*Contribution from the Istituto di Chimica Generale, University of Padova, Padova, Italy*

# The *cis* Effect of Amines in Displacements of Ligands in Planar Platinum(II) Complexes

**L. Cattalini, G. Marangoni, and A. Cassol**

*Received November 30, 1968*

*The kinetics of displacement, by various reagents, of the coordinated chloride from complexes of the type* trans-$[Pt(am)_2Cl_2]$ *(am = pyridine derivative) have been followed in methanol at 30°. The results have been discussed in terms of* cis *effect of the amine ligands.*

## Introduction

The mechanistic role of amines acting as entering nucleophiles or leaving groups in substitution reactions at square-planar complexes of platinum(II), palladium(II) and gold(III) has been studied in a number of cases during the last few years.[1] It has been found that the free energy of activation decreases linearly with the basicity ($pK_a$) of the entering amine or increases linearly with the basicity of the leaving amine.

The absence of information concerning the role of the amine ligands behaving as non-participating ligands induces us to study the kinetics of the processes:

$$trans\text{-}[Pt(am)_2Cl_2] + Y^- \rightarrow trans\text{-}[Pt(am)_2ClY] + Cl^- \qquad (1)$$

where the two amine ligands, *cis* to the replaceable group, and the entering nucleophile are systematically changed. The results are reported and discussed in this paper.

## Experimental Section

*Materials*: The platinum(II) complexes used in this investigation were prepared by the method reported in the literature for the *trans*-$[Pt(py)_2Cl_2]$ complex.[2] The analytical data are summarized in Table 1. The salts NaI, NaBr, NaSCN as well as pyridine and thiourea were all commercial products reagent grade. The solvent methanol was purified by distillation after refluxing over $Mg(OCH_3)_2$ to remove water.

*Kinetics.* The complexes obey Beer's law and are stable in methanol. Known volumes of methanolic solutions of the substrate and reagent were brought separately at 30° and mixed in the thermostated cell of a double beam Optica-CF4R recording spectrophotometer. The reactions were followed by measuring the changing optical density in the U.V. region of the spectrum over a period of time. The system and the kinetic trend are exactly the same as previously reported[3] for the complex *trans*-$[Pt(py)_2Cl_2]$.

**Table I.** Analytical data for the complexes *trans*-$[Pt(am)_2Cl_2]$.

| Amine | C% calc. | C% Found. | H% Calc. | H% Found. | N% Calc. | N% Found. |
|---|---|---|---|---|---|---|
| 4-CN-pyridine | 30.4 | 30.1 | 1.69 | 1.73 | 11.8 | 11.5 |
| 4-Cl-pyridine | 24.6 | 24.8 | 1.64 | 1.60 | 5.73 | 5.78 |
| 4-$CH_3$-pyridine | 32.1 | 29.9 | 3.12 | 3.17 | 6.25 | 6.16 |

**Table II.** Pseudo first order rate constants for the reactions (1) in methanol at 30°.

| *Cis* amine ligands. | Entering group | concn. $10^2 \times M$ | $10^3 \times k_{obs}$ $sec^{-1}$ |
|---|---|---|---|
| 4-CN-pyridine | $SCN^-$ | 0.876 | 14 |
| | | 0.292 | 4.47 |
| | | 0.177 | 2.68 |
| 4-CN-pyridine | $I^-$ | 0.43 | 5.07 |
| | | 0.215 | 2.76 |
| | | 0.1075 | 1.5 |
| 4-CN-pyridine | $Br^-$ | 39.5 | 10.5 |
| | | 9.9 | 2.36 |
| | | 5.64 | 1.49 |
| 4-Cl-pyridine | $SCN^-$ | 1.76 | 10.2 |
| | | 0.88 | 5.2 |
| | | 0.44 | 2.6 |
| 4-Cl-pyridine | $I^-$ | 1.0 | 3.48 |
| | | 0.5 | 1.77 |
| | | 0.25 | 0.8 |
| 4-Cl-pyridine | $Br^-$ | 50.2 | 4.44 |
| | | 25.1 | 2.21 |
| | | 12.54 | 1.11 |
| 4-Cl-pyridine | py | 199 | 1.84 |
| | | 99.5 | 0.93 |
| 4-$CH_3$-pyridine | $SCN^-$ | 7.71 | 15.5 |
| | | 3.35 | 7.56 |
| | | 1.675 | 3.58 |
| 4-$CH_3$-pyridine | $I^-$ | 9.167 | 7.15 |
| | | 6.11 | 4.5 |
| | | 4.583 | 3.65 |
| | | 3.055 | 1.82 |
| 4-$CH_3$-pyridine | py | 199 | 1.15 |
| | | 99.5 | 0.575 |
| | | 115.3 | 0.767 |
| 4-$CH_3$-pyridine | thiourea | 0.286 | 1.5 |
| | | 0.143 | 0.75 |

