Photochemistry of Planar Four-co-ordinate Palladium(II) Complexes. Part 2.[1] *trans–cis* Isomerization of Dihalogenobis(tri-n-propylphosphine)palladium(II) in Solution

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The photoisomerization of *trans*-dihalogenobis(tri-n-propylphosphine)palladium(II) complexes has been studied in various solvents. The quantum yields depend strongly both on the nature of the co-ordinating halide and on the excitation wavelength. The photochemical results are discussed in terms of the possible mechanisms for the *trans–cis* photoisomerization of square-planar complexes. Photolysis of *cis*-$[\mathrm{Pd(PPr^n_3)_2Cl_2}]$ yields the chloro-bridged complex, $[\mathrm{Pd_2(PPr^n_3)_2Cl_4}]$.

INVESTIGATIONS on photoisomerization of square-planar complexes have dealt mainly with platinum(II) derivatives.[2–7] Analogous studies on palladium(II) complexes, to our knowledge, have never been reported; this is probably due to the high reactivity of square-planar palladium(II) complexes, which usually rapidly achieve isomeric equilibrium in solution.[8,9]

We have made a preliminary report[10] that u.v. irradiation of methanol solutions of the complex *trans*-$[\mathrm{Pd(PPr^n_3)_2Cl_2}]$ causes extensive conversion into the *cis*-isomer, equation (1), and subsequently into the bridged compound $[\mathrm{Pd_2(PPr^n_3)_2Cl_4}]$. In this paper, we report in

$$trans\text{-}[\mathrm{Pd(PPr^n_3)_2Cl_2}] \underset{\text{heat}}{\overset{h\nu}{\rightleftharpoons}} cis\text{-}[\mathrm{Pd(PPr^n_3)_2Cl_2}] \qquad (1)$$

some detail on the quantum efficiency of equation (1), noting especially the effect of changing the co-ordinating halide and the excitation wavelength. We also examined the influence of solvent on the composition of the photostationary state, to ascertain whether polar solvents favour the *cis* isomer. The effects of adding free halide and tri-n-propylphosphine were also noted. (These various effects could be particularly important in many catalysis mechanisms and it is known that small amounts of various species poison the catalysts.) Finally, the mechanism of the photoisomerization was studied in a series of solvents by ^{1}H and ^{31}P n.m.r., electronic, and i.r. spectroscopy and by conductometric methods.

EXPERIMENTAL

Preparation of the Complexes.—The complex *trans*-$[\mathrm{Pd(PPr^n_3)_2Cl_2}]$, (1a), was prepared according to literature procedures.[11] Complexes *trans*-$[\mathrm{Pd(PPr^n_3)_2Br_2}]$, (2a), and *trans*-$[\mathrm{Pd(PPr^n_3)_2I_2}]$, (3a) were obtained from (1a) by metathetic exchange in methanol. Recrystallizations were carried out until the compounds were pure, according to i.r., ^{1}H n.m.r., and ^{31}P n.m.r. spectra.

cis-$[\mathrm{Pd(PPr^n_3)_2Cl_2}]$, (1b).[12] A nitromethane solution (10^{-2} mol dm^{-3}) of (1a) was irradiated in a quartz reaction vessel using a PCQ (photochemical quartz) mercury lamp for 2 h at room temperature. The *trans–cis* mixture was concentrated with a stream of N_2 to minimum volume and diethyl ether was added to give a crystalline precipitate.

After filtration the solid was washed with diethyl ether, dried, and identified as the *cis* isomer by spectral methods (^{1}H n.m.r., i.r., and electronic spectroscopy).

Photochemical preparation of $[\mathrm{Pd_2(PPr^n_3)_2Cl_4}]$, (4). A methanol solution (20 cm^3, 5×10^{-3} mol dm^{-3}) of (1b) was placed in a quartz vessel and irradiated at 280 nm for 10 h. The solvent was removed under reduced pressure to yield a crude residue which consisted of a mixture of (4) and $\mathrm{PPr^n_3}$. After recrystallisation from methanol–diethyl ether, the solid was identified as the bridged compound $[\mathrm{Pd_2(PPr^n_3)_2Cl_4}]$ by comparison with an authentic sample.[13] No formation of (4) was observed at 20 °C in the dark; instead, as previously reported,[10] some conversion of (1b) to (1a) occurred in the dark.

