Reaction of $[Pt(C_2H_4)Cl_3]^-$ with Bipyridyl

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Abstract: Displacements by uncharged chelating ligands (L–L) on the trichloro(ethylene)platinate(II) ion have been studied in acidic aqueous methanol at 24.6°. For the reaction with bipyridyl (N–N) two identifiable steps were found. Whereas the rate of the first step depends on the concentration of both Zeise's salt (I) and entering group, the rate of the second step was found to be independent of the ligand concentration. A reaction mechanism is proposed involving a bimolecular attack of the reagent on the trichloro(ethylene)platinate(II) ion to give the positively charged *cis*-$[Pt(C_2H_4)(N–N)Cl]^+$ (II), which then undergoes the olefin replacement, leading to the thermodynamically stable *cis*-$[Pt(N–N)Cl_2]$ (III). Evidence from kinetic studies for the rather labile intermediate II is presented.

Of relatively recent origin are the developments in the important research field concerning the chemistry of the d^8 transition metal ions. This rapidly expanding interest is due mainly to the chemical versatility of such systems. Thus, d^8 transition metal ions form fairly stable organo,[1,2] hydrido,[3–7] and olefin complexes;[8–14] they undergo nucleophilic substitutions,[15–17] electron-transfer reactions,[18] and electrophilic attack.[19–22] The combination of these properties, involving an interplay of kinetic and thermodynamic factors, renders these metal ions the most effective catalysts for the activation of inert saturated molecules (*e.g.*, H_2) and for the addition of unsaturated molecules (*e.g.*, olefins, carbon monoxide, acetylene, etc.) in the homogeneous phase.[23–26]

The present work is devoted to the kinetic study of some new labile platinum(II)–olefin complexes.

Whereas negatively charged four-coordinate planar platinum(II)–olefin complexes are fairly stable, less frequent is the occurrence of uncharged compounds. Among the last named, stable dihalide, dialkyl, and diaryl platinum(II)–diene complexes have been isolated.[9,27–30] In addition, trichloro(ethylene)platinate(II) ion reacts under rather mild conditions with some amino acids to give stable, neutral compounds. Thus, recently Panunzi, *et al.*,[31] succeeded in isolating monomeric complexes of the type $[Pt(C_2H_4)$(amino acid anion)Cl] in which the nitrogen of the amine group is believed to be bonded to the metal in the *trans* position to the olefin. However, to the best of our knowledge, no stable positively charged platinum(II)–olefin complex with chelate ligands has been reported. Only with monodentate ligands has a cationic, rather unstable, Pt(II)–ethylene complex of formula $[Pt(C_2H_4)(NH_3)(py)Cl]^+$ been obtained.[32] No reaction occurs between olefins and positive or neutral Pt(II) compounds. Thus, whereas allyl alcohol (reacting as an olefin) is a good entering group toward anionic Pt(II) complexes, it does not appear to react at all with $[Pt(NH_3)_3Cl]^+$.[33]

At this stage, therefore, any attempt to provide a satisfactory explanation for the difference in the behavior of these complexes (whether in terms of effective nuclear charge or of a combination of other effects) requires a preliminary study of the factors affecting the lability of positive platinum(II)–olefin complexes. Strictly related to this is the study of the reaction mechanism for the replacements of negative groups from platinum(II)–olefin complexes by chelating ligands.

This paper reports kinetic investigations of the chloride displacements on the trichloro(ethylene)platinate(II) ion with some neutral chelating agents having nitrogen and/or oxygen as donor atoms. The rate of formation of a cationic platinum(II)–olefin complex and that of the replacement of its coordinated ethylene have been determined.

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Experimental Section

Materials. The Zeise's salt used in this investigation was prepared from K_2PtCl_4 by the method of Cramer.[25] To the tetrachloroplatinate(II) ion in aqueous solution acidified with HCl was added stannous chloride. The mixture was stirred and ethylene was introduced at about 1.5 atm. The crystals obtained by cooling the solution were washed with cold methanol, and the residue was recrystallized from 0.2 *N* hydrochloric acid to remove potassium chloride and then from ethanol. The complex was dried in a desiccator over KOH pellets and H_2SO_4 and stored in the dark.

