creases in energy with respect to the ground ${}^6A_1$ state as the ligand field strength *increases*. The absence of the band in the salen complexes could then be explained by assuming that the ligand field strength is weaker than in the polyimines and is high enough in energy to be masked by the charge-transfer bands. It does not seem likely that the ligand field strength in the salen complexes would be less than in beryl (six oxides), but the effects of the lower symmetry in the salen complexes cannot be estimated. There is some small additional absorption in the tail of the charge-transfer bands (around 12,000–14,000 cm^{-1}) which could be due to this transition, although, if this is true, the intensity is appreciably less than in the polyimine systems. Further, the similarity in isomer shifts for all of these binuclear complexes to each other and to that found for [Fe(terpy)Cl$_3$] suggests that, to the extent that the isomer shifts in closely related compounds are indicative of spin state, all of them are $S = {}^5/_2$ systems.

Conclusions

On the basis of the data presented it seems clear that [Fe(terpy)Cl$_3$] and [Fe(terpy)$_2$](ClO$_4$)$_3$ are monomeric high- and low-spin Fe(III) complexes, respectively. The new binuclear complex [Fe$_2$(terpy)$_2$O](NO$_3$)$_4$·H$_2$O and the complex [Fe$_2$(bipy)$_4$O](SO$_4$)$_2$·3.5H$_2$O are analogous to the well-established phenanthroline system. The magnetic as well as the Mössbauer and electronic spectral data presented in this paper can be explained assuming an $S = {}^5/_2$ ground state for each iron. We believe, however, that the data for the phenanthroline, bipyridine, and particularly terpyridine complexes suggest the possibility that the ground state for each iron is a spin quartet, unlike the salen data which are only compatible with a sextet ground state. More work needs to be done on these and on similar systems in order to resolve the problem.

Acknowledgments. Support of the National Science Foundation under Grants GP-7510 and GP-5039 is gratefully acknowledged. Research at Brookhaven National Laboratory was carried out under the auspices of the U. S. Atomic Energy Commission. One of us (W. M. R.) wishes to thank the Chemistry Department of Brookhaven National Laboratory for a research assistantship under the Summer Student Program and the National Institutes of Health for a predoctoral fellowship. We also thank Mr. Gary Long for some of the magnetic measurements.

Nucleophilic Reactivity in Substitution Reactions of Square-Planar Metal Complexes. III. Kinetic Evidence for the Accumulation of a Reaction Intermediate in Nucleophilic Substitutions in Rhodium(I) Complexes

L. Cattalini, R. Ugo, and A. Orio

*Contribution from Istituto di Chimica Generale ed Inorganica,
University of Padua, Padua, Italy.* *Received February 23, 1968*

Abstract: The kinetics of the nucleophilic displacement of the stibine from the complex [Rh(1,5-cyclooctadiene)Cl(SbR$_3$)] (R = *p*-tolyl) by amines (am) are reported. The reactions occur in two steps, the first corresponding to the rapid formation of a five-coordinated species; the second, which is slower, to its dissociation to give the product [Rh(1,5-cyclooctadiene)Cl(am)]. This is the first direct evidence for the accumulation of a five-coordinate reaction intermediate in square-planar substitution. The effect on the kinetics of changing the chelate olefin, the leaving group, the ligand *cis* to the leaving group, the entering group, and the solvent is also reported and discussed.

Ligand substitution reactions in coordination compounds occur with a variety of mechanisms, depending on the nature of the reagents, the solvent, the coordination number, etc. The behavior of planar complexes of d^8 transition metal ions such as Rh(I), Pt(II), Pd(II), and Au(III) appears to be simple, in the sense that the substrates generally undergo bimolecular substitution with transition states in which both the entering and leaving groups are bonded to the metal.