Chemicals.—All solvents were Merck Spectro materials. After drying and distillation (from molecular sieves or P_4O_{10}), each solvent was stored in a stoppered dark glass bottle.

Apparatus.—Irradiation at 254 nm was carried out with a HANOVIA NM 15/44 low-pressure lamp. Monochromatic light of 280, 313, 333, 365, and 405 nm was obtained from a high-pressure HANAU Q 400 mercury lamp and the appropriate Bausch and Lomb interference filters.

Infrared spectra were recorded on a Perkin-Elmer 257 instrument using 0.2-mm CsBr cells and, for 200—700 cm^{-1}, with paraffin mulls between CsI discs.

Hydrogen-1 n.m.r. and ^{31}P n.m.r. spectra were recorded at 90 MHz (Bruker WH 90) for *ca.* 10^{-2} mol dm^{-3} solutions.

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 taken periodically to the spectrophotometer for optical measurements. The initial concentration of the reagent complex was selected in order to ensure the maximum light absorption compatible with the spectrophotometric kinetic measurements to be performed.

All kinetic runs were carried out under zero-order experimental conditions in order to facilitate the calculation of quantum yields. The quantum yield calculation was always based on two actinometric measurements[14] performed in the reaction cell before and after each photochemical run.

Photolyses were carried out in aerated, degassed (by freeze-pump-thaw cycles), and oxygenated (saturated with

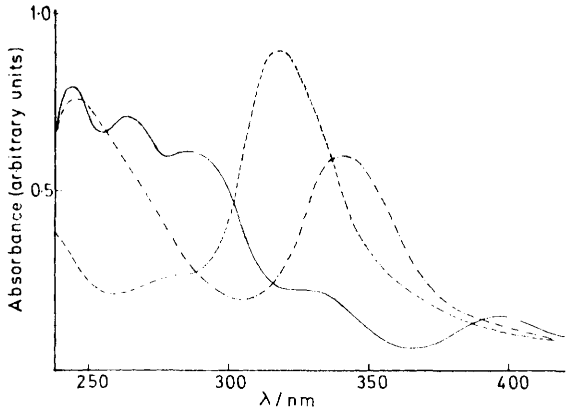

FIGURE 1 Electronic spectra of the complexes in MeOH: *trans*-$[Pd(PPr^n{}_3)_2I_2]$ (——) (5×10^{-5} mol dm^{-3}); *trans*-$[Pd(PPr^n{}_3)_2Cl_2]$ (– – – –) (5×10^{-5} mol dm^{-3}); *trans*-$[Pd(PPr^n{}_3)_2Br_2]$ (– · – · –) (5×10^{-5} mol dm^{-3})

oxygen through bubbling) solutions. The quantum yields of photoreactions were unaffected by the presence of oxygen.

Hydrogen-1 and ^{31}P n.m.r. spectra were recorded immediately after solution preparation and subsequent to irradiation times to check for rearrangement processes.

TABLE 1

Absorption data (298 K) for dihalogenobis(tri-n-propylphosphine)palladium(II) complexes in MeOH

Complex	Band A $\tilde{\nu}_{max.}$/cm^{-1}	Band B $\tilde{\nu}_{max.}$/cm^{-1}
$[Pd(PPr^n{}_3)_2Cl_2]$	31 847	44 400
		42 016 (sh)
$[Pd(PPr^n{}_3)_2Br_2]$	29 070	40 325
		37 879 (sh)
$[Pd(PPr^n{}_3)_2I_2]$	25 160	37 736
		34 483
		30 303

RESULTS

Electronic Spectra.—The spectra of (1a), (2a), and (3a) are shown in Figure 1 and compiled in Table 1. All show two intense bands, one centred at around 300—400 nm, assigned [15-17] to a halogen→metal charge transfer (band A), and one centred around 220—290 nm assigned to a phosphorus→metal charge transfer (band B). A general red shift for band A in going from the chloro- to the bromo- and to the iodo-complexes is evident.

