

THERMALLY-REVERSIBLE PHOTOISOMERIZATION OF *trans*-DINITROBIS(TRI-*n*-PROPYLPHOSPHINE)PALLADIUM(II)

G. GUGLIELMO, V. RICEVUTO,

Dipartimento di Chimica Inorganica e Struttura Molecolare, Università di Messina, 98100 Messina (Italy)

P. BERGAMINI, S. SOSTERO and O. TRAVERSO

Istituto Chimico, Università di Ferrara, Via Borsari 46, 44100 Ferrara (Italy)

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Summary

UV irradiation of *trans*-dinitrobis(tri-*n*-propylphosphine)palladium(II) in MeOH yields a photostationary *trans-cis* mixture which reverts quantitatively in the dark to the *trans*-form. The *cis*-isomer, which can be isolated in crystalline form by irradiation of *trans*-species in *n*-hexane, has been characterized by UV, IR ¹H and ³¹P NMR spectroscopy. Irradiation of a 1/1 mixture of *trans*-[(P*n*Bu₃)₂Pd(NO₂)₂] and *trans*-[(P*n*Pr₃)₂Pd(NO₂)₂] gives almost entirely a 1/1 mixture of the corresponding *cis*-isomer, indicating an intramolecular process.

Introduction

Cis-trans photoisomerization of square planar palladium(II) complexes can, in some cases, take place reversibly in either direction but often takes place in only one direction [1,2]. Systems undergoing photoisomerization in both directions, thus eventually achieving in a photostationary state, are the dihalobis(tertiary phosphine)palladium(II) complexes [2,3], L₂PdX₂ (L = PEt₃, P*n*Pr₃, P*n*Bu₃; X = Cl, Br). The relative concentrations of the *cis*- and *trans*-isomers at the photostationary state are a function of the solvent, but for a particular solvent the steady-state *cis/trans* ratio is the same whether approached from a pure *cis*- or from a pure *trans*-isomer. We demonstrate here the potential of photoirradiation as a means of preparing unstable isomeric forms at ambient temperature by photolysis of *trans*-[(P*n*Pr₃)₂Pd(NO₂)₂] (Ia).

Experimental

Compounds. *trans*-[(P*n*Pr₃)₂Pd(NO₂)₂] (Ia) and *trans*-[(P*n*Bu₃)₂Pd(NO₂)₂] were prepared by literature procedures [4]. Merck spectroquality solvents were degassed by bubbling in N₂ followed by freeze-pump-thaw cycles.

Apparatus. The electronic absorption spectra and the absorbance changes for the quantum yields measurements were recorded on a Cary 17 spectrometer and a Perkin-Elmer 323 UV-visible spectrometer, respectively. Infrared absorption spectra were recorded on a Perkin-Elmer 257 instrument. Photolysis was carried out with use of 250 W XENON LAMP equipped with f/3.4 Applied Photophysics monochromator. ^1H NMR and ^{31}P NMR spectra were recorded with a Bruker VH 90 spectrometer. Conductivity measurements were performed at 18°C using a Radiometer CDM 3 instrument adapted in-house for use during direct irradiation of the solutions.

Procedures. The irradiations were performed at 20°C on magnetically stirred solutions, which were periodically taken to the spectrophotometer for optical measurements. The initial concentration of the reagent complex was selected to ensure maximum light absorption compatible with the spectrophotometric kinetic measurements to be performed.

All kinetic runs were carried out under zero-order conditions in order to facilitate calculations of the quantum yields [2]. The quantum yield calculation was based on two actinometric measurements [5] performed in the reaction cell before and after each photochemical run.

Results

Photolysis of $\text{trans}-[(\text{PPr}_3^n)_2\text{Pd}(\text{NO}_2)_2]$ (Ia). No thermal isomerization of (Ia) to the *cis* form was observed during several days at 20°C . No thermal reaction

