

Photoisomerization of Chlorophenylbis(triethylphosphine)platinum(II)

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The photochemical isomerization of cis- and trans-Pt(PEt₃)₂PhCl in acetonitrile solution has been investigated and the quantum yields determined under various experimental conditions. The overall results indicate two essential features of the studied process: a) the photochemical isomerization occurs through a mechanism different from the thermal one and involves only excited electronic state; b) the cis → trans and the trans → cis conversion must proceed by distinctly different mechanisms, the first probably through an intramolecular twisting from a low lying state of ligand field and the latter through a dissociative path from a charge transfer state.

Introduction

In the photochemical investigation of square planar platinum(II) complexes a *cis-trans* geometric isomerization has been frequently observed [1, 2]. This reaction has been interpreted either in terms of an intramolecular twisting mechanism through an intermediate of tetrahedral geometry, or in terms of an intermolecular mechanism involving solvent molecules or dissociate ligand. The prevailing mechanism seems to depend on the particular system studied. For example both complexes Pt(gly)₂ [3] and Pt(py)₂Cl₂ [4] undergo *cis* → *trans* photoisomerization, the first by an intramolecular pathway and the latter by a mixed mechanism, involving an intermolecular dissociative pathway and an intramolecular twisting.

In the case of the Pt(PEt₃)₂Cl₂ complex, two possible pathways have been suggested for the reversible *cis-trans* photoisomerization: one involves a triplet state with tetrahedral geometry [5], another involves a trigonal bipyramid containing a solvent molecule [5, 6]. In a more recent investigation of this complex [7], it was proposed that the isomerization originated from low lying states of the ligand field, with the *trans* → *cis* conversion implying a triplet state and the *cis* → *trans* a singlet state.

In this context we considered it of interest to undertake a photochemical investigation of square planar aryl-platinum(II) complexes of the type PtL₂ArX (where L = tertiary phosphine, X = halogen). These complexes are generally inert in aprotic solvents, but rapidly undergo *cis* → *trans* isomerization in protic solvents or in the presence of traces of the free ligand, L [8a]. Kinetic studies have shown that the uncatalyzed isomerization proceeds via a dissociative asynchronous mechanism in which the rate determining step is the breaking of the Pt–X bond to yield a three-coordinate intermediate responsible for the *cis* → *trans* conversion [8b–d].

In the present work we investigate the photochemical reversible isomerization of Pt(PEt₃)₂PhCl in acetonitrile solvent, through measurements of quantum yields under various experimental conditions.

Experimental

Materials

The complexes *trans*- and *cis*-[Pt(PEt₃)₂PhCl] were prepared and purified by the methods reported in the literature [9].

Benzophenone, triphenylene and ferrocene (Baker) were suitable for sensitizer use. Acetonitrile was of spectroscopic grade. All other common chemicals were reagent grade.

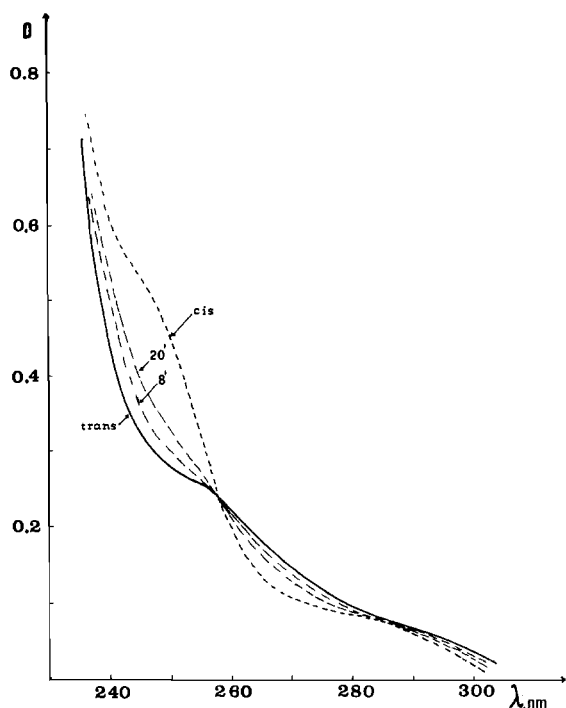
Apparatus

The light sources and the general equipment to obtain the radiations of desired wavelength were the same as previously described [10]. The intensity of the incident light measured by ferric oxalate actinometer was of the order of 10⁻⁷ Nhν/min.