However, even though the rates of these processes generally follow a first-order dependence on both the concentrations of the substrate and entering reagent, it has been suggested[1,2] that the intimate mechanism is not a synchronous interchange of ligands. Langford and Gray[1] suggest an associative mechanism, with a five-coordinated intermediate that represents the incipient coordination unsaturation of the four-coordinate d^8 system. In the past few years indirect kinetic evidence supporting this point of view has been reported,[3] and the same argument has been used as a possible explanation of the difference in the kinetic behavior of platinum(II) and gold(III) complexes.[4]

In a preliminary communication[5] we reported some

---

[1] C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965.

[2] F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reaction," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967.

[3] (a) U. Belluco, R. Ettore, F. Basolo, R. G. Pearson, and A. Turco, *Inorg. Chem.*, **5**, 591 (1966); (b) U. Belluco, M. Graziani, M. Nicolini, and P. Rigo, *ibid.*, **6**, 721 (1967); (c) L. Cattalini and M. Martelli, *Gazz. Chim. Ital.*, **97**, 498 (1967).

[4] L. Cattalini, A. Orio, and M. L. Tobe, *J. Am. Chem. Soc.*, **89**, 3130 (1967).

[5] L. Cattalini, A. Orio, R. Ugo, and F. Bonati, *Chem. Commun.*, 48 (1967).

direct kinetic evidence for the accumulation of a reaction intermediate in the reaction

$$[\mathrm{Rh}(1{,}5\text{-cyclooctadiene})\mathrm{Cl}(\mathrm{SbR_3})] + \mathrm{am} \longrightarrow [\mathrm{Rh}(1{,}5\text{-cyclooctadiene})\mathrm{Cl}(\mathrm{am})] + \mathrm{SbR_3}$$

where R = *p*-tolyl. This research has been extended and the final results are reported and discussed in this paper.

Results

Separately prepared solutions of [Rh(1,5-cyclooctadiene)Cl(SbR$_3$)] (R = *p*-tolyl) and the amine were brought to the reaction temperature and mixed to start the reaction, which was followed spectrophotometrically. There was an immediate change of spectrum which was followed by a relatively slow change. The final products were shown to be the amino complexes [Rh(1,5-cyclooctadiene)Cl(am)] by comparing the spectra at the end of the reaction with those of authentic separately prepared specimens. Moreover, these amino complexes could be isolated from the reaction mixture in reasonable yield when the substitutions were carried out in more concentrated solutions. Thus it is the stibine ligand that is replaced in this reaction. When the amines react with the complexes [Rh(1,5-cyclooctadiene)Br(SbR$_3$)] and [Rh(norbornadiene)Cl(SbR$_3$)], the reaction course is similar.

All the reactions were carried out in the presence of a large excess of the entering amine, in order to achieve pseudo-first-order conditions. The kinetics of the second step were followed. This obeyed a first-order rate law, and the rate constants (k) were obtained from the slope of the plot of log $(D_t - D_\infty)$ *vs.* time, where D_t and D_∞ are the optical densities of the reaction mixture at time t and at the end of the reaction, respectively, measured at a wavelength in the near-ultraviolet region where there is an adequate change in absorbance. Measurements carried out at different wavelengths give the same value for the rate constant.

The results are summarized in Table I. In each case the rate of the reaction depended upon the nature of the entering amine and not upon its concentration.

Table I. First-Order Rate Constants,[a] k, for the Reactions of Replacement by Amines of SbR$_3$ (R = *p*-tolyl) from Rh(I) Complexes

