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A Kinetic Study of the Reactivity of a Series of Amines with the Neutral Rhodium(I) Complex, Chlorocycloocta-1,5-Diene Piperidine Rhodium(I)

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The rates of nucleophilic displacement of piperidine by a series of amines, from the complex chlorocycloocta-1,5-diene piperidine rhodium(I), have been determined in methanol. A linear free energy relationship is observed for this displacement, independent of whether chelating or monodentate amines are used. The intercept of the rate vs. concentration plot of the entering amine is found to be different for monodentate amines as opposed to chelating diamines. An explanation of this anomoly is presented.

Introduction

The majority of substitution reactions on square planar d^8 substrates results in the general rate law[1]:

$$\text{Rate} = (k_s + k_y[Y])[\text{Substrate}] \qquad (1)$$

where the second-order rate constant k_y refers to the bimolecular attack of Y on the substrate and the first-order rate constant k_s to the bimolecular attack of the solvent, S, as shown in Figure 1.[1,2]

The presence of a contribution due to the reaction controlled by the rate constant k_{-s} has been observed only in a few cases.[3,4] This scheme requires k_s to be dependent on the nature of the substrate and solvent but not on the nature of Y. There are examples of processes in which either $k_s \gg k_y[Y]$[5] or $k_y[Y] \gg k_s$[6] resulting in a simplification of the two-term rate law.

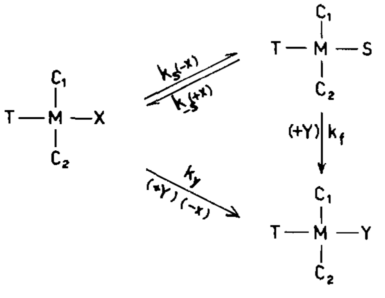


Figure 1.

In the study by Robb[4] *et al.,* the reaction controlled by the constant k_{-s} only became apparent when added amounts of the leaving groups were varied. The ratio of the rate constants, k_{-s}/k_f, was found to be 0.23 and it is obvious that as this ratio approaches unity, k_{-s} will play a more dominant role in the overall reaction scheme.

In this study just such a situation occurs and it is found that the first order rate constant is no longer just a function of the solvent but is also a function of the nature of Y. This has been interpreted in terms of the k_{-s}/k_f ratio being greater than unity.

In an attempt to elucidate the relative importance of bond-making and bond-breaking in Rh^I d^8 systems we have varied the basicity of a series of entering amines on a common Rh^I substrate. Good linear free energy plots of the nucleophilic displacement rates, k_y, vs. pK_a of the entering amine have been obtained. The discriminating ability for this "bond-making" linear free energy plot are compared to those obtained for "bond-breaking" reported earlier by us.[7]

Experimental

Materials

The diolefinic piperidine complex has been synthesised according to the method of Chatt[8] by treating $[CODRhCl]_2$ in CH_2Cl_2 with a calculated amount of piperidine. The final product of the reaction, namely cycloocta-1,5-diene chelate diamine rhodium cationic species in the case of the reaction with 2,2′-bipyridyl and 4,4′-dimethyl-2,2′-bipyridyl were prepared as the hexafluorophosphate salt[9], microanalysed and their visible spectra used to ensure that this was indeed the species being formed. In the case of the reaction with monodentate amines, the product, namely cycloocta-1,5-diene bisamine rhodium cationic species were prepared as the hexafluorophosphate salts and microanalysed. Table I shows the microanalytical results.

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

TABLE I. Microanalytical data for the complexes

Amine	Complex Formulae	Microanalytical results			
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
4,4′-Dimethyl-2,2′-bipyridyl	$C_{20}H_{24}N_2RhPF_6$	Required:	C: 44.46;	H: 4.48;	N: 5.19
		Found:	C: 44.15;	H: 4.50;	N: 5.23
Pyridine	$C_{18}H_{22}N_2RhPF_6$	Required:	C: 42.04;	H: 4.31;	N: 5.45
		Found:	C: 42.21;	H: 4.29;	N: 5.51
β-Picoline	$C_{20}H_{26}N_2RhPF_6$	Required:	C: 44.25;	H: 4.80;	N: 5.17
		Found:	C: 44.10;	H: 4.85;	N: 5.35
γ-Picoline	$C_{20}H_{26}N_2RhPF_6$	Required:	C: 44.25;	H: 4.80;	N: 5.17
		Found:	C: 43.84;	H: 4.91;	N: 5.43
α-Picoline	$C_{20}H_{26}N_2RhPF_6$	Required:	C: 44.25;	H: 4.80;	N: 5.17
		Found:	C: 44.02;	H: 4.91;	N: 4.95

