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Kinetics of β-Hydrogen Elimination from *cis*-Chloro(n-alkyl)bis(triethylphosphine)platinum(II) Complexes

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In the course of our studies on the uncatalyzed isomerization of *cis*-[Pt(PEt$_3$)$_2$RCl] complexes in protic solvents, we found that when R = C_2H_5 the rate of isomerization is very much greater than that of the analogous methyl or aryl compounds [1]. Since inductive or steric factors cannot account for this large difference of reactivity, we started a detailed kinetic study of the isomerization of complexes in which R comes from a series of linear or branched alkyl groups, with the aim of investigating the sensitivity of the process to the length of the chain and/or to the availability of β hydrogens. During this study we found that the n-propyl and the n-butyl derivatives, in addition to spontaneous isomerization, undergo thermal decomposition through a concurrent pathway with isopropanol as solvent. Addition of very small amounts of chloride ions produces mass-law retardation of the isomerization until, at concentrations of chloride greater than 0.01 *M*, the sole reaction is the decomposition of the starting material into *trans*-[Pt(PEt$_3$)$_2$HCl] isolated in a quantitative yield and characterized by elemental analysis, u.v., I.R., and ^{1}H n.m.r. spectra.

The kinetics of decomposition, followed by repetitive scanning of the spectra in the u.v. region, obey a first-order rate law until well over 90% of the reaction and are independent of the concentration of the complex. They are unaffected by chloride ion in solution in the range of concentrations examined (0.01–0.2 *M*). Abstract factor analysis of the spectral changes [2] has shown the presence of only two independently-absorbing species in solution in the wavelength range studied, *viz.* the alkyl substrate and the hydride product.

TABLE I. First-Order Rate Constants and Activation Parameters for the Thermal Decomposition of *cis*-[Pt(PEt$_3$)$_2$RCl] Complexes in Isopropanol Containing 0.1 *M* LiCl.

R = n-propyl		R = n-butyl	
t, °C	10^4 k_{obs}, s^{-1}	t, °C	10^4 k_{obs}, s^{-1}
11.5	1.01	11.5	1.35
15.3	1.72	15.3	2.27
20.0	3.35	20.0	5.08
25.2	6.0	25.2	9.30
29.6	10.6	29.6	14.8
$\Delta H^{\neq}$ = 21.2 ± 0.2 Kcal mol^{-1}		$\Delta H^{\neq}$ = 22.4 ± 1 Kcal mol^{-1}	
$\Delta S^{\neq}$ = – 2 ± 0.8 e.u.		$\Delta S^{\neq}$ = +2.7 ± 0.1 e.u.	

The formation of the platinum–hydride compound has also been followed by monitoring the Pt–H stretching frequency at 2216 cm^{-1}, using a barium fluoride cell and a computer-aided infrared spectrometer. The appearance of the volatile decomposition products was followed by GLC, after quenching with HCl samples taken at various times. In the case of the n-propyl derivative the only volatile product was 1-propene, while for the n-butyl derivative we observed the formation of 1-butene, *cis*-2-butene and *trans*-2-butene. The ratio of the three butenes is 22.3:22.3:1 respectively when the reaction is carried out at 20 °C, and does not change appreciably with the temperature. No alkanes are produced in these reactions. The kinetic results obtained using these different techniques were indistinguishable, within experimental error.

Addition of triethylphosphine to solutions of the complexes rises a new catalyzed pathway for the isomerization which predominates over the decomposition. The *trans*-[Pt(PEt$_3$)$_2$(n-alkyl)Cl] species are stable under the same experimental conditions which promote the facile decomposition of the *cis* isomers.

All these findings can be summarized in Scheme 1.

The spontaneous isomerization of the alkyl complexes in the neat solvent may proceed according to the well-established mechanism which involves as rate-determining step the dissociative loss of the chloride to give a T-shaped PtL_2R^+ 3-coordinate intermediate [3]. An incipient interaction of the β-hydrogens of the alkyl group with the metal assists the formation of the platinum cation which, however, interconverts into a geometrically distinct '*trans*-like' T structure before a complete β-extraction can take place. This is in line with the low energy barrier found for the fluxionality of coordinatively unsaturated reaction intermediates such as $H(PH_3)_2Pt^+$ [4a], Me_3Au [4b], $Et_2(PEt_3)Pt$ [4c].

