$Co(H_2O)_6^{3+}$ and $Mn(H_2O)_6^{3+}$ reactions, it is likely that pathways involving electronically excited states of the reactants need to be invoked, at least in the case of the $Co(H_2O)_6^{3+}$ reactions. Analogous considerations may also be relevant to the $Mn(H_2O)_6^{2+/3+}$ exchange, but in the absence of a direct measurement of the $Mn(H_2O)_6^{2+/3+}$ exchange constant, we have focused our attention on the $Co(H_2O)_6^{2+/3+}$ system.

In order to rationalize the $Co(H_2O)_6^{3+}$ results in terms of an outer-sphere mechanism, it is necessary that the thermal population of ligand-field excited states (of $Co(H_2O)_6^{3+}$ or $Co(H_2O)_6^{2+}$) provide a viable reaction pathway. For an inner-sphere water-bridged mechanism,[38] viable pathways are obtained through superexchange coupling of LMCT states or, perhaps, through actual oxidation of the bridging water molecule to form a hydroxyl-bridged transition state. A more complete characterization of these systems must await the results of spectroscopic and structural studies currently in progress.

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Registry No. $Mn(H_2O)_6^{3+}$, 18976-26-6; $Os(4,4'-(CH_3)_2bpy)_3^{2+}$, 33247-24-4; $Os(phen)_3^{2+}$, 31067-98-8; $Os(bpy)_3^{2+}$, 23648-06-8; $Os(5\text{-}Cl\text{-}phen)_3^{2+}$, 71692-76-7; $Fe(bpy)_3^{2+}$, 15025-74-8; $Ru(4,4'-(CH_3)_2bpy)_3^{2+}$, 32881-03-1; $Ru(bpy)_3^{2+}$, 15158-62-0; $Ru(5\text{-}NO_2phen)_3^{2+}$, 54360-17-7; $Mn(H_2O)_6^{2+}$, 15365-82-9; $Fe(H_2O)_6^{2+}$, 15365-81-8; $Ni(H_2oxime)^{2+}$, 55188-31-3; $Ni([14]aneN_4)^{2+}$, 68344-00-3; $Ni(Me_6[14]\text{-}4,11\text{-}dieneN_4)^{2+}$, 18444-42-3.

Supplementary Material Available: Plots of $k_0(K_{1h} + [H^+])$ vs. $[H^+]$ for the reduction of Mn(III) by OsL_3^{2+} complexes (supplementary Figure 1) and by Ni(II) macrocycles (supplementary Figure 2) and kinetic data for the oxidation of ML_3^{2+} complexes (Table SI) and Fe^{2+} (Table SII) by Mn(III) and for the reduction of Co(III) by Mn^{2+} (Table SIII) (5 pages). Ordering information is given on any current masthead page.

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Ligand Substitution Kinetics and Equilibria in the Systems Formed by Tetrabromoaurate(III) Anion and Heterocyclic Nitrogen Donors

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The kinetics of the forward and reverse reactions $[AuBr_4]^- + am = [AuBr_3(am)] + Br^-$ has been studied in 95/5 vol % methanol/water mixtures at 25.0 °C for am = pyridine and a variety of substituted pyridines. When there is methyl substitution on both the 2- and 6-positions, the low stability of the amine complexes precludes a study of the kinetics of their formation. However, they can be prepared and the kinetics of their decomposition are reported. The second-order rate constants for the forward and reverse reactions depend upon the amine basicity and take the form $\log k^f_2 = a(pK_a) + b$ and $\log k^r_2 = -a'(pK_a) + b'$, where a and a' are independent of the extent of ortho substitution in the ligand. In contrast to the case for the chloro analogues, the reactions in both directions are retarded by 2(6)-methyl substituents in the pyridine ring, manifested by a change in b and b'.

Introduction

During the past 20 years, ligand substitution processes at planar tetracoordinate d^8 gold(III) complexes have been studied, frequently with chloride as either leaving group or entering nucleophile, both in simple systems involving complexes of monodentate ligands and in those involving bi- or polydentate chelating molecules.[3] Apart from some cases where bromide ion has been used as nucleophile[4] and the solvolysis of $[AuBr_4]^-$ anion in water,[5] a relatively small amount of data is available for gold(III) systems involving bromide as ligand(s) or nucleophile.