Kinetic Experiments

The kinetics were followed using a Cary 15 spectrophotometer. Measured, thermostated aliquots of the substrate and amine solutions were mixed by an injection technique in a cell housed in a constant temperature cell holder. An excess concentration of the amine was used in order to achieve pseudo-first-order conditions. The optical density change due to chelating diamines was monitored at 480 nm, the absorption maxima of the species being formed, whereas for monodentate amines, the wavelength used was 345 nm in order to maximize the optical density change.

Results

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

$$k_{obs} = k_l + k_y\,[\text{Amine}] \qquad (2)$$

The slope of the plot of k_{obs} vs. amine concentration gives a value for k_y whilst the intercept gives a value for k_l.

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

Table IV summarizes the activation parameters, k_y values at 25° C and the pK_a (in water) of the entering amine.

Using equation (5), which will be developed later on in the discussion, a value of $(k_{-s}/k_f)[\text{Am}]$ has been computed and these values are shown in Table V, together with the values of k_{-s}/k_f calculated, assuming that the leaving amine concentration is the same as that of the complex.

TABLE II. Data for the reaction CODRhCl(Pip) + Amine→ at different added amine concentrations and temperatures

Temperature (° C)	[Amine] (*M*)	$10^2 k_{obs}$ (sec^{-1})
4,4′-Dimethyl-2,2′-bipyridyl:		
14.5	0.0092	3.61
	0.0169	5.81
	0.0234	7.68
	0.0290	9.26
	0.0338	11.22
	0.0450	13.89
	0.0553	17.30
	0.0625	19.55
	0.0676	21.70
	0.0740	22.97
9.7	0.0092	3.18
	0.0169	5.07
	0.0234	6.42
	0.0290	8.00
	0.0338	9.35
	0.0450	11.67
	0.0553	14.37
	0.0625	16.32
	0.0676	17.30
	0.0740	19.25
4.0	0.0090	2.05
	0.0161	3.33
	0.0230	4.45
	0.0285	5.73
	0.0332	6.55
	0.0443	8.75
	0.0543	10.30
	0.0614	11.83
	0.0664	13.00
	0.0725	14.17

Temperature (° C)	[Amine] (M)	10^2k_{obs} (sec^{-1})
Pyridine:		
20.0	0.0266	21.0
	0.0400	24.8
	0.0533	30.0
	0.0676	33.8
	0.0824	40.8
	0.1099	50.1
	0.1373	60.1
14.0	0.0266	14.4
	0.0400	17.1
	0.0533	20.6
	0.0661	23.3
	0.0824	27.7
	0.1099	31.0
	0.1373	38.6
5.8	0.0266	9.8
	0.0400	12.0
	0.0533	13.1
	0.0666	15.9
	0.0687	16.6
	0.0824	18.7
	0.1099	21.6
	0.1373	27.4
β-Picoline:		
20.0	0.0268	18.4
	0.0401	23.8
	0.0535	30.2
	0.0662	36.0
	0.0669	35.5
	0.0794	40.5
	0.1059	52.0
	0.1324	62.0
14.0	0.0268	13.7
	0.0401	18.2
	0.0535	22.2
	0.0662	25.3
	0.0669	26.6
	0.0794	29.8
	0.1059	36.2
	0.1324	45.5
5.8	0.0268	7.5
	0.0401	10.4
	0.0535	12.2
	0.0662	14.7
	0.0669	15.9
	0.0794	18.7
	0.1059	21.4
	0.1324	27.5
γ-Picoline:		
20.0	0.0266	18.8
	0.0399	25.4
	0.0532	30.8
	0.0664	37.4
	0.0665	37.1
	0.0798	44.3
	0.1064	57.7
	0.1329	60.0
14.0	0.0266	14.2
	0.0399	19.3
	0.0532	23.9
	0.0665	30.1
	0.0798	34.8
	0.1064	43.3
	0.1329	55.1
5.8	0.0266	8.9
	0.0399	11.8
	0.0532	14.8
	0.0665	18.4
	0.0798	22.3
	0.1064	26.2
	0.1329	33.9
α-Picoline:		
20.0	0.268	11.0
	0.402	13.3
	0.536	18.1
	0.670	21.2
	0.671	21.6
	0.805	25.6
	1.074	32.1
	1.342	40.7
14.0	0.268	7.1
	0.402	8.4
	0.536	11.2
	0.670	13.2
	0.671	13.2
	0.805	16.4
	1.074	18.9
	1.342	24.0
5.8	0.268	4.1
	0.335	4.3
	0.469	6.1
	0.536	6.6
	0.603	7.1
	0.670	7.8
	0.805	9.0
	1.074	12.0
	1.342	14.4