The complexes of the type *cis*-$[Pt(L\text{-}L)Cl_2]$ are all known compounds and have been prepared by the methods reported in the literature. The references are the following: *cis*-$[Pt(bipyridyl)Cl_2]$,[34] *cis*-$[Pt(oxyquinoline)Cl_2]$,[35] and *cis*-$[Pt(ethylenediamine)Cl_2]$.[36] Each one was characterized by elemental analysis and by comparison of its ultraviolet spectrum with published values, when available.

Methanol purified by distillation over $(CH_3O)_2Mg$ and redistilled water were used as solvents. Other materials were reagent grade products.

Kinetics. The reactions were followed by measuring the changes in optical density in the ultraviolet region of the spectrum over a period of time. Freshly prepared solutions of $K[Pt(C_2H_4)Cl_3]\cdot H_2O$ were used for each kinetic run. Known volumes of thermostated solutions of the complex and the reagent were mixed in a 1-cm quartz cell placed in the thermostated compartment of an Optica CF-4 recording spectrophotometer. The reference cell contained all the reagents, except the complex. From the recorded near-ultraviolet spectra, a suitable wavelength was chosen and the kinetics were followed at the appropriate wavelength by recording the change in optical density as a function of time. Any single kinetic run was carried out under pseudo-first-order conditions, and the first-order rate constants, k_{obsd}, were calculated from slopes of the linear plots of log $(A_\infty - A_t)$ *vs.* time (*A* is the optical density). In all the reactions the ionic strength was maintained constant by adding lithium perchlorate.

Results and Discussion

All the reactions were performed in 95% aqueous methanol to which was added hydrochloric acid. No aqueous solution could be used because of the very low solubility of some species. The reaction mixture was kept acidified to prevent aquation of the Zeise's salt. It is known, in fact, that trichloro(ethylene)platinate(II) ion rapidly undergoes appreciable aquation according to the equilibrium

$$[Pt(C_2H_4)Cl_3]^- + H_2O \leftrightarrows \mathit{trans}\text{-}[Pt(C_2H_4)(H_2O)Cl_2] + Cl^- \qquad (1)$$

The aquo complex, in turn, undergoes acid dissociation, yielding its conjugate base, *trans*-$[Pt(C_2H_4)(OH)Cl_2]^-$, which is thought to be an unstable species.[37,38] Thus, all the kinetic runs were carried out in the presence of sufficient hydrochloric acid to force the above equilibrium far enough to the left to ignore the presence of aquo and hydroxo complexes.

In each kinetic run pseudo-first-order conditions were provided by adding a large excess of the amine entering group to the acidified solution of the complex. Although in all cases the concentration of the free amine was smaller than that of the substrate, it was kept constant all during the course of the reaction by the establishment of the acid–base equilibrium: amine $+ H^+ \leftrightarrows$ amine H^+. The concentration of the unprotonated entering group was graphically determined by using the well-known logarithmic concentration diagram procedure.

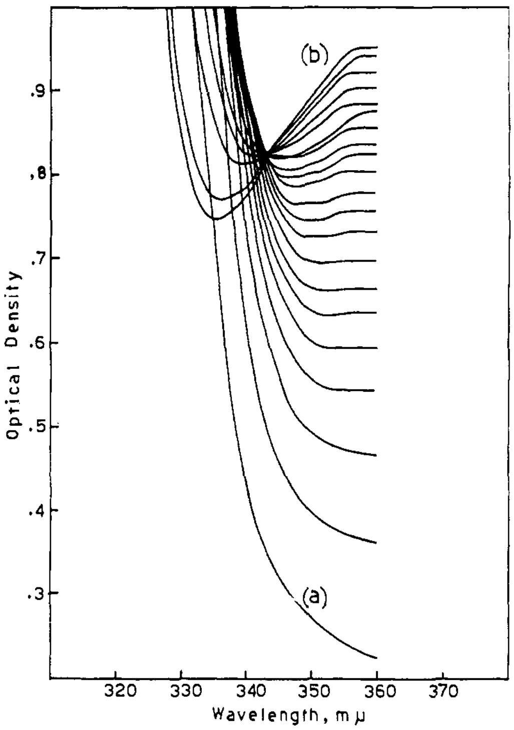

Figure 1. Optical density changes for the reaction of Zeise's salt ($\sim 5 \times 10^{-5}$ *M*) and bipyridyl (10^{-3} *M*) in acidic aqueous methanol (HCl 4×10^{-3} *M*) at 24.6°. The first stage is over in a matter of 150 sec: (a) spectrum of the reaction mixture after 10 sec; (b) final spectrum.