Amine	pK_a[b]	Solvent	Temp, °C	[am], M	10^2k, sec^{-1}
(1) Substrate = [Rh(1,5-cyclooctadiene)Cl(SbR$_3$)]					
3-Cyanopyridine	1.38	Acetoxyphenone	25	*a*	1.53
		Cyclohexanone	25	*a*	1.7
		Acetone	16	*a*	0.54
		Acetone	25	*a*	1.58
		Acetone	35	*a*	5.1
3-Chloropyridine	2.84	Acetone	25	*a*	1.93
Pyridine	5.17	Acetone	25	0.004	2.41
				0.016	2.45
				0.08	2.46
				0.16	2.39
				0.32	2.44
				0.64	2.38
		Methanol	25	*a*	1.65
		ClCH$_2$CH$_2$Cl[c]	25	*a*	2.03
4-Methylpyridine	6.02	Acetone	25	*a*	2.66
Morpholine	8.4	Acetone	25	*a*	3.68
n-Butylamine	10.7	Acetone	25	*a*	4.57
(2) Substrate = [Rh(1,5-cyclooctadiene)Br(SbR$_3$)]					
3-Cyanopyridine	1.38	Acetone	25	*a*	1.17
3-Chloropyridine	2.84	Acetone	25	*a*	1.38
Pyridine	5.17	Acetone	25	*a*	1.73
4-Methylpyridine	6.02	Acetone	25	*a*	2.3
(3) Substrate = [Rh(norbornadiene)Cl(SbR$_3$)]					
3-Cyanopyridine	1.38	Acetone	25	*a*	1.7
3-Chloropyridine	2.84	Acetone	25	*a*	2.05
Pyridine	5.17	Acetone	25	*a*	2.7
4-Methylpyridine	6.02	Acetone	25	*a*	2.9
Morpholine	8.4	Acetone	25	*a*	4.0

[a] These values represent the average of the rate constants obtained in several kinetic runs over a range of concentration of the amine. The agreement is always as close as that shown in the entry of pyridine on the first substrate in acetone at 25°. [b] The values of pK_a refer to the acid, amH$^+$ in water. [c] Data obtained with fresh solutions of the amine in the solvent.

Discussion

The general rate law for the process

$$\mathrm{L_3M{-}X + N \longrightarrow L_3M{-}N + X}$$

corresponding to the replacement of the ligand X coordinated to M in a planar substrate by N is

$$\text{rate} = (k_1 + k_2[\mathrm{N}])[\mathrm{L_3M{-}X}]$$

It has been shown quite clearly[1,2] that the path of the reaction controlled by the first-order constant k_1 is due to nucleophilic attack by the solvent (S), according to the scheme

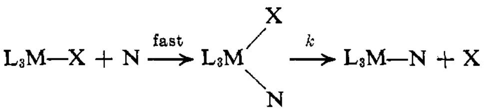
$$\mathrm{L_3M{-}X + S \xrightarrow{k_1} L_3M{-}S + X}$$

$$\mathrm{L_3M{-}S + N \xrightarrow{fast} L_3M{-}N + S}$$

Therefore it should be possible, in principle, to find a system where $k_1 \gg k_2[\mathrm{N}]$ so that the rate is independent on the concentration of the entering group N. Many such examples have been found, *e.g.*, $[\mathrm{PtCl_4}]^{2-} + {}^{36}\mathrm{Cl}^-$,[6] all reactions involving hydroxide as entering group on Pt(II) derivatives, and so on.

However, this cannot be the case for the reactions reported in this paper even though the rates are zero order with respect to the entering amine. The mechanism by way of the solvolytic path not only requires the rate to be independent of the nature of the reagent but also, for a particular substrate, to be independent of its nature. Furthermore the rate might be sensitive to the nucleophilic properties of the solvent. The results in Table I show that the rate changes significantly and systematically with the nature of the entering amine whereas it is not seriously affected by the nature of the solvent.

These results indicate that the two stages of reaction that have been observed correspond to a fast association of the reagents to yield a relatively inert five-coordinated intermediate that then expels the stibine in the slow step. The rate constants in Table I relate to these dissociative processes.



$$\mathrm{L_3M{-}X + N \xrightarrow{fast} L_3M\!\begin{smallmatrix}X\\ \\ N\end{smallmatrix} \xrightarrow{k} L_3M{-}N + X}$$

The energy profile corresponding to this process is of the type in Figure 1. The position of the minimum indicates that the intermediate is more stable than the

---

[6] L. F. Grantham, T. S. Elleman, and J. S. Martin, Jr., *J. Am. Chem. Soc.*, 77, 2965 (1955); see also L. Cattalini, A. Orio, and M. Nicolini, *ibid.*, 88, 5734 (1966).