TABLE III. Values of k_y and k_1 obtained for the reaction CODRhCl(Pip) + Am → at different temperatures

Entering amine	Temperature (°C)	$k_y(M^{-1}sec^{-1})$	$k_1(sec^{-1})$	$10^3 \times$ Complex concentration (M)
4,4′-Dimethyl-2,2′-bipyridyl	14.5	3.05	0.75×10^{-2}	–
	9.7	2.55	0.60×10^{-2}	–
	4.0	1.90	0.40×10^{-2}	–
Pyridine	20.0	3.60	0.110	2.037
	14.0	2.34	0.081	
	5.8	1.57	0.055	
β-Picoline	20.0	4.16	0.080	2.045
	14.0	2.94	0.068	
	5.8	1.85	0.039	
γ-Picoline	20.0	4.86	0.058	2.040
	14.0	3.83	0.043	
	5.8	2.39	0.025	
α-Picoline	20.0	0.267	0.037	2.048
	14.0	0.166	0.027	
	5.8	0.099	0.013	

TABLE IV. Activation parameters for the reaction CODRhCl(Pip) + Am →

Entering amine	$k_y^{25°C}(M^{-1}sec^{-1})$	ΔH^* (kcal mole^{-1})	ΔS^* (e.u.)	pK_a[b]
4,4′-Dimethyl-2,2′-bipyridyl[e]	4.78	6.78	–32.8	5.20[c]
Pyridine	4.95	8.95	–24.9	5.09
β-Picoline	5.59	10.47	–20.1	5.68
γ-Picoline	6.41	9.71	–22.2	6.02
α-Picoline	0.36[d]	10.89	–24.0	6.10
2,2′-Bipyridyl[a]	3.71	6.69	–36.5	4.30

[a] Results from reference 4.

[b] pK_a of the conjugate acid in water.

[c] Estimated using the fact that a methyl group in the γ position changes the pK_a by ~.9 units i.e. *cf.* pyridine and γ-picoline.

[d] This is consistent with a steric factor (Δ) = 1.7.

[e] The values of k_s obtained were ~10% lower than the true values because in order to dissolve this diamine, 10% CH_2Cl_2 had to be added.

TABLE V. Ratios of k_{-s}/k_f at various temperatures for the reaction CODRhCl(Sol) + Am →

Entering amine	Temperature (°C)	$k_{-s}/k_f[Am]$[a] (moles)	$(k_{-s}/k_f)_{25°C}$	Entering amine	Temperature (°C)	$k_{-s}/k_f[Am]$[a] (moles)	$(k_{-s}/k_f)_{25°C}$
Pyridine	20.0	0.0271	13.05	γ-Picoline	20.0	0.0094	4.86
	14.0	0.0312			14.0	0.0090	
	5.8	0.0323			5.8	0.0086	
β-Picoline	20.0	0.0162	10.36	α-Picoline	20.0	0.0918	54.9
	14.0	0.0204			14.0	0.1115	
	5.8	0.0192			5.8	0.0869	

[a] Data for the k_s values at different temperatures were taken from reference 4 for the reaction CODRhCl(Pip) + Bipy →

Discussion

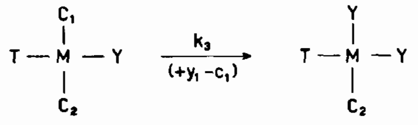
In the case of the chelating diamines, the results conform to the well-known rate law found for most substitution reactions of square planar complexes as shown in equation (1). This is as expected since the ratio of k_{-s}/k_f has been determined[4] as 0.23 for the case when 2,2′-bipyridyl is the entering nucleophile and thus a contribution due to the reaction pathway characterized by k_{-s} will be negligible.

However, in the case where the incoming nucleophile is a monodentate amine (with a pK_a lower than that of the leaving group, piperidine, implying that they are weaker nucleophiles) one would expect the ratio k_{-s}/k_f to be greater than unity, and one can no longer neglect the pathway characterized by k_{-s}.