Spectrophotometric measurements were performed with an Optica CF4 N1 spectrophotometer with a cell compartment thermostatted at 25 ± 0.1 °C.

TABLE I. Electronic Spectra of $[\text{Pt}(\text{PEt}_3)_2\text{PhCl}]$ in Acetonitrile Solution.

	λ , nm		Assignment
<i>cis</i> - $[\text{Pt}(\text{PEt}_3)_2\text{PhCl}]$	280	1600	d-d; CTTM
	245	9900	CTTM
<i>trans</i> - $[\text{Pt}(\text{PEt}_3)_2\text{PhCl}]$	290	1250	d-d; CTTM
	255	5300	CTTM

Fig. 1. Spectral changes of *trans*- $[\text{Pt}(\text{PEt}_3)_2\text{PhCl}]$ in acetonitrile solution under 254 nm irradiation. The numbers on the curves give the irradiation time in minutes.

Procedures

Photolysis was carried out in acetonitrile solutions deaerated, aerated and saturated with oxygen or xenon. Samples were introduced into standard spectrophotometric cells, which were sealed, after deoxygenation with pure nitrogen or after saturation either with oxygen or xenon and then irradiated at the desired wavelength. During irradiation the solutions were stirred with a small magnetic stirrer. The photolysis kinetics were followed spectrophotometrically in suitable absorption regions.

For solutions of absorbance greater than 2 at the irradiating wavelength, the quantum yield values were calculated from the initial rate of the conversion. For solutions of low concentration with absorbance less than 1 the quantum yield values were calculated (Zimmerman's method [11]) by the conversion

kinetics and by the composition of the photostationary state, obtained from both directions.

Experiments of quenching and sensitization were carried out in deaerated solutions and the irradiation was performed at suitable wavelengths.

Results

Electronic Spectra

The spectra of *trans*- and *cis*- $[\text{Pt}(\text{PEt}_3)_2\text{PhCl}]$, reported in Table I, show two unresolved absorption bands, which can be approximately assigned on the basis of their intensity and of previous assignments made for square planar d^8 systems [12]. The intense band, that can be noted as shoulder in the ultraviolet region, corresponds to a charge transfer transition of ligand to metal type, which involves an excitation of a halogen lone pair π electron to a d orbital on the metal. This assignment is supported by the shift toward the red observed for the band in the corresponding *cis* and *trans* bromo and iodo complexes. The weaker band observed on the low energy side can be ascribed to a ligand field transition: the relatively high intensity is due to the close charge transfer band overlapping.

No luminescence emission was observed down to liquid air temperature.

Photochemical Behavior

Preliminary experiments indicated that the pure *trans* or *cis*- $[\text{Pt}(\text{PEt}_3)_2\text{PhCl}]$ in acetonitrile solution undergoes photolysis on irradiation at 254 nm.

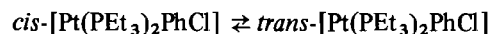
No thermal reaction was observed under the experimental conditions adopted.

The photoreaction was followed by recording spectra at various intervals, as shown in Fig. 1.

The isosbestic point and the successive spectra matched those of a mixture of *trans* and *cis* isomers of total concentration equal to that of the starting isomer. In dilute solutions, the same photostationary state was attained independently of the nature of the initial isomer.

In order to confirm that the photoreaction was a clean *cis* \rightleftharpoons *trans* photoisomerization, the components of a photolysed solution were isolated by thin layer silica gel chromatography using as solvent petroleum ether (40–70 °C)–ethyl ether mixture 80:20. The isolated compounds were identified as *trans* and *cis* isomer by UV spectra. No side compound was detectable by chromatography.

The photoreaction is therefore interpreted as the reversible photoisomerization



Acetonitrile solutions of the two isomers were irradiated under various experimental conditions to

TABLE II. Effect of the Wavelength on the Quantum Yields^a of Photoisomerization of [Pt(PEt₃)₂PhCl] in Deaerated Acetonitrile Solution.

$\lambda_{\text{exc.}}$	$\phi_{c \rightarrow t}$	$\phi_{t \rightarrow c}$
254	0.096	0.048
280	0.097	0.023
313	0.095	<10 ⁻³

^aError about 4%.

observe the influence of the irradiation wavelength, of the initial isomer concentration, of oxygen or xenon, of tetraethylammonium chloride, of sensitizer or quencher. The irradiation was carried out at three different wavelengths corresponding to the region of the charge transfer (254 nm), charge transfer and ligand field (280 nm) and ligand field (313 nm) transitions, Table II.