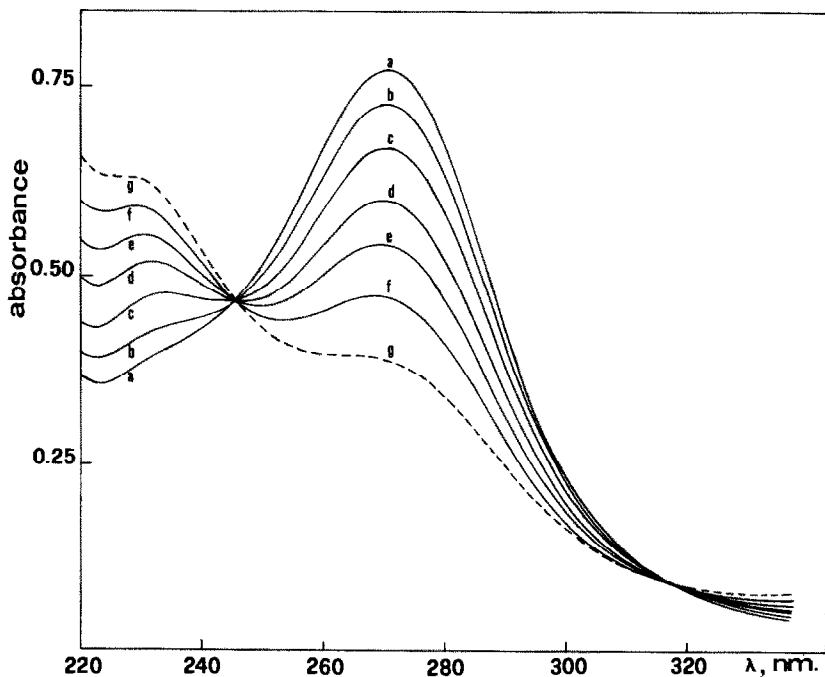
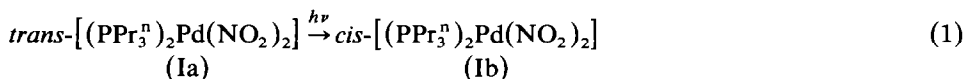


Fig. 1. Spectral changes during irradiation (λ 285 nm) of a 3.35×10^{-5} M solution of $\text{trans}-[(\text{PPr}_3^n)_2\text{Pd}(\text{NO}_2)_2]$ in MeOH: (a) no irradiation; (b) irradiation time of 10 s; (c) 20 s; (d) 40 s; (e) 60 s; (f) 80 s; (g) spectrum of *cis*- $[(\text{PPr}_3^n)_2\text{Pd}(\text{NO}_2)_2]$.

(isomerization or decomposition) was observed in solution in the presence of NO_2^- or free PPr_3^n . Photolysis (λ 254, 285, 313, 320, 330 nm) of methanol solution of Ia induced a UV spectral change with a clearly defined isosbetic point at 245 nm and with a final spectrum identical with that for authentic *cis*- $[(\text{PPr}_3^n)_2\text{Pd}(\text{NO}_2)_2]$ (Ib). (Fig. 1).

Interruption of irradiation led to a quantitative return to (Ia). From the absorption spectrum of the *trans*-isomer (Ia) and the spectrum of the photostationary equilibrium obtained by irradiation at 313 nm in MeOH, the UV spectrum of the *cis*-complex (Ib) was obtained. The spectrum of Ib obtained by this procedure [6] matched that of pure Ib prepared by our photochemical method (see the preparation of *cis*-isomer).

These results and the ^{31}P NMR spectral profile of the photoreactions (see ^{31}P NMR experiments) indicate that the only photochemical process occurring is that shown in eq. 1.



NMR experiments. Photolysis (250 W Xe arc) of Ia in CD_3OD for 9 h leads to gradual disappearance of the ^{31}P resonance of Ia (-8.64 ppm) and emergence of a new peak at -22.57 ppm. Such a downfield shift is typical of the *cis*-isomer of established *cis-trans* pairs in phosphine palladium(II) complexes [1,2]. In the dark the new species decays with first-order kinetics to reform quantitatively the -8.64 ppm peak of Ia. Such uncatalyzed thermal isomerization is similar to that observed for L_2PdX_2 ($\text{L} = \text{PEt}_3, \text{PPr}_3^n, \text{PBu}_3^n$; $\text{X} = \text{Cl}, \text{Br}$) complexes [2].

Isolation of the cis-isomer Ib. Two procedures were employed: (a) Silver nitrate (0.040 g) was added to a solution of *cis*- $[(\text{PdCl}_2(\text{PPr}_3^n)_2)]$ (0.0498 g) in MeOH. The AgCl formed was filtered off and an excess of KNO_2 was added to the filtrate. The resultant precipitate was filtered off, washed with *n*-hexane, and dried in vacuo to give the product Ib: IR (Nujol) $\nu(\text{NO}_2)$ as.: 1460, 1385, 1330, 1320; $\nu(\text{NO}_2)$ sym. 1310; $\nu(\text{NO}_2)$ bend.: 850, 840 cm^{-1} .

(b) Irradiation (λ 313 nm) of an *n*-hexane solution of the *trans*-isomer Ia resulted in precipitation of the *cis* isomer Ib as it formed ($\sim 18\%$ yield). Identification of the *trans*- and *cis*-isomers (Ia and Ib) was mainly by ^1H and ^{31}P NMR spectroscopy (Table 1). The ^{31}P spectrum of *cis*-Ib shows a singlet at -22.57 ppm in CDCl_3 . Ultraviolet spectra in MeOH showed λ_{max} at 270 nm ($\epsilon = 11.4 \times 10^3$) and 240sh ($\epsilon = 18.8 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). Proton NMR data are listed in Table 1.