A mathematical treatment of the reaction scheme shown in Figure 1 results in the following expression:

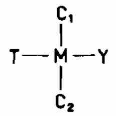
$$k_{obs} = k_s + (k_y k_{-s}/k_f)[X] + k_y[Y] \qquad (3)$$

In the actual kinetic scheme the product in Figure 1 will react further, viz.:



$$T-\overset{C_1}{\underset{C_2}{M}}-Y \xrightarrow[(+Y_1,\,-C_1)]{k_3} T-\overset{Y}{\underset{C_2}{M}}-Y \qquad (4)$$

but the rate constant k_3 does not alter the relationship given in equation (3), provided that $k_3[Y]$ is rapid i.e. assuming a steady state appromination for the species



$$T-\overset{C_1}{\underset{C_2}{M}}-Y$$

It is suggested that the k_1 value obtained when the entering nucleophile is a monodentate amine, corresponds to the non-functional (in Y) expression given by:

$$k_1 = k_s + (k_y k_{-s}/k_f)[X] \qquad (5)$$

This expression has been used to calculate k_{-s}/k_f ratios and the results are shown in Table V.

Discriminating values, α, for the nucleophilic substitution of monodentate amines on the solvolysed substrate have been calculated using the expression:

$$\alpha = \frac{\log k_{-s}/k_f}{\Delta pK_a} = \frac{\log k_{-s} - \log k_f}{\Delta pK_a} \qquad (6)$$

where ΔpK_a is given by pK_a(piperidine) – pK_a(entering amine).

TABLE VI. Discrimination (α) values and steric factor (Δ) for the reaction CODRhCl(Sol) + Am→

Entering amine	Discrimination value	Average α value	Steric factor Δ
Pyridine	0.186	0.17	
β-Picoline	0.187		
γ-Picoline	0.132		
α-Picoline	0.347	–	0.90

These values are shown in Table VI. The high α value obtained when the entering amine is α picoline is explained in terms of the steric hindrance parameter Δ, due to an α methyl blocking group. By a consideration of Figure 2, the Δ value can be calculated via the expression:

$$\Delta = \{pK_a(\text{piperidine}) - pK_a(\alpha \text{ picoline})\}(\alpha' - \alpha) \qquad (7)$$

where α is the average discriminating value obtained for the unhindered amines and α' that obtained using equation (6) for α picoline.

The Δ value obtained is also shown in Table VI and agrees remarkably well with Δ values found in other square-planar d^8 systems.[10–12]

Recently we published[7] a paper where the leaving group (a monodentate amine) was systematically varied whilst keeping the entering group the same. The linear free energy plots for k_s and k_y revealed α values of -0.3 and -0.08, respectively. A linear free energy plot of the logarithm of k_y vs. the pK_a of the entering group is shown in Figure 3. The discrimination or α value is 0.17. In addition, the discrimination or α value for the reaction of amines with the solvolysed species CODRhCl(Sol) yields a value of 0.17. All of these values are within the limits found for other square-planar d^8 systems.[10–12]

If we assume that we can separate the overall free energy changes into individual contributions (bond-making and bond-breaking) and into external factors (ionic strength etc.) we can interpret these discrimination values as implying that bond-making in the transition state plays a more important role in governing the overall rate of reaction than bond-breaking. However, Miller[13] has pointed out that this assumption (of individual contributions) is not always valid since there will be "crossterms"; that is, a change in one variable will alter the magnitude of the response to change in some other variable.

In the study of $[Pt(Bipy)(NO_2)X]$[14,15] both the nature of the entering groups and leaving groups were varied systematically. Plots of $\log k_2$ vs. n^o_{Pt} of the entering nucleophiles gave parallel straight lines, one for each substrate, implying that the free-energy change relative to any one of the reactions can be obtained by adding to a constant value, a contribution relative only to the nature of the leaving group and a contribution relative only to the nature of the entering group. This indicates that the bond-making and bond-

