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Displacement of Neutral Nitrogen Donors by Chloride in $AuCl_3$(3R-py) (3R-py = *meta*-Substituted Pyridine): Comparison between *meta*- and *para*-Substituted Pyridines by Kinetics and DFT Calculations

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The kinetics of the process $AuCl_3(3R\text{-py}) + Cl^- \rightarrow AuCl_4^- + 3R\text{-py}$ (3R-py = one of a number of *meta*-substituted pyridines covering a wide range of basicity) have been studied in methanol at 25 °C. The reactions obey the usual two-term rate law observed in the substitution reactions of 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 of ca. –0.6 already found for *para*-substituted pyridines (4R-py). Until now the two groups of bases have been considered to behave in the same manner in their displacement from Au^{III} and Pt^{II} by various nucleophiles but, on the contrary, the reactivity of the two classes of N donors is slightly different and follows the order: 4R-py > 3R-py. This kinetic result is explained on the basis of an energetic difference between the frontier orbitals of the $AuCl_3$(3R-py) and $AuCl_3$(4R-py) derivatives.

Introduction

The chemical features of (pyridine)gold(III) complexes are currently of interest from both a catalytic[1] and mechanistic point of view: in particular, the reactivity of gold(III)[2–5] in the reactions with N-donor bases has been widely studied, mainly involving pyridine and substituted pyridines (R-py) as entering or leaving groups. The same types of reactions have also been studied for platinum(II) derivatives[6–10] and it was observed that the substitution reactions (1), (2) and (3) take place with an associative mechanism, where the rate constants for the forward and the reverse reactions obey the general relationship $k_{obs} = k_1 + k_2$[nucleophile], which is usual for nucleophilic substitutions of planar four-coordinate d^8 metal complexes.[11]

$$AuCl_4^- + R\text{-py} \rightleftharpoons AuCl_3(R\text{-py}) + Cl^- \qquad (1)$$

$$[LPtCl]^+ + R\text{-py} \rightleftharpoons [LPt(R\text{-py})]^{2+} + Cl^- \qquad (2)$$

[L = 2,6-bis(methylsulfanylmethyl)pyridine,[5] bis(2-pyridylmethyl) sulfide,[7] 2,2′:6′,2′′-terpyridine,[9] biacetylbis(*N*-methyl-*N*-phenyl)-oxazone[8]]

$$LPtCl_2 + R\text{-py} \rightleftharpoons [LPt(R\text{-py})Cl]^+ + Cl^- \qquad (3)$$

[L = 1,2-bis(phenylsulfanyl)ethane[6]]

The k_1 term is the first-order rate constant for the nucleophilic attack on the substrate by the solvent, whereas k_2 is the second-order rate constant for the nucleophilic attack on the substrate by the nucleophile. The k_2 constants are remarkably influenced by the nature of R-py, indicating that the discriminating ability of gold(III) and platinum(II) complexes is good. In both the forward and reverse reactions a linear free-energy relationship, $\log k_2 = \alpha pK_a$ + constant, occurs between the rate constant and the basicity of R-py, that is the pK_a of the conjugated acid $[H(R\text{-py})]^+$. Steric retardation is observed for pyridines containing one or two *ortho* groups (usually called hindered pyridines) and these effects are in many cases approximately additive. Moreover, we studied the kinetics of the reaction $AuCl_3(nu) + Cl^- \rightarrow AuCl_4^- + nu$ (nu = five-membered N-donor heterocycles such as thiazole, oxazole, imidazole and their derivatives)[4] and the results were compared, under the same experimental conditions, with studies where the leaving groups are pyridines.[3] 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.

