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Steric Effects upon Chelate Ring-opening and Ring-closure Substitution Reactions of (*o*-Dimethylaminophenyldimethylarsine)rhodium(III) Complexes

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The kinetics of the reversible reaction (i) have been studied in methanol [amine = NH_3, $NMeH_2$, $NEtH_2$, NPr^nH_2,

$$trans\text{-}[RhL_2Cl_2]^+ + \text{amine} \rightleftharpoons mer\text{-}[RhL(L')(\text{amine})Cl_2]^+ \qquad (i)$$

NBu^nH_2, $N(CH_2Ph)H_2$, NPr^iH_2, NBu^iH_2, NBu^sH_2, or $N(CH_2Bu^t)H_2$; L and L' = *o*-dimethylaminophenyldimethylarsine-*NAs* and -*As* respectively]. The pseudo-first-order rate constant of the approach to equilibrium exhibits the form $k_{obs.} = k_{(t\rightarrow m)}[\text{amine}] + k_{(m\rightarrow t)}$. The rate constant of the forward reaction (i) is scarcely affected by the nature of the entering primary amine. On the other hand, the rate constant of the reverse reaction is strongly dependent on the leaving amine, the change of reactivity being satisfactorily rationalized in terms of changes of the amine steric hindrance, in agreement with a dissociative mode of activation.

IN a previous paper[1] we have reported the results of a series of kinetic investigations on the reversible system (1) † in methanol (L and L' = *o*-dimethylaminophenyldimethylarsine-*NAs* and -*As* respectively; amine =

$$trans\text{-}[RhL_2Cl_2]^+ + \text{amine} \underset{k(m\rightarrow t)}{\overset{k(t\rightarrow m)}{\rightleftharpoons}} mer\text{-}[RhL(L')(\text{amine})Cl_2]^+ \qquad (1)$$

pyridine or substituted pyridine), where the forward reaction involves the opening of a chelate ring and coordination of the amine at the site vacated by the leaving NMe_2 arm of the chelate ligand. It was found that the rate constant of the forward reaction is scarcely affected by the nature of the entering group, apart from *ortho*-substituted pyridines which exhibit a comparatively low reactivity. Conversely, the rate constant of the reverse reaction is strongly dependent on the leaving amine, according to relationship (2), found at 25 °C. Once again, an anomalous behaviour was observed for *ortho*-

$$\log k_{(m\rightarrow t)} = -0.52\ pK_a - 0.90 \qquad (2)$$

substituted pyridines, whose complexes react faster than expected from equation (2), suggesting that steric requirements might play an important role in determining the rate of the interconversion described by equation (1).

In order to elucidate this point we have carried out a kinetic investigation of system (1) in methanol using amine = ammonia and aliphatic primary amines (NRH_2; R = Me, Et, Pr^n, Bu^n, CH_2Ph, Pr^i, Bu^i, Bu^s, or CH_2Bu^t) which exhibit rather similar basicities, but significantly different steric hindrances.

EXPERIMENTAL

Materials.—The complex *trans*-$[RhL_2Cl_2][NO_3]$ was prepared as described elsewhere.[2] New complexes of general formula *mer*-$[RhL(L')(\text{amine})Cl_2][ClO_4]$ were prepared by treating at room temperature a concentrated methanolic solution of *trans*-$[RhL_2Cl_2][NO_3]$ (20—30 g dm^{-3}), under stirring, with a sufficient excess of amine to ensure that reaction (1) went to completion. At the end of the reaction the solution was treated with few cubic centimetres of a saturated aqueous solution of $Na[ClO_4]$ followed by ten volumes of water. The analytical data for the yellow materials which suddenly separated were fully consistent with the required products (Table 1). Complexes with $N(CH_2Bu^t)H_2$, NBu^sH_2, and NPr^iH_2 were always highly contaminated by the starting *trans* parent complex (20—70%), mainly because of unfavourable equilibrium constants (see Table 3). The i.r. spectra (Nujol mulls) of the pure products (Table 1) in the 140—500 cm^{-1} region showed only one strong Rh–Cl band at 350 cm^{-1} (at 350 cm^{-1} also for *trans*-$[RhL_2Cl_2][NO_3]$), characteristic of the asymmetric stretching for a *trans* Cl–Rh–Cl unit.[3]