When, many years ago, we studied[6,7] the kinetics of the processes of the type

$$[AuCl_4]^- + am \rightarrow [Au(am)Cl_3] + Cl^-$$

(where am is an heterocyclic nitrogen donor of the group of pyridine) the corresponding study of the $[AuBr_4]^-$ system seemed to be a trivial extension of the work and was not pursued. However, in the course of a routine examination of this system we found that the change in behavior, on changing from the chloro to the bromo system, was much more significant than we had anticipated and so the kinetics of the forward and reverse reactions, for the process

$$[AuBr_4]^- + am \rightleftarrows [Au(am)Br_3] + Br^-$$

in 95/5 vol % methanol/water at 25 °C, are reported in this paper.

Experimental Section

Materials. The various pyridines are all reagent grade products (Aldrich), which were distilled, when necessary, over KOH pellets. $HAuCl_4\cdot 3H_2O$, HBr, LiBr, and methanol were all reagent grade products (Engelhard and Hoechst).

$HAuBr_4\cdot 5H_2O$, Hydrogen Tetrabromoaurate(III) Pentahydrate. The compound was prepared by treating $HAuCl_4\cdot 3H_2O$ (3 g) dissolved in water (10 cm^3) with a large excess of HBr. After the color had changed from yellow to dark red, the solution was allowed to evaporate completely in the dark in a desiccator over NaOH. The dark red, very hygroscopic, crystalline product was obtained in virtually 100% yield; mp 80 °C dec.

$[AuBr_3(C_5H_5N)]$, Tribromo(pyridine)gold(III). In a typical preparation $HAuBr_4\cdot 5H_2O$ (0.2 g, 0.35 mmol) dissolved in water (10 cm^3) was first neutralized with the stoichiometric amount of $NaHCO_3$ and then treated with a slight excess of pyridine (0.03 g, 0.38 mmol) dissolved in methanol (5 cm^3), with stirring. After a few minutes, the red precipitate that formed was filtered off, washed with methanol and diethyl ether, and dried under a vacuum; yield 80%. The product can be crystallized from hot methanol.

The other complexes of the type $[AuBr_3(am)]$ were synthesized in the same way. The analytical data are summarized in Table I.

Kinetics. The kinetics were followed by measuring the absorbance changes of the reaction mixture with time by using a Varian-Cary 219

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[1] Università di Venezia.
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Table I. Analytical Data for the Complexes of the Type $[AuBr_3(am)]$

amine	empirical formula	anal. found (calcd) % C	% H	% N
2,4,6-trimethylpyridine	$AuBr_3C_8H_{11}N$	17.1 (17.21)	2.05 (1.99)	2.58 (2.51)
2,3,6-trimethylpyridine	$AuBr_3C_8H_{11}N$	18.0 (17.21)	2.00 (1.99)	2.43 (2.51)
2,6-dimethylpyridine	$AuBr_3C_7H_9N$	15.5 (15.45)	1.60 (1.67)	2.70 (2.58)
2,4-dimethylpyridine	$AuBr_3C_7H_9N$	15.2 (15.45)	1.70 (1.67)	2.64 (2.58)
2,3-dimethylpyridine	$AuBr_3C_7H_9N$	15.7 (15.45)	1.62 (1.67)	2.48 (2.58)
3,4-dimethylpyridine	$AuBr_3C_7H_9N$	15.7 (15.45)	1.65 (1.67)	2.49 (2.58)
3,5-dimethylpyridine	$AuBr_3C_7H_9N$	15.4 (15.45)	1.71 (1.67)	2.55 (2.58)
2-methylpyridine	$AuBr_3C_6H_7N$	13.4 (13.59)	1.30 (1.33)	2.78 (2.64)
4-methylpyridine	$AuBr_3C_6H_7N$	13.2 (13.59)	1.31 (1.33)	2.55 (2.64)
pyridine	$AuBr_3C_5H_5N$	11.8 (11.63)	1.01 (0.98)	2.68 (2.72)
3-chloropyridine	$AuBr_3ClC_5H_4N$	10.5 (10.91)	0.78 (0.73)	2.65 (2.55)
4-cyanopyridine	$AuBr_3C_6H_4N_2$	13.0 (13.32)	0.78 (0.75)	5.32 (5.18)

and/or a Perkin-Elmer Coleman 575 spectrophotometer. In each kinetic run the concentration of the entering nucleophile was large enough to provide pseudo-first-order conditions and the value of the observed rate constants k_{obsd} (reported in Tables II and III) were calculated as the slopes of the plots of log $(A_t - A_\infty)$ vs. time, where A_t and A_∞ are the absorbances of the reaction mixture at 392 nm, by a nonlinear regression program based on the Gauss–Newton algorithm with an HP 85 computer.