In recent work[5] involving reaction (1) we compared the lability of three different groups of N donors: (I) 4-substituted pyridines; (II) 4-substituted pyridines with a more extended π-system; and (III) sp^3 nitrogen-donor bases. The first group includes pyridine, 4-bromopyridine, 4-chloropyridine, 4-methylpyridine, 4-methoxypyridine, 4-aminopyridine and 4-(dimethylamino)pyridine, while the second group includes the derivatives of cyanopyridine, isonicotinic acid, methyl isonicotinate and 4-acetylpyridine. The lability

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of these pyridines is considerably lower than that of the third group of derivatives, i.e. the sp^3 ligands piperidine, cyclohexylamine and morpholine. Pyridines I and II obey the linear relationship $\log k_2 = \alpha pK_a$ + constant with $\alpha \approx -0.6$, but the reactivity of the two groups differ by about 2.3 $kJ\,mol^{-1}$ in the order: pyridines I > pyridines II. These differences were attributed to a ground-state stabilization due to the π back-donation from the filled orbitals of the metal atom to the antibonding orbitals of the pyridine ligands.

In some kinetic studies involving reactions (1), (2) and (3)[2,3,7,8] *meta*-substituted pyridines (3R-py) were also considered and their reactivity appeared similar to that of group I pyridines, but during our latest work regarding reaction (1),[5] trying to study *meta*-substituted pyridines like 3-methylpyridine and 3-chloropyridine, we found kinetic data that was not completely comparable with those of *para*-substituted pyridines. In order to determine whether these differences have a chemical meaning, the kinetics of the displacement of the nitrogen ligand by chloride from $AuCl_3$(3R-py) substrates in methanol at 25 °C are reported and the results are compared with those of ref.[5] The discussion is supported by ground-state DFT calculations performed on the $AuCl_3$(3R-py) and $AuCl_3$(4R-py) derivatives and the different reactivity of the coordinated *meta*- and *para*-substituted pyridines is correlated with a slight, systematic difference between the energies of the frontier orbitals of the corresponding gold(III) complexes.

Results and Discussion

When a methanolic solution of the neutral $AuCl_3$(3R-py) substrate was allowed to react with an appropriate excess of chloride, repetitive scanning of the spectrum in the region 240–360 nm showed that the reaction evolves with time in a first-order fashion leading to the substitution of the neutral base by a chloride ion. The presence of well-maintained isosbestic points, whose position depends 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. Addition of $LiClO_4$ indicated that primary salt effects were absent and secondary effects were negligible; thus, no further attempt to maintain a constant ionic strength was made. The reactions were studied in the presence of 0.1 $mol\,dm^{-3}$ CH_3SO_3H. Preliminary experiments showed that, at constant chloride concentration, the rate of reaction was not dependent on the concentration of acid over the range 0.02–0.2 $mol\,dm^{-3}$. The acid simply serves to protonate the released ligand, to prevent the reverse reaction and to force the reaction to completion. All the reactions were studied in the presence of a sufficient excess of chloride over the substrate to provide pseudo-first-order conditions. It is to be noted that these experimental conditions are the same as those used in ref.[5] The rate constants were determined in the usual way from the change in absorbance as a function of time at a conve-

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

3R-py	$[Cl^-]/mol\,dm^{-3}$	$10^3 k_{obs}/s^{-1}$[a]	3R-py	$[Cl^-]/mol\,dm^{-3}$	$10^3 k_{obs}/s^{-1}$[a]
3-Chloropyridine	0.0005	27.7 ± 0.1	3-phenylpyridine	0.001	1.93 ± 0.03
	0.0010	29.6 ± 0.1		0.002	2.28 ± 0.01
	0.0015	31.5 ± 0.1		0.003	2.81 ± 0.01
	0.0020	36.5 ± 0.2		0.004	3.27 ± 0.02
	0.0025	38.3 ± 0.1		0.005	3.76 ± 0.04
3-Bromopyridine	0.0005	17.0 ± 0.1	3-hydroxymethylpyridine	0.001	1.05 ± 0.01
	0.0010	20.2 ± 0.2		0.002	1.26 ± 0.01
	0.0015	23.0 ± 0.1		0.003	1.60 ± 0.02
	0.0020	28.0 ± 0.2		0.004	1.94 ± 0.01
	0.0025	30.5 ± 0.1		0.005	2.22 ± 0.03
3-Iodopyridine	0.0005	10.1 ± 0.2	3-methoxypyridine	0.001	1.39 ± 0.01
	0.0010	12.2 ± 0.1		0.002	1.64 ± 0.02
	0.0015	14.2 ± 0.1		0.003	2.05 ± 0.03
	0.0020	15.7 ± 0.2		0.004	2.35 ± 0.04
	0.0025	18.1 ± 0.1		0.005	2.68 ± 0.03
3-Fluoropyridine	0.0005	17.2 ± 0.1	3-methylpyridine	0.001	0.63 ± 0.02
	0.0010	19.9 ± 0.2		0.002	0.77 ± 0.01
	0.0015	22.5 ± 0.1		0.003	0.93 ± 0.03
	0.0020	24.9 ± 0.1		0.004	1.08 ± 0.01
	0.0025	27.9 ± 0.3		0.005	1.24 ± 0.02