TABLE 1

Analytical data (%) for *mer*-$[RhL(L')(\text{amine})Cl_2][ClO_4]$; calculated values are given in parentheses

Amine	C	N	H	Cl
NH_3	33.8	5.55	5.00	14.0
	(32.4)	(5.65)	(4.75)	(14.4)
$NMeH_2$	33.0	5.45	5.10	14.4
	(33.4)	(5.55)	(4.95)	(14.1)
$NEtH_2$	33.9	5.35	5.35	14.1
	(34.4)	(5.45)	(5.10)	(13.8)
NPr^nH_2	35.2	5.25	5.45	13.6
	(35.3)	(5.35)	(5.30)	(13.6)
NBu^nH_2	35.6	5.10	5.50	13.7
	(36.2)	(5.25)	(5.45)	(13.4)

Liquid amines were purified by distillation over K[OH] pellets. An aqueous solution (16.5 mol dm^{-3}) of ammonia rather than pure ammonia was used. Methanol was dried over magnesium methoxide.

Preparation of the Reaction Mixtures; Evaluation of the Reaction Rates and Equilibria.—Stock solutions of amines and ammonia were prepared by diluting titrated methanolic solutions. The reaction mixtures were prepared by mixing appropriate volumes of thermostatted stock solutions of *trans*-$[RhL_2Cl_2][NO_3]$ (prepared by weight), amine, and methanol directly in 1-cm silica cells maintained in the thermostatted cell compartment of either a Beckman DK 2A or an Optica CF4R spectrophotometer. Weighed amounts of the *mer* complexes were dissolved directly in the

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† The *mer* designation of the reaction product has been adopted to emphasize that the amine and the *trans* chlorides are in the same meridional plane.

reaction cell when the *mer* ⟶ *trans* conversion was examined. At suitable time intervals the spectrum of the reacting mixture was scanned in the 280—360 nm region, where the course of the reaction was revealed by significant changes of absorbance and was also characterized by the presence of isosbestic points (in the region between 308 and 315 nm). Relatively fast reactions were followed by recording the absorbance against time at a selected wavelength (285 or 290 nm).

The starting concentration of the rhodium(III) complexes in the reacting mixture was kept in the range 7 × 10^{-5}— 2 × 10^{-4} mol dm^{-3}. The ranges of concentration for the entering amines in the reactions of *trans*-$[RhL_2Cl_2]^+$ were 8.93 × 10^{-3}—4.46 × 10^{-2} (NH_3), 5.00 × 10^{-3}—4.17 × 10^{-2} ($NMeH_2$, $NEtH_2$, and NBu^iH_2), 2.50 × 10^{-3}—4.17 × 10^{-2} (NPr^nH_2), 5.00 × 10^{-3}—5.83 × 10^{-2} (NBu^nH_2), 1.00 × 10^{-2}— 4.17 × 10^{-1} [$N(CH_2Ph)H_2$], 1.00 × 10^{-1}—8.33 × 10^{-1} (NPr^iH_2), 2.60 × 10^{-1}—8.30 × 10^{-1} (NBu^sH_2), and 1.00 × 10^{-2}—8.33 × 10^{-2} mol dm^{-3} [$N(CH_2Bu^t)H_2$]. At least five kinetic runs were carried out at each temperature for each entering group. In the case of the *mer* ⟶ *trans* conversions at least four runs were carried out in methanol at each temperature for any single complex.

