Contribution from the Centro di Chimica e Tecnologia Composti Metallorganici Elementi di Transizione del C.N.R., Facoltà di Chimica Industriale, Università di Bologna, 40136 Bologna, Italy.

Olefin Replacement by Bipyridyl in Platinum(II) Olefin Complexes

R. Pietropaolo, P. Uguagliati, M. Graziani, and U. Belluco

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A kinetic study of the reaction of $[Pt(ol)Cl_3]^-$ (ol = allylNH_3^+, allylPEt_3^+, allylSO_3^-, pent-4-enylNH_3^+) with bipyridyl (Bipy) in acidic 95% aqueous methanol to give cis–$[Pt(Bipy)Cl_2]$ *is reported. The rate law takes the form $1/k_{obs} = k' + k''(Cl^-)/(Bipy)$, where k_{obs} is the pseudo-first-order rate constant. The proposed mechanism involves slow formation of the solvato species $[Pt(ol)(S)Cl_2]$ followed by slow reaction with Bipy to give the final product with replacement of the coordinated olefin.*

Introduction

In a previous paper[1] we found that the reaction of Zeise's salt, $K[Pt(C_2H_4)Cl_3]$, with bipyridyl (Bipy) to give *cis*–$[Pt(Bipy)Cl_2]$ in aqueous methanol under kinetic conditions proceeds through formation of the labile cationic intermediate $[Pt(Bipy)(C_2H_4)Cl]^+$ in a bimolecular step. Such intermediate then undergoes first-order loss of the coordinated olefin to yield the final substitution product. We attributed the instability of cationic olefin complexes of platinum(II) to a reduced metal→olefin π back-bonding. Recently, an analogous kinetic study was reported[2] for the reaction of $K[Pt(ac)Cl_3]$ (ac = 2,5-dimethyl-3-hexyne-2,5-diol) with bipyridyl in 90% aqueous methanol, in which the formation of a labile cationic platinum-acetylene intermediate was postulated.

We shall now report on a kinetic investigation of the reaction of bipyridyl with the olefin complexes $[Pt(ol)Cl_3]^-$ (ol = allylNH_3^+, allylSO_3^-, allylPEt_3^+, and pent-4-enylNH_3^+) to give *cis*–$[Pt(Bipy)Cl_2]$ in acidic 95% aqueous methanol.

Experimental Section

Materials. The starting olefin complexes were prepared by literature methods.[3] All other materials were reagent grade chemicals.

Kinetic Measurements. The reactions were carried out in 95% aqueous methanol at 25°C at 0.2 *M* ionic strength ($LiClO_4$) in the presence of variable amounts of hydrochloric acid, lithium chloride, and bipyridyl. Details of this procedure have been described earlier.[1] Complex concentration was *ca.* 10^{-4} *M*.

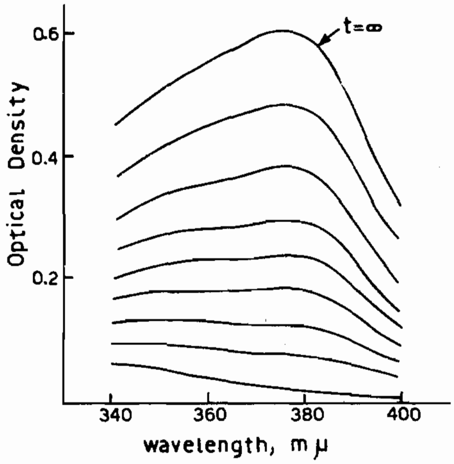

Figure1. Spectral changes during the reaction of $[Pt(AllylNH_3)Cl_3]$ with Bipyridyl in 95% aqueous methanol. $[Bipy]_0 = 5.67\times10^{-3}$ *M*; $[HClO_4] = 0.1515$ *M*; $[Cl^-] = 0.05$ *M*.

Progress of the reaction was followed with a Beckmann DK-2A recording spectrophotometer equipped with thermostatted cell compartment. Spectral changes in the near-ultraviolet region were monitored, one single stage of spectrophotometric change being observed. Optical density readings were taken at various time intervals at *ca.* 375 mμ, where the absorptions of the starting $[Pt(ol)Cl_3]^-$ and of the product *cis*–$[Pt(Bipy)Cl_2]$ differed most widely (Fig. 1). The spectrum of the latter was compared to that of an authentic sample independently prepared.[4] The pseudo-first-order rate constants, k_{obs} (sec^{-1}), were calculated from the slopes of linear plots of log ($A_\infty - A_t$) *vs.* time (A is the optical density).