[a] The indicated errors were obtained from the nonlinear least-squares fit of the experimental data to $D_t = D_\infty + (D_0 - D_\infty)\exp(-k_{obs}t)$ (D_0 = absorbance after mixing the reactants, D_∞ = absorbance at completion of reaction). Each experimental measurement was repeated at least twice.

nient wavelength and the observed rate constants, k_{obs}, are collected in Table 1.

The observed rate constants, k_{obs}, obey the general relationship $k_{obs} = k_1 + k_2$[nucleophile], usually found for substitution in gold(III) complexes. The k_1 terms, which refer 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,[12] are usually quite small and contribute little to the reactions. The k_2 terms are the second-order rate constants for the direct attack of the nucleophile, Cl^-, at the substrate and were determined by a linear regression of the k_{obs} values vs. the chloride concentration. As expected from previous studies on gold(III) substitution reactions,[2–5] the pseudo-first-order rate constant values, k_{obs}, mainly depend upon the k_2 values, which are reported in Table 2 together with the pK_a values of $H[(3R\text{-}py)]^+$ taken from ref.[13]

In Figure 1 the plots of log k_2 vs. pK_a of the leaving 3R-py are shown, together with the data for the simple pyridine and the *para*-substituted pyridines 4R-py in the same pK_a range (see ref.[5] for log k_2 and pK_a values of these nitrogen donors).

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

3R-py	k_2/dm^{3}mol s^{-1}[a]	pK_a of $[H(3R\text{-}py)]^+$
$AuCl_3$(3-chloropyridine)	5.6 ± 0.6	2.84
$AuCl_3$(3-bromopyridine)	6.9 ± 0.4	2.84
$AuCl_3$(3-iodopyridine)	3.9 ± 0.1	3.25
$AuCl_3$(3-fluoropyridine)	5.28 ± 0.09	2.97
$AuCl_3$(3-methylpyridine)	0.153 ± 0.002	5.52
$AuCl_3$(3-phenylpyridine)	0.46 ± 0.02	4.80
$AuCl_3$(3-hydroxymethylpyridine)	0.30 ± 0.01	5.00
$AuCl_3$(3-methoxypyridine)	0.33 ± 0.01	4.91

[a] Errors were obtained from the linear regression of k_{obs} values vs. chloride concentration.

As depicted in Figure 1, a linear relationship, log $k_2 = \alpha pK_a$ + constant, is obeyed for both the *meta*-substituted (3R-py) and *para*-substituted (4R-py) pyridines, with $\alpha \approx -0.6$. Coordinated *meta*-substituted pyridines appear to be slightly less reactive than the *para*-substituted ones, even if the difference between the reactivity of the two groups of pyridines is quite small ($\Delta \approx 0.18$) and corresponds to about 1 kJ mol^{-1}. The chemical behaviour of the unsubstituted pyridine in its displacement by chloride from Au^{III} is comparable to that of the *para*-substituted pyridines.