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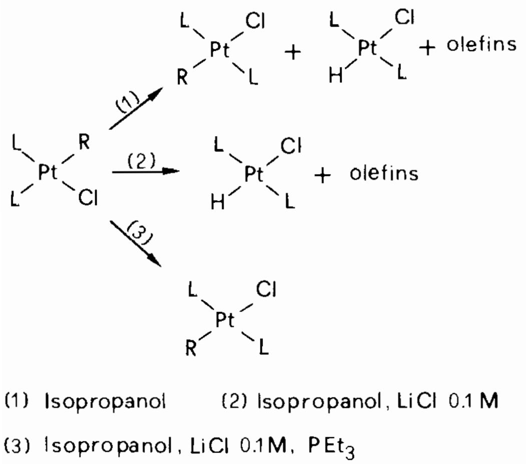

Scheme. I. Reaction pathways for *cis*-chloro(n-alkyl)bis(triethylphosphine)platinum(II) complexes under different experimental conditions.

The parallel thermal decomposition is relatively unaffected by the presence of excess of chloride ion in solution, suggesting that the process occurs via an independent unimolecular pathway. This latter process fits all characteristics required to a model system for mechanistic studies, in that it involves a direct examination of β-elimination of alkyl ligands and takes place under mild conditions; both the starting material and the final metal hydride product being stable enough to be isolated as pure compounds and only alkenes are formed. The studies of Whitesides *et al.*, to which we owe the most definitive evidence for the implication of β-hydrogens in the decomposition of platinum(II) alkyls, have shown interestingly that the thermal decomposition of *cis*-dialkylbis(triethylphosphine)platinum(II) complexes [5] in apolar solvents requires more drastic conditions and leads to platinum(0) products through a transient platinum(II)–hydride species whose existence is only inferred. The complexes *trans*-$[Pt(PEt_3)_2EtCl]$ [6a] and *trans*-$[Pt(PEt_3)_2EtBr]$ [6b] afford ethylene and the corresponding platinum hydrides only as a result of pyrolysis at 180 °C.

The great versatility of the *cis*-$[Pt(PEt_3)_2$(n-alkyl)-Cl] system has been evidenced also by some preliminary GLC tests of the decomposition of the n-butyl derivative in a variety of polar and non-polar aprotic solvents. The rate of thermal decomposition as well as the relative ratio of the three butenes are markedly influenced by the nature of the solvent. Addition of iodide ions to the solution of the complex produces an enormous acceleration of its rate of decomposition even in the less effective solvents, influencing at the same time the distribution of the butene products in favor of the formation of 1-butene. For instance, *trans*-$[Pt(PEt_3)_2HI]$ is formed soon after mixing acetone solutions of LiI and *cis*-$[Pt(PEt_3)_2$(n-Butyl)Cl], with 1-butene as the main volatile product (85%).

Summing up, the most important conclusion which can be drawn from these preliminary results is that the *cis*-$[Pt(PEt_3)_2$(n-alkyl)(halide)] complexes, by contrast with the relative inertness of their *trans* analogs, undergo a facile β-hydride elimination, whose rate is almost unaffected by the length of the aliphatic chain (see data in Table I) but which depends very much on the nature of the halide ion and of the reaction medium. The essential features of the process appear to differ greatly from those found in the decomposition of the corresponding *cis*- dialkyl complexes [5]. Coordinative unsaturation about the metal seems to be a pre-requisite for ready thermal decomposition of transition metal alkyls [7]. A dissociative loss of the phosphine is the main feature in the mechanism proposed for the decomposition of dialkyl [5] and di(cycloalkyl) [8] bis(phosphine)platinum(II) complexes in non-donor solvents. However, in our case, a proper study of the effect of the phosphine seems to be prevented by its role as catalyst of isomerization and we must take into account that the process occurs even in donor solvents and in the presence of good nucleophiles. A definite assessment of the mechanism and of the steps in which the β-hydrogens are implicated must await the extension of the study to compounds containing chelating phosphines, labelled alkyls and other halide groups.

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