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A Kinetic Study of the Reactivity of 2,2'-Bipyridyl wiht a Series of Neutral Rhodium(I) Amine Complexes of the Formula Chlorocycloocta-1,5-diene Amine Rhodium(I)

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The rates of solvolysis and of nucleophilic displacement by 2,2'-bipyridyl have been determined for a series of compounds of the type chlorocycloocta-1,5-diene amine rhodium(I). A linear relationship is observed between the logarithm of both k_s, the rate constant for solvolysis, and k_y, the rate of nucleophilic displacement of the monodentate amine by 2,2'-bipyridyl, and the basicity of the monodentate leaving amine.

Introduction

In recent years the investigation of the kinetics of substitution in square-planar d^8 complexes has been dominated by an attempt to correlate the nucleophilicity (in the case of general ligands) or basicity (in the case of amines) to the rates of reactions. In the former case a large amount of work has been done with Pt^{II}[1] complexes, achieving a great degree of success where it has been found that a good correlation does exist using different Pt^{II} substrates. However, this approach has produced disappointing results in the case of Au^{III} systems. This marked difference between Pt^{II} and Au^{III} has been ascribed to the fact that for gold substrates the activation step is strongly dependent upon the nature of the substrate,[2] essentially forcing the adoption of the view that each system is unique in its behaviour and can only be treated as such.

Systematic studies on the reactivity of amines towards square-planar substrates of Pt^{II},[3] Pd^{II},[4] and Au^{III}[5] have been done and have allowed a comparison to be made between the various metal complex systems. However, little work has been done on two of the remaining members of the d^8 systems of the platinum metals, Rh^I and Ir^I, with regard to a systematic study of the effect of the basicity of amines on their reactivity. Cattalini *et al.*[6] studied the reaction of (COD)RhCl(SbR_3) (where COD represents cycloocta-1,5-diene) with various amines. In their study, the accumulation of a five coordinate intermediate was detected which led to a rate which was non-functional with respect to the concentration of the incoming amine but which was dependent on its nature.

We[7] have recently reported the reaction of (COD)-RhCl(Piperidine) with 2,2'-bipyridyl in methanol and have subsequently extended this study to cover a range of leaving amines. The results obtained form the basis of this report.

Experimental Section

Materials. The diolefinic amine complexes were prepared according to the method of Chatt[8] by treating $[CODRhCl]_2$ in CH_2Cl_2 with calculated amounts of the amine. The product of all the kinetic runs, namely the $[CODRh(Bipy)]^+$ moiety was prepared as the hexafluorophosphate salt by the method of Cocevar[9] *et al.* All species were fully characterised and microanalysed, and the results are shown in Table I.

All other chemicals used were A.R. grade and the amines were purified by distillation over KOH.

Kinetic Experiments. The complex and bipyridyl solutions were thermostated in a constant temperature water-bath for a sufficiently long time to allow the solvolysis equilibrium to be established in the complex containing solution. A measured aliquot of the complex solution was transferred to a cell housed in a constant temperature cell holder fitted to a Cary 15 spectrophotometer. Working at a wavelength of 480 mμ, the absorption λ_{max} of the product $[COD\text{-}Rh(Bipy)]^+$, a measured amount of bipyridyl solution was injected into the rhodium solution. An excess of bipyridyl was used in order to achieve pseudo-first-order conditions. A trace of the change in optical density with time was monitored until no further change in optical density occurred whereupon the results were graphically analysed from plots of ℓn (OD_t-

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Table I. Microanalytical data for the complexes.

