$1,2\text{-}B_{10}C_2H_{10}$ in 30 ml of anhydrous ether added to a suspension of 5.0 g (5.4 mmol) of $[(C_6H_5)_3P]_3RhCl$ in 50 ml of ether. The yield of pure product, red-violet crystals, was 4.0 g (87%), mp 178–181° dec.

$1\text{-}[(PPh_3)_2Rh]\text{-}7\text{-}CH_3\text{-}1,7\text{-}(\sigma\text{-}B_{10}C_2H_{10})$, III. This complex was prepared from 8.22 mmol of $1\text{-}Li\text{-}7\text{-}CH_3\text{-}1,7\text{-}B_{10}C_2H_{10}$ (25 ml ether) and 2.5 g (2.7 mmol) of $[(C_6H_5)_3P]_3RhCl$ suspended in 30 ml of ether. The yield of pure product, orange crystals, was 1.5 g (70%), mp 182–184° dec.

$1\text{-}[(PPh_3)_2Rh]\text{-}7\text{-}C_6H_5\text{-}1,7\text{-}(\sigma\text{-}B_{10}C_2H_{10})$, IV. Complex IV was prepared in the same manner from 9.0 mmol of $1\text{-}Li\text{-}7\text{-}C_6H_5\text{-}1,7\text{-}B_{10}C_2H_{10}$ and 2.5 g (2.7 mmol) of $[(C_6H_5)_3P]_3RhCl$. The yield of pure product, orange crystals, was 1.7 g (75%), mp 167–168° dec.

$1\text{-}[(PPh_3)_2Rh(C_6H_5CN)]\text{-}2\text{-}C_6H_5\text{-}1,2\text{-}(\sigma\text{-}B_{10}C_2H_{10})$, V. A solution of 3.0 mmol of C_6H_5CN in 10 ml of dry diethyl ether was added under an argon atmosphere at 25° to a stirred suspension of 0.42 g (0.5 mmol) of $1\text{-}[(PPh_3)_2Rh]\text{-}2\text{-}C_6H_5\text{-}1,2\text{-}(\sigma\text{-}B_{10}C_2H_{10})$ in 10 ml of ether. In the course of the reaction the deep red color turned to orange. After stirring for 4 hr at room temperature, the reaction mixture was rotary evaporated to an orange solid. The solid thus obtained was dissolved in 10 ml of dry CH_2Cl_2 under argon atmosphere and then reprecipitated by addition at 0° of 5 ml of ethanol. The yield of pure product was essentially quantitative. The orange crystals melted at 150–152° with decomposition.

$1\text{-}[(PPh_3)_2Rh(CO)]\text{-}2\text{-}C_6H_5\text{-}1,2\text{-}(\sigma\text{-}B_{10}C_2H_{10})$, VI. Under argon, a solution of 9.0 mmol of $1\text{-}Li\text{-}2\text{-}C_6H_5\text{-}1,2\text{-}B_{10}C_2H_{10}$ in 25 ml of dry ethyl ether was slowly added at 0° to a stirred suspension of 2.5 g (3.61 mmol) of $[(C_6H_5)_3P]_2Rh(CO)Cl$ in 30 ml of ether. The mixture was stirred for 4 hr at 0° and the yellow precipitate separated by filtration in an argon atmosphere was washed with dry *n*-hexane. Further purification was performed by recrystallization from benzene–*n*-hexane. The yield of pure product, yellow crystals, was 2.5 g (80%), mp 126–127° dec;

$1\text{-}[(PPh_3)Rh(CO)_2]\text{-}2\text{-}C_6H_5\text{-}1,2\text{-}(\sigma\text{-}B_{10}C_2H_{10})\cdot{}^1/_2CH_2Cl_2$, VII. A suspension of 0.38 g (0.45 mmol) of $1\text{-}[(PPh_3)_2Rh]\text{-}2\text{-}C_6H_5\text{-}1,2\text{-}(\sigma\text{-}B_{10}C_2H_{10})$ in 10 ml of dry benzene at 25° was treated with carbon monoxide at 1 atm. The deep red color rapidly turned yellow and a fine yellow precipitate was formed. The precipitate was collected by filtration under CO atmosphere and washed with a little methanol. The crude product was further purified by recrystallization under CO atmosphere from $CH_2Cl_2\text{–}CH_3OH$. The yield of dichloromethane-solvated product was essentially quantitative. The bright yellow crystals melted at 176° with decomposition. The half molecule of CH_2Cl_2 present was found by gas chromatographic analysis. The complex is unstable in solution and can be handled only under an atmosphere of carbon monoxide.