Results and Discussion

Fresh solutions of $H[AuBr_4]\cdot 5H_2O$ or $[AuBr_3(am)]$ in 95/5 vol % methanol/water closely follow Beer's law, but the absorption spectra, measured in the range 280–410 nm, change with time as a consequence of solvolysis. In order to avoid the presence of solvato species in the reaction mixture, the reactions involving $H[AuBr_4]$ or $[AuBr_3(am)]$ were started by adding a very small amount of the solid substrate, from a capillary tube, directly to the solution of the nucleophile in the thermostated spectrophotometer cell. The solid dissolves immediately upon shaking the mixture, and there is no interference with the kinetic runs. The concentration of the substrate in the reaction mixture, which could be calculated from the initial absorbance by knowing its extinction coefficient, was always less than 10^{-4} mol dm^{-3}, so that the nucleophile concentration was always large enough to provide pseudo-first-order conditions. Some reactions were started by adding a small, known amount (20 μL) of more concentrated solution of the substrate dissolved in CH_2Cl_2 to the solution of the nucleophile (3 cm^3) in the cell. This alternative technique leads to exactly the same results.

In the cases when bromide ion displaces the coordinated nitrogen donor, preliminary experiments carried out at low nucleophile concentration in the region 280–410 nm clearly indicate, through the development of well-defined isosbestic points around 360 nm (the exact wavelength depending on the nature of am), that a single reaction stage is involved. The final spectra show the characteristic maximum of $[AuBr_4]^-$ at 392 nm and are identical with those of a mixture of $[AuBr_4]^-$, excess Br^-, and am measured under the same experimental conditions. There is therefore no doubt that the processes followed do correspond to the displacement by bromide of the coordinated nitrogen donor.

In the reverse processes, i.e. when excess nitrogen donor is reacting with $[AuBr_4]^-$, the same isosbestic point develops and the spectral changes are exactly the reverse of the previous ones. However, at longer time, one can observe in some case a second reaction stage taking place, probably indicating further substitution. Fortunately this second stage is always too slow to interfere with the first one.

Reactions. $[AuBr_4]^- + am \rightarrow [AuBr_3(am)] + Br^-$. The experimental data reported in Table II show that in every case the system obeys the rate law $k_{obsd} = k^f_1 + k^f_2[am]$, which is usual for ligand substitutions at planar tetracoordinate complexes.[3] The values of the specific rate constants k^f_1 and k^f_2, obtained from an unweighted linear least-squares treatment of k_{obsd} vs. [am], are summarized in Table IV, together with the data for the corresponding reactions at $[AuCl_4]^-$, taken from the literature.[6] Data could not be obtained for nitrogen donors having $pK_a < 5$ or a large steric hindrance (i.e. with the group of 2,6-dimethylpyridines) since, in these cases, even in the presence of the large excess of nucleophile the amount of $[AuBr_3(am)]$ at equilibrium is small and the absorbance changes associated are too small to provide reliable rate constants.

Table II. First-Order Rate Constants, k_{obsd}, for the Reactions $[AuBr_4]^- + am \rightarrow [AuBr_3(am)] + Br^-$ in 95/5 vol % $MeOH/H_2O$ and at 25 °C[a]

am	10^3[am], mol dm^{-3}	k_{obsd}, s^{-1}
pyridine	1.42	23 ± 1
	4.27	46 ± 1
	5.34	54 ± 1
	7.11	68.4 ± 0.6
	10.7	96 ± 2
	14.2	125 ± 5
3-methylpyridine	1.14	26.7 ± 0.2
	2.29	39.2 ± 0.4
	4.29	58.8 ± 0.9
	5.72	72 ± 1
	11.4	127 ± 3
4-methylpyridine	1	19.3 ± 0.5
	1.99	27.8 ± 0.5
	3.73	48.6 ± 0.8
	4.98	62 ± 1
	7.46	91 ± 1
	9.95	121 ± 4
	14.9	177 ± 6
3,5-dimethylpyridine	1.39	24.4 ± 0.5
	2.78	38.7 ± 0.3
	4.18	55.6 ± 0.5
	5.23	69 ± 1
	6.97	90.5 ± 0.6
	13.9	184 ± 5
3,4-dimethylpyridine	1.15	21.3 ± 0.2
	3.46	51.2 ± 0.7
	4.32	65.3 ± 0.8
	5.76	85 ± 3
	11.5	164 ± 2
2-methylpyridine	3.16	8.23 ± 0.06
	6.32	12.05 ± 0.06
	15.5	23.8 ± 0.1
	31.6	44.1 ± 0.5
	79	102 ± 1
	158	202 ± 2
2,3-dimethylpyridine	13.8	40.3 ± 0.2
	27.6	62.6 ± 0.4
	41.5	83.9 ± 0.4
	55.3	107 ± 1
	111	191 ± 3
2,4-dimethylpyridine	9.61	22.8 ± 0.5
	16.0	33.1 ± 0.8
	32.0	65.3 ± 0.4
	72.1	136 ± 1
	96.1	180 ± 3

[a] Substrate concentration always less than 10^{-4} mol dm^{-3}.