The observed rate constants, $k_{obs.}$, and the equilibrium constants, K_{eq}, were determined as previously described for the reactions with pyridines.[1]

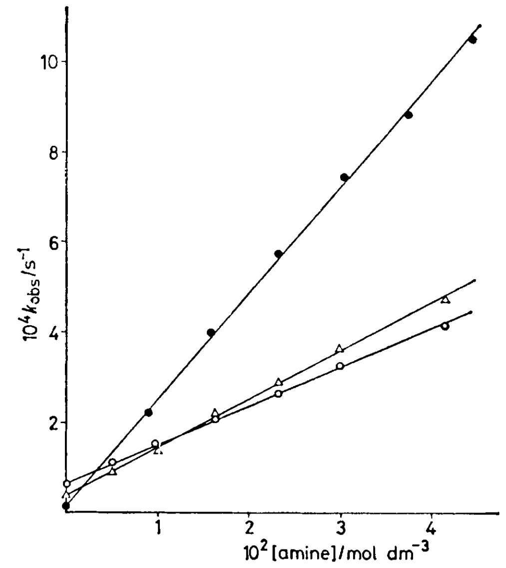

FIGURE 1 Dependence of the observed rate constants of the approach to equilibrium, $k_{obs.}$, on the entering amine for the reaction of *trans*-$[RhL_2Cl_2]^+$ with NH_3 (●), $NMeH_2$ (△), and $NEtH_2$ (○) in methanol at 25.0 °C. Data at [amine] = 0 refer to the $k_{obs.}$ of the *mer*→*trans* conversion of the individual complexes

RESULTS

The complexes *mer*-[RhL(L')(amine)Cl_2][ClO_4] examined in this paper [amine = NH_3, $NMeH_2$, $NEtH_2$, NPr^nH_2, NBu^nH_2, $N(CH_2Bu^t)H_2$, NBu^sH_2, or NPr^iH_2] * release the co-ordinated amine when dissolved in methanol, yielding quantitatively *trans*-$[RhL_2Cl_2]^+$, according to stoicheiometry (1) and following a first-order rate law under our experimental conditions.

TABLE 2

Rate constants and activation parameters for the reactions *trans*-$[RhL_2Cl_2]^+$ + amine $\rightleftharpoons$ *mer*-$[RhL(L')(amine)Cl_2]^+$

Amine	θ_c/°C	$k_{(t\to m)}$/$dm^3\,mol^{-1}\,s^{-1}$	$\Delta H_{(t\to m)}^{\ddagger}$/kJ mol^{-1}	$\Delta S_{(t\to m)}^{\ddagger}$/J $K^{-1}\,mol^{-1}$	$k_{(m\to t)}$/s^{-1}	$\Delta H_{(m\to t)}^{\ddagger}$/kJ mol^{-1}	$\Delta S_{(m\to t)}^{\ddagger}$/J $K^{-1}\,mol^{-1}$
NH_3	25.0	2.34 × 10^{-2}	73	−30	1.38 × 10^{-5}	120	63
	35.0	6.72 × 10^{-2}			6.74 × 10^{-5}		
	45.0	1.61 × 10^{-1}			3.04 × 10^{-4}		
$NMeH_2$	25.0	1.08 × 10^{-2}	78	−21	3.45 × 10^{-5}	114	52
	45.0	8.34 × 10^{-2}			6.64 × 10^{-4}		
$NEtH_2$	25.0	8.73 × 10^{-3}	74	−36	6.08 × 10^{-5}	123	86
	45.0	6.10 × 10^{-2}			1.46 × 10^{-3}		
NPr^nH_2	25.0	1.07 × 10^{-2}	77	−24	8.19 × 10^{-5}	120	78
	35.0	3.20 × 10^{-2}			4.40 × 10^{-4}		
	45.0	8.10 × 10^{-2}			1.82 × 10^{-3}		
NBu^nH_2	25.0	1.00 × 10^{-2}	77	−24	7.55 × 10^{-5}	120	79
	35.0	2.91 × 10^{-2}			3.94 × 10^{-4}		
	45.0	7.59 × 10^{-2}			1.70 × 10^{-3}		
NBu^iH_2	25.0	1.10 × 10^{-2}	80	−13	2.53 × 10^{-4}	111	59
	45.0	9.00 × 10^{-2}			4.53 × 10^{-3}		
$N(CH_2Bu^t)H_2$	25.0	1.54 × 10^{-2}	66	−58	9.24 × 10^{-4}		
	35.0	3.94 × 10^{-2}			3.80 × 10^{-3}	103	42
	45.0	8.75 × 10^{-2}			1.33 × 10^{-2}		
$N(CH_2Ph)H_2$	25.0	2.01 × 10^{-2}	70	−43	1.63 × 10^{-4}	113	61
	45.0	1.26 × 10^{-1}			3.04 × 10^{-3}		
NBu^sH_2	20.0				6.00 × 10^{-3}	95	37
	25.0	5 × 10^{-3} *			1.25 × 10^{-2}		
	30.0				2.18 × 10^{-2}		
NPr^iH_2	20.0				2.16 × 10^{-3}	101	50
	25.0	5 × 10^{-3} *			4.50 × 10^{-3}		
	30.0				9.35 × 10^{-3}		
	35.0				1.60 × 10^{-2}		