Results and Discussion

The reactions

$$[Pt(ol^n)Cl_3]^- + \text{Bipyridyl} \rightarrow cis\text{–}[Pt(\text{Bipyridyl})Cl_2] + ol^n + Cl^-$$

ol = allylNH_3^+, allylPEt_3^+, pent-4-enylNH_3^+; n = +1
ol = allylSO_3^-; n = −1

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(1) P. Uguagliati, U. Belluco, U. Croatto, and R. Pietropaolo, *J. Am. Chem. Soc.*, *89*, 1336 (1967).
(2) J. Hubert and T. Theophanides, *Inorg. Chim. Acta*, *3*, 391 (1969).
(3) a) R. G. Denning and L. M. Venanzi, *J. Chem. Soc.*, 3241 (1963). b) D. V. Claridge and L. M. Venanzi, *ibid.*, 3419 (1964). c) R. G. Denning, F. R. Hartley, and L. M. Venanzi, *ibid.*, (A), 324 (1967). d) R. M. Milburn and L. M. Venanzi, *Inorg. Chim. Acta*, 2, 97 (1968).

Table I. Rate Data for the Reactions: $[Pt(Olefin)Cl_3]^- + Bipyridyl \longrightarrow [Pt(Bipyridyl)Cl_2] + Olefin + Cl^-$ in 95% Aqueous Methanol, at 25°C. $\mu = 0.2\,M$

Complex	$[H^+]$ M	$[Cl^-]$ M	$[ClO_4^-]$ M	$10^2[Bipy]_0$ [a] M	$10^6[Bipy]$ [b] M	$\frac{10^{-4}[Cl^-]}{[Bipy]}$	10^3k_{obs} sec^{-1}	$10^{-2}\frac{1}{k_{obs}}$ sec
$[Pt(allylNH_3)Cl_3]$	0.2	0.2	—	0.52	1.00	20.0	1.0	10.0
	0.2	0.2	—	0.96	2.00	10.0	1.45	6.9
	0.2	0.2	—	2.45	5.60	3.6	2.20	4.5
	0.2	0.2	—	3.82	9.43	2.1	2.75	3.6
	0.1515	0.05	0.1515	0.57	1.56	3.2	2.10	4.7
	0.1515	0.05	0.1515	1.29	3.76	1.3	2.65	3.8
	0.1515	0.05	0.1515	1.81	5.40	0.9	2.77	3.6
	0.1515	0.05	0.1515	2.58	8.23	0.6	2.90	3.4
	0.105	0.098	0.105	0.42	1.60	6.0	1.80	5.5
	0.105	0.098	0.105	0.70	2.86	3.4	2.20	4.5
	0.105	0.098	0.105	1.40	6.16	1.6	2.90	3.4
	0.105	0.098	0.105	2.80	14.50	0.7	3.00	3.3
$[Pt(allylSO_3)Cl_3]^{2-}$	0.2	0.2	—	0.59	1.22	16.6	3.45	2.9
	0.2	0.2	—	0.93	1.92	10.4	4.60	2.2
	0.2	0.2	—	1.86	4.00	5.0	6.10	1.6
	0.2	0.2	—	3.73	9.03	2.2	8.10	1.2
	0.1515	0.05	0.1515	0.51	1.40	3.7	7.50	1.3
	0.1515	0.05	0.1515	1.28	3.70	1.4	9.50	1.1
	0.1515	0.05	0.1515	1.78	5.31	0.9	10.00	1.0
	0.1515	0.05	0.1515	2.55	8.10	0.6	10.50	0.9
	0.105	0.098	0.105	0.39	1.50	6.4	6.10	1.6
	0.105	0.098	0.105	0.64	2.60	3.7	8.40	1.2
	0.105	0.098	0.105	1.29	5.60	1.8	9.30	1.1
	0.105	0.098	0.105	2.57	13.00	0.8	11.60	0.9
$[Pt(allylPEt_3)Cl_3]$	0.2	0.2	—	0.59	1.20	16.6	0.81	12.4
	0.2	0.2	—	0.93	1.92	10.4	1.08	9.2
	0.2	0.2	—	1.86	4.05	5.0	1.65	6.0
	0.2	0.2	—	2.63	5.98	3.2	2.07	4.8
	0.2	0.2	—	3.73	9.04	2.2	2.40	4.2
	0.1515	0.05	0.1515	0.57	1.56	3.2	1.80	5.5
	0.1515	0.05	0.1515	1.81	5.42	0.9	2.40	4.2
	0.1515	0.05	0.1515	2.59	8.23	0.6	2.60	3.8
	0.105	0.098	0.105	0.39	1.50	6.4	1.60	6.3
	0.105	0.098	0.105	0.64	2.60	3.7	2.05	4.9
	0.105	0.098	0.105	1.29	5.60	1.8	2.50	4.0
	0.105	0.098	0.105	2.57	13.00	0.8	2.70	3.7
$[Pt(pentenylNH_3)Cl_3]$	0.2	0.2	—	0.58	1.19	16.8	2.00	5.0
	0.2	0.2	—	0.99	2.08	9.6	3.50	2.8
	0.2	0.2	—	1.93	4.26	4.7	6.40	1.6
	0.2	0.2	—	2.69	6.22	3.2	8.20	1.2
	0.2	0.2	—	3.82	9.43	2.1	10.00	1.0
	0.1515	0.05	0.1515	0.51	1.40	3.6	7.1	1.4
	0.1515	0.05	0.1515	1.28	3.67	1.4	13.7	0.7
	0.1515	0.05	0.1515	1.79	5.34	0.9	15.0	0.65
	0.1515	0.05	0.1515	2.55	8.06	0.6	16.2	0.6
	0.105	0.098	0.105	0.42	1.60	6.1	5.6	1.8
	0.105	0.098	0.105	0.70	2.85	3.4	8.7	1.2
	0.105	0.098	0.105	1.40	6.10	1.6	15.0	0.7
	0.105	0.098	0.105	2.80	14.50	0.7	22.0	0.5