Amine	Complex Formulae		Micronalytical results			
Piperidine:	$C_{13}H_{23}NRhCl$	Required:	C: 47.06;	H: 7.00;	N: 4.22;	Cl: 10.71
		Found:	C: 46.52;	H: 6.94;	N: 4.33;	Cl: 10.80
Cyclohexamine:	$C_{14}H_{25}NRhCl$	Required:	C: 48.62;	H: 7.30;	N: 4.05;	Cl: 10.82
		Found:	C: 48.58;	M: 7.44;	N: 4.18;	Cl: 10.24
Ammonia:	$C_8H_{15}NRhCl$	Required:	C: 36.50;	H: 5.75;	N: 5.32;	Cl: 13.48
		Found:	C: 36.30;	H: 5.48;	N: 4.91;	Cl: 13.52
Morpholine:	$C_{12}H_{21}NORhCl$	Required	C: 42.85;	H: 6.27;	N: 4.15;	Cl: 10.54
		Found:	C: 42.91;	H: 6.22;	N: 4.22;	Cl: 10.96
n-Propylamine:	$C_{11}H_{21}NRhCl$	Required:	C: 43.26;	H: 6.92;	N: 4.59;	Cl: 11.61
		Found:	C: 42.93;	H: 6.61;	N: 4.26;	Cl: 11.66
Iso-Propylamine:	$C_{11}H_{21}NRhCl$	Required:	C: 43.26;	H: 6.92;	N: 4.59;	Cl: 11.61
		Found:	C: 43.17;	H: 6.86;	N: 4.18,	Cl: 11.82
di-N-butylamine:	$C_{16}H_{31}NRhCl$	Required:	C: 51.14;	H: 8.32;	N: 3.73;	Cl: 9.44
		Found:	C: 51.25;	H: 8.26;	N: 3.63;	Cl: 9.43
2,2′-Bipyridyl·	$C_{18}H_{20}N_2RhPF_6$	Required:	C: 42.20;	H: 3.93;	N: 5.47	
		Found:	C: 42.41;	H: 4.04;	N: 5.31	

$OD_{\infty})^{10}$ *vs.* time. The final spectrum was measured and compared to the spectrum obtained using pure [CODRh(Bipy)]PF_6.

Results

Table II shows the k_{obs} values obtained at different bipyridyl concentrations and temperatures. These data are consistent with a two-term rate law of the form:

$$k_{obs} = k_s + k_y[\mathrm{Bipy}] \qquad (1)$$

The slope of the plot of k_{obs} *vs.* bipyridyl concentration gives a value for k_y, whilst the intercept gives a value for k_s.

Table II. Data for the reaction CODRhCl(Am)+N N→ at different bipyridyl concentrations and temperatures. Complex Concentration < $10^{-3}M$

Temperature (°C)	[Bipy] (*M*)	10^2k_{obs}(sec^{-1})
CODRhCl(Cyclohexamine):		
21.0	0.0089	4.4
	0.0163	6.7
	0.0184	7.7
	0.0226	8.9
	0.0280	10.7
	0.0337	12.8
	0.0449	17.0
	0.0467	17.3
	0.0576	21.0
	0.0606	22.3
	0.0673	25.2
	0.0842	29.7
11.0	0.0089	3.00
	0.0163	4.3
	0.0184	5.5
	0.0226	5.4
	0.0280	6.6
	0.0337	8.3
	0.0449	10.4
	0.0467	10.7
	0.0576	12.7
	0.0606	12.9
	0.0673	14.1
	0.0842	18.3
5.1	0.0089	2.2
	0.0163	3.3
	0.0184	3.8
	0.0226	4.2
	0.0280	5.0
	0.0326	5.9
	0.0337	5.8
	0.0467	7.7
	0.0576	9.4
	0.0606	10.0
	0.0673	10.9
	0.0842	13.5
CODRhCl(n-propylamine):		
20.5	0.0092	5.1
	0.0168	7.7
	0.0234	9.6
	0.0288	11.5
	0.0337	13.3
	0.0428	16.3
	0.0494	18.3
	0.0612	22.1
	0.0714	25.3
	0.0780	27.5
14.5	0.0092	3.67
	0.0168	5.6
	0.0234	7.2
	0.0288	8.4
	0.0337	10.1
	0.0428	12.7
	0.0494	14.1
	0.0612	17.0
	0.0714	19.9
	0.0780	21.6
6.1	0.0092	2.5
	0.0168	3.67
	0.0234	5.0
	0.0288	5.9
	0.0337	6.8
	0.0428	8.1
	0.0494	9.6
	0.0612	11.5
	0.0714	13.4
	0.0780	14.5
CODRhCl(Morpholine):		
20.0	0.0091	10.2
	0.0167	13.6
	0.0189	14.0
	0.0231	16.1
	0.0286	19.0
	0.0334	21.0
	0.0356	22.0