To explain the experimental data obtained from the kinetic measurements, ground-state DFT B3PW91 calculations were performed on $AuCl_3$(py), $AuCl_3$(3R-py) and $AuCl_3$(4R-py) derivatives. Particular interest was devoted to the frontier orbitals of the gold complexes and Table 3 reports the energy values of the HOMOs and LUMOs for all

Table 3. Energy values of the frontier orbitals of the $AuCl_3$(py), $AuCl_3$(3R-py) and $AuCl_3$(4R-py) complexes.

R-py	HOMO [eV]	LUMO [eV]
$AuCl_3$(4-methoxypyridine)	–0.27672	–0.14997
$AuCl_3$(4-chloropyridine)	–0.28573	–0.16001
$AuCl_3$(4-methylpyridine)	–0.27872	–0.15209
$AuCl_3$(4-bromopyridine)	–0.28541	–0.15964
$AuCl_3$(pyridine)	–0.28183	–0.15564
$AuCl_3$(3-bromopyridine)	–0.28584	–0.16068
$AuCl_3$(3-methoxypyridine)	–0.27946	–0.15314
$AuCl_3$(3-chloropyridine)	–0.28629	–0.16108
$AuCl_3$(3-methylpyridine)	–0.27759	–0.15129
$AuCl_3$(3-iodopyridine)	–0.28525	–0.15992
$AuCl_3$(3-fluoropyridine)	–0.28619	–0.16087
$AuCl_3$(3-phenylpyridine)	–0.27953	–0.15325
$AuCl_3$(3-hydroxymethylpyridine)	–0.27917	–0.15274

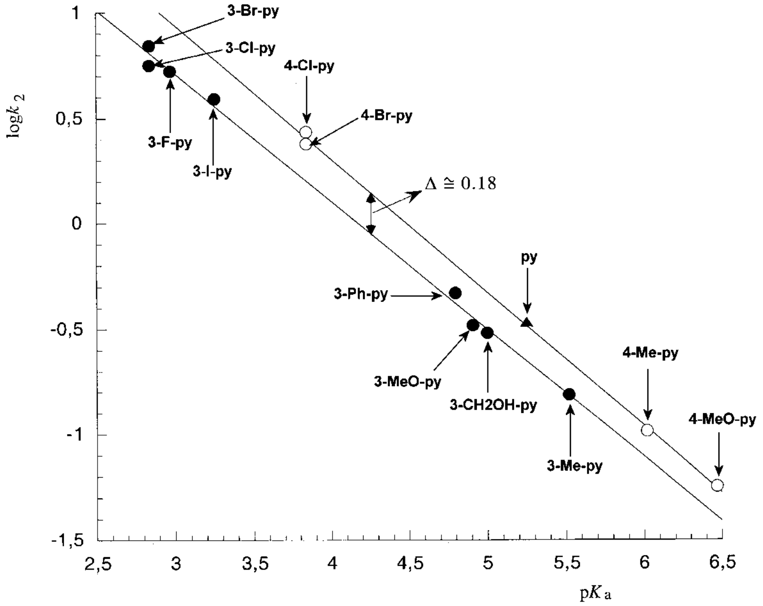

Figure 1. Plots of log k_2 for the reaction $AuCl_3(R\text{-}py) + Cl^- \rightarrow AuCl_4^- + R\text{-}py$ against pK_a of $[H(R\text{-}py)]^+$: (▲) R-py = pyridine; (○) R-py = 4-chloropyridine, 4-methoxypyridine, 4-methylpyridine, 4-bromopyridine; (●) R-py = 3-chloropyridine, 3-bromopyridine, 3-fluoropyridine, 3-iodopyridine, 3-methylpyridine, 3-phenylpyridine, 3-hydroxymethylpyridine, 3-methoxypyridine.