Errors: $k \pm 3\%$, $\Delta H^{\ddagger}$ ±4 kJ mol^{-1}, $\Delta S^{\ddagger}$ ±12 J K^{-1} mol^{-1}.

* Error, ±20%.

The reactions of *trans*-$[RhL_2Cl_2]^+$ with amines do not go to completion under the experimental conditions adopted (with the exception of reactions with ammonia) and the concentration of the reaction product at equilibrium is enhanced by increasing the amine concentration, according

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* The high contamination by *trans*-$[RhL_2Cl_2]^+$ of the complexes containing the last three amines did not affect either the stoicheiometry or the rate law of the reactions.

TABLE 3

Equilibria constants, K_{eq}, the quotients $k_{(t \rightarrow m)}/k_{(m \rightarrow t)}$, and thermodynamic parameters of the reactions *trans*-$[RhL_2Cl_2]^+$ + amine $\rightleftharpoons$ *mer*-$[RhL(L')(amine)Cl_2]^+$

Amine	θ_c / °C	K_{eq} / $dm^3\ mol^{-1}$	$\Delta H^{\ominus}$ / $kJ\ mol^{-1}$	$\Delta S^{\ominus}$ / $J K^{-1}\ mol^{-1}$	$k_{(t \rightarrow m)}/k_{(m \rightarrow t)}$ / $dm^3\ mol^{-1}$	$\Delta H_{(t \rightarrow m)}$ / $kJ\ mol^{-1}$	$\Delta S_{(t \rightarrow m)}$ / $J\ K^{-1}\ mol^{-1}$
NH_3	25.0				1 700	−46	−92
	35.0				997		
	45.0				530		
$NMeH_2$	25.0	284	−41	−91	313	−36	−73
	45.0	100			126		
$NEtH_2$	25.0	132	−41	−96	144	−48	−122
	45.0	47			41.8		
NPr^nH_2	25.0	107	−41	−98	131	−42	−102
	35.0	58			72.7		
	45.0	38			44.5		
NBu^nH_2	25.0	140	−45	−109	132	−43	−103
	35.0	70			73.6		
	45.0	45			44.7		
NBu^iH_2	25.0	42.4	−31	−72	43.5	−31	−72
	45.0	19.4			19.9		
$N(CH_2Bu^t)H_2$	25.0	17	−33	−86	16.7	−37	−99
	35.0	12			10.4		
	45.0	7.4			7.42		
$N(CH_2Ph)H_2$	25.0	118			123		
	45.0	37	−46	−114	41.4	−43	−104
NBu^sH_2	25.0	0.8			0.4		
NPr^iH_2	25.0	1			1		

Errors: K_{eq} ±10%, ΔH ±8 kJ mol^{-1}, ΔS ±25 J K^{-1} mol^{-1}.