As is usual for these processes,[8] the second-order rate constants k_2 refer to the direct bimolecular displacement of a coordinated bromide by the entering nucleophile, whereas the first-order rate

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(8) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed., Wiley: New York, 1966.

Table III. First-Order Rate Constants, k_{obsd}, for the Reactions $[AuBr_3(am)] + Br^- \rightarrow [AuBr_4]^- + am$ in 95/5 vol % $MeOH/H_2O$ and at 25 °C[a]

am	$10^4[Br^-]$, mol dm^{-3}	10^3k_{obsd}, s^{-1}
pyridine	2	33.2 ± 0.7
	5	50.2 ± 0.7
	8	68.6 ± 0.8
	10	78.8 ± 0.6
	20	139 ± 1
4-methylpyridine	5	25.3 ± 0.2
	10	43.4 ± 0.2
	16	58.8 ± 0.8
	30	103 ± 1
	50	167 ± 2
	80	269 ± 6
3-methylpyridine	2	24.5 ± 0.8
	5	33.8 ± 0.8
	8	41 ± 1
	10	48.0 ± 0.4
	20	76.3 ± 0.6
35-dimethylpyridine	5	19.8 ± 0.3
	8	26.9 ± 0.4
	10	31.6 ± 0.4
	20	52 ± 1
	50	106 ± 2
	100	205 ± 3
3,4-dimethylpyridine	5	16.6 ± 0.2
	8	22.3 ± 0.2
	10	25.3 ± 0.3
	20	40.0 ± 0.3
	100	188 ± 2
2-methylpyridine	10	16.9 ± 0.3
	20	25.8 ± 0.3
	50	54.4 ± 0.7
	80	78 ± 2
	100	96.3 ± 0.4
2,3-dimethylpyridine	10	9.8 ± 0.1
	20	17.3 ± 0.2
	50	35.5 ± 0.4
	80	52.7 ± 0.4
	100	67.9 ± 0.6
	20	136 ± 1
2,4-dimethylpyridine	1	7.3 ± 0.1
	2	12.7 ± 0.1
	8	42.5 ± 0.1
	10	52.1 ± 0.5
	20	103 ± 1
	40	203 ± 5
2,6-dimethylpyridine	5.36	2.50 ± 0.04
	10.1	3.4 ± 0.1
	20.1	5.08 ± 0.09
	40.3	9.2 ± 0.1
	80	17.3 ± 0.1
	101	21.8 ± 0.8
2,3,6-trimethylpyridine	5	1.60 ± 0.03
	10	2.49 ± 0.05
	20	3.99 ± 0.02
	50	8.37 ± 0.06
	100	16.0 ± 0.3
2,4.6-trimethylpyridine	7.5	1.37 ± 0.05
	10	1.60 ± 0.01
	25	3.7 ± 0.1
	50	6.7 ± 0.2
	100	13.2 ± 0.1

[a] Substrate concentration always less than 10^{-4} mol dm^{-3}.

Table IV. Specific Rate Constants, k_1 and k_2, for the Reactions $[AuBr_4]^- + am \rightarrow [Au(am)Br_3] + Br^-$ in 95/5 vol % $MeOH/H_2O$ and at 25 °C[a]

am	pK_a	10^3k_1, s^{-1}	k_2, mol^{-1} dm^3 s^{-1}
2,4-dimethylpyridine	6.99	5 ± 1	1.82 ± 0.05 (0.325)
2,3-dimethylpyridine	6.57	19.4 ± 0.6	1.55 ± 0.05
2-methylpyridine	6.10	4.0 ± 0.4	1.25 ± 0.01 (0.227)
3,4-dimethylpyridine	6.44	5.8 ± 0.7	13.7 ± 0.1 (2.9)
3,5-dimethylpyridine	6.34	3 ± 2	12.9 ± 0.2 (2.5)
3-methylpyridine	5.68	16.4 ± 0.5	9.73 ± 0.08 (2.0)
4-methylpyridine	6.02	5.6 ± 0.7	11.3 ± 0.1 (2.1)
pyridine	5.17	11.7 ± 0.4	7.94 ± 0.05 (1.6)

