Photochemical isomerization of platinum(II) complexes containing phosphine and carbonyl ligands: $Pt(CO)(PR_3)X_2$ ($X = Cl, Br, I$)

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Abstract

The photo-induced *cis–trans* isomerization of $Pt(CO)(PR_3)X_2$, where $X = Cl$, Br and I; $PR_3 = PEt_3$, $PMePh_2$ and PPh_3, has been studied in chloro-hydrocarbon solvents, with emphasis on the chloro–triethyl complexes. Photo-induced dimerization was a concurrent reaction to varying degrees for the complexes. In chloroform and carbon tetrachloride, an induction period was observed for isomerization. Addition of carbon monoxide enhanced isomerization but suppressed dimerization, while continuous purging with nitrogen produced the opposite effects. For *cis*-$Pt(CO)(PEt_3)Cl_2$, the quantum yield of *cis–trans* conversion was about 0.6 at different wavelengths of incident light; it was invariable towards the presence of oxygen or 1,3-pentadiene, but increased to about 0.8 in the presence of carbon monoxide introduced at different pressures. These results indicate that isomerization takes place from a singlet state of relatively long lifetime, with metal–carbonyl bond breaking as the first step, followed by catalysis of the reaction by the free ligand.

Introduction

The photochemical isomerization of square-planar platinum(II) complexes often proceeds through a different pathway than the corresponding thermal process [1]. Thus for complexes of the type PtL_2X_2, where X stands for an anionic ligand such as a halide and L for a neutral species such as a phosphorus or a sulfur donor ligand, the thermal *cis–trans* conversion is usually catalysed by free ligands [2–4], and commonly proceeds either through a consecutive ligand displacement mechanism or a pseudo-rotation mechanism [5, 6]. On the other hand, the photochemical isomerization normally proceeds in the absence of added ligands and by far the most commonly proposed pathway is an intramolecular twisting mechanism [7–9].

A different type of reaction pattern has been reported by Anderson and Cross for carbonyl complexes of the type $Pt(PR_3)(CO)X_2$ [10]. For these complexes the thermal isomerization proceeds spontaneously but only in the *trans* to *cis* direction. Experimental results indicated an autocatalysed path involving the elimination of CO ligand as the first step, followed by isomerization through catalysis by the free CO. It has also been found that the *cis–trans* isomerization of these complexes can be initiated photochemically, but detailed studies for the photochemical reaction have so far not been made [10].

In view of the fact that metal–carbonyl bond dissociation is a common photochemical primary process for many complexes containing the carbonyl ligand [11], it is of interest to investigate the nature of the photochemical isomerization of the $Pt(PR_3)(CO)X_2$ complexes. In this work we report a study of the photochemical isomerization of these complexes in chloro-hydrocarbon solvents. The results indicate that, contrary to other systems, an intermolecular mechanism involving the participation of the free carbonyl ligand is a major route for the photo-initiated isomerization.

Experimental

Materials

The complexes *cis*-$Pt(PEt_3(CO)Cl_2$ (**I**), *cis*-$Pt(PMePh_2)(CO)Cl_2$ (**II**) and *cis*-$Pt(PPh_3)(CO)Cl_2$ (**III**) were prepared from the corresponding chloro-bridged complexes *trans*-$[Pt_2Cl_4(PR_3)_2]$ according to the methods reported in the literature [12]. The complexes *cis*-$Pt(PEt_3)(CO)Br_2$ (**IV**) and *cis*-$Pt(PEt_3)(CO)I_2$ (**V**) were prepared by metathesis of the chloro complex in acetone [12]. The results of elemental analyses are given in Table 1.

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TABLE 1. Elemental analyses of the complexes

Complex	Calc. (%)			Found (%)		
	C	H	Halide	C	H	Halide
I	20.40	3.67	17.20	20.22	3.67	16.92
II	34.00	2.65	14.35	33.80	2.69	14.54
III	41.02	2.72	12.75	40.78	2.64	13.30
IV	16.78	3.02	31.87	16.62	2.94	31.84
V	14.13	2.54	42.65	14.06	2.49	39.45

Solid samples of the *trans* form of the chloro complexes $Pt(PR_3)(CO)Cl_2$ were prepared by passing carbon monoxide through solutions of the corresponding dimers in chloroform or benzene, followed by solvent removal through slow evaporation [10]. However, appreciable conversion to the *cis* form was found to occur overnight even when the solid samples were stored at −10 °C. For photolysis experiments, millimolar solutions of the *trans* complexes were prepared by bubbling carbon monoxide through solutions of the dimers for periods not exceeding 2 min. It was found that the *trans* isomers could be generated quantitatively in solution in this manner.