[a] Analytical concentration; [b] Unprotonated Bipyridyl.

proceed rapidly and smoothly to completion in 95% aqueous methanol at 25°C in a single observable stage in the presence of hydrochloric acid and lithium chloride. Kinetic runs were carried out at three different values of chloride and proton concentrations, corresponding to three sets of experiments for each complex studied. Within each set of runs, $[Cl^-]$ and $[H^+]$ were kept constant as the analytical concentration of bipyridyl was changed. This amounted to changing the concentration of free, unprotonated bipyridyl in each run, as calculated from the appropriate analytical proton concentration and the pK_A of bipyridyl (aqueous solution).[5] In each kinetic run pseudo-first-order conditions were provided by using a large excess of the entering bipyridyl. In fact, in all cases the concentration of free ligand, though smaller than that of the substrate, was kept constant throughout the course of the reaction by the rapid establishment of the equilibrium:

$$Bipy + H^+ \rightleftharpoons Bipy{-}H^+$$

In this way the effect of changes of the $[Cl^-]/[Bipy]$ ratio on the reaction rate could be observed. Pseudo-first-order rate constants, k_{obs} (sec^{-1}), at various such ratios are listed in Table I.

On plotting $1/k_{obs}$ *vs* $[Cl^-]/[Bipy]$, straightlines with non-zero intercepts were obtained showing that

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(4) G. T Morgan and F. H. Burstal, *J. Chem. Soc.*, 965 (1934).
(5) For a discussion of this procedure see Ref. 1.

Table II. Values of Intercepts (k', sec) and Slopes (k'', sec) of Plots of $1/k_{obs}$ *vs* $[Cl^-]/[Bipy]$

Complex	$[H^+]$ *M*	$[Cl^-]$ *M*	$[ClO_4^-]$ *M*	10^{-2} k' sec	10^3 k'' sec
$[Pt(allylNH_3)Cl_3]$	0.2	0.2	—	3.0	3.8
	0.1515	0.05	0.1515	3.2	4.5
	0.105	0.098	0.105	3.0	4.2
$[Pt(allylSO_3)Cl_3]^{2-}$	0.2	0.2	—	0.9	1.15
	0.1515	0.05	0.1515	0.95	1.10
	0.105	0.098	0.105	0.87	1.10
$[Pt(allylPEt_3)Cl_3]$	0.2	0.2	—	3.0	5.9
	0.1515	0.05	0.1515	3.3	6.1
	0.105	0.098	0.105	3.1	5.1
$[Pt(pentenylNH_3)Cl_3]$	0.2	0.2	—	0.4	2.7
	0.1515	0.05	0.1515	0.4	2.7
	0.105	0.098	0.105	0.32	2.4

the rate data fit the relationship

$$1/k_{obs} = k' + k''[Cl^-]/[Bipy] \qquad (1)$$

(see Fig. 2). As expected, the couples of k′ and k″ values (intercept and slope) for each set of runs on a given complex are in satisfactory agreement with each other within experimental error (see Table II).