It is clear that the energy of the radiation influences the *trans* → *cis* conversion, but does not affect the reverse process.

The quantum yields were independent of the initial isomer concentration in the range 10⁻³–10⁻⁵ M.

The photostationary state by direct irradiation was within the experimental limits in agreement with that calculated by the relationship

$$\frac{[cis]_e}{[trans]_e} = \frac{\epsilon_t \phi_{t \rightarrow c}}{\epsilon_c \phi_{c \rightarrow t}}$$

The effects of the oxygen, xenon or chloride were studied irradiating at 254 nm. The presence of oxygen significantly reduced the value of $\phi_{t \rightarrow c}$ (in aerated or oxygen saturated solutions $\phi_{t \rightarrow c} = 0.032$), whereas the $\phi_{c \rightarrow t}$ value was not affected. The presence of heavy atom xenon increased the quantum yield of the *trans* → *cis* conversion (in xenon saturated solutions $\phi_{t \rightarrow c} = 0.067$), while the quantum yield for the reverse process remained unchanged. The addition of tetraethylammonium chloride did not cause any significant change in the isomerization quantum yields.

Attempts of sensitization experiments were carried out with triphenylene and benzophenone by irradiation at 254 and 333 nm respectively. The relative concentrations of both *cis* and *trans* substrates (3 × 10⁻⁴ M) and sensitizers (0.5 × 10⁻³ and 0.028 M respectively) assured that the irradiation was almost completely absorbed by the sensitizer. No photo-reaction under these conditions was observed.

A set of runs was performed with solutions of starting *trans* or *cis* isomer (10⁻³ M) containing various concentrations (10⁻³–3 × 10⁻⁴ M) of ferrocene. In the experimental conditions the 254 nm

irradiation was absorbed almost completely by the initial isomer. The results were rather surprising. The conversion *trans* → *cis* underwent rapid reduction until zero as the concentration of the ferrocene increased from 0.3 × 10⁻³ to 10⁻³ M. No change of the ferrocene or decomposition product was detectable. By way of contrast, irradiation of the *cis* isomer solutions in the same conditions gave rise to an unidentified photodecomposition product, which absorbed at wavelengths longer than 300 nm. Chromatography tests indicated that at the same time some *cis* → *trans* conversion was taking place.

Discussion

From the overall results two points especially emerge:

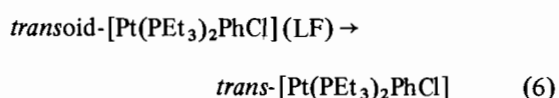
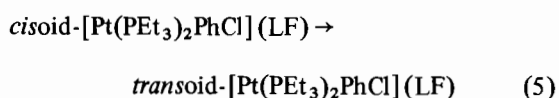
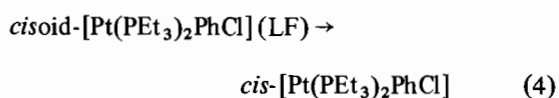
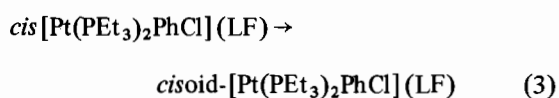
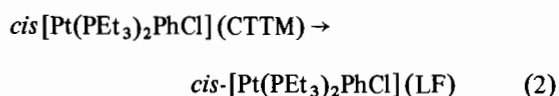
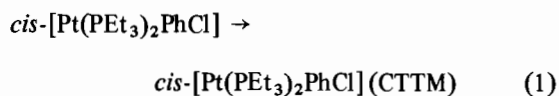
a) the photochemical isomerization of [Pt(PEt₃)₂PhCl] is reversible and is not affected by chloride concentration: this means that the photochemical process occurs through a mechanism different from the thermal one, which suffers mass law retardation by chloride. Therefore the photoisomerization involves only excited electronic states.

b) Wavelength of irradiation and other factors such as presence of oxygen or xenon, addition of ferrocene, influence in different ways the *trans* → *cis* and *cis* → *trans* reactions. This indicates that the two isomerizations occur through two different pathways.