Table II. (Continued)

	0.0491	28.0
	0.0609	34.1
	0.0710	38.2
17.0	0.0091	8.9
	0.0167	10.8
	0.0189	12.0
	0.0231	13.7
	0.0286	15.2
	0.0334	17.7
	0.0356	18.3
	0.0474	22.0
	0.0491	22.7
	0.0609	26.7
10.8	0.0091	4.1
	0.0167	5.5
	0.0189	6.7
	0.0231	7.3
	0.0286	8.8
	0.0334	9.9
	0.0356	10.6
	0.0474	13.6
	0.0491	14.8
	0.0609	16.7
	0.0639	17.8
	0.0710	19.3
	0.0879	24.0
5.6	0.0091	2.3
	0.0167	3.7
	0.0189	4.4
	0.0231	4.8
	0.0286	5.6
	0.0334	6.7
	0.0356	7.3
	0.0474	9.0
	0.0491	9.7
	0.0609	11.8
	0.0639	12.6
	0.0710	13.3
	0.0879	17.2
CODRhCl(Ammonia):		
15.2	0.0091	6.5
	0.0167	8.3
	0.0231	10.2
	0.0286	12.0
	0.0334	13.1
	0.0491	18.0
	0.0639	22.2
	0.0710	24.2
	0.0879	29.3
9.2	0.0091	5.7
	0.0167	6.1
	0.0194	6.7
	0.0231	7.1
	0.0286	8.3
	0.0334	9.5
	0.0356	10.0
	0.0474	12.0
	0.0491	12.6
	0.0609	15.3
	0.0710	17.2
	0.0879	21.6
4.0	0.0091	3.0
	0.0167	4.1
	0.0194	5.0
	0.0231	4.9
	0.0286	5.7
	0.0334	6.4
	0.0356	6.7
	0.0491	8.8
	0.0609	10.5
	0.0639	10.9
	0.0710	12.1
	0.0879	14.4
CODRhCl(iso-Propylamine):		
20.5	0.0092	4.6
	0.0168	5.9
	0.0234	8.1
	0.0288	9.9
	0.0337	11.3
	0.0428	14.0
	0.0494	17.0
	0.0612	19.8
	0.0714	22.2
	0.0780	25.5
	0.0892	28.2
14.5	0.0092	3.0
	0.0168	4.8
	0.0234	6.1
	0.0288	7.5
	0.0337	8.8
	0.0428	10.8
	0.0494	12.7
	0.0612	15.2
	0.0714	18.1
	0.0780	19.4
6.4	0.0092	2.1
	0.0168	3.1
	0.0234	4.3
	0.0288	5.0
	0.0337	5.8
	0.0428	7.4
	0.0494	8.6
	0.0612	10.4
	0.0714	11.8
	0.0780	13.0
CODRhCl(di-n-Butylamine):		
20.0	0.0144	5.9
	0.0189	7.7
	0.0223	8.7
	0.0251	9.1
	0.0289	10.8
	0.0380	13.3
	0.0449	15.8
	0.0506	17.4
	0.0523	18.3
	0.0577	20.5
	0.0686	22.5
	0.0756	26.9
	0.0813	26.5
	0.0895	30.2
	0.0915	30.4
14.1	0.0092	3.0
	0.0168	4.8
	0.0234	6.5
	0.0288	7.8
	0.0337	8.8
	0.0428	10.5
	0.0494	12.8
	0.0612	15.4
	0.0714	18.0
	0.0780	19.3
6.1	0.0092	1.7
	0.0168	3.4
	0.0234	4.4
	0.0288	5.4
	0.0337	5.9
	0.0428	7.7
	0.0494	8.7
	0.0612	10.8
	0.0714	12.5
	0.0780	13.6

Table III shows the values of k_s and k_y obtained at different temperatures from which the activation parameters were calculated.