N.B. The concentration of the complex in the reaction mixture was always of the order of magnitude of $10^{-5}$ *M*.

---

[1] L. Cattalini and al: *Inorg. Chem. 5,* 1145, 1517, 1674 (1966); 6, 75, 280 (1967); *La Chim. e l'Ind. (Milan) 49,* 625, 1337 (1967).

[2] G. B. Kauffman, *Inorg. Syn. 7,* 251 (1963).

[3] U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Am. Chem. Soc. 87,* 241 (1965).

The kinetics were carried out in the presence of excess nucleophile in order to provide pseudo first order conditions. When the entering group is pyridine the reaction leads to the monosubstituted products but, for the entry of $Br^-$, $I^-$, $SCN^-$ and thiourea there is only one kinetic stage leading to the disubstituted products. This is in accordance with the *trans* labilizing effect sequence: thiourea, SCN, I, Br > > Cl > py as already reported for the pyridine complex.[3]

The pseudo first order rate constants, $k_{obs}$, have been obtained from the linear plot of $\log(D_t - D_\infty)$ *vs.* time, where $D_t$ and $D_\infty$ are the optical densities of the reaction mixture at time t and at the end of the reaction respectively and are summarized in Table II.

**Table III.** Second order rate constants, $k_2$, relative to the processes (1) in methanol at 30°.

| Complex | Nucleophile | $10^3 \times k_2$, $M^{-1} \times sec^{-1}$ |
|---|---|---|
| *trans*-$[Pt(4\text{-}CN\text{-}py)_2Cl_2]$ | $SCN^-$ | 1,600 |
| | $I^-$ | 1,180 |
| | $Br^-$ | 25 |
| *trans*-$[Pt(4\text{-}Cl\text{-}py)_2Cl_2]$ | $SCN^-$ | 574 |
| | $I^-$ | 340 |
| | $Br^-$ | 8.86 |
| | py | 0.925 |
| *trans*-$[Pt(4\text{-}CH_3py)_2)Cl_2]$ | $SCN^-$ | 197 |
| | $I^-$ | 78 |
| | py | 0.58 |
| | thiourea | 5,250 |

The reactions obey the usual two-term rate law[4] rate = $(k_1 + k_2[Y])[\text{substrate}]$ (Y = entering nucleophile) and the second order rate constants, $k_2$, are reported in Table 3. The $k_1$, term provides such a minor contribution when compared to the $k_2[Y]$ contribution that the values are seriously affected by experimental error. The $k_2$ values are summarized in Table III.

## Discussion

As is usual in platinum(II) substitutions, the plot of log $k_2$ vs. the $n_{Pt}$ index of the entering nucleophile is linear for each of the substrates examined.[3] The slopes of these lines (« *s* » = nucleophilic discrimination factor) are reported in Table 4.