Reagent or analytical grade solvents dichloromethane, chloroform and carbon tetrachloride were re-distilled before use.

Apparatus

A xenon illuminator (Varian LX15OUV) and a medium pressure mercury lamp (Hanovia 616A) were used as light sources for photolysis. A Bausch and Lomb high intensity grating monochromator and Oriel interference filters were used to isolate light of the desired wavelengths.

Ultraviolet spectra and absorbance values were measured on a Shimadzu 260 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer A1300 instrument.

Procedure

Photolysis was carried out in quartz cells. Solutions were either aerated, degassed, or treated with carbon monoxide. For quantitative addition of carbon monoxide, a solution was first degassed, and the gas was admitted at a known pressure. During photolysis, UV or IR spectra or absorbance values in the UV region were taken at regular intervals. Quantum yields were determined by using the potassium oxalate actinometer [13]. Each calculation of quantum yield was based on two actinometry determinations performed before and after a photochemical run.

Results and discussion

Spectra

The UV spectra of *cis*$Pt(PR_3)(CO)Cl_2$ ($PR_3 = PEt_3$, $PMePh_2$, PPh_3) all showed an intense band around 250 nm. The spectra of the corresponding *trans* complexes were also similar to each other in that they all showed a strong band around 250 nm and a weaker one near 300 nm. Figure 1 shows the spectra of *cis*- and *trans*-$Pt(PEt_3)(CO)Cl_2$. The spectral features of all the complexes are summarized in Table 2. Note that there is a general red shift of the first intense band in going from the chloro, bromo, to the iodo compounds in their *cis* form, indicating that the band is due to a ligand to metal

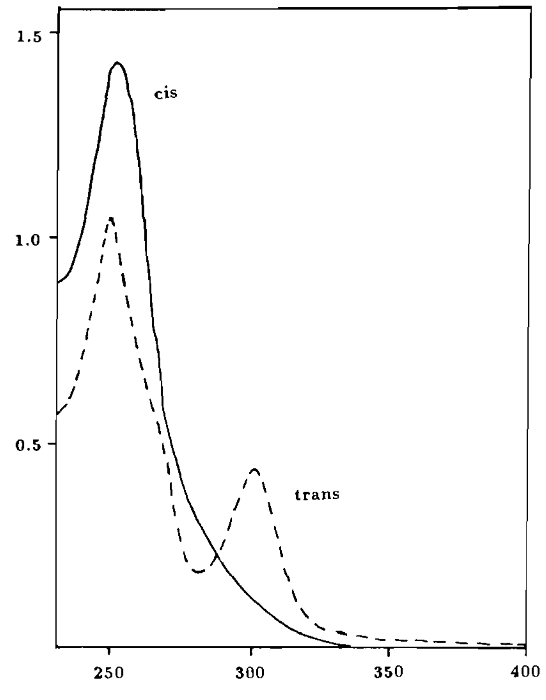

Fig. 1. Spectra of *cis*- and *trans*-$Pt(CO)(PEt_3)Cl_2$ in dichloromethane. Concentration of each solution: 2.22×10^{-4} M.

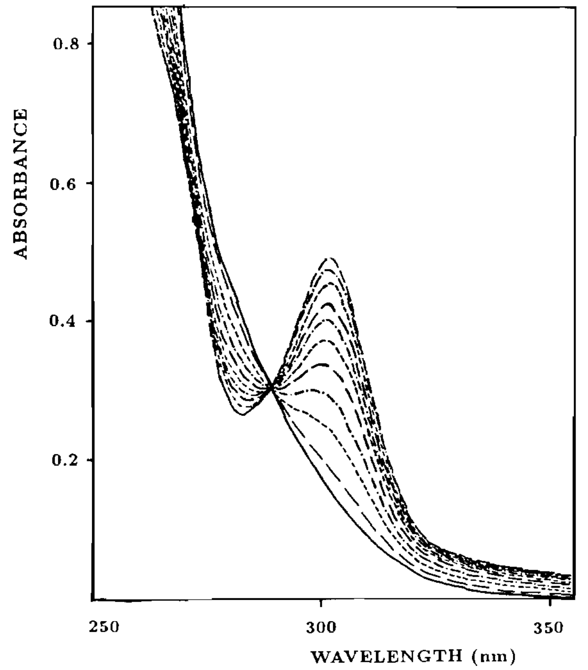

Fig. 2. Spectral changes during photolysis of Pt(CO)(PEt$_3$)Cl$_2$ in dichloromethane at 254 nm. Solid line: initial solution, conc. = $2.79–10^{-4}$ M. Total irradiation time: 17.5 min.