to the reversibility of the systems. These reactions follow a pseudo-first-order rate law, with an observed rate constant of the approach to equilibrium, $k_{obs.}$, which is related to the amine concentration by relationship (3) (Figure 1). Such a relationship is expected when the reversible system (1) involves second-order forward and first-order reverse

$$k_{obs.} = k_a + k_b[\text{amine}] = k_{(m \rightarrow t)} + k_{(t \rightarrow m)}[\text{amine}] \qquad (3)$$

reactions. The values of the rate constants k_a, obtained by extrapolation, are very close to those of $k_{(m \rightarrow t)}$, obtained from *mer* ⟶ *trans* conversions (see Figure 1). Moreover, the quotients k_b/k_a are fairly similar to the values of the equilibrium constants, K_{eq}, obtained from spectrophotometric measurements (Table 3). These results lead to the assignment of k_a as $k_{(m \rightarrow t)}$ and of k_b as $k_{(t \rightarrow m)}$, as in the second form of equation (3). In Table 2 the values of $k_{(t \rightarrow m)}$ and $k_{(m \rightarrow t)}$ are listed together with the corresponding activation parameters. The values of K_{eq}, together with $k_b/k_a = k_{(t \rightarrow m)}/k_{(m \rightarrow t)}$, are listed in Table 3.

DISCUSSION

The results obtained show that the rate of the *trans* ⟶ *mer* reactions is scarcely affected by the nature of the entering amine (Table 2). On the other hand, the *mer* ⟶ *trans* conversions, and also the equilibrium constants (Table 3), are strongly dependent on the nature of the leaving amine. In particular, the activation free energy of the conversion, $\Delta G_{(m \rightarrow t)}^{\ddagger}$, is linearly related to the standard free energy of the reaction, $\Delta G_{(m \rightarrow t)}^{\ominus}$ according to relationship (4). The high value of α

$$\Delta G_{(m \rightarrow t)}^{\ddagger} = \alpha \Delta G_{(m \rightarrow t)}^{\ominus} + \beta \qquad (4)$$

(0.84) suggests the occurrence of an extension of the Rh–amine bond in the activated complex, in agreement with the proposition of a dissociative mode of activation for these conversions.[4-6] Similar behaviour has previously been found for the reactions with substituted pyridines.[1]

However, the changes of activation free energy and standard free energy must be related to different factors when either aliphatic or heterocyclic amines are considered. Thus, the σ-donor ability of pyridine and *meta*- and *para*-substituted pyridines, which exhibit similar steric hindrance, was found to be the primary factor responsible for both the kinetic and thermodynamic behaviour of *mer* ⟶ *trans* conversions. The same factor cannot be invoked for ammonia and the primary amines considered here, since they exhibit very similar σ-donor abilities [with some difference for NH_3 and $N(CH_2Ph)H_2$] however they are measured, *i.e.* in terms of pK_a,[7] gas-phase basicities,[8] or sums of the Taft σ^* values of the groups bonded to nitrogen.[9] It seems reasonable to suggest that differences in steric hindrance are responsible for both the kinetic and thermodynamic behaviour observed. Recently, some Russian workers [10-12] have taken the values of the Taft steric constant, E_s, for hydrocarbon substituents CRR′R″ as a measure of the steric effect of the isosteric amines, NRR′R″, E_N. A plot of log $k_{(m \rightarrow t)}$ against E_N (Figure 2) shows a fairly satisfactory linear relationship for eight ligands, such that an increase of steric hindrance of the amine (*i.e.*, according to the definition, a lowering of E_N) increases the readiness of *mer*-$[RhL(L')(amine)Cl_2]^+$ to undergo loss of amine and conversion into *trans*-$[RhL_2Cl_2]^+$, in agreement with the dissociative mode of activation proposed above for this reaction.[13] According to such a mode of activation, changes in the σ-donor ability of the leaving amine are also likely to be important in affecting the rate, as previously found for substituted pyridines. However, the amines considered here are too similar in this respect to allow such a contribution to be examined. The complexes with NBu^iH_2 and $N(CH_2Bu^t)H_2$ appear to be comparatively more labile than expected from their E_N values (Figure 2), possibly owing to the steric contribution of the branched β-methyl groups of these amines. These groups do not appear to affect the rates in the organic reactions performed to evaluate the $E_s (= E_N)$ values, but they are likely to be important when the amine is bonded to Rh^{III}, the co-ordination site being very crowded because of the presence of four *cis* groups and the NMe_2 end of the unidentate L′.