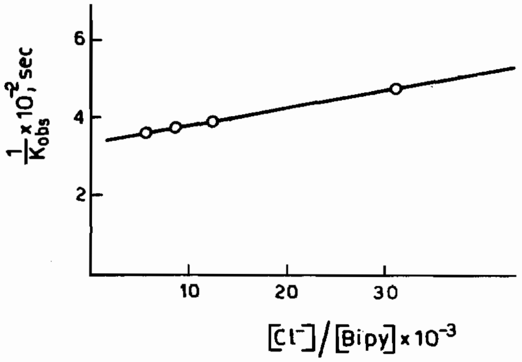

Figure 2. Plot of $1/k_{obs}$ *vs* $[Cl^-]/[Bipy]$ for the reaction of $[Pt(AllylNH_3)Cl_3]$ with Bipyridyl. $[H^+] = 0.1515$ *M*; $[Cl^-] = 0.05$ M.

In analogy with the reaction of Zeise's salt,[1] a mechanism consistent with the observed rate law (1) is proposed in the following scheme in which the charge on the coordinated olefin has been omitted for simplicity:

$$\underset{(\mathbf{I})}{[Pt(ol)Cl_3]^-} + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \underset{(\mathbf{II})}{\textit{trans}\text{—}[Pt(ol)(S)(Cl_2]} + Cl^-$$

$$(\mathbf{II}) + Bipy \xrightarrow{k_2} \underset{(\mathbf{III})}{[Pt(ol)(Bipy)Cl]^+} + Cl^- + S$$

$$(\mathbf{III}) \xrightarrow[-ol,\ +Cl^-]{fast} \underset{(\mathbf{IV})}{\textit{cis}\text{—}[Pt(Bipy)Cl_2]}$$

Since no intermediates in appreciable concentration could be detected in the course of reactions, the steady-state approach can be applied to this scheme. The resultant rate law takes the form

$$k_{obs} = \frac{k_1k_2[Bipy]}{k_{-1}[Cl^-]+k_2[Bipy]} \qquad (2)$$

the reverse of which is expressed by eq. 1 where $k' = 1/k_1$ and $k'' = k_{-1}/k_1k_2$. Therefore, the ratio k'/k'' is a measure of the relative effectiveness of bipyridyl over chloride in competing for intermediate (**II**) (*ca.* 10^4).

The conversion (**I**)→(**II**) involves rate controlling solvolysis of the starting olefin complex with replacement of a *trans*-labilized chloride by a solvent molecule. The ensuing solvato complex (**II**) will then undergo bimolecular attack by the entering bidentate ligand with replacement of the solvent and of a further chloride to give the labile intermediate (**III**) (probably through prior slow replacement of the solvent *trans* to the coordinated olefin followed by rapid closure of the chelate ring;[1,2,6] this two-step sequence is not reported in the scheme for the sake of brevity). Finally, intermediate (**III**) decomposes rapidly to the reaction product (**IV**) by releasing the coordinated olefin. Unfortunately, there appears to be no clear cut trend relating to the nature of the olefins for data in Table II, so that their rationalization is not immediate.

The kinetic behaviour of these $[Pt(ol)Cl_3]^-$ complexes toward replacement of the coordinated olefin by bipyridyl is at striking variance with that of $[Pt(C_2H_4)Cl_3]^{-1}$ and $[Pt(ac)Cl_3]^-$ (ac = 2,5-dimethyl-3-hexyne-2,5-diol).[2]. In both these latter cases, in fact, no prior solvolysis step was observed; further, under specific conditions a labile intermediate could be detected in one stage of the overall reaction with bipyridyl, whose decomposition to the end product could be followed kinetically. It appears therefore that (i) the *trans*-labilizing power of the olefins examined in this work is greater than that of ethylene and of the substituted acetylene, (ii) the collapse of the intermediate $[Pt(ol)(Bipy)Cl]^+$ to *cis*—$[Pt(Bipy)Cl_2]$ is always faster than its formation when the coordinated olefin bears solubilizing groups such as NH_3^+, PEt_3^+, SO_3^-. It is likely that both these facts originate from an involved interplay of steric, electronic, and solvation effects which at present are hard to disentangle.

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(6) See Ref. 41 and 42 in Ref. 1.