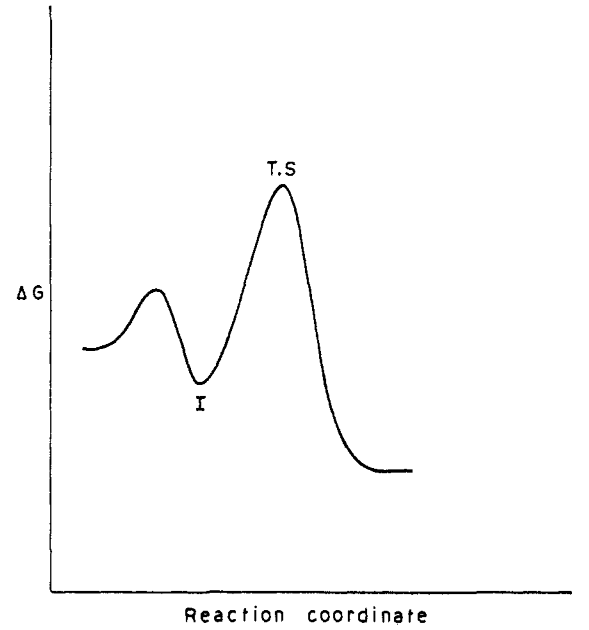


Figure 1. Type of energy profile for the substitutions reported.

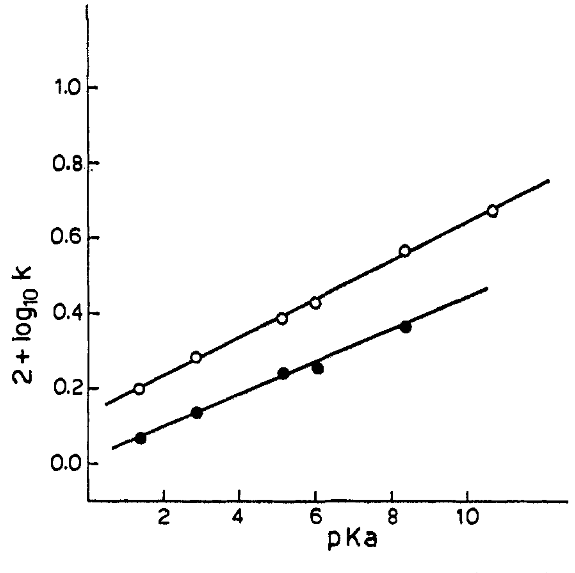


Figure 2. Plot of log k against the pK_a of the associate amine (see text): ○, substrate having Cl *cis* to the leaving stibine; ●, substrate having Br *cis* to the leaving stibine.

unassociated reagents but less stable than the final products. Experimental evidence in support of the initial fast association can be found when the optical density calculated by extrapolating the plots of log $(D_t - D_\infty)$ back to zero time (see Results) are compared with the optical density calculated from the known spectrum of the starting complex measured in the absence of amine. There is a considerable difference. In the reactions between 3-cyanopyridine and [Rh(1,5-cyclooctadiene)Cl(SbR_3)], this extrapolation was carried out at a number of different wavelengths and it allowed a rough estimation of the spectrum of the intermediate, which shows similar features to that of the five-coordinated rhodium(I) species.[7] Furthermore, on following the kinetics of this reaction at very low amine concentrations (comparable to that of the complex), the rate of the first step is reduced to some extent, as might be expected for a bimolecular process, and the change of optical density with time is characteristic of two overlapping stages.

The activation parameters for the reaction with 3-cyanopyridine were calculated from the data in Table I. They are $\Delta H^{\ddagger} = 19.4$ kcal/mole and $\Delta S^{\ddagger} = -1.4$ eu/mole, respectively. The entropy change is large in comparison to the values usually obtained in square-planar substitution (from -14 to -34 eu/mole for the reactions at platinum(II) complexes[2]) and is consistent with the dissociative nature of the slow step of the substitution.