Photolysis of (1a), (2a), *and* (3a).—No thermal isomerization of (1a), (2a), or (3a) to the *cis* forms was observed to occur over several weeks at room temperature (20 °C). No thermal reaction (isomerization or decomposition) was observed in solution after several days in the presence of X^- (Cl, Br, or I) or free $PPr^n{}_3$.

On irradiation (λ = 254, 313, 333, 365, or 405 nm) of methanol solutions of (1a), a gradual spectral change is observed (Figure 2). The absorption at the maximum at 314 nm decreases and a new absorption band appears with a pronounced maximum at 254 nm; the spectra show an isosbestic point at 288 nm. The observed spectral variations can be assigned to a *trans* ⟶ *cis* isomerization for the following reasons: (*i*) by maintaining the irradiated solutions in the dark, the original u.v. absorption spectrum of (1a) is re-established; (*ii*) the change in the ^{31}P n.m.r. spectrum of (1a) which accompanies the spectral change upon irradiation is characteristic (see ^{31}P n.m.r. results); and (*iii*) by applying the procedure outlined by Fischer,[18] the u.v. absorption spectrum of *cis*-$[Pd(PPr^n{}_3)_2Cl_2]$, (1b), was obtained from the absorption spectrum of the *trans* isomer (1a) and the spectrum of the photostationary equilibrium, as obtained from irradiation at 313 nm in MeOH. The spectrum of (1b) obtained by this procedure matched that of pure (1b) prepared by our photochemical method [12] (Figure 2).

Phosphorus-31 *N.M.R. Measurements.*—A 3 h irradiation (λ = 254 nm) of (1a) (5×10^{-2} mol dm^{-3} in CD_2Cl_2) gave the following ^{31}P n.m.r. changes: original solution, −9.00 p.p.m. (relative to H_3PO_4); irradiated solution, reduced intensity at −9.00 p.p.m., new peak at −23.3 p.p.m. The observed downfield shift of the ^{31}P resonance is the same as found in the *trans* ⟶ *cis* isomerization of similar complexes.[9] A ^{31}P n.m.r. profile of the photoreaction indicated the absence of the free-ligand ^{31}P resonance at 33 p.p.m.[19] The electronic and ^{31}P n.m.r. experimental results taken together indicate that the sole photochemical reaction which occurs is reaction (2).

$$\underset{(1a)}{trans\text{-}[Pd(PPr^n{}_3)_2Cl_2]} \xrightarrow{h\nu} \underset{(1b)}{cis\text{-}[Pd(PPr^n{}_3)_2Cl_2]} \quad (2)$$

Photolysis of cis-$[Pd(PPr^n{}_3)_2Cl_2]$, (1b).—Irradiation (254 nm) of methanolic (1b) gave no photochemical isomerization to (1a); the only product isolated was $[Pd_2(PPr^n{}_3)_2Cl_4]$ (4) which has been formulated as the chloro-bridged derivative on the basis of elemental analysis and spectroscopic properties. The ^1H n.m.r. spectrum ($[^2H_4]$MeOH) shows bands attributable to the methylene groups at 1.95 p.p.m. and 1.80 p.p.m. and to the methyl group at 1.27 p.p.m. The integrated absorption of the proton resonances virtually matched that expected for compound (4).

The *trans* structure of the bridged palladium chloro-complex (4) was verified by the skeletal stretching frequencies [20] in the 200—500 cm^{-1} region *viz.*, 440, 418, 355 (Pd–Cl terminal stretching), 300 (Pd–Cl, bridging *trans* to Cl stretching), and 254 (Pd–Cl, bridging *trans* to $PPr^n{}_3$). An ^1H n.m.r. profile of photoreaction indicated a gradual formation of free $PPr^n{}_3$.