Absorption of CO by $1\text{-}[(PPh_3)_2Rh]\text{-}2\text{-}C_6H_5\text{-}1,2\text{-}(\sigma\text{-}B_{10}C_2H_{10})$. In a standard gas absorption apparatus 10 ml of dry benzene was saturated with carbon monoxide at 1 atm pressure and 25°. Then the rhodium–carborane complex (0.1–0.15 g) was tipped into the solvent from a bucket and the additional carbon monoxide uptake at 25° was measured. The uptake stopped after 10 min and the absorption was found to correspond to 1.44 mol of CO/mol of complex II (72% of the calculated value). The isolated product was identified as complex VII, mp 175–176° dec. The absorption was measured also at 18° and 1 atm and the uptake was found to correspond to 1.88 mol of CO/mol of complex II (94% of the calculated value).

Absorption of CO by $1\text{-}[(PPh_3)_2Rh(CO)]\text{-}2\text{-}C_6H_5\text{-}1,2\text{-}(\sigma\text{-}B_{10}C_2H_{10})$. The absorption of CO was performed in the same conditions above reported. The uptake stopped after 10 min and the absorption at 25° was found to correspond to 0.64 mol of CO/mol of complex VI. The product isolated was identified as the complex VII, mp 175–176° dec.

Acknowledgment. We thank Mr. F. Bergamin for technical assistance in the preparation of the carboranes.

Registry No. I, 43202-53-5; II, 43202-54-6; III, 43202-55-7; IV, 43164-55-2; V, 43202-56-8; VI, 43202-57-9; VII, 43202-58-0; $[(C_6H_5)_3P]_3RhCl$, 14694-95-2; *trans*-$[(C_6H_5)_3P]_2Rh(CO)Cl$, 15318-33-9; $1\text{-}Li\text{-}2\text{-}CH_3\text{-}1,2\text{-}B_{10}C_2H_{10}$, 32630-05-0; $1\text{-}Li\text{-}2\text{-}C_6H_5\text{-}1,2\text{-}B_{10}C_2H_{10}$, 41655-52-1; $1\text{-}Li\text{-}7\text{-}CH_3\text{-}1,7\text{-}B_{10}C_2H_{10}$, 32630-07-2; $1\text{-}Li\text{-}7\text{-}C_6H_5\text{-}1,7\text{-}B_{10}C_2H_{10}$, 42012-25-9.

Contribution from Centro di Chimica e Tecnologia dei Composti Metallorganici degli Elementi di Transizione,
Consiglio Nazionale Ricerche, Facolta Chimica Industriale, The University, Calle Larga, Venice, Italy

Mechanism of the Reaction of Zeise's Salt with DL-α-Alanine

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The reaction of Zeise's anion, $[Pt(C_2H_4)Cl_3]^-$, with DL-α-alanine (AlaH) to give *N-trans*-$[Pt(Ala)(C_2H_4)Cl]$ in water at 25° proceeds stepwise. In the pH range 3.2–4.0, *i.e.*, at very low concentrations of the anionic form of the amino acid, one single stage is observed. This involves bimolecular reactions of both $[Pt(C_2H_4)Cl_3]^-$ and the aquo species *trans*-$[Pt(C_2H_4)(H_2O)Cl_2]$ to give the intermediate *N-trans*-$[Pt(Ala)(C_2H_4)Cl_2]^-$ in which the alaninate anion is linked to platinum only through the nitrogen-bearing end. This step is followed by the more rapid closure of the chelate ring by the carboxylate end to give *N-trans*-$[Pt(Ala)(C_2H_4)Cl]$. The second-order rate constants for the reactions of Zeise's anion and its aquo complex with Ala are $6.1 \pm 3.5 \times 10^3$ and $1.70 \pm 0.15 \times 10^5$ M^{-1} sec^{-1}, respectively. In the pH range 6–9, *i.e.*, when Ala is the predominant amino acid species, the first step becomes too fast to measure, thus enabling the subsequent closure of the chelate ring to be studied kinetically. The first-order rate constant for this intramolecular process is $6.11 \pm 0.14 \times 10^{-3}$ sec^{-1}.