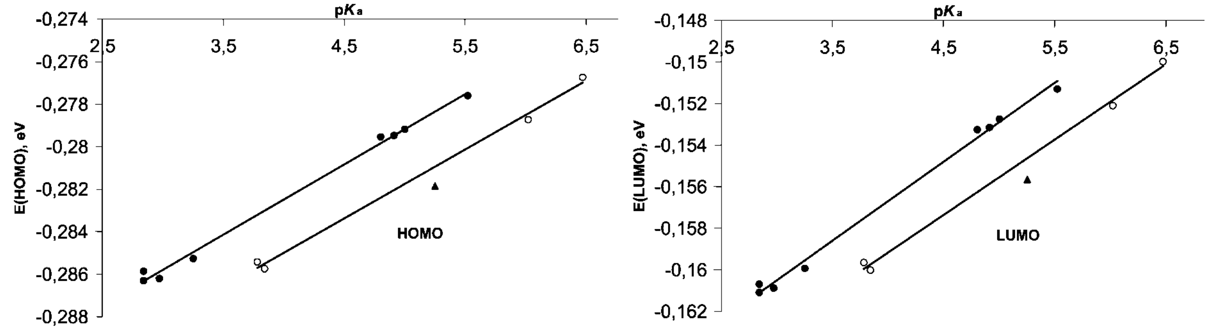

Figure 2. Plots of the (R-py) HOMO and LUMO energies against the pK_a of [H(R-py)]$^+$: (▲) R-py = pyridine; (○) R-py = 4-chloropyridine, 4-methoxypyridine, 4-methylpyridine, 4-bromopyridine; (●) R-py = 3-chloropyridine, 3-bromopyridine, 3-fluoropyridine, 3-iodopyridine, 3-methylpyridine, 3-phenylpyridine, 3-hydroxymethylpyridine, 3-methoxypyridine.

the considered species, while in Figure 2 the plots of HOMO and LUMO vs. pK_a of the leaving 3R-py are shown.

Linear correlations between the frontier orbital energies and pK_a values were found, in particular for the *para*-substituted pyridine (4R-py) derivatives where the equations are $E(\text{HOMO}) = 0.0032 \pm 0.0002\ \text{p}K_a - 0.2979 \pm 0.0008$ and $E(\text{LUMO}) = 0.0036 \pm 0.0002\ \text{p}K_a - 0.1737 \pm 0.0008$, while for the *meta*-substituted pyridine (3R-py) complexes the same equations are $E(\text{HOMO}) = 0.0031 \pm 0.0001\ \text{p}K_a - 0.2957 \pm 0.0004$ and $E(\text{LUMO}) = 0.0038 \pm 0.0001\ \text{p}K_a - 0.1719 \pm 0.0005$. As depicted in Figure 2, the gradients of the plots of the HOMO or LUMO energies vs. pK_a are almost the same for both the 3R- and 4R-pyridines, while there is a significant difference (about 0.002 eV) in their intercepts. The computational results for the pyridine complex AuCl$_3$(py) are comparable to those of the AuCl$_3$(4R-py) derivatives, as was also the case with the chemical behaviour (see Figure 1). The comparison of Figure 1 and Figure 2 appears to indicate a relation between the kinetic and theoretical data, suggesting that the different reactivity of the two groups of ligands considered, 3R-py and 4R-py, could be ascribed to the different energies of the frontier orbitals depicted in Figure 2.

In the reaction studied, i.e. the nucleophilic attack of Cl$^-$ on AuCl$_3$(R-py) and the consequent displacement of the nitrogen ligand, a large role should be played by the lowest unoccupied molecular orbitals of the gold complexes and the filled atomic orbitals of the chloride ion. All the calculated LUMO energy values fall in the range –0.14997 eV to –0.16108 eV and the AuCl$_3$(3R-py) LUMOs are about 0.002 eV higher than those of the AuCl$_3$(4R-py) complexes. The three 3p atomic orbitals of Cl$^-$ have a calculated energy of –0.02709 eV, while the 3s atomic orbital corresponds to an energy value of –0.47949 eV (see Figure 3). On supposing that the observed minor reactivity of the AuCl$_3$(3R-py) complexes, compared to that of the AuCl$_3$(4R-py) derivatives, corresponds to a greater energy difference between the LUMOs of the AuCl$_3$(3R-py) species and the interacting Cl$^-$ atomic orbital, it is to be concluded that the 3s atomic orbital of the chloride ion plays an important role in the nucleophilic attack. Using a pseudo-Valence-Bond description to better explain this last conclusion regarding the reaction studied, Cl$^-$ appears to interact with the gold(III) complexes using a hybrid atomic orbital with a strong s character and, consequently, an energy value lower than those of the LUMOs of the gold complexes, as depicted in Figure 3.