In Table IV, the activation parameters, k_s and k_y values at 25°C together with the pK_a (in water) of the leaving amine are compiled.

Table III. Values of k_s and k_y obtained for the reaction CODRhCl(Am)+$\widehat{N\ N}$→at different temperatures.

Leaving Amine	Temperature	$k_y(M^{-1}sec^{-1})$	$10^2k_s(sec^{-1})$
Cyclohexamine	21.0	3.35	1.58
	11.0	2.02	1.0
	5.1	1.48	0.9
n-propylamine	20.5	3.23	2.2
	14.5	2.61	1.1
	6.1	1.75	0.83
Morpholine	20.0	4.50	6.0
	17.0	3.48	5.6
	10.8	2.51	1.67
	5.6	1.57	1.0
Ammonia	15.2	2.96	3.34
	9.2	2.14	2.34
	4.0	1.47	1.6
Iso-propylamine	20.5	3.00	1.33
	14.5	2.40	0.83
	6.4	1.59	0.63
di-n-butylamine	20.0	3.22	1.3
	14.1	2.37	0.83
	6.1	1.65	0.58

Table IV.

Amine	k_y25°C$(M^{-1}sec^{-1})$	k_s25°C(sec^{-1})	ΔFk_y^*	ΔFk_s^*	ΔHk_y^*	ΔHk_s^*	ΔSk_y^*	ΔSk_s^*	pK_a[a]
Piperidine[e]	3.71	1.76×10^{-2}	16.69	19.82	6.69	11.41	—35.5	—28.2	11.12
Cyclohexamine	4.07	1.81×10^{-2}	16.60	19.81	7.92	7.01	—29.1	—42.8	10.64
Ammonia	5.32	6.31×10^{-2}	16.45	19.10	9.41	9.99	—24.4	—31.6	9.25
Morpholine[f]	6.07	$9.8\ \times10^{-2}$	16.40	18.82	10.51	19.00	—19.8	+ 0.6	8.40
n-Propylamine	3.89	$2.2\ \times10^{-2}$	16.68	19.71	6.31	8.61	—34.7	—37.2	10.6[b]
Iso-Propylamine	3.66	1.63×10^{-2}	16.71	19.69	6.65	8.20	—33.7	—38.5	10.6[c]
di-n-Butylamine	4.02	1.71×10^{-2}	16.61	19.86	7.35	8.95	—31.0	—36.6	11.0[d]

[a] pK_a of the conjugate acid in water. [b] pK_a value taken to be the same as n-butylamine. [c] pK_aobtained from reference (18). [d] pK_a value taken to be the same as for diethylamine. [e] Results from reference (7). [f] No attempt has been made to rationalise the differences in activation parameters because this represents the upper limit of our technique.

Discussion

In all cases there was an initial fast reaction which could not be measured using conventional techniques. It was suggested earlier[7] that this fast reaction was the attack by 2,2′-bipyridyl on the solvolysed species, (COD)RhCl(Solvent)ie as depicted by k_f in the scheme shown in Figure 1 below.

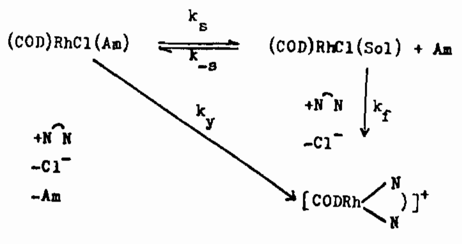

Figure 1.

where COD represents cycloocta-1,5-diene, Am represents monodentate amine, and $\widehat{N\ N}$ represents the chelating diamine, 2,2′-bipyridyl.