Introduction

The stability of the metal-olefin bond in platinum(II) complexes as related to the formal charge on the complex has been the subject of studies in the past few years. While negative and neutral π-olefin complexes of Pt^{II} with monodentate ligands had long been known, only recently have π-olefin Pt^{II} complexes with bidentate ligands been described, of the type $[Pt(\text{amino acid})(C_2H_4)Cl]$.[1-3] In these complexes the coordinated olefin may be in a trans position either to the nitrogen or to the oxygen atom of the amino acid. Upon treatment with aqueous hydrochloric acid, these complexes dissociate completely into Zeise's anion and the amino acid. Facile exchange of the coordinated olefin also takes place.[3c,4] No examples of nucleophilic attack on the coordi-

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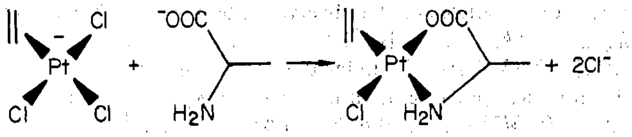
(4) For a survey see U. Belluco, "Organometallic and Coordination Chemistry of Platinum," Academic Press, London, 1973, Chapter VI.

nated olefin in these neutral complexes have been reported so far.

Cationic π-olefin complexes of Pt^{II} are comparatively unstable, such as $[Pt(NH_3)(pyridine)(C_2H_4)Cl]^+$ [5] and *trans*-$[Pt(PR_3)_2(H)(C_2H_4)]^+$.[6] Results of our kinetic studies on the reaction of Zeise's anion and its analogs $[Pt(olefin)Cl_3]^-$ (olefin = ethylene;[7] allyl-Z;[8] Z = NH_3^+, PEt_3^+, SO_3^-) with neutral bidentate ligands (N-N = bipyridyl, ethylenediamine) giving $[Pt(N\text{-}N)Cl_2]$ indicated that olefin replacement to the final product occurred through the intermediacy of the highly unstable cationic species $[Pt(N\text{-}N)(olefin)Cl]^+$. This mechanism was confirmed independently in the case of the reaction of Bukhovets' anion $[Pt(ac)Cl_3]^-$ (ac = 2,5-dimethyl-3-hexyne-2,5-diol) with bipyridyl[9] for which the cationic intermediate [Pt(bipy)(ac)Cl]Cl could be isolated in the solid state. Also, cationic complexes of the type [Pt(ac′)(en)Cl]Cl (ac′ = an acetylene derivative, en = ethylenediamine) were reported.[10] All these species are unstable toward replacement of the π-bonded acetylene by chloride, which results in their conversion to $[Pt(N\text{-}N)Cl_2]$.

In the wake of these findings and of our previous results, we anticipated that the use of a monoanionic bidentate ligand such as an amino acid anion (L-L) in the reaction of $[Pt(L_\pi)Cl_3]^-$ (L_π = olefin, acetylene, carbon monoxide, isocyanide, etc.) would allow us to halt the mechanistic pathway sequence at the stable neutral intermediate $[Pt(L\text{-}L)(L_\pi)Cl]$. Therefore, we have carried out a kinetic study of the reaction



(DL-α-alaninate)

in water at 25° and shall report on the results herein. The results for other L_π complexes will be described in a forthcoming paper.

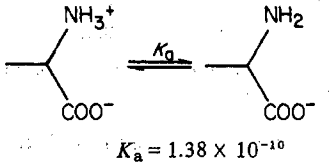
Experimental Section

Materials. The reaction product, *N-trans*-$[Pt(C_2H_4)(Ala)Cl]$ (Ala = DL-α-alaninate anion), was prepared by the reaction of Zeise's salt with the amino acid in basic medium according to the literature methods.[1,3a] All other chemicals were of reagent grade purity. Doubly distilled water was used as the solvent.

Kinetics. The progress of the reaction of $[Pt(C_2H_4)Cl_3]^-$ or of *trans*-$[Pt(C_2H_4)(H_2O)Cl_2]$ (see further) with alanine was followed with an Optica CF-4 recording spectrophotometer equipped with a thermostated cell compartment where the temperature was controlled within ±1°. Spectral changes in the range 330–270 mμ were monitored. Details of the procedure were described elsewhere.[7,8] In each kinetic run the final spectrum of the reaction mixture was identical with that of an authentic sample of *N-trans*-$[Pt(C_2H_4)(Ala)Cl]$. All kinetic runs were carried out at the required pH by the use of conventional buffer systems (potassium dihydrogen phosphate–phosphoric acid for pH 3–4; borax–boric acid for pH 8; total buffer concentration 0.1 *M*). The ionic strength was adjusted to 0.3 *M* by addition of lithium chloride or perchlorate.