TABLE 1
 ^1H NMR PARAMETERS FOR $[(\text{PPr}_3^n)_2\text{Pd}(\text{NO}_2)_2]^{a,b}$

Parameter	<i>trans</i> -Ia ^c	<i>cis</i> -Ib ^d
$\delta(\text{PPr}_3^n)$ (ppm)	1.10(t) 1.62(m) 1.95(m)	1.05(t) 1.58(m) 1.75(m)

^a t = Triplet, m = multiplet. ^b Although the resonances are described simply as multiplets (due to coupling with both P and CH_2), the actual patterns are different for Ia and Ib isomers. ^c In CD_3OD solution. ^d In CDCl_3 solution.

TABLE 2

QUANTUM YIELDS FOR THE PHOTOREACTION OF *trans*-[(PPr₃ⁿ)₂Pd(NO₂)₂] IN METHANOL AT VARIOUS IRRADIATION WAVELENGTHS

λ_{irr} (nm)	254	270	320
Φ	0.004	0.025 0.026 ^a	0.055 0.056 ^b

^a In the presence of NO₂⁻ (3×10^{-5} mol dm⁻³). ^b In the presence of small amounts of PPr₃ⁿ.

Mechanistic studies

Attempts to assess the roles of inter- and intra-molecular pathways in the photochemically induced *trans-cis*-isomerization involved the following experiments.

(i) *Photolysis*. Photolysis in CD₃OD of a 1/1 (molar) mixture of *trans*-[(PPr₃ⁿ)₂Pd(NO₂)₂] and *trans*-[(PBu₃ⁿ)₂Pd(NO₂)₂] gave a ³¹P NMR spectrum indicating 75–80% conversion into *cis*-[(PPr₃ⁿ)₂Pd(NO₂)₂] and *cis*-[(PBu₃ⁿ)₂Pd(NO₂)₂], together with a very small resonance consistent with formation of a trace of mixed complexes.

Thermolysis of the mixture of *trans* complexes was examined by ³¹P NMR spectroscopy in methanol solution; on heating, small quantities of the *cis*-isomers were formed, i.e. *cis*-[(PPr₃ⁿ)₂Pd(NO₂)₂], *cis*-[(PBu₃ⁿ)₂Pd(NO₂)₂] while the major new product was *trans*-[(PPr₃ⁿ)(PBu₃ⁿ)Pd(NO₂)₂].

(ii) *Quantum yields*. Quantitative measurements were performed under various experimental conditions. The presence of NO₂⁻ and/or free PPr₃ⁿ affects neither the band positions in the electronic spectrum nor the course of photoreaction for Ia. Quantum yields for the photoisomerization Ia → Ib as a function of irradiation are shown in Table 2.

(iii) *Conductivity measurements*. Measurements of the conductivity of the irradiated (λ 320 nm) methanolic solutions of Ia (alone or in the presence of PPr₃ⁿ) gave a very low value compared with those of 1/1 electrolytes [2].

Discussion

The ³¹P NMR data and the electronic spectral variations indicate that upon irradiation of Ia in MeOH a photostationary state is set up which contains up to 65% *cis*-isomer at 20 °C. Irradiation of n-hexane solutions of the *trans*-isomer leads to deposition of the pure *cis*-isomer Ib, albeit in rather lower yields. The effect of solvent on the *cis/trans* ratio reflects solvent polarity, with MeOH favoring the dipolar *cis*-isomer over the non-polar *trans*-isomer, while the *cis* isomer Ib precipitates in the non-polar solvent n-hexane.

The Ia → Ib isomerization may be either intramolecular or intermolecular process [2,7]. The most significant result is that irradiation of the mixture of *trans*-[(PPr₃ⁿ)₂Pd(NO₂)₂] and *trans*-[(PBu₃ⁿ)₂Pd(NO₂)₂] indicates a predominantly intramolecular process. Furthermore, the lack of influence of NO₂⁻ or PPr₃ⁿ on the quantum yields indicates that the photochemical isomerization is not subject to retardation. Additionally, it was observed that the conductivity of the irradiated solutions never reached that of a 1/1 electrolyte even when an excess of PPr₃ⁿ was

added. The results of conductometric studies and the independence of the quantum yields of added NO_2^- and PPr_3^n are therefore complementary, and both indicate the absence of an ionic pathway for the photoinduced isomerization. On the basis of these results the simplest intramolecular process appears to be a "twist" mechanism, in which the initial Ia complex rearranges to its isomer Ib via an intermediate or transition state having a tetrahedral configuration [2,7].

The electronic absorption spectrum of Ia revealed little about the nature of photoactivated state, since no well-resolved bands were observed. The spectrum contains a shoulder on the long-wavelength side (300–330 nm) of the massive ligand-centered transitions at higher energies. The active excited state leading to isomerization must come from the transition [2], probably LF, which appears as shoulder in the 300–330 nm spectral region, since a larger quantum yield can be obtained by irradiation in this region.

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