The low discriminating ability of *trans*-$[RhL_2Cl_2]^+$ towards primary amines in the *trans* ⟶ *mer* conversions is also consistent with the proposed occurrence of a very weak interaction between Rh^{III} and the incoming amine in the activated complex, which is the same in the case of the reverse reaction.

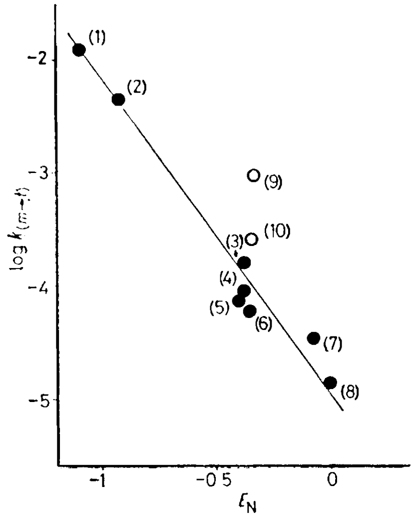

FIGURE 2 Dependence of log $k_{(m \rightarrow t)}$ on the steric constant, E_N, of the leaving amine [NBu^sH_2 (1), NPr^iH_2 (2), $N(CH_2Ph)H_2$ (3), NPr^nH_2 (4), NBu^nH_2 (5), $NEtH_2$ (6), $NMeH_2$ (7), NH_3 (8), $N(CH_2Bu^t)H_2$ (9), and NBu^iH_2 (10)] for the *mer* ⟶ *trans* conversion in methanol at 25.0 °C

All the above results are consistent with the dissociative mechanism [equation (5)] tentatively proposed

$$\begin{aligned} & trans\text{-}[RhL_2Cl_2]^+ + \text{amine} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \\ & \underset{\substack{\text{five-co-ordinate}\\ \text{intermediate}}}{[RhL(L')Cl_2]^+} + \text{amine} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \\ & \qquad mer\text{-}[RhL(L')(\text{amine})Cl_2]^+ \qquad (5) \end{aligned}$$

in a previous paper,[1] which involves a reversible opening of one end of the chelate rings (k_1 and k_2 rate terms) followed by reversible attack of the entering amine (k_3 and k_4 rate terms) on the five-co-ordinate rhodium(III) intermediate. In this scheme it is assumed that the five-co-ordinate intermediate is sufficiently long lived to exchange its outer-sphere ligands many times before its conversion into the starting complex or the reaction product. In this case the pseudo-first-order rate constant of the approach to equilibrium is given by equation (6), which simplifies to the form found experimentally [equation (3)] provided $k_2 \gg k_3$ [amine].* Therefore,

$$k_{obs.} = \frac{k_1k_3[\text{amine}]}{k_2 + k_3[\text{amine}]} + \frac{k_2k_4}{k_2 + k_3[\text{amine}]} \qquad (6)$$

the rate terms $k_{(t \rightarrow m)}$ and $k_{(m \rightarrow t)}$ give the values of k_1k_3/k_2 and k_4 respectively. Thus, the term related to the dissociative rate-determining step of the *mer* ⟶ *trans* conversions, $k_4 = k_{(m \rightarrow t)}$, is expected to increase with increasing steric hindrance of the leaving group.[13] On the other hand, the independence of $k_{(t \rightarrow m)}$ of the amine implies that the k_3 rate term is also independent of the amine and indicates that the degree of the Rh ··· amine interaction in the activated complex of the related reaction step is almost independent of the incoming ligand, and that this interaction is negligible.

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* At the present time no new information is available, other than that previously referred to,[1] to allow one to discriminate between a *D* or an I_d mechanism. If an I_d mechanism operates, equation (6) would also include the formation constant of the encounter complexes.

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