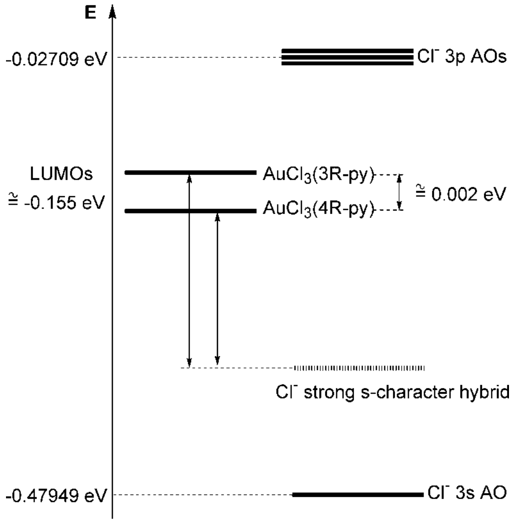

Figure 3. Plot of the Cl$^-$ 3s and 3p AOs and the AuCl$_3$(R-py) (R-py = 3R-py and 4R-py) LUMO energy levels.

Concluding Remarks

The comparison of the results of the kinetic measurements on the process AuCl$_3$(R-py) + Cl$^-$ → AuCl$_4^-$ + R-py, where R-py are *para*-substituted pyridines 4R-py and *meta*-substituted pyridines 3R-py, enabled the observation of a slightly different behaviour for these two types of pyridines, the latter type being less reactive. Moreover, by means of DFT calculations the kinetic results were correlated to a small energy difference of the frontier orbitals of the AuCl$_3$(4R-py) and AuCl$_3$(3R-py) derivatives.

Experimental Section

Materials: Compound $KAuCl_4{\cdot}2H_2O$ was prepared from pure gold foil (99.99%). Pure reagent-grade products [LiCl, $LiClO_4$, CH_3SO_3H (Aldrich)] were used without further purification. Pyridines were recrystallized or distilled before use when necessary. Anhydrous MeOH was obtained by distillation from 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, respectively).

Instruments: Electronic spectra and kinetic measurements were obtained with a Perkin–Elmer Lambda 15 spectrophotometer. ^1H NMR spectra were obtained with Bruker Avance 300 and/or Bruker AC 200 spectrometers. COSY, NOESY and homonuclear decoupling experiments were performed to improve the characterization of the complexes. The conductivity of 1×10^{-3} mol dm^{-3} solutions 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(3-methylpyridine)gold(III) was first characterized by Cattalini and Tobe,[3] but the preparation of the complexes of 3-fluoropyridine, 3-bromopyridine, 3-chloropyridine, 3-iodopyridine, 3-phenylpyridine, 3-(hydroxymethyl)pyridine and 3-methoxypyridine is described here for the first time. All the complexes were prepared by the following method: $KAuCl_4{\cdot}2H_2O$ (0.415 g, 1 mmol) was dissolved in water (20 mL) and an equimolar amount of the nitrogen-donor base, dissolved in a small volume of water (3 mL), was added dropwise whilst stirring. The yellow precipitate that formed almost immediately was filtered off, washed three times with water (10 mL) and dried in vacuo. The complexes were nonconductive in organic solvents. Yields were in all cases nearly quantitative (>95%). Analytical and ^1H NMR data are collected in Tables 4 and 5, respectively.