[a] Values for the corresponding chloro systems[6] in methanol are given in parentheses.

constants k_1 can be attributed to the rate-determining solvolytic reaction

$$[AuBr_4]^- + S \xrightarrow{k^f_1} [AuBr_3(S)] + Br^-$$

(S being a solvent molecule), which is followed by the fast displacement of S by the nitrogen donor

$$[AuBr_3(S)] + am \rightarrow [AuBr_3(am)] + S$$

The k^f_1 rate constants ought to be independent of the nature of the nucleophile. The relatively large scatter of the k^f_1 values in Table IV is probably due to the fact that they are measured as intercepts in the plots of k_{obsd} vs. [am] and are then affected by large experimental errors since they only contribute significantly to k_{obsd} at the lowest of the nucleophile concentrations used. If we omit the two anomalous high values and take the average value of the rest, $k^f_1 = 5 \times 10^{-3}$ s^{-1}; this is greater than the value of $k^f_1 = 5 \times 10^{-4}$ s^{-1} obtained under the same experimental conditions for the solvolytic contribution to the rate law in the substitution reactions of $[AuCl_4]^-$.[9] The greater lability of the bromo complex as compared to that of the chloro complex is obviously due to a combination of the kinetic trans + cis effects and lability of bromide as compared to that of chloride.

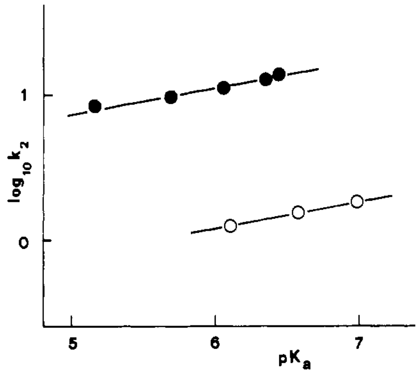

Figure 1. Plot of log k_2 vs. pK_a for the reactions of displacement of one bromide from $[AuBr_4]^-$ by heterocyclic nitrogen donors: (○) unhindered pyridines; (●) 2-methylpyridines.

A plot of log k_2 vs. the basicity of the entering nucleophile (Figure 1) (measured as usual as the pK_a of the conjugate acid amH^+ in water at 25 °C) reveals that the nitrogen donors can be divided into two groups, the first formed by pyridines with no ortho substituents and the second by 2-methylpyridines. Both groups obey a linear free energy relationship of type

$$\log k_2 = a(pK_a) + b \tag{1}$$

with the same value of a, 0.183 ± 0.004, and the steric retardation factor $(b_1 - b_2)$ is 0.97 ± 0.06.

These data allow a proper comparison between the kinetic behaviors of $[AuBr_4]^-$ and $[AuCl_4]^-$. The greater reactivity of $[AuBr_4]^-$, observed in the solvolytic reaction, is maintained in the reactions with the heterocyclic bases, and it is of great interest to note that the ratio of the values of k_2 for a particular base remain within the range 4.7–5.6 without any apparent systematic variation. Thus the change from $[AuCl_4]^-$ to $[AuBr_4]^-$ does not lead to any significant change in the nucleophilic discriminating ability or in the steric retardation factor.

$[AuBr_3(am)] + Br^- \rightarrow [AuBr_4]^- + am$. The values of k_{obsd} reported in Table III indicate that the systems obey the usual relationship $k_{obsd} = k^r_1 + k^r_2[Br^-]$. The values of the specific rate constants k^r_1 and k^r_2 are summarized in Table V, together with the data for the corresponding $[AuCl_3(am)]$ and *trans*-$[Au(CN)_2Cl(am)]$ complexes in their reactions with bromide, taken

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[9] Canovese, L.; Cattalini, L.; Marangoni, G.; Tobe, M. L. *J. Chem. Soc. Dalton Trans.*, in press.

Table V. Specific Rate Constants, k_1 and k_2, for the Reactions $[Au(am)Br_3] + Br^- \rightarrow [AuBr_4]^- + am$ in 95/5 vol % $MeOH/H_2O$ and at 25 °C[a]