**Table IV.** Nucleophilic discrimination factor *s* for the substrate of the type *trans*-$[Pt(am)_2Cl_2]$ (methanol, 30°) and basicity ($pK_a$) of the *cis* amine

| Amine | $pK_a$ | s |
|---|---|---|
| 4-CN-pyridine | 1.9 | 1.1 |
| 4-Cl-pyridine | 3.84 | 1.033 |
| pyridine | 5.17 | $^a$ 1.00 |
| $4\text{-}CH_3$-pyridine | 6.02 | 0.955 |

$^a$ This substrate is the standard complex for the $n_{Pt}$ scale.[3]

The first observation is that there is a linear relationship between *s* and $pK_a$ of the *cis* amine ligands, the discrimination increasing with decreasing $pK_a$, according to the expression:

$$s = -0.035\ (pK_a) + \text{constant} \qquad (2)$$

In the literature, there are two sets of data relative to the *cis* effect in platinum(II) substitutions; these refer to the reactions:[3,5,6]

$$trans\text{-}[PtL_2Cl_2] + Y^- \rightarrow trans\text{-}[PtL_2ClY] + Cl^-$$

and

$$[Pt(bipy)(C)Cl] + Y^- \rightarrow [Pt(bipy)(C)Y] + Cl^-$$

In these two cases the sequences

$$PEt_3(1.65) > AsEt_3(1.25) > SeEt_2(1.05) > py(1.00) > pip(0.91)$$

and

$$NCS(1.3) > N_3(0.95) > NO_2(0.87) > Cl(0.75)$$

have been found for the effect of the *cis* ligands (2L and C respectively) on the nucleophilic discrimination factor (reported in parenthesis). The conclusions of these researches were: (i) the *cis* effect can be rationalized in terms of the influence of the *cis* partners on the ability of the substrate to discriminate between different entering groups and (ii) the substrates which show greater discrimination are those containing *cis* ligands capable of delocalizing negative charge away from the center of the reaction during the formation of the transition state, either because they can interact with the metal *via* π bonding or because they are high in the micropolarizability scale.[6]

The present results are in agreement with the above conclusions in so far as the smaller the basicity of the *cis* amines the greater the nucleophilic discrimination factor, altough the difference is only marginal in this case. It is of interest to note that the relationship (2) involves a thermodynamic property, namely $pK_a$, whereas it was not possible to correlate rate data for reactions of the complexes of the type *trans*-$[PtL_2Cl_2]$ with such non-kinetic properties under the same experimental conditions.[3] It was necessary to use the kinetically determined parameter, $n_{Pt}$, that the *cis* ligand would have reacting as a nucleophile; this being thought to be a measure of its micropolarizability or else a qualitative evaluation of σ plus π interactions. The present relationship is probably due to the fact, which has been already pointed out in the study of the reactivity of amines towards platinum(II) complexes,[1] that the micropolarizability of the amines is constant.

The small value of the coefficient in the expression (2) can be interpreted as a consequence of the relatively small importance of basicity in reactions of complexes of « soft » metal ions, such as $Pt^{II}$. The major effect of varying the $pK_a$ of the *cis* amine ligands

---

(4) C. H. Langford and H. B. Gray, « Ligand Substitution Processes », W. A. Benjamin Inc., Ney York, N. Y. (1965); F. Basolo and R. G. Pearson « Mechanism of Inorganic Reactions », 2nd ed., J. Wiley and S. Inc., New York, N. Y. (1967).

(5) L. Cattalini and M. Martelli, *Inorg. Chim. Acta*, *1*, 189 (1967).

(6) L. Cattalini, A. Orio, and M. Nicolini, *J. Am. Chem. Soc.* *88*, 5734 (1966).

is therefore the increase in reactivity with decreasing basicity. This is consistent with the idea that a decreasing ability to transfer charge to the metal is better able to accomodate the increase in electron density caused by the entry of the fifth ligand in the transition state. Bearing in mind that the originally *cis* ligands occupy the apical positions in the transition state, there may be some significance in the observation that the *cis* effect responds more to basicity whereas the *trans*, entering group and leaving group effect respond more to micropolarizability. This response of *cis* effect to ligand basicity was also observed in reactions of gold(III) complexes.[7]

*Aknowledgments.* We thank Dr. M. L. Tobe for helpful discussions.

(7) L. Cattalini, A. Orio, and M. L. Tobe, *Inorg. Chem.* 6, 75 (1967).