Results and Discussion

In the pH range 3–4, $[Pt(C_2H_4)Cl_3]^-$ reacts with DL-α-alanine to give *N-trans*-$[Pt(C_2H_4)(Ala)Cl]$ in a single observable stage of spectrophotometric change. In each kinetic run pseudo-first-order conditions were provided by the addition of a large excess of the amino acid to the starting complex. Although in all cases the concentration of the anionic form of the amino acid, $H_2NCH\text{-}(CH_3)COO^-$ (Ala), was much smaller than that of the platinum substrate (~10^{-9} *M* *vs.* 7.5 × 10^{-4} *M*), it was kept constant throughout each kinetic run by the continuously and simultaneously maintained equilibrium 1. Under these conditions pseudo-first-



(1)

$K_a = 1.38 \times 10^{-10}$

order rate constants, k^{I}_{obsd}, were calculated from the slopes of linear plots of log $(A_\infty - A_t)$ *vs.* time (A = optical density). Table I lists rate constants for some different concentrations of Ala, which were obtained either by changes in total amino acid concentration at a constant pH or by changes in pH at a constant analytical amino acid concentration. The concentrations of the anionic form of the amino acid, [Ala], were calculated according to equilibrium 1 by eq 2, where C_0 =

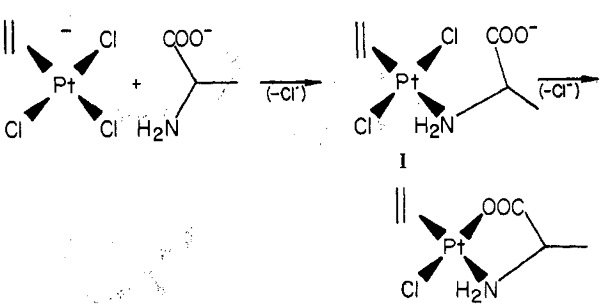
$$[Ala] = K_aC_0/(K_a + [H^+]) \qquad (2)$$

total amino acid concentration in the range 1.5–3 × 10^{-2} *M*. The K_a for alanine was taken from the literature.

On plotting k^{I}_{obsd} *vs.* [Ala] at constant added chloride concentration (10^{-2} *M*), a straight line with negligible intercept within experimental error is obtained. Least-squares analysis gave a value of 5.21 ± 0.34 × 10^4 M^{-1} sec^{-1} for the slope of this plot. Therefore, the kinetics obey the rate law in (3),

$$k^{I}_{obsd} = k[Ala] \qquad (3)$$

indicating that the anionic form of the amino acid which bears the free unprotonated amine group is the kinetically active species which attacks the platinum complex. We suggest that this stage involves displacement of the trans-labilized chloride in Zeise's anion by the free amine group to give the intermediate I, followed by the more rapid closure of the chelate ring by the carboxylate group which gives the final product II. On the other hand, Zeise's anion undergoes



I

(4)

II

the aquation reaction 5.[11-15] The value of the equilibrium

$$[Pt(C_2H_4)Cl_3]^- + H_2O \rightleftharpoons trans\text{-}[Pt(C_2H_4)(H_2O)Cl_2] + Cl^- \qquad (5)$$

III

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Table I. Pseudo-First-Order Rate Constants, $k^{\mathrm{I}}_{\mathrm{obsd}}$ (sec^{-1}), for the Reaction $[\mathrm{Pt(C_2H_4)Cl_3}]^-$ + Ala → *N-trans*-$[\mathrm{Pt(Ala)(C_2H_4)Cl}]$ + $2\mathrm{Cl}^-$ in Water at 25° [a]

$10^2\times$ [Alanine],[b] M	$10^4[\mathrm{H}^+]$, M	$10^2[\mathrm{Cl}^-]$, M	10^9[Ala], M	$10^4k^{\mathrm{I}}_{\mathrm{obsd}}$, sec^{-1}
1.5	100.00	1.00	0.21	<0.05
1.5	3.16	1.00	6.56	3.90
1.5	1.58	1.00	13.10	7.00
1.0	2.34	1.00	5.90	3.37
3.0	2.34	1.00	17.70	9.40
1.5	2.34	10.00	8.85	1.04
1.5	2.34	3.00	8.85	1.84
1.5	2.34	1.50	8.85	3.22
1.5	2.34	1.00	8.85	4.86
1.5	2.34	0.75	8.85	6.05

[a] Platinum complex concentration 7.5×10^{-4} M; $\mu = 0.3$ M.
[b] Total amino acid concentration.