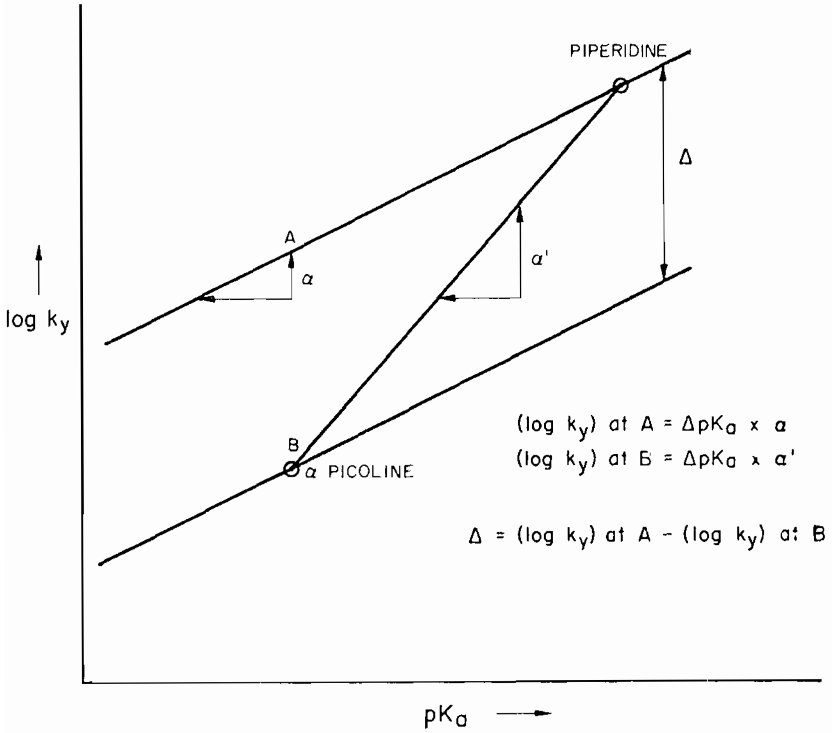


Figure 2.

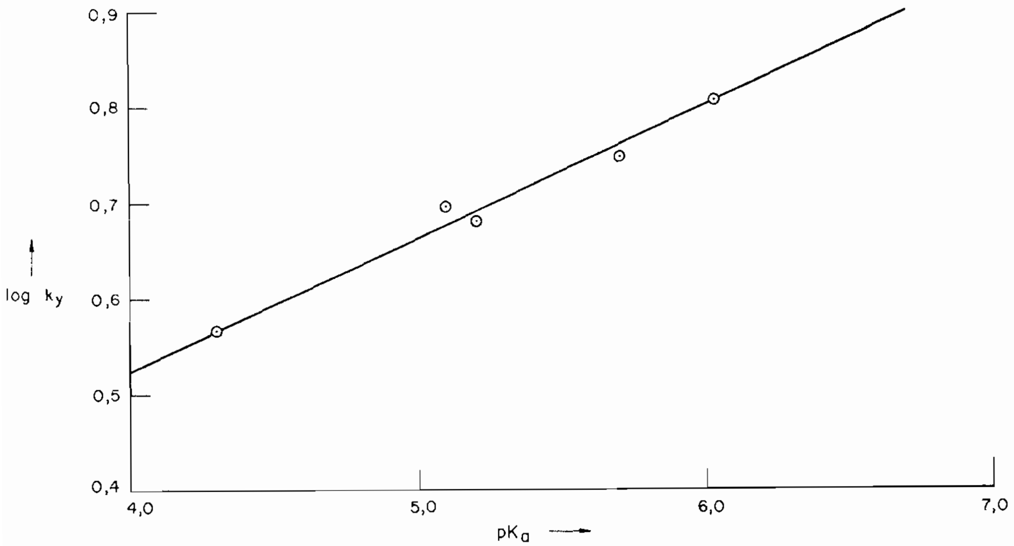


Figure 3.

breaking aspects of the substitution are relatively independent of each other. This seems to be also true for Pd^{II} complexes[16] but is no longer valid when comparing the Au^{III} systems. In the study of $AuCl_3(Am)$[17] reacting with thioethers, varying both the leaving amines and the entering thioethers, straight parallel lines were obtained (logk_2 vs. pK_a values) only for the most reactive thioethers. In other words, only by increasing the nucleophilicity of the entering thioethers can a situation be achieved in which bond-breaking and bond-making effects are separated sufficiently to give "platinum-like" behaviour.

Since the relative stability of the intermediate with respect to the transition state seems to be controlled by the effective nuclear charge of the central metal ion[18], one expects the separation of the overall free energy changes into bond-breaking and bond-making components for rhodium(I) to be more complete than for Pt^{II}.