charge transfer transition. In the IR region all complexes showed the sharp CO stretching at approximately 2100 cm^{-1}, with the *trans* species showing slightly higher frequencies than the *cis*, as expected since in the *trans* complexes the carbonyl and the phosphine ligands would both compete for the back-donation of electron from the metal. There was also a decreasing trend in the frequency of CO stretching in going from the chloro, bromo, to the iodo complex, in accord with the increasing electron donating tendency of the ligands.

Isomerization of Pt(PR$_3$)(CO)X$_2$

Solutions of *cis*-Pt(PR$_3$(CO)Cl$_2$ in the chloro-hydrocarbon solvents carbon tetrachloride, chloroform and dichloromethane could be kept for days. Upon irradiation with UV light *cis* to *trans* conversion took place, as indicated by the changes in the UV or IR spectra. Figure 2 shows the UV spectra changes for *cis*-Pt(PEt$_3$)(CO)Cl$_2$ during irradiation. Similar changes were also observed for *cis*-Pt(PMePh$_2$)(CO)Cl$_2$ and *cis*-Pt(PPh$_3$)(CO)Cl$_2$ in the presence of added carbon monoxide. For these solutions the absorbance data treated according to the graphical method of Coleman *et al.* [14] gave straight lines passing through the origin, confirming the presence of only two absorbing species during irradiation.

In chloro-hydrocarbon solvents *trans*-Pt(PR$_3$)(CO)Cl$_2$ gradually isomerised to the *cis* at room temperatures. Irradiation of the solutions accelerated the process. However while the thermal isomerization proceeded only in the *trans* to *cis* direction, the light-induced process proceeded towards a photostationary state. These observations were in agreement with the results of Anderson and Cross [10].

Irradiation of solutions of *cis*-Pt(PEt$_3$)(CO)X$_2$ (X = Br or I) in dichloromethane resulted in conversion to the *trans*, showing characteristic UV spectral changes similar to those exhibited by the chloro complexes, with isosbestic points at 303 and 328 nm for the bromo and iodo complexes, respectively. In the IR spectra, a new band at 2125 cm^{-1} was observed

TABLE 2. UV and IR spectroscopic characteristics of complexes in dichloromethane

Complex		λ_m (nm)^a	$\epsilon \times 10^{-3}$ (M^{-1} cm^{-1})	ν(CO) (cm^{-1})
Pt(CO)(Ph$_3$)Cl$_2$	*cis*	257(sh)	12.3	2105
	trans	305	1.65	2133
		254(sh)	8.94	
Pt(CO)(PMePh$_2$)Cl$_2$	*cis*	254(sh)	12.4	2116
	trans	304	2.15	2140
		252(sh)	11.9	
Pt(CO)(PEt$_3$)Cl$_2$	*cis*	252	6.16	2107
	trans	302	1.87	2132
		250	4.53	
Pt(CO)(PEt$_3$)Br$_2$	*cis*	295(sh)	2.20	2100
		258	7.05	
Pt(CO)(PEt$_3$)I$_2$	*cis*	340(sh)	3.37	2089
		286	7.06	

$^a\lambda$ = wavelength of maximum absorption; sh = shoulder.

for the bromo and one at 2111 cm^{-1} for the iodo species, these were slightly higher than those observed for the starting compounds and could be assigned to the CO stretching of the *trans* species.

Thermal and photo-induced dimerization

Apart from isomerization, the complexes $Pt(CO)(PR_3)Cl_2$ also exhibit different degrees of dimerization to the corresponding chloro-bridged complexes *trans*-$\{Pt(PR_3)Cl_2\}_2$. There were several salient features which may be summarized as follows.