The mechanism of ligand displacement observed in these Rh(I) complexes might appear unusual in square-planar substitution. However, it is in accord with the conclusions reached by comparing the kinetic behavior of Pt(II) and Au(III) complexes,[4] *i.e.*, with the concept that the utilization of five orbitals for covalent bonding becomes progressively easier as the effective nuclear charge of the central atom decreases, on going from Au(III) to Pt(II) and from Pt(II) to Rh(I).[8]

Having established the mechanism, we have tried to change the reacting system systematically, in order to examine the effect of structural variation on the rate of substitution. The changes examined were in (a) the nature of the entering amine, (b) the chelating diolefin, (c) the ligand *cis* to the leaving group, and (d) the leaving group.

There is a linear relationship between the reactivity (expressed in terms of log k) and the σ donor properties of the entering amine (expressed in terms of the pK_a of the conjugate acid) for each of the complexes examined (Figure 2). The same type of behavior has been observed in respect to the second-order rate constants for the reactions of amines with planar Pt(II), Pd(II), and Au(III) substrates.[9] This indicates that also in the case of Rh(I) there is not significant π interaction between the metal and the heteroaromatic amine, in spite of the lower oxidation state of the metal. This is further supported by the fact that the data for the two nonaromatic amines lie on the same straight line (Figure 2).

The slight increase of the reactivity as the basicity of the associated amine becomes larger is probably due to the fact that the greater donation of charge to the metal favors the dissociation of the Sb–Rh bond, either through a destabilization of the intermediate or a stabilization of the transition state.

A relative stabilization of the intermediate should also explain the difference in the behavior of the chloro and bromo complexes. When bromide is *cis* to the stibine in the starting complex instead of chloride, there is a relatively small decrease of both the reactivity and the discrimination between the various amines (Figure 2). The values of the slopes in Figure 2 are 0.051 and 0.043 for the Cl and Br complexes, respectively. The bromide being more polarizable than the chloride enables the intermediate to absorb the perturbation due to electron donation from the amine more readily and

---

[7] L. M. Venanzi, private communication.

[8] R. S. Nyholm, *Proc. Chem. Soc.*, 273 (1961); R. S. Nyholm and M. L. Tobe, *Experientia, Suppl.*, 9, 112 (1965).

[9] L. Cattalini, A. Orio, and A. Doni, *Inorg. Chem.*, 5, 1517 (1966); L. Cattalini, M. Nicolini, and A. Orio, *ibid.*, 5, 1674 (1966); L. Cattalini, A. Doni, and A. Orio, *ibid.*, 6, 280 (1967); L. Cattalini, A. Orio, and M. Martelli, *Chim. Ind.* (Milan), 49, 625 (1967).

reduces its importance in controlling the rate of dissociation of the stibine.

As can be seen from the data in Table I, the change of the chelate diolefin from 1,5-cyclooctadiene to norbornadiene does not appreciably affect the kinetic behavior. There is a small increase in the reactivity which could be related to the different chelating properties of the two diolefins, but the discrimination between different entering amines remains practically the same. Changing the nature of the aromatic group R in the stibine (from *p*-tolyl to phenyl) does not influence the rate to any significant extent.

However, drastic changes are observed when triphenylphosphine or triphenylarsine is present instead of the stibine. The kinetics of the corresponding reactions are not reported, since the displacement of phosphine and arsine is too fast to be followed by our techniques. However, it could be seen that, whereas under the conditions used the displacement of phosphine was reversible, that of the arsine (and the stibine) was not. In the absence of data for the phosphine and arsine systems it would not be wise to suggest any special reason why the stibine bonded to Rh(I) promotes such a peculiar behavior. However, there might be some connection with the observation that equilibria of the type

$$[Rh(CO)L_2Cl] + L \rightleftarrows [Rh(CO)L_3Cl]$$

leading to the formation of five-coordinated species are found[10] when $L = SbR_3$ but not when it is a phosphine or an arsine.

Experimental Section

The olefinic stibine complexes have been synthetized according to the method of Wilkinson[11] by treating $[(diolefin)RhX]_2$[12] in CH_2Cl_2 with the calculated amount of Sb(*p*-tolyl)$_3$. After evaporating nearly all the solvent, the compounds were obtained by adding *n*-hexane.