This is further borne out by the fact that when amines of high pK_a's are used, implying a stronger metal amine bond present, one expects the equilibrium

$$(COD)RhCl(Am) \underset{k_{-s}}{\overset{k_s}{\rightleftharpoons}} (COD)RhCl(Sol)+Am$$

to lie further over to the left and thus the percentage of the overall change in optical density involved in this fast reaction would be relatively small. However, when lower pK_a amines are used, the equilibrium will lie more to the right, resulting in a larger percentage change due to the fast reaction. This is in fact observed. For example, at 5.0°C, the percentage of this fast reaction for (COD)RhCl(piperidine) is 29.4 percent whilst for (COD)RhCl(Morpholine) it is 79.6 percent.

Since it is a fact that the optical density change due to the slower nucleophilic attack by the bipyridyl on the initial substrate (*i.e.* the reaction characterised by k_y) becomes vanishingly small for the lower pK_a amines, this study was limited to amines having a $pK_a > 8.4$. This unfortunately precludes the study of amines having α and α,α′ substituents so that no information on the steric effects of methyl groups in the α positions can be included in this report. Stopped-flow measurements are presently underway to augment this situation and will be covered in a future paper.

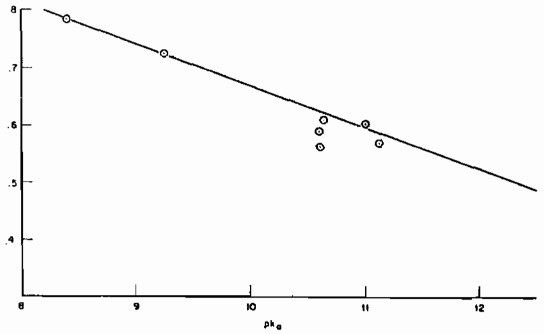

Figure 2.

A further consequence of this decreasing optical density change for the lower pK_a amines is that the experimental errors become larger for these amines.

Linear free energy plots were obtained for both the nucleophilic substitution by bipyridyl (as measured by k_y) and for the solvolysis (as measured by k_s). These plots are shown in Figures 2 and 3, respectively. It is evident that the rate of the relevant reaction changes significantly and systematically with the naure of the leaving amine. The values obtained for the complexes where the leaving amines are n-propylamine and iso-propylamine do not seem to correlate as well as the others. The reason for this is not immediately apparent but could be due to slight differences in their pK_a values in methanol as opposed to water.

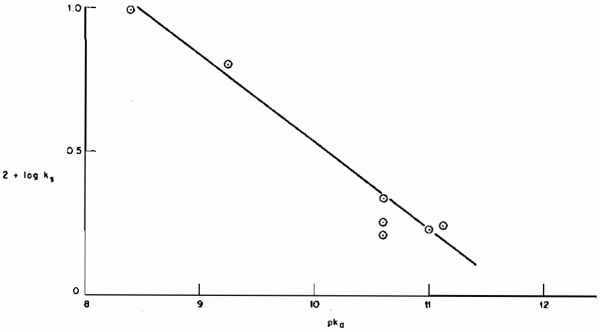

Figure 3.

Although the pK_a's used were those for the relevant amine in water, the work of Hall[11] on the determination of the base strengths of amines in nonprotolytic solvents shows that the base strength in water is a reliable index of the base strength in organic solvents. However, it must be noted at this point that the slopes of the linear free energy plots, or the discriminating ability, α, will include a term which is equal to the proportionality constant for the pK_a as measured in water and the solvent in which the kinetic study is made. This means that one can only compare values of these slopes when the kinetics are done in the same solvent unless the proportionality constant is known.