am	pK_a	10^4k_1, s^{-1}	k_2, $mol^{-1}\ dm^3\ s^{-1}$
2,4,6-trimethylpyridine	7.48	3.3 ± 0.3	0.129 ± 0.001 (*11*)
2,3,6-trimethylpyridine	7.25	9.4 ± 0.5	0.151 ± 0.001
2,6-dimethylpyridine	6.75	11 ± 1	0.203 ± 0.003 (3.5, *5.4*)
2,4-dimethylpyridine	6.99	24 ± 4	5.02 ± 0.02 (2.48 *3.9*)
2,3-dimethylpyridine	6.57	20 ± 1	6.6 ± 0.1
2-methylpyridine	6.1	90 ± 10	8.8 ± 0.1
3,4-dimethylpyridine	6.44	60 ± 10	18.1 ± 0.2
3,5-dimethylpyridine	6.34	125 ± 6	19.3 ± 1 (*6.5*)
3-methylpyridine	5.68	187 ± 3	28.8 ± 0.2 (7.2, *7.2*)
4-methylpyridine	6.02	100 ± 10	31.2 ± 0.3 (5.7)
pyridine	5.17	200 ± 8	59.6 ± 0.4 (13.4, *37*)

[a] Data for the corresponding chloro systems $[Au(am)Cl_3]$ and (in italics) *trans*-$[AunCN)_2Cl(am)]$ in their reactions with bromide ion[7] in methanol are given in parentheses.

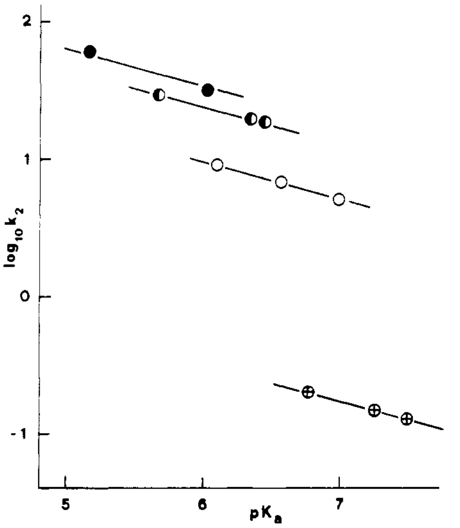

Figure 2. Plot of log k_2 vs. pK_a for the reactions of displacement of the coordinated heterocyclic nitrogen donor from $[AuBr_3(am)]$ by bromide ion: (○) unhindered pyridines; (◑) 3-methylpyridines; (●) 2-methylpyridines; (⊗) 2,6-dimethylpyridines.

from the literature.[7] These studies can be extended to the displacement of 2,6-dimethylpyridines even though the study of their formation in 95/5 vol % $MeOH/H_2O$ is prevented by the unfavorable position of equilibrium. This is due to the fact that the neutral species $[AuBr_3(am)]$can be easily obtained from water, in which they are virtually insoluble, and it is this low solubility compared to that of $HAuBr_4$ that tips the balance under preparative conditions.

It is in this reaction that the main and somewhat unexpected difference between the chloro and bromo systems is found. Both the $k^r{}_1$ and $k^r{}_2$ rate constants are significantly affected by steric hindrance, an effect not observed in the reactions of the corresponding trichloro or *trans*-dicyano–chloro species. The difference between second-order rate constants for the reaction of the chloro and bromo substrates is most dramatic.

In the reactions of displacement of the nitrogen donor from $[AuCl_3(am)]$ by bromide ion in methanol the second-order rate constants k_2 are roughly related to the basicity of the leaving group, but there was no systematic effect that can be attributed to steric hindrance from methyl substituents in the 2- and 6-positions, and it was suggested that the steric effects did not change on going from the ground state to the transition state.[6,7]

Table VI. Equilibrium Constants for the Processes $[AuX_4]^- + am \rightleftarrows [Au(am)X_3] + X^-$ in 95/5 vol % $MeOH/H_2O$ and at 25 °C

am	pK_a	*K*	
		X = Cl[a]	X = Br
pyridine	5.17	3.84	0.133 ± 0.002
3-methylpyridine	5.68	10.2	0.338 ± 0.004
4-methylpyridine	6.02	21.9	0.370 ± 0.004
3,5-dimethylpyridine	6.34	27.8	0.671 ± 0.01
3,4-dimethylpyridine	6.44		0.76 ± 0.01
2-methylpyridine	6.10	2.39	0.133 ± 0.002
2,3-dimethylpyridine	6.57		0.234 ± 0.004
2,4-dimethylpyridine	6.99	12.6	0.362 ± 0.005
2,6-dimethylpyridine	6.75	0.77	
2,4,6-trimethylpyridine	7.48	3.80	

[a] Data from ref 6 in methanol.