[(1,5-cyclooctadiene)RhCl(SbR$_3$)] (R = *p*-tolyl) is a yellow compound. *Anal.* Calcd for $RhC_{29}ClH_{33}Sb$: C, 54.2; H, 5.1. Found: C, 54.9; H, 5.0.

[(1,5-cyclooctadiene)RhBr(SbR$_3$)] is an orange compound. *Anal.* Calcd for $RhBrC_{29}H_{33}Sb$: C, 50.7; H, 4.8. Found: C, 50.9; H, 4.8.

[(norbornadiene)RhCl(SbR$_3$)] is a yellow compound. *Anal.* Calcd for $RhC_{28}ClH_{29}Sb$: C, 53.8; H, 4.6. Found: C, 54.0; H, 4.4.

The kinetics were followed spectrophotometrically. Known volumes of thermostated solutions of the complex and the reagent were mixed in the thermostated compartment of an Optica-CF4 double-beam recording spectrophotometer. The spectra changes characteristic of the reacting system were first determined by scanning the near-ultraviolet region at known intervals. Once the spectrum changes were characterized and a suitable wavelength chosen to study the reaction, the kinetics were followed by setting the wavelength at the chosen value and recording the changes of optical density as a function of time.

Acknowledgment. We thank the Italian Council for Research (C.N.R., Rome) for financial support.

---

[10] R. Ugo, F. Bonati, and S. Cenini, to be submitted for publication.

[11] M. A. Bennet and G. Wilkinson, *J. Chem. Soc.*, 1418 (1961).

[12] J. Chatt and L. M. Venanzi, *ibid.*, 4735 (1957).

The Crystal Structure and Molecular Conformation of Bis(N-*t*-butylsalicylaldiminato)palladium(II)[1]

V. W. Day,[2] M. D. Glick, and J. L. Hoard[3]

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850.

Received February 24, 1968

Abstract: A three-dimensional X-ray structure analysis of crystalline bis(N-*t*-butylsalicylaldiminato)palladium(II) leads to a centrosymmetric, but markedly "stepped," conformation for the molecule. The parallel mean planes of the salicylaldimine residues are separated by 1.72 Å and each plane is inclined 35.6° to the planar quasi-square coordination group. Conformational details of the *t*-butyl-substituted chelate rings, longer than normal values for some bond lengths, and shorter than usual nonbonding distances, are suggestive of pronounced steric strains within the molecule. The monoclinic unit cell of the crystal has $a = 19.38$, $b = 7.78$, $c = 14.71$ Å, $\beta = 108.8°$, and contains four molecules; calculated and measured densities are 1.45 and 1.44 g/cc, and the space group is C2/c. Reflections lying for the most part within the Cu Kα limiting sphere were photographically recorded with Mo Kα radiation; intensities were visually estimated. Structure determination utilized Patterson and Fourier syntheses, followed by anisotropic full-matrix least-squares refinement. A conventional R of 0.070 for the 1254 independent reflections was obtained.

The reasons for undertaking a structural investigation of the diamagnetic bis(N-*t*-butylsalicylaldiminato)palladium(II) chelate are best presented against the background provided by recent studies of the bis(N-alkylsalicylaldiminato) chelates of nickel(II). The Ni(II) complexes display a rather complicated magnetic behavior that is correlated with the existence of stereochemically distinctive, yet energetically comparable, diamagnetic and paramagnetic (triplet) species of each chelate.[4] In each of the several known crystal-

---

[1] This investigation was supported in part by National Science Foundation Grant GP-6710X, by Public Health Research Grant 2-RO1-GM09370 from the National Institutes of Health, General Medical Sciences, and by the Advanced Research Projects Agency.

[2] National Science Foundation Predoctoral Trainee, 1965–1969.

[3] Author to whom correspondence should be addressed.

[4] See R. Holm, A. Chakravorty, and G. O. Dudek, *J. Am. Chem. Soc.*, 86, 379 (1964), for a comprehensive discussion with numerous references to pertinent earlier papers.