Although most of the work involving linear free energy plots on metal substrates has been done in methanol, a variety of solvents have been used in organic studies. Thus one finds for alkylating agents, slopes of 0.2 for the chloroacetate ion in methanol,[12] 0.78 for ethyl chloroformate[13] in 85% aqueous acetone and 0.22 for 3-bromopropanol[13] in water, where the pK_a's of the reacting moiety has been determined in the specific solvent used. However, in the case of kinetic studies on metal complexes, the pK_a values used are invariably those obtained in aqueous solution, irrespective of the solvent being used in the study.[14]

It has generally been found that this discriminating value is smaller for inorganic substrates than for organic ones. Thus, although in organic reactions, a low discriminating value implies that bond making in the transition state is not very important, as proposed by Hudson,[15] this has been explained[16] in terms of the fact that, in general, the "softer" metal complexes discriminate in favour of the polarizability of the entering reagent rather than its basicity.

Our results show significant differences in the discriminating ability, α, for the two reaction pathways. The α value associated with the displacement of amines by bipyridyl is smaller than that involving solvolysis (.07 as opposed to .3).

This deviation in the α values could possibly be a consequence of the fact that in the one case a chelatinggroup is the attacking nucleophile whilst in the other it is a monodentate solvent group. However, subsequent work[17] has shown that the rate of nucleophilic substitution of a chelating diamine is governed, as for the monodentate amines, by the lowest pK_a value of the chelate, implying that the rate determining step is that of the first nitrogen group entering with the subsequent ring closing step being rapid.

A possible explanation is that this deviation in α values reflects the more dominant role that is played in the rate determining step, by the leaving group, when the entering group is a weak nucleophile.

Pictorially this can be envisaged using the energy profiles depicted in Figures 4 and 5. Thus in the case of the solvolysis reaction, the bond-breaking step becomes relatively more important than in the direct substitution step. More correctly, the bond-making step in the solvolysis reaction becomes of lesser importance because of its inherent weakness.

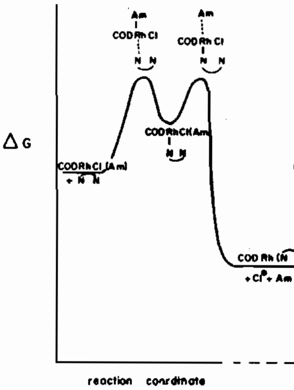

Figure 4. For the reaction CODRhCl(Am)+$\overset{\frown}{\text{N N}}$→

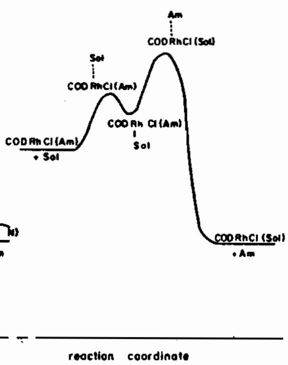

Figure 5. For the reaction CODRhCl(Am)+Solvent→

We cannot, of course, make any comment on the relative importance of bond-making and bond-breaking at this stage, but this will be done in a forthcoming publication where the leaving amine remains the same and the entering amine is systematically varied.[17]

In all the cases studied there is no indication of a stable five-coordinate intermediate being formed. This suggests that, in the energy profile of our reaction, the minimum does not lie at a lower energy than the start-

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ing position. This is a point of difference to that suggested by Cattalini *et al.*[6] for the reaction of (COD)-RhCl(SbR$_3$) with various amines.

It is interesting that diethylamine proved to belong to the Group II amines, *i.e.* having a single methyl blocking group in the α position, when reacted with [Pt(Bipy)Cl$_2$],[3] whereas in our study even di-n-butylamine behaves as a Group I type amine, *i.e.* no apparent steric hindrance, as one would expect.

It was hoped that by studying n-propylamine and iso-propylamine, steric effects other than those associated with α blocking would be observed. It can be seen from the kinetic data that, within experimental error, no effect is observed.