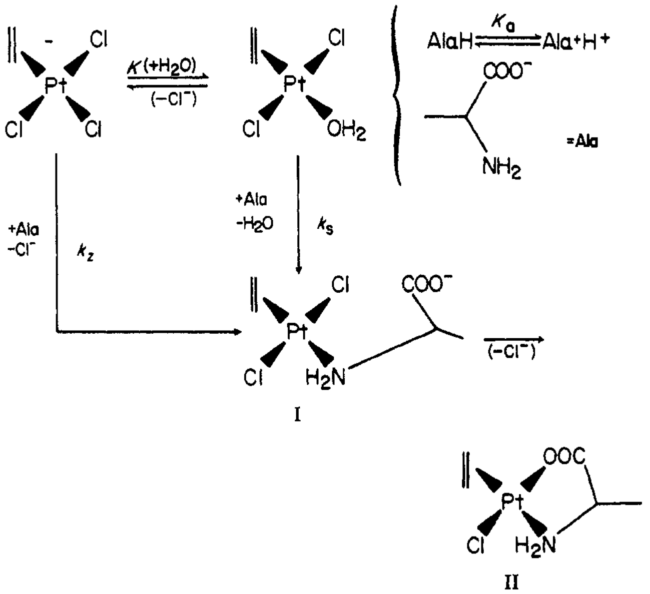
quotient, K, for this aquation has been found to be 2.6×10^{-3} M at 25°.[15] In the expectation that the aquo complex III also would react with Ala at comparable rates, kinetic runs were carried out at chloride concentrations ranging from 7.5×10^{-3} to 10^{-1} M at pH 3.63 and [Ala] = 8.85×10^{-9} M in order to study the effect of added chloride on rates (Table I). On plotting the $k^{\mathrm{I}}_{\mathrm{obsd}}$ values for these experiments *vs.* inverse chloride concentration a straight line with finite intercept was obtained (Figure 1). This straight line begins to level off at $[\mathrm{Cl}^-] \lesssim 7.5 \times 10^{-3}$ M, that is, where the concentration of the chloride ion released as in eq 4 becomes comparable with that of the chloride added. Least-squares analysis of the linear portion gave a slope of $4.17 \pm 0.41 \times 10^{-6}$ M sec^{-1} and an intercept of $5.4 \pm 3.1 \times 10^{-5}$ sec^{-1}.

These results indicate an overall rate law of the form

$$k^{\mathrm{I}}_{\mathrm{obsd}} = \left\{a + (b/[\mathrm{Cl}^-])\right\}[\mathrm{Ala}] \qquad (6)$$

A reasonable mechanism accounting for these results is

Scheme I



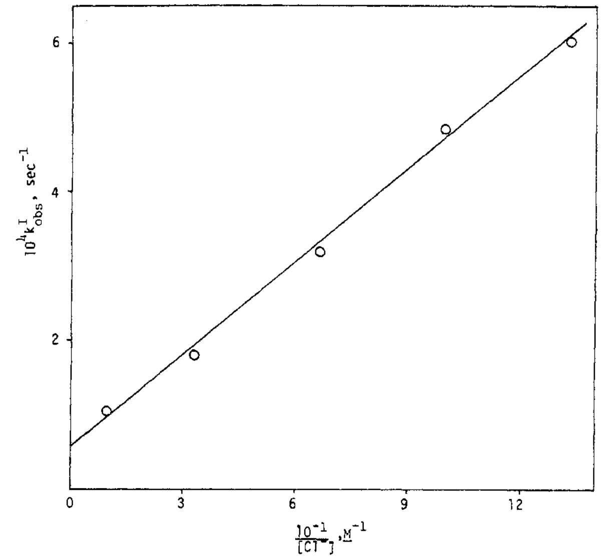


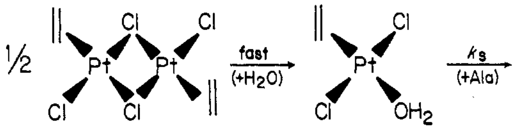
Figure 1. Dependence of $k^{\mathrm{I}}_{\mathrm{obsd}}$ on inverse chloride ion concentration; $[\mathrm{H}^+] = 2.34 \times 10^{-4}$ M, [Ala] = 8.85×10^{-9} M.

