 (3.04)	23.0 (23.1)
(4-methoxypyridine)$AuCl_3$	$C_6H_7AuCl_3NO$	17.5 (17.5)	1.62 (1.71)	3.31 (3.40)	25.6 (25.8)
(4-aminopyridine)$AuCl_3$	$C_5H_6AuCl_3N_2$	15.1 (15.1)	1.39 (1.52)	7.13 (7.05)	26.9 (26.8)
[4-(dimethylamino)pyridine]$AuCl_3$	$C_7H_{10}AuCl_3N_2$	19.6 (19.8)	2.21 (2.37)	6.47 (6.58)	24.8 (25.0)
(4-cyanopyridine)$AuCl_3$	$C_6H_4AuCl_3N_2$	17.6 (17.7)	1.23 (0.99)	6.72 (6.88)	17.6 (17.7)
(4-acetylpyridine)$AuCl_3$	$C_7H_7AuCl_3NO$	19.7 (19.8)	1.49 (1.66)	3.34 (3.30)	25.0 (25.1)
(methyl isonicotinate)$AuCl_3$	$C_7H_7AuCl_3NO_2$	19.3 (19.1)	1.61 (1.60)	3.24 (3.18)	24.3 (24.1)
(isonicotinic acid)$AuCl_3$	$C_6H_5AuCl_3NO_2$	16.7 (16.9)	0.99 (1.18)	3.37 (3.28)	25.0 (24.9)
(piperidine)$AuCl_3$	$C_5H_{11}AuCl_3N$	15.3 (15.5)	2.76 (2.85)	3.71 (3.61)	27.2 (27.4)
(morpholine)$AuCl_3$	$C_4H_9AuCl_3NO$	12.3 (12.3)	2.54 (2.32)	3.32 (3.59)	27.1 (27.2)
(cyclohexylamine)$AuCl_3$	$C_6H_{13}AuCl_3N$	18.0 (17.9)	3.27 (3.26)	3.46 (3.48)	26.3 (26.4)

Table 5. ^1H NMR spectroscopic data for the complexes.