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

Complex	C	H	N	Cl
$AuCl_3$(3-fluoropyridine)	15.2 (15.0)	1.27 (1.01)	3.51 (3.50)	26.5 (26.6)
$AuCl_3$(3-bromopyridine)	12.8 (13.0)	0.62 (0.87)	3.11 (3.04)	23.3 (23.1)
$AuCl_3$(3-chloropyridine)	14.3 (14.4)	1.10 (0.97)	3.34 (3.36)	(34.2) (34.0)
$AuCl_3$(3-methylpyridine)	18.1 (18.2)	1.63 (1.78)	3.72 (3.53)	27.0 (26.8)
$AuCl_3$(3-iodopyridine)	11.7 (11.8)	0.69 (0.79)	2.91 (2.76)	20.7 (20.9)
$AuCl_4$(3-phenylpyridine)	41.7 (41.9)	2.11 (1.93)	3.12 (2.97)	22.7 (22.6)
$AuCl_3$(3-hydroxymethylpyridine)	17.3 (17.5)	1.76 (1.71)	3.41 (3.40)	25.9 (25.8)
$AuCl_3$(3-methoxypyridine)	17.6 (17.5)	1.51 (1.71)	3.44 (3.39)	26.0 (25.8)

Kinetics: Reactions were initiated by adding a 0.015 mol dm^{-3} acetone solution (10–20 µL) of the substrate complex, $AuCl_3$(3R-py), to a methanolic solution of chloride ion (3 mL) that had previously been 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 a suitable wavelength (320 nm) as a function of time. Pseudo-first-order rate constants (k_{obs} [s^{-1}]) were obtained either from the gradient of plots of $\log(D_t - D_\infty)$ vs. time or from a nonlinear least-squares fit of the experimental data to $D_t = D_\infty + (D_0 - D_\infty)\exp(-k_{obs}t)$, where D_0, D_∞ and k_{obs} are the parameters that have to be optimized (D_0 = absorbance after mixing the reactants, D_∞ = absorbance at completion of reaction).

Computational Details: The computational geometry optimizations of the $AuCl_3$(3R-py) and $AuCl_3$(4R-py) complexes were performed in vacuo using the hybrid DFT B3PW91 method[14] without sym-