(i) The *cis* complexes in solution were stable and showed no sign of change. Irradiation of *cis*-$Pt(CO)(PEt_3)Cl_2$ in chloro-hydrocarbon solvents led only to isomerization. In the absence of added carbon monoxide, irradiation of the complexes with more bulky ligands, viz. *cis*-$Pt(CO)(PPh_3)Cl_2$ and *cis*-$Pt(CO)(PMePh_2)Cl_2$, resulted in isomerization as well as some dimerization, as indicated by the appearance of spectral bands around 275 and 337 nm.

(ii) The slow isomerization of *trans*-$Pt(CO)(PR_3)Cl_2$ in chloro-hydrocarbon solvents when the solutions were kept in the dark was also accompanied by some dimerization. When the *trans* complexes were dissolved in methanol, the spectra obtained were those of the dimers, indicating that dimerization was complete and instantaneous.

(iii) Irradiation of the *trans* complexes in chloro-hydrocarbon solvents accelerated both the *trans* to *cis* conversion and dimerization.

(iv) For both the *cis* and *trans* complexes in chloro-hydrocarbon solvents, addition of free carbon monoxide enhanced isomerization but suppressed dimerization, both in the thermal and photo-initiated processes (*vide infra*).

(v) When irradiation of *cis*-$Pt(PR_3)(CO)Cl_2$ in chloro-hydrocarbon solvents was performed with continuous bubbling of nitrogen, isomerization became slower, at the same time dimerization was enhanced. This applied also to the complex with the triethyl phosphine ligand.

Dimerization in these complexes probably takes place through a dissociative path with initial formation of a three-coordinate species.

$$Pt(CO)(PR_3)Cl_2 \rightleftharpoons Pt(PR_3)Cl_2 + CO \tag{1}$$

$$Pt(PR_3)Cl_2 + Pt(CO)(PR_3)Cl_2 \longrightarrow \text{dimer} + CO \tag{2}$$

$$2Pt(PR_3)Cl_2 \longrightarrow \text{dimer} \tag{3}$$

The first step is reversible, as implied by the effect of added carbon monoxide and that of continuous purging with nitrogen. The fact that the *trans* complexes were more prone towards dimerization is also in accordance with such a dissociative pathway, as a strong *trans* effect, soft, and π-acid ligand like phosphine would weaken the platinum–carbon monoxide linkage.

The observation of rapid dimerization in methanol probably indicates that the three-coordinate species is stabilized by solvation, or that dimerization occurs through the intermediacy of the solvent coordinated species $Pt(PR_3)Cl_2(MeOH)$.

A similar mechanism has been proposed by Courtot and co-workers [15] for the photo-induced dimerization of $Pt(amine)(olefin)Cl_2$ complexes, leading to the formation of $\{PtCl_2(amine)\}_2$. When the monomeric complex was irradiated in an oxygen-donor solvent, the species $PtCl_2(amine)(solvent)$ was formed and could be isolated at low temperatures. In halogenated solvents at room temperatures, the solvent coordinated species suffers loss of the oxygen-donor ligand with formation of the dichloro-bridged diplatinum complex [15c].

Induction period

For *cis*-$Pt(CO)(PEt_3)Cl_2$ in chloro-hydrocarbon solvents, as isomerization was the only reaction during photolysis, it was possible to measure spectrophotometrically the concentration of the *trans* isomer as a function of irradiation time. It was noted that with carbon tetrachloride and chloroform as solvents, an induction period was required for the *cis* to *trans* conversion. A typical plot is shown in Fig. 3. This phenomenon was not due to the presence of solvent impurity, as repeated fractionation of the solvent did not result in the elimination or shortening of the induction period. In dichloromethane, where the

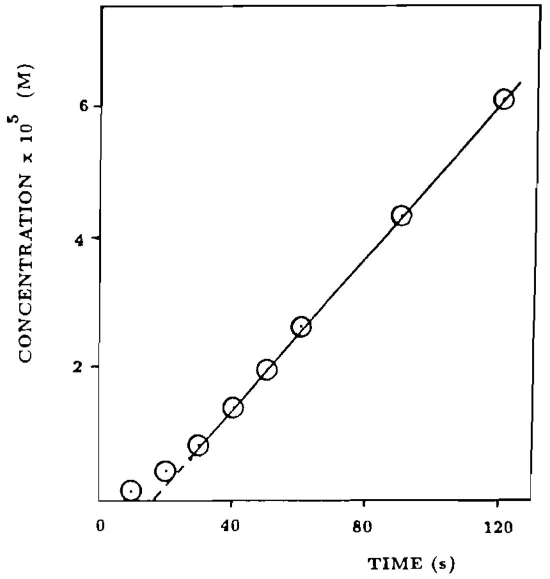

Fig. 3. Increase of concentration of *trans*-$Pt(CO)(PEt_3)Cl_2$ during photolysis of the *cis* isomer in chloroform at 254 nm. Initial concentration of *cis* complex: 6.97×10^{-4} M.