Complex	^1H NMR, $(CD_3)_2CO$, 298 K
(pyridine)$AuCl_3$[a]	8.89 (dd, 2 H, $^3J_{HH}$ = 6.5, $^4J_{HH}$ = 1.5 Hz, H_α); 8.33 (tt, 1 H, $^3J_{HH}$ = 7.8, $^4J_{HH}$ = 1.5 Hz, H_γ); 7.89 (dd, 2 H, $^3J_{HH}$ = 6.5, ^3J = 7.8 Hz, H_β)
(4-methylpyridine)$AuCl_3$	8.90 (d, 2 H, $^3J_{HH}$ = 6.2 Hz, H_α); 7.80 (d, 2 H, $^3J_{HH}$ = 6.2 Hz, H_β); 2.62 (s, 3 H, CH_3)
(3,5-dimethylpyridine)$AuCl_3$	8.74 (s, 2 H, H_α); 8.05 (s, 1 H, H_γ); 2.52 (s, 6 H, CH_3)
(4-chloropyridine)$AuCl_3$	9.14 (d, 2 H, $^3J_{HH}$ = 7.0 Hz, H_α); 8.13 (d, 2 H, $^3J_{HH}$ = 7.0 Hz, H_β)
(4-bromopyridine)$AuCl_3$	9.04 (d, 2 H, $^3J_{HH}$ = 6.8 Hz, H_α); 8.27 (d, 2 H, $^3J_{HH}$ = 6.8 Hz, H_β)
(4-methoxypyridine)$AuCl_3$	8.85 (d, 2 H, $^3J_{HH}$ = 7.3 Hz, H_α); 7.46 (d, 2 H, $^3J_{HH}$ = 7.3 Hz, H_β); 4.16 (s, 3 H, CH_3)
(4-aminopyridine)$AuCl_3$	8.25 (d, 2 H, $^3J_{HH}$ = 7.1 Hz, H_a); 6.91 (d, 2 H, $^3J_{HH}$ = 7.1 Hz, H_b); 7.06 (br. s, 2 H, NH_2)
[4-(dimethylamino)pyridine]$AuCl_3$	8.28 (d, 2 H, $^3J_{HH}$ = 7.8 Hz, H_α); 6.91 (d, 2 H, $^3J_{HH}$ = 7.8 Hz, H_β); 3.26 (s, 6 H, NMe_2)
(4-cyanopyridine)$AuCl_3$	9.47, 8.46 (AA′BB′ spin system, 4 H, $^3J_{AB} = {}^3J_{A'B'}$ = 6.5, $^4J_{AA'} = {}^4J_{BB'}$ = 2.0 Hz, *aromatic protons*)
(4-acetylpyridine)$AuCl_3$	9.33, 8.37 (AA′BB′ spin system, 4 H, $^3J_{AB} = {}^3J_{A'B'}$ = 7.0, $^4J_{AA'} = {}^4J_{BB'}$ = 2.0 Hz, *aromatic protons*); 2.80 (s, 3 H, CH_3)
(isonicotinic acid)$AuCl_3$	9.36, 8.43 (AA′BB′ spin system, 4 H, $^3J_{AB} = {}^3J_{A'B'}$ = 6.9, $^4J_{AA'} = {}^4J_{BB'}$ = 1.5 Hz, *aromatic protons*)
(methyl isonicotinate)$AuCl_3$	9.36, 8.42 (AA′BB′ spin system, 4 H, $^3J_{AB} = {}^3J_{A'B'}$ = 7.3, $^4J_{AA'} = {}^4J_{BB'}$ = 1.0 Hz, *aromatic protons*); 4.05 (s, 3 H, CH_3)
(piperidine)$AuCl_3$	3.63 (br. s, 1 H, *NH*); 3.56 (m, 4 H, CH_2-*N*); 2.00–1.50 (m, 6 H, CH_2)
(morpholine)$AuCl_3$	4.03 (m, 4 H, CH_2-*O*); 3.56 (m, 4 H, CH_2-*N*); 3.80 (br. m, 1 H, *NH*)
(cyclohexylamine)$AuCl_3$	3.92 (s, very br., 2 H, NH_2); 2.48 (br. m, 1 H, *CH*-*N*); 1.62 (m, 4 H, CH_2); 1.39 (m, 4 H, CH_2); 1.19 (m, 2 H, CH_2)

[a] CD_3NO_2, 298 K.

lengths as a function of time. Pseudo-first-order rate constants (k_{obs}, s^{-1}) were obtained either from the gradient of plots of $\log(D_t - D_\infty)$ versus time or from a nonlinear least-squares fit of experimental data to $D_t = D_\infty + (D_0 - D_\infty)\exp(-k_{obs}t)$ with D_0, D_∞ and k_{obs} as the parameters to be optimized (D_0 is absorbance after mixing the reactants, D_∞ is absorbance at completion of reaction).

Computational Details: The computational geometry optimizations of the $AuCl_3$(am) complexes were performed in vacuo using the hybrid DFT B3PW91 method[11] without symmetry constraints, in combination with the polarized, single-ζ core, triple-ζ valence 6-311G** basis set on the elements of the first rows of the periodic table and the ECP-based SDD basis set on Au.[12] The "restricted" formalism was applied in all calculations, together with tight convergence criteria. All the resultant stationary points were characterized as true minima (i.e., no imaginary frequencies). All calculations were carried out at CINECA (Centro Italiano di Supercalcolo, Bologna, Italy) using IBM p5-575 computers with 64-bit IBM Power5 processors, which operated at 1.9 GHz frequency. The software used was the Gaussian '03.[13] The Natural Bond Orbitals analysis[14] was performed during our studies, using the NBO version 3.1 implemented in Gaussian 03. Unfortunately, the software separated all our complexes into three different fragments, $[AuCl_2]^{x+}$, $[Cl]^{y-}$ and $[pyridine]^{(y-x)+}$, leading to uncorrected results; for example the apparent d^{10} configuration of the gold centres. For this reason, no discussion based on the NBO analysis was helpful for this work.

Supporting Information (see also the footnote on the first page of this article): Selected geometry data and energies for the prepared gold(III) complexes.

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