shown in Scheme I with a rate law of the form

$$k^{\mathrm{I}}_{\mathrm{obsd}} = \left\{\frac{k_sK + k_z[\mathrm{Cl}^-]}{K + [\mathrm{Cl}^-]}\right\}[\mathrm{Ala}] \qquad (7)$$

Equation 7 reduces to the observed rate law of eq 6, where $a = k_z$ and $b = k_sK$, when $[\mathrm{Cl}^-] \gg K = 2.6 \times 10^{-3}$ M. Hence, as [Ala] = 8.85×10^{-9} M under the conditions prevailing at the graphical plotting of eq 6, the values k_z and k_sK are $6.1 \pm 3.5 \times 10^3$ M^{-1} sec^{-1} and $4.70 \pm 0.45 \times 10^2$ sec^{-1}.

The rate constant for the second-order reaction of the aquo complex III with Ala, k_s, was measured directly from kinetic runs where Zeise's dimer, $[\mathrm{Pt(C_2H_4)Cl_2}]_2$, was the initial platinum substrate. In fact, this dimer is known to be converted essentially completely into the monomeric aquo species III when dissolved in water.[15]



III

$$\mathrm{I} \longrightarrow \mathrm{II} \qquad (8)$$

Pseudo-first-order initial rate constants, k'_{obsd}, for the reaction of III with Ala at 25° in the absence of added chloride in the pH range 3.2–3.8 are listed in Table II. Again, only the conversion III → I could be followed in the pH range of study, step I → II being faster. As expected, a straight line was obtained on plotting k'_{obsd} *vs.* [Ala] as calculated from eq 2 for a constant total alanine concentration of 1.5×10^{-2} M, according to the rate law of (9). No intercept was observed

$$k'_{\mathrm{obsd}} = k_s[\mathrm{Ala}] \qquad (9)$$

within experimental error. The least-squares slope, k_s, is $1.70 \pm 0.15 \times 10^5$ M^{-1} sec^{-1}. From this constant and from the above product k_sK, a value of $2.76 \pm 0.51 \times 10^{-3}$ M for K is deduced. The agreement of this value with that determined by independent thermodynamic measurements on Zeise's salt ($2.6 \pm 0.2 \times 10^{-3}$ M at 25°)[14,15] provides a good check on the mechanism proposed in Scheme I. In particular, it lends support to the assumption of the trichloro-di-

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Table II. Pseudo-First-Order Rate Constants, k'_{obsd} (sec^{-1}), for the Reaction *trans*-$[Pt(C_2H_4)(H_2O)Cl_2]$ + Ala → *N-trans*-$[Pt(Ala)(C_2H_4)Cl]$ + H_2O + Cl^- in Water at 25° [a]

$10^4[H^+]$, *M*	10^9[Ala], *M*	$10^4k'_{obsd}$, sec^{-1}
5.55	3.73	7.0
3.16	6.56	12.0
2.34	8.85	15.5
1.63	12.69	22.4

[a] No chloride added; total alanine concentration 1.5×10^{-2} *M*, platinum complex concentration *ca.* 7.5×10^{-4} *M*; $\mu = 0.3$ *M* (lithium perchlorate).

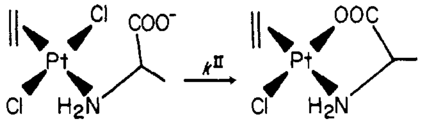
chloroaquo equilibrium, (5), as the one responsible for the observed reaction rates.

The mechanism in Scheme I involves bimolecular displacement of either chloride or water trans to ethylene by the amino group of the entering amino acid anion *via* parallel second-order routes, *i.e.*, k_z and k_s, to the intermediate I. An overall second-order kinetic pattern results from the solvolysis of the platinum substrate being faster than subsequent reaction of the aquo species with the entering nucleophile. This is at variance with the customary behavior of platinum complexes toward nucleophilic displacements, where solvolysis is the rate-determining step for the solvent-assisted reaction pathway.[16] This may well be simply due to the extremely low concentration of nucleophile (Ala) compared to that of water. The experimental rate constant related to the reactivity of Zeise's anion toward Ala, k_z, is affected by a rather larger standard deviation than the k_s term. To the extent that a comparison is feasible, the aquo complex appears to react at a rate which is some 30 times greater than that of Zeise's parent chloride, reflecting the higher lability of water as a leaving group.[17]