In the present case, the plot of log k_2 vs. the basicity of the leaving groups (Figure 2) shows that steric hindrance is of overwhelming importance. Four parallel lines can be identified, each one referring to an expression

$$\log k_2 = -a'(\mathrm{p}K_a) + b' \qquad (2)$$

with the same value of $a' = 0.27$ and with different b'values. The most reactive systems are those where pyridine and 4-methylpyridine are displaced, $b'_1 = 3.16$. A small steric retardation can be observed for pyridines having methyl group(s) in the 3- and/or 5-positions of the ring ($b'_2 = 3.01$, $b'_1 - b'_2 = 0.15$). This steric effect is typical of very crowded systems and has been observed in reactions at palladium(II)[10] and platinum(II) substrates.[11] A relatively large retardation is given by pyridines having a single 2(6)-methyl group in a position ($b'_3 = 2.62$, $b'_1 - b'_3 = 0.54$), and a very large retardation is observed in cases where methyl groups occupy the 2- and 6-positions.

In a comparison of the reactivities of $[AuCl_3(am)]$, *trans*-$[Au(CN)_2Cl(am)]$, and $[AuBr_3(am)]$ with respect to the displacement of am by Br^-, it should be pointed out that the previous studies were made in dry methanol. However, if one ignores this small difference in solvent composition, the data in Table V show that the unhindered bromo complexes are some 4 times more labile than their chloro equivalents (which matches the reactions of $[AuX_4]^-$ with pyridines), the 2(6)-monosubstituted species are more reactive by a factor of 2, and the 2,6-disubstituted species are less reactive by a factor of nearly 20. The *trans*-$[Au(CN)_2Cl(am)]$ complexes are some 1.5–2 times more labile than those of $[AuCl_3(am)]$ and show no systematic variation with steric hindrance either. The major difference between the rate constants for the reactions

$$[AuCl_3(am)] + Cl^- \rightarrow [AuCl_4]^- + am$$

$$[AuBr_3(am)] + Br^- \rightarrow [AuBr_4]^- + am$$

when am is an unhindered pyridine is due to the nucleophilicity of Cl^- and Br^-.

In the systems

$$[AuBr_4]^- + am \rightleftarrows [AuBr_3(am)] + Br^-$$

the ratios between the second-order rate constants for the forward and reverse reactions give the values of the equilibrium constants, *K*, which are reported in Table VI, together with the values for the corresponding chloro systems. The plot of log *K* vs. the basicity of the various nitrogen donors gives obviously again a group of parallel lines, which obey the relationship

$$\log K = A(\mathrm{p}K_a) + B$$

with $A = 0.455$ and different values of *B*, depending upon steric hindrance.

In the case of the chloro systems the values of the equilibrium constants, with the exception of that for 2,6-dimethylpyridine ($K = 0.77$), are always larger than 1, the most thermodynamically stable neutral complex being that containing the most basic and less hindered nitrogen donor (3,5-dimethylpyridine, $K = 27.8$).

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In the case of the bromo systems the values of the equilibrium constants are always smaller than 1 and also decreases with decreasing ligand basicity and increasing bulkiness. The 3-methyl-substituted pyridine complexes are marginally more stable than the 4-substituted complexes because the minor retardation seen in their displacement is not found in their formation. This fact explains why the reactions of the 2,6-dimethylpyridines and of the nucleophiles having $pK_a < 5$ with $[AuBr_4]^-$ could not be kinetically studied under our experimental conditions.

The larger stability of the chloro systems as compared to that of the bromo is mainly due to the fact that the affinity of Au(III) for pyridines lies between that for chloride and bromide and the variation of the other ligands in the complex has a minor effect, except insofar as the response to ligand bulkiness is affected.

Conclusions. As was pointed out when the study was first made, the lack of steric hindrance effects in the displacement of am from $[AuCl_3(am)]$ by chloride (and other nucleophiles) indicates that the steric hindrance in the rate-determining transition state is not significantly greater than that in the final product, and it was suggested that the Au–N bond was fully developed in the rate-determining transition state and that the main source of repulsion was between the 2(6)-methyl groups and the *cis* ligands (which become axial in the transition state). The observation of strong steric effects in the reactions of $[AuBr_3(am)]$ with Br^- (albeit less marked than in those of the reverse reactions) tells us that the transition state is more crowded than both the reagents ground state and the products state. In order to avoid the paradoxical conclusion that there is less steric repulsion in $[AuBr_3(am)]$ than in $[AuCl_3(am)]$, we conclude that the 2(6)-methyl groups can no longer lie in the plane of the former complexes and therefore interfere with the two bromides in the trigonal plane of the transition state. A number of studies to examine this question in detail have suggested themselves, and these are now in progress.