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

Complex	^1H NMR, $(CD_3)_2CO$, 298 K
$AuCl_3$(3-fluoropyridine)	δ = 9.30 (dd, 1 H, $^3J_{H,F}$ = 2.8 Hz, $^4J_{H,H}$ = 2.2 Hz, 2-H), 9.10 (d, 1 H, $^3J_{H,H}$ = 5.8 Hz, 6-H), 8.39 (ddd, 1 H, $^3J_{H,H}$ = 8.4 Hz, $^3J_{H,F}$ = 8.2 Hz, $^4J_{H,H}$ = 2.2 Hz, 4-H), 8.16 (ddd, 1 H, $^3J_{H,H}$ = 5.8 Hz, $^3J_{H,H}$ = 8.4 Hz, $^3J_{H,F}$ = 5.0 Hz, 5-H) ppm
$AuCl_3$(3-bromopyridine)	δ = 9.42 (d, 1 H, $^4J_{H,H}$ = 2.1 Hz, 2-H), 9.21 (dd, 1 H, $^3J_{H,H}$ = 6.0 Hz, $^4J_{H,H}$ = 1.0 Hz, 6-H), 8.67 (ddd, 1 H, $^3J_{H,H}$ = 8.4 Hz, $^4J_{H,H}$ = 2.1 Hz, $^4J_{H,H}$ = 1.0 Hz, 4-H), 8.03 (dd, 1 H, $^3J_{H,H}$ = 6.0 Hz, $^3J_{H,H}$ = 8.4 Hz, 5-H) ppm
$AuCl_3$(3-chloropyridine)	δ = 9.34 (d, 1 H, $^4J_{H,H}$ = 2.3 Hz, 2-H), 9.17 (dd, 1 H, $^3J_{H,H}$ = 6.0 Hz, $^4J_{H,H}$ = 1.1 Hz, 6-H), 8.55 (ddd, 1 H, $^3J_{H,H}$ = 8.3 Hz, $^4J_{H,H}$ = 2.3 Hz, $^4J_{H,H}$ = 1.1 Hz, 4-H), 8.09 (dd, 1 H, $^3J_{H,H}$ = 6.0 Hz, $^3J_{H,H}$ = 8.3 Hz, 5-H) ppm
$AuCl_3$(3-methylpyridine)	δ = 8.96 (s, 1 H, 2-H), 8.93 (d, 1 H, $^3J_{H,H}$ = 6.0 Hz, 6-H), 8.24 (d, 1 H, $^3J_{H,H}$ = 7.9 Hz, 4-H), 7.88 (dd, 1 H, $^3J_{H,H}$ = 6.0 Hz, $^3J_{H,H}$ = 7.9 Hz, 5-H), 2.58 (s, 3 H, CH_3) ppm
$AuCl_3$(3-iodopyridine)	δ = 9.50 (d, 1 H, $^4J_{H,H}$ = 1.8 Hz, 2-H), 9.20 (dd, 1 H, $^3J_{H,H}$ = 5.8 Hz, $^4J_{H,H}$ = 1.0 Hz, 6-H), 8.79 (ddd, 1 H, $^3J_{H,H}$ = 8.4 Hz, $^4J_{H,H}$ = 1.8 Hz, $^4J_{H,H}$ = 1.0 Hz, 4-H), 7.87 (dd, 1 H, $^3J_{H,H}$ = 5.8 Hz, $^3J_{H,H}$ = 8.4 Hz, 5-H) ppm
$AuCl_4$(3-phenylpyridine)	δ = 9.50 (d, 1 H, $^4J_{H,H}$ = 2.1 Hz, 2-H), 9.11 (dd, 1 H, $^3J_{H,H}$ = 6.0 Hz, $^4J_{H,H}$ = 1.0 Hz, 6-H), 8.69 (ddd, 1 H, $^3J_{H,H}$ = 6.2 Hz, $^4J_{H,H}$ = 2.1 Hz, $^4J_{H,H}$ = 1.0 Hz, 4-H), 8.09 (dd, 1 H, $^3J_{H,H}$ = 6.0 Hz, $^3J_{H,H}$ = 6.2 Hz, 5-H), 7.97–7.79 (m, 3 H, Ph), 7.75–7.52 (m, 2 H, Ph) ppm
$AuCl_3$(3-hydroxymethylpyridine)	δ = 9.06 (s, 1 H, 2-H), 8.99 (d, 1 H, $^3J_{H,H}$ = 6.0 Hz, 6-H), 8.35 (d, 1 H, $^3J_{H,H}$ = 7.9 Hz, 4-H), 7.95 (dd, 1 H, $^3J_{H,H}$ = 6.0 Hz, $^3J_{H,H}$ = 7.9 Hz, 5-H), 5.17 (br. s, 1 H, OH), 4.90 (s, 2 H, CH_2) ppm
$AuCl_3$(3-methoxypyridine)	δ = 8.90 (d, 1 H, $^4J_{H,H}$ = 2.4 Hz, 2-H), 8.71 (dd, 1 H, $^3J_{H,H}$ = 5.4 Hz, $^4J_{H,H}$ = 1.0 Hz, 6-H), 7.99 (ddd, 1 H, $^3J_{H,H}$ = 8.2 Hz, $^4J_{H,H}$ = 2.4 Hz, $^4J_{H,H}$ = 1.0 Hz, 4-H), 7.92 (dd, 1 H, $^3J_{H,H}$ = 8.2 Hz, $^3J_{H,H}$ = 5.4 Hz, 5-H), 4.09 (s, 3 H, CH_3) ppm

metry 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 and I.[15] The "restricted" formalism was applied in all calculations. All the resultant stationary points were characterized as true minima (i.e. no imaginary frequencies). A B3PW91/6-311+G** calculation (the same was used for the complexes, with the addition of sp diffuse functions) was applied to obtain the energies of the filled atomic orbitals of the chloride ion. All calculations were carried out at CINECA (Centro Italiano di Supercalcolo, Bologna, Italy) using IBM p5-575 computers with 64-bit IBM Power5 processors operating at 1.9 GHz. The software used was the Gaussian 03 program.[16]

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