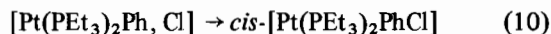
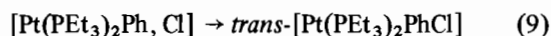
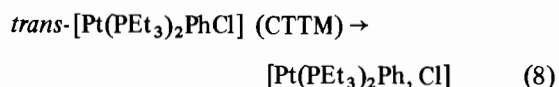
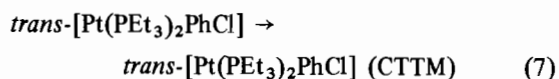
For the *cis* → *trans* photoisomerization the absence of wavelength effects suggests that the conversion takes place from the same state regardless of the nature of the initial populated state. This means that when excited to a charge transfer state or to an upper ligand field state, the *cis* molecule undergoes rapid radiationless transitions and reaches the low lying state with unitary efficiency, where *cis* → *trans* isomerization occurs. This hypothesis is supported by appreciable spectroscopic evidence of efficient communication between the charge transfer and ligand field bands.

Spectroscopic studies [13] of some square platinum(II) complexes have already evidenced that d–d excitation of an electron destabilizes the planar arrangement towards a tetrahedral structure. Moreover a MO study [14] aiming at elucidating the geometrical nature of the excited state responsible for the *cis*–*trans* isomerization of the Pt(gly)₂ complex [3] has shown that the potential surface of the electronic lower excited state has a tetrahedral geometry with two minima corresponding respectively to a *cisoid* and a lower *transoid* configuration, separated by an energy barrier which allowed *cis* → *trans* conversion and not the reverse. Assuming that a similar electronic situation is operative for the ligand field states of Pt(PEt₃)₂PhCl, a mechanism for the *cis* → *trans* photoisomerization may involve intra-

molecular twisting by the paths (1)–(5). The *cis* molecule excited to upper states (1) decays to ligand field states (2) where it is equilibrated in the *cisoid* tetrahedral minima (3). This latter can competitively either decay to the *cis* ground state (4) or undergo conversion to the *transoid* tetrahedral minima (5), which eventually decays to the *trans* ground state (6). As far as the multiplicity of the reactive state is concerned no evidence for a triplet state was provided, because of the absence of oxygen and xenon effects and of the ambiguous results obtained with ferrocene.



The main feature of the *trans* to *cis* photoisomerization is its close dependence on the type of the irradiated band: the isomerization takes place only when the irradiation is performed at wavelengths (254 and 280 nm) corresponding to pure or mixed transfer charge transitions, the quantum yields being strongly dependent on the energy of the exciting radiation. No reaction was observed for irradiation in the ligand field region (313 nm). Therefore it appears that the transfer charge state reached upon irradiation is the precursor of the *trans* → *cis* conversion. The general scheme for the *trans* → *cis* photoisomerization can be adequately described by the paths (7)–(10).



It could be assumed that for excitation in the charge transfer band the CTTM species formed can undergo homolytic fission at the weakened metal–halogen bond. Thus a solvent trapped ‘radical pair’ is formed by metallo-fragment of three-coordinate Pt and halogen radical. The three-coordinate fragment can either recombine with the dissociate ligand to form the *trans* product (9) or undergo a distortion of the coordinate ligands toward a ‘*cis*-like’ structure which eventually takes up Cl yielding the *cis* product (10). This path requires a small energy barrier for the interconversion of ‘*cis*-like’ and ‘*trans*-like’ T shaped structures inside the radical pair. However there are no reasons to exclude that the halide reentry can occur at a more symmetrical trigonal intermediate. It should be kept in mind that a distinction cannot be made between an intramolecular process and such a dissociative isomerization pathway provided that it occurs in the solvent cage.

The oxygen, ferrocene and xenon effects are not of easy interpretation. At first sight these effects seem to indicate the involvement in the *trans* → *cis* isomerization of a species of triplet multiplicity: this could be a non spectroscopic CTTM state (which precedes formation of the radical pair) of relatively lower energy and sensible to quenchers [15]. If this is the case, the observed inefficiency of sensitizers could be attributed to inadequate energies. However, the scattering of data could suggest either a collateral catalytic path or the occurrence of an unidentified intermediate scavenged by oxygen and ferrocene. At present any of the mentioned hypotheses cannot be dismissed on the basis of our experimental data.

In conclusion the two processes cannot crossover for the following reasons:

a) the pathway of *cis* → *trans* conversion cannot be operative for *trans* → *cis* conversion, owing to the energy barrier height (reaction 3) between *transoid* and *cisoid* minima in the ligand field state;

b) the pathway of *trans* → *cis* conversion cannot be attained by the *cis* isomer, because the singlet transfer charge state undergoes radiationless decays with unitary efficiency to ligand field state.

Acknowledgment

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