Having established this we can now analyse the results obtained for the CODRh(Am)Cl system. When we vary the entering amine, both the substrates CODRh(Sol)Cl and CODRh(Pip)Cl yield linear free energy plots having essentially the same discrimination ability i.e. $\alpha = 0.17$. This suggests that we have a situation in which the separation of bond-breaking and bond-making is sufficiently "platinum-like" to consider their roles separately, as expected.

When the entering nucleophile is bipyridyl and the leaving amines are varied systematically, a linear free energy plot having an α value of -0.08 is obtained. This suggests that the energy profile is as shown in Figure 4, where the bond between the metal and the entering amine is partially formed in the transition state and its formation plays a greater role in determining the rate. This type of energy profile was also suggested for the entry of thioethers in the complex [Pt(Bipy)(NO_2)X].[15]

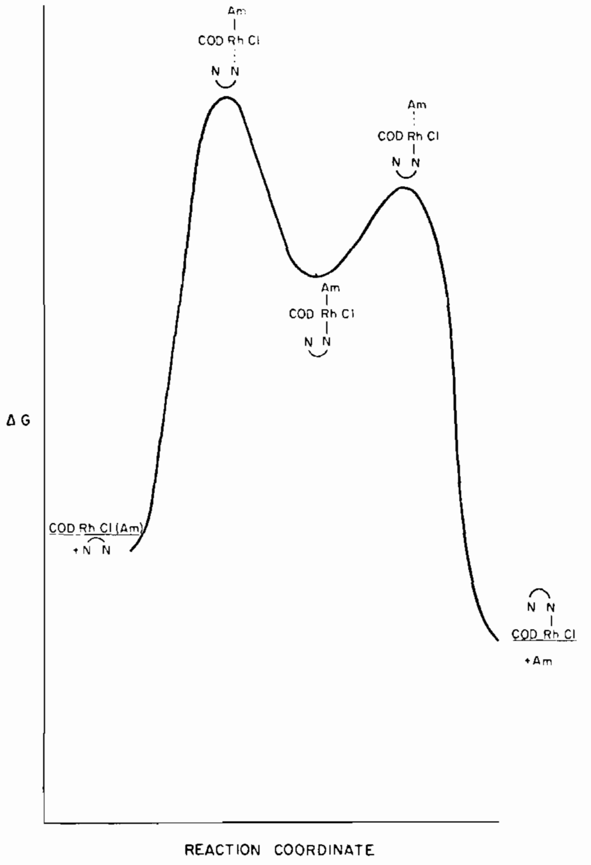


Figure 4. Reaction coordinate diagram for the rate determining step of the reactions:

$$\mathrm{CODRhCl(Am)} + \overset{\frown}{\mathrm{MN}} \rightarrow \mathrm{CODRh}(\overset{\frown}{\mathrm{NH}})$$

or

$$\mathrm{CODRhCl(Am)} + \mathrm{Am'} \rightarrow \mathrm{CODRh(Am')_2}$$

However, the large discrimination value ($\alpha = -0.30$) obtained for the reaction

$$\mathrm{CODRh(Am)Cl + Sol \rightarrow CODRh(Sol)Cl + Am}$$

seems to contradict this scheme. This anomaly can best be explained analogously to that of the Au^{III} [17] case in which only the entry of the most reactive thioethers resulted in parallel lines for the linear free energy plots. Thus in the rhodium(I) case, when the entering nucleophile is very weak (a solvent in our case) the assumption that the bond-making and bond-breaking steps can be considered as independent is no longer valid. This results in this abnormally high α value. Completely analogous behaviour was found for the complex $AuCl_3$(Am)[17], where weak entering nucleophiles resulted in higher α values. The various reaction profiles possible for substitution in square-planar complexes, and their relation to the bond-breaking and bond-making separations have been considered by Tobe.[19]

Further support for the reaction profile shown in Figure 4 is forthcoming when one considers the steric factor Δ. α Picoline as the entering amine, exhibits Δ values of 1.7 and 0.9 when the substrate is CODRh (Pip)Cl and CODRh(Sol)Cl, respectively. However, when the leaving amine is di-n-butylamine, no steric effect is apparent (as opposed to the steric effect found for diethylamine when reacting with Pt(Bipy)Cl_2).[20] This could be interpreted in terms of the fact that the Rh–N bond is nearly the same in the transition state and in the final amine complex so that the energy barrier for the free rotation of the bulky ligand is acting in the same way in destabilising the transition state and the ground state of the reverse process.

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