Both k_s and k_z are greater than the second-order rate constant for displacement of the chloride trans to ethylene in Zeise's anion by bipyridyl[7] (1.45×10^3 M^{-1} sec^{-1} at 25° in 95% aqueous methanol). This is not unexpected, since the nucleophilic ability of the primary amine group of alanine is greater than that of the tertiary nitrogen of bipyridyl. In any case, this work combined with our previous investigations[7,8] will show that the second-order rate constants for displacement of aquo or chloride ligands trans to ethylene or substituted olefins in $[Pt(olefin)Cl_2X]^{n+}$ (X = H_2O, Cl) by chelating nitrogen-donor ligands are generally quite high, a result of the high trans-labilizing power of olefins. Indeed, only by drastically reducing the effective concentration of the basic nitrogen-bearing end of the entering bidentate ligand through massive protonation were we able to slow down reaction rates to a level accessible to customary spectrophotometric measurements.

The possibility of affecting the rate of entry of alanine into $[Pt(C_2H_4)Cl_3]^-$ by mere adjustment of pH so that successive stages may become detectable offered us a means of determining the rate of ring closure for the conversion of intermediate I to the final product II. In fact, when the kinetics are carried out in the pH range 8-9 where the whole of alanine is present as the unprotonated anion, formation of an intermediate is immediate, as indicated by the disappearance of the initial spectrum within the time of mixing of reactants. Within the same time a new absorption, corresponding to the intermediate, appears which then slowly increases in intensity to give a final spectrum which is identical with that of II.

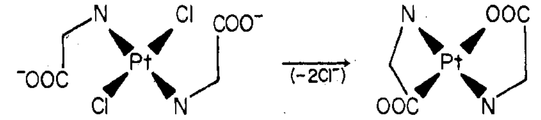
The rate of this slower second stage is independent of alanine, chloride, and hydrogen ion concentration in the pH range of study. The first-order rate constant for this monomolecular step, k^{II}, is $6.11 \pm 0.14 \times 10^{-3}$ sec^{-1} as an average of several kinetic measurements. We suggest that this step involves the internal ring closure in intermediate I effected by the carboxylate end of monodentate *N*-coordinated alanine displacing a chloride cis to ethylene.



I II

(10)

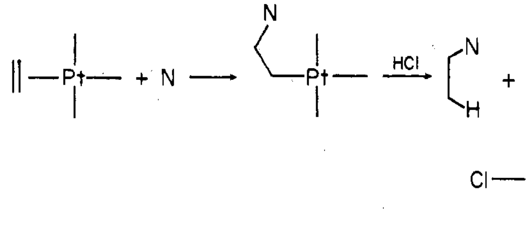
In other words, the overall reaction Scheme I appears to consist of two consecutive reactions (Zeise's anion and III → I and I → II) in which the observed rate constants for the successive steps, while of comparable magnitude, can be made sufficiently different to allow the occurrence of the separate steps to be detected and their rates measured. The observed rate constant for the ring closure in (10), k^{II}, is comparable with the analogous rate constants for chelate ring closure by the carboxylate end in *trans*-$[Pt(H_2NCH_2COO^-)_2Cl_2]^{2-}$ giving $[Pt(H_2NCH_2COO)_2]$.[18]



(11)

These ring-closing reactions, effected by a carboxylate group, are much slower than expected, since in reactions involving polydentate entering groups the chelate ring closes almost always very rapidly.[19-21] The poor nucleophilic ability of COO^- is probably responsible for this behavior. Nonetheless, a kinetic chelate effect must still be operative in ring closures (10) and (11), since their rate constants are far greater than those relating to the entry of monodentate carboxylate ligands into platinum(II).

We have also observed a further slower reaction of the final chelate product II with excess alanine at pH >9, having a rate which appears to increase markedly with pH and alanine concentration. A study of this reaction is underway, but it can be surmised that it involves displacement of coordinated ethylene in II by one further alanine giving eventually the bischelate amino acid complex $[Pt(Ala)_2]$. Alternatively, one might envisage this stage as involving direct nucleophilic attack of the amino group of alanine on the coordinated olefin to give a platinum-carbon σ-bonded aminoalkyl complex such as is known to occur in Pt^{II}-olefin complexes reacting with aliphatic amines.[22] Reaction 12 is a general



(12)

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feature of platinum(II)-olefin complexes and takes place usually under very mild conditions in nonaqueous solvents such as dichloromethane and acetone. The resulting aminoalkyl complexes undergo cleavage of the platinum-carbon σ bond upon treatment with aqueous hydrochloric acid to give olefin-free complexes and the *N*-alkylated derivatives of the attacking amine. Incidentally, the reaction of Zeise's salt with alanine described in this paper might also have involved initial nucleophilic attack of the amino group on ethylene to give an aminoalkyl platinum complex. However, this is not actually the case since the reaction product is exclusively *N*-*trans*-[Pt(Ala)(C_2H_4)Cl],[1,3a] which is completely dissociated in 3 *N* HCl to give back the starting $[Pt(C_2H_4)Cl_3]^-$. Apparently, formation of an aminoalkyl complex in this case is unfavored (i) by the use of water as a solvent which effectively deactivates the amino group by solvation and (ii) by the negative charge on the substrate complex.