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Registry No. $[AuBr_3$(2,4,6-trimethylpyridine)], 97374-28-2; $[AuBr_3$(2,3,6-trimethylpyridine)], 97374-29-3; $[AuBr_3$(2,6-dimethylpyridine)], 21113-12-2; $[AuBr_3$(2,4-dimethylpyridine)], 21113-14-4; $[AuBr_3$(2,3-dimethylpyridine)], 97374-30-6; [AuBr(3,4-dimethylpyridine)], 97374-31-7; $[AuBr_3$(3,5-dimethylpyridine)], 21113-13-3; $[AuBr_3$(2-methylpyridine)], 21113-09-7; $[AuBr_3$(4-methylpyridine)], 21113-11-1; $[AuBr_3$(pyridine)], 21524-04-9; $[AuBr_3$(3-chloropyridine)], 97374-32-8; $[AuBr_3$(4-cyanopyridine)], 21113-16-6; $[AuBr_4]^-$, 14337-14-5; $HAuBr_4$, 17083-68-0; pyridine, 110-86-1; 3-methylpyridine, 108-99-6; 4-methylpyridine, 108-89-4; 3,5-dimethylpyridine, 591-22-0; 3,4-dimethylpyridine, 583-58-4; 2-methylpyridine, 109-06-8; 2,3-dimethylpyridine, 583-61-9; 2,4-dimethylpyridine, 108-47-4; 2,6-dimethylpyridine, 108-48-5; 2,3,6-trimethylpyridine, 1462-84-6; 2,4,6-trimethylpyridine, 108-75-8; bromine, 7726-95-6.

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Phosphine-Ligated Copper(I) Derivatives of Dicarbahexaborane(8) and 2,3-Dimethyldicarbahexaborane(8)

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The reactions of $K[R_2C_2B_4H_5]$, where $R_2 = (H)_2$ or $(CH_3)_2$, with $[(C_6H_5)_3P]_2CuBr\cdot{}^1/_2C_6H_6$ or $[(C_6H_5)_2PCH_2]_2CuI$ afford respectively $[(C_6H_5)_3P]_2CuC_2B_4H_7$ (I), $[(C_6H_5)_3P]_2Cu(CH_3)_2C_2B_4H_5$ (II), $[(C_6H_5)_2PCH_2]_2CuC_2B_4H_7\cdot CH_2Cl_2$ (III), and $[(C_6H_5)_2PCH_2]_2Cu(CH_3)_2C_2B_4H_5\cdot{}^1/_2CH_2Cl_2$ (IV). The species were characterized by boron-11 and proton NMR spectroscopies. Complexes I–IV exist as the nido-pentagonal-pyramidal cupriocarboranes in which the phosphine-ligated copper(I) electrophile has replaced a bridging proton in the parent carborane and thus occupies a bridging position between two basal boron atoms. Infrared spectral data may be interpreted to suggest the presence of copper–hydrogen–boron bridge bonds between the copper atom and the adjacent terminal hydrogens on basal boron atoms. Studies of the solution properties of the complexes I–IV in CD_2Cl_2 by ^{31}P NMR spectroscopy indicate that extensive phosphine ligand-exchange processes occur at temperatures down to −100 °C.

Introduction

The Brønsted acidity of bridging hydrogen atoms in boron hydrides[1,2] and the related carboranes[3,4] is now well established. The resulting conjugate bases each possess at least one boron–boron bond that is susceptible to insertion of Lewis acids.[5] The Lewis acids range from simple species such as H^+ and BH_3[6,7] through more complex main-group[5,8] and transition-metal moieties.[1,9]

Since the first transition-metal–borane complex, $[(C_6H_5)_3P]_2CuB_5H_8$, was prepared from B_5H_9,[10] many systems involving the insertion of transition-metal moieties into a basal boron–boron bond of the square-pyramidal *nido*-borane have been reported. Examples for the related nido-pentagonal-pyramidal species are not so well-known. The metalloboranes $[(C_6H_5)_3P]_2CuB_6H_9$,[10a] prepared from the $[B_6H_9]^-$ anion, and $[(C_6H_5)_3P]_2CuB_5H_8Fe(CO)_3$,[11] prepared from the $[B_5H_8Fe(CO)_3]^-$ ion, have been reported. For both species, infrared spectra[10a,11,12] suggest the presence of a copper–hydrogen–boron bridge bond and, in the case of the latter, the presence of this bridge bond is indicated by the crystal structure. The carborane anion $[C_2B_4H_7]^-$, which is isostructural and isoelectronic with $[B_6H_9]^-$ and $[B_5H_8Fe(CO)_3]^-$ in terms of the polyhedral skeletal electron pair theory,[13] forms

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