photoinduced isomerization proceeded more rapidly under comparable conditions, an induction period was not apparent.

Quantum yield and mechanism

The values of the quantum yield for *cis* to *trans* conversion in dichloromethane were measured for the complex *cis*-$Pt(CO)(PEt_3)Cl_2$, for which photodimerization was not an important concurrent process. The quantum yield data measured under different conditions are presented in Table 3. The data indicate that the yield is independent of wavelength. The fact that the same value was obtained for aerated and degassed solutions implies that there was no effect of dissolved oxygen, a potential triplet state quencher. Addition of another quencher, *trans*-1,3-pentadiene, also did not have appreciable effect on the yield. On the other hand, the yield increased by a constant factor of about thirty percent upon addition of carbon monoxide, with pressure of the gas varying from 12 to 209 mm Hg.

The effect of added carbon monoxide shows that the *cis–trans* isomerization is catalysed by the presence of the free ligand. In the light of this effect, the induction period observed in the absence of the added gas can be attributed to the initial formation of the free ligand required for isomerization. The absence of any effect of dissolved oxygen and 1,3-pentadiene indicates that the reaction probably originates from a singlet state. The constancy of quantum yield with respect to varying incident wavelength is in line with the anticipation that the same excited state should be populated upon light absorption, since the same spectral band was irradiated over the range of wavelength covered. The constancy of quantum yield observed with the addition of carbon monoxide implies that even at the lowest free ligand concentration, practically all the excited state species react with the free ligand, leading to isomerization. Thus the excited state must be relatively long-lived. The value of 0.8 for the quantum yield probably reflects a high efficiency of the catalysed process.

The experimental results thus are in accordance with the following scheme for the photo-induced isomerization

$$cis \xrightarrow{h\nu} cis^* \tag{4}$$

$$cis^* \longrightarrow M + CO \tag{5}$$

$$cis^* \xrightarrow{CO} trans \tag{6}$$

$$cis^* \longrightarrow cis \tag{7}$$

where the asterisk denotes the excited species, and M a three-coordinate species.

In the presence of added carbon monoxide, reaction (6) is the dominant step for the excited species and reaction (7) would become unimportant. Reaction (6) indicates that the *cis–trans* conversion is brought about by an intermolecular, rather than intramolecular, process of the excited species. The reaction may proceed through either the pseudo-rotation or the consecutive displacement mechanism. Although the present data do not shed much light on the nature of the process, the fact that the reaction occurred in relatively non-polar solvents would suggest that the pseudo-rotation of the five-coordinate species $Pt(PR_3)(CO)_2X_2$ is more likely to be operative than the consecutive displacement mechanism, which would involve an ionic intermediate species $[Pt(PR_3)(CO)_2X^+]X^-$. It thus appears that the photo-induced isomerization of these carbonyl complexes takes place via a pathway similar to that of the thermal process [10].

TABLE 3. Quantum yields of isomerization of *cis*-$Pt(CO)(PEt_3)Cl_2$ in dichloromethane

Run	λ (nm)	Conc. × 10^3 (M)[a]	P_{CO} (mm Hg)	$\Phi_{C \to T}$
1	254	2.02		0.62
2	254	0.801		0.58
3[b]	245	0.815		0.62
4[b]	254	0.416		0.62
5	254	0.416	12	0.83
6	254	0.416	64	0.82
7	254	0.416	106	0.79
8	254	0.416	209	0.79
9	265	2.02		0.61
10	265	0.806		0.61
11	313	2.01		0.60
12[c]	313	1.93		0.61
13	313	1.21		0.59

[a] Initial concentration of the platinum complex. [b] In degassed solution. [c] In degassed solution in the presence of 6.70×10^{-3} M of 1,3-pentadiene.

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