Registry No. K[Pt(C_2H_4)Cl_3], 12012-50-9; DL-alanine, 302-72-7; *trans*-[Pt(C_2H_4)(H_2O)Cl_2], 12275-01-3; *N-trans*-$[Pt(Ala)(C_2H_4)Cl_2]^-$, 42996-29-2; *N-trans*-[Pt(Ala)(C_2H_4)Cl], 42996-30-5.

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Nuclear Magnetic Resonance Study of a Platinum-Ethylene Complex in a Liquid Crystal Solvent

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The nmr spectrum of the olefin resonance of *trans*-(py)(C_2H_4)$PtCl_2$ dissolved in a nematic solution of poly-γ-benzyl-L-glutamate and methylene chloride has been observed. In C_{2v} symmetry only two ordering parameters are required. As a result the three interproton coupling constants will determine one structure parameter. For a rigid molecule the ratio of the H-H distance of geminal hydrogens to the H-H distance of hydrogens cis to each other on the C-C skeleton could be determined. This analysis of the spectrum reported here gave a ratio for the olefin moiety in solution which compares quite favorably to previously reported results in the solid state. It is expected that dynamic processes are present in the system studied. However, conditions under which this method of analysis is still valid are discussed. Severely overlapping resonances were found and the standard method of analysis could not be used. A method was developed in which the spectrum intensities, rather than transition frequencies, were fit.

Transition metal-olefin complexes have been widely studied,[1-3] and several workers have discussed the structure of the olefin moiety in these complexes.[2,4,5] Recent crystal structure studies have shown that in Zeise's salt[6] and in (C_5H_5)Rh(C_2H_4)(C_2H_4)[7] the C-H bonds are bent back away from the metal center. Figure 1 shows the ethylene in the conformation found in the solid-state studies. It was of interest to determine features of the geometry of a platinum-olefin complex in solution for several reasons. One is that the olefin rotates about the platinum-olefin bond in solution[2] and several authors have suggested[2,8] there is a variation in the binding of the olefin with rotation. The platinum orbitals are proposed to be best suited for bonding to the olefin when the olefin C-C axis is perpendicular to the plane of the two chlorines and L in Figure 1. The geometry within the ethylene moiety is expected to be sensitive to the particular conditions of overlap and bonding between the metal and the olefin. Thus, in solution, the ethylene might assume a number of geometries in time and, on the average, exhibit a structure different from that observed in the solid state. MO calculations[5] have predicted that the olefin spends most of its time with its C-C axis parallel to the y axis. Another reason these systems are interesting is that ligand exchange has been observed in solution,[3] though the olefin remains bound to platinum, at least on the nmr time scale. This dynamic process could possibly affect the average olefin geometry as well if the olefin geometry is a sensitive function of the metal environment in solution.

A technique suited to measuring structural parameters in solution is nuclear magnetic resonance spectroscopy in a nematic liquid crystal solvent,[9] but the method is subject to some limitations. Foremost are the experimental ones; the molecule must be soluble in the nematic solvent but must not decompose in it. With these considerations in mind, the complex *trans*-Pt(C_2H_4)(py)Cl_2 (hereafter referred to as I) was chosen and its spectrum examined in several commercially available liquid crystal solvents. None gave a usable spectrum. The complex was found to be soluble in the nematic phase of a mixture of poly-γ-benzyl-L-glutamate (PBLG) and CD_2Cl_2, and reproducible spectra were obtained. This particular solvent is very weakly orienting and, as a result, energy absorption occurs over a narrow range of frequencies, and hence extensive overlap of peaks is observed. For this reason, the usual frequency-fitting procedures are of no use in the spectral analysis. Instead, we developed a procedure in which the spectrum intensity at various frequencies was fit by a calculated intensity at that frequency which would result from the set of calculated peaks. Lorentzian line shapes of identical line width were assumed. A discussion of this assumption is presented in the Appendix.

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