In absence of reliable pK_a values for the base employed in aqueous methanol, we have been forced to use pK_a values determined in aqueous solution. This assumption appears to be quite reasonable since it has been found, on the basis of potentiometric determinations, that the base strength of amines in water is a reliable index of their base strength in aprotic solvents.[39] This should be also true for methanol which has a greater similarity to water than nonprotolytic solvents. Such an approximation can affect the value of the bimolecular constant, k^I (see below), but it does not invalidate the mechanistic implications.

By scanning the spectrum in the ultraviolet region from time to time during the course of the reaction with bipyridyl, it could be seen that there were two observable stages of spectrophotometric change. Previous experiments using reaction mixtures with relatively high concentrations of free unprotonated bipyridyl showed also that the first stage of the reaction was over within a few seconds, as shown by the drastic change of the initial spectrum (Figure 1). An isosbestic point was developed at 344 mμ after the first-stage completion. Thus, in other kinetic runs, by taking optical density measurements at this wavelength, the second stage of the reaction could be ignored, and the values of k^I_{obsd} corresponding to the first stage of the reaction were determined. The rate constants of the second stage, k^{II}_{obsd}, were obtained by calculating at wavelengths where the difference in optical density between the spectra of the products of the two stages

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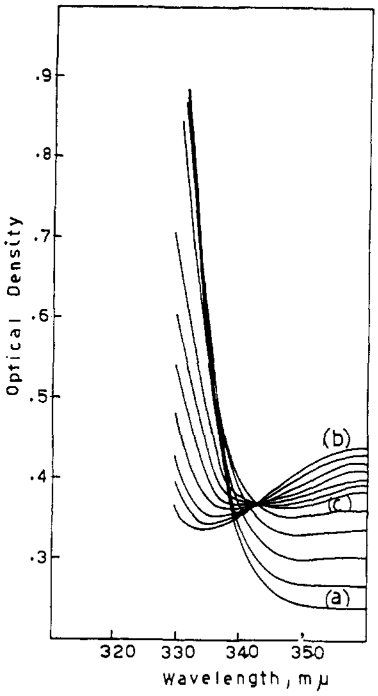

Figure 2. Optical density changes for the reaction of Zeise's salt (~2.5 × 10^{-5} *M*) and bipyridyl (10^{-3} *M*) in acidic aqueous methanol (HCl 2.5 × 10^{-3} *M*) at 24.6°: (a) spectrum of the reaction mixture after 60 sec; (b) final spectrum; (c) probable spectrum of *cis*-$[Pt(C_2H_4)(N\text{-}N)Cl]^+$.

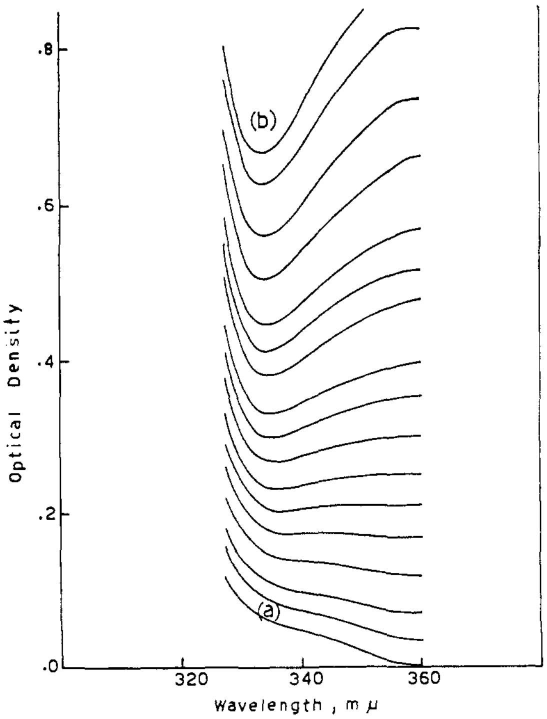

Figure 3. Optical density changes for the reaction of Zeise's salt (~5 × 10^{-5} *M*) and bipyridyl (10^{-3} *M*) in the presence of HCl (1.27 × 10^{-1} *M*) at 24.6°. The first state is slower than the second one: (a) spectrum of the reaction mixture after 10 sec; (b) final spectrum.

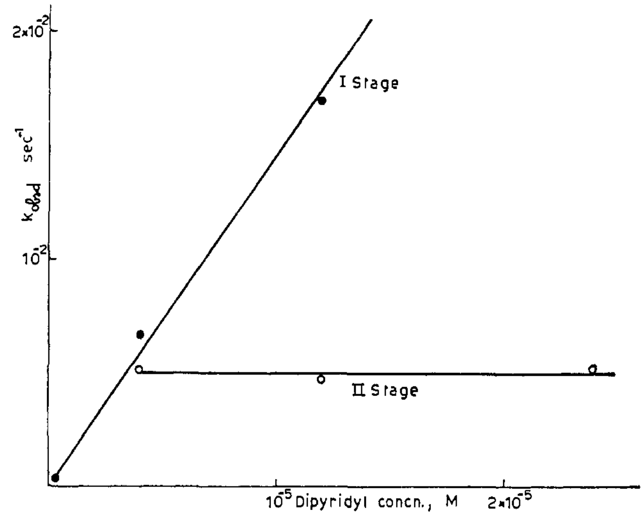

Figure 4. Plots of k_{obsd} for the two stages of the reaction between Zeise's salt and bipyridyl *vs.* unprotonated entering-group concentration.

of the over-all reaction was largest (Figure 2). The customary treatment for consecutive reactions was applied in this case. At relatively high concentrations of hydrochloric acid (*i.e.*, very low concentrations of unprotonated bipyridyl), the first stage of the reaction becomes slower than the second one, and as a consequence the isosbestic point disappears (Figure 3). The observed rate constants relative to the single two stages (eq 2) are reported in Table I.

$$[Pt(C_2H_4)Cl_3]^- + \text{N-N} \xrightarrow{k^{I}} \text{intermediate} \xrightarrow{k^{II}} cis\text{-}[Pt(\text{N-N})Cl_2] \quad (2)$$

As shown by these rate data, the first-step rate (k^{I}_{obsd}) depends upon the concentration of the free bipyridyl, whereas the rate of the subsequent step (k^{II}_{obsd}) is unaffected by changes in bipyridyl concentration. By plotting the pseudo-first-order rate constants *vs.* the bipyridyl concentration, two straight lines are obtained, as is shown in Figure 4. For the first step of the reaction, the observed rate constants therefore fit the relationship

$$k^{I}_{obsd} = k^{I}[\text{bipyridyl}] \quad (3)$$

This is the same kinetic expression found for the substitution reactions in planar Pt(II) complexes, except for the missing first-order rate constant (k_1, sec^{-1}),[40] which in this case is too small to be measured. However, even here one can accept the reaction mechanism usually adopted for displacements on four-coordinate planar platinum(II) substrates.[15–17] The values of the

Table I. Rates of Reaction 2 in Acidic Aqueous Methanol at 24.6°[a]

HCl concn, *M*	Unprotonated bypyiridyl concn, *M*	k^{I}_{obsd}, sec^{-1}	k^{II}_{obsd}, sec^{-1}
0.127	3.0 × 10^{-7}	4.0 × 10^{-4}	...
0.01	4.0 × 10^{-6}	6.7 × 10^{-3}	5.0 × 10^{-3}
0.004	1.2 × 10^{-5}	1.7 × 10^{-2}	4.8 × 10^{-3}
0.0025	2.4 × 10^{-5}	...	5.1 × 10^{-3}

[a] Complex concentration ~5 × 10^{-5} *M*; analytical bipyridyl concentration 10^{-3} *M*; ionic strength = 0.2 *M* with $LiClO_4$.

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single specific rate constants are $k^{I} = 1.45 \times 10^3$ M^{-1} sec^{-1} and $k^{II} = 5 \times 10^{-3}$ sec^{-1}.

Because of the higher *trans* effect of the ethylene in comparison to the chloride, one can reasonably assume that in the trichloro(ethylene)platinate(II) ion the chloride ion in the position *trans* to ethylene is the most labile one. This is also confirmed by the reaction of Zeise's salt with many charged and uncharged monodentate ligands.[38] We suggest that the first stage of the reaction must involve a bimolecular substitution of such a chloride ion by the bipyridyl, followed by a fast chelation in *cis* position leading to the rather labile, positive *cis*-$[Pt(C_2H_4)(N\text{–}N)Cl]^+$. In line with this, it is noteworthy that in reactions involving polydentate entering groups, the chelate ring closes almost always very rapidly.[41,42] The cationic intermediate undergoes a subsequent bimolecular substitution of the ethylene by the solvent (S) which is then rapidly replaced by chloride ion. Thus, the final product is identified as the thermodynamically stable *cis*-$[Pt(N\text{–}N)Cl_2]$. The rate constant of the second stage (k^{II}, sec^{-1}) must therefore be a pseudo-first-order rate constant for a reaction path controlled by the solvent. k^{II}_{obsd} is, in fact, independent of the chloride concentration. It is of interest that the ethylene was found to be evolved only during the course of the second stage of the reaction. The proposed reaction mechanism of the overall process is shown in Figure 5.

We think that this evidence clearly shows the existence and the chemical identity of a novel, positively charged platinum(II)–olefin complex, of the type *cis*-$[Pt(C_2H_4)(N\text{–}N)Cl]^+$. Unfortunately, it was not possible to trap it by adding at −70° salts of bulky univalent anions, such as $B(C_6H_5)_4^-$ and $SbCl_6^-$, to an acidified methanolic solution of $K[Pt(C_2H_4)Cl_3]$ and bipyridyl. Thus, since any other attempt of direct chemical identification of the kinetic product (II) was unsuccessful, its nature was deduced from kinetic considerations. In Figure 2 a spectrum (c) is reported of a reaction mixture allowed to react for a sufficient time under the right conditions to convert practically all the Zeise's salt into the *bona fide* intermediate (II). This therefore would be the most probable spectrum of *cis*-$[Pt(C_2H_4)(N\text{–}N)Cl]^+$ in the near-ultraviolet region.

Finally, kinetics of the reaction between Zeise's salt and some other chelating ligands, such as 8-oxyquinoline and ethylenediamine, were carried out under experimental conditions similar to those used for the reaction with bipyridyl. In these cases a cationic labile platinum(II)–olefin compound could not be detected since the two expected reaction stages do not differ sufficiently to be identifiable. The reaction with ethylenediamine (en), however, may involve the formation of a transient, ethylenediamine-bridged complex, $[(Pt(C_2H_4)Cl_3)_2en]$, as found under preparative conditions.[43]

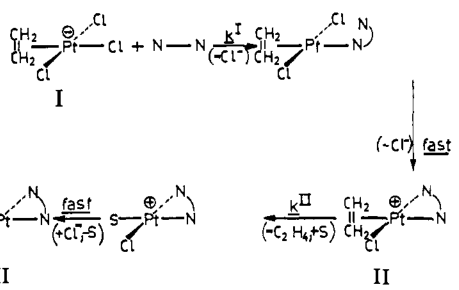

Figure 5. Proposed mechanism for the reaction of Zeise's salt with bipyridyl.

As far as the easier replacement of the ethylene from cationic platinum(II)–olefin complexes in comparison with their neutral and anionic parent compounds is concerned, one can argue that this behavior may be accounted for by considering that the ability of the olefins to participate in π interactions will be very dependent on the oxidation state of the metal and its effective nuclear charge. Consequently, with cationic complexes where back-donation of negative charge by way of π bonding from metal to olefin will probably decrease, the replacement of the olefin becomes easier. It is of interest, moreover, that the aromaticity of the platinum α-diimine chelate ring[42] in *cis*-$[Pt(C_2H_4)(N\text{–}N)Cl]^+$ produces a lower electron density along the platinum–olefin bond. This turns out to be an additional cause of weakening of this bond due to the consequent decrease of the back-bonding to the olefin.

Thus, one can conclude that stability of platinum–olefin complexes depends upon the simultaneous existence of both σ bonding from the olefin to the metal and π back-bonding from the metal to the olefin. When π bonding is drastically reduced, as in the case of cationic complexes of platinum(II) with olefins, the stability of the platinum–olefin bond greatly decreases despite the enhancement of the σ donor ability of the olefin.

Recent investigations by Venanzi, *et al.*,[44] have been directed toward the determination of the relative significance of π bonding *vs.* σ bonding in metal–olefin bond stability. The $\Delta S°$ and $\Delta H°$ values of formation were measured for complexes of the type $[Pt(olefin^+)Cl_3]$ in aqueous solutions. Values obtained supported the assumption that the olefin σ-donor ability was a less significant factor than the π-acceptor property in affecting the stability of the platinum–olefin bond.

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