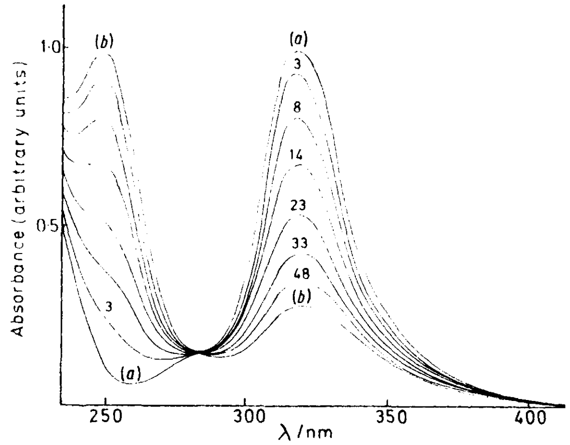

FIGURE 2 Photochemically induced u.v. spectral changes of *trans*-$[Pd(PPr^n{}_3)_2Cl_2]$ (6.75×10^{-5} mol dm^{-3}): (*a*), initial spectrum; (*b*), spectrum of authentic *cis*-$[Pd(PPr^n{}_3)_2Cl_2]$. Numbers refer to the irradiation time in minutes; $\lambda_{irr.}$ = 313 nm

These results indicate the occurrence of photoreaction (3).

$$2\ cis\text{-}[\mathrm{Pd(PPr^n_3)_2Cl_2}] \xrightarrow{h\nu} [\mathrm{Pd_2(PPr^n_3)_2Cl_4}] + 2\ \mathrm{PPr^n_3} \quad (3)$$

Photolysis of trans-[Pd(PPr$^n_3$)$_2$X$_2$] [X = Br, (2a); X = I, (3a)].—Deaerated methanol solutions of (2a) and (3a) were irradiated with 254—450 nm light in order to examine any variation in reaction pattern as compared to the chloro-complex (1a). Both spectral profiles showed an isosbestic point at 336 nm characteristic of the *trans–cis* isomerization. The absorbance data plotted according to the method of Coleman *et al.*[21] gave straight lines passing through the origin, confirming the presence of only two absorbing species during photolysis. Phosphorus-31 n.m.r. and electronic studies of irradiated solutions of (2a) and (3a) gave spectral changes identical to those obtained for (1a). These experimental results indicate the occurrence of reaction (2) for (2a) and (3a) as well.

Quantum Yields.—Quantitative measurements were performed under various experimental conditions. The presence of X$^-$ and/or free PPr$^n_3$ affects neither the band positions in the electronic spectra nor the course of photoreactions for (1a), (2a), and (3a). Quantum yields for the photoreactions as a function of irradiation are given in Table 2.

The data collected in Table 2 show three significant features: (*i*) the quantum yields show a wavelength dependence when $\lambda_{\text{irr.}} \leqslant 313$ nm; (*ii*) the order: $\Phi_{\text{isom.}}$ (1a) > $\Phi_{\text{isom.}}$ (2a) > $\Phi_{\text{isom.}}$ (3a); (*iii*) the quantum yields are virtually independent of the presence of X$^-$ and/or PPr$^n_3$.

TABLE 2

Quantum yields for the photoisomerization process of the complex *trans*-[Pd(PPr$^n_3$)$_2$X$_2$] (X = Cl, Br, or I) in methanol at several wavelengths of irradiation

$\lambda_{\text{irr.}}$/nm	Cl	Br	I
254	0.45	0.18	
313	0.19	0.11	0.02
	0.18 [a]		
	0.19 [b]		
333	0.18	0.12	0.02
365	0.19	0.12	0.03
405	0.19	0.11	0.02

[a] In the presence of Cl$^-$ (10^{-2} mol dm^{-3}). [b] In the presence of small amounts of tri-n-propylphosphine. Estimated error ±5%.

DISCUSSION

The systematic pattern of electronic and ^{31}P n.m.r. changes shows that the only photoproduct which is formed upon irradiation of (1a) is the *cis* complex, (1b). The quantum yields for (1a)⟶(1b) conversion show a wavelength dependence, and clearly the large quantum yield resulting from photolysis of (1a) at 254 nm [irradiation in the region of the CTTM (charge transfer to metal) band, P ⟶ Pd] leads to population of a reactive state inaccessible to 313 nm radiation; moreover this state does not deactivate efficiently to the lower energy states of band B and the LF (ligand-field) transitions. The same trend of weak internal conversion between CTTM and LF excited states was observed previously for square-planar platinum(II) complexes.[22]

The electronic character of the excited states of palladium(II) complexes, *viz.* $\sigma_{\mathrm{Pd}}{}^{n} \longrightarrow \sigma_{\mathrm{Pd}}{}^{*} \longrightarrow \pi_{\mathrm{Pd}}{}^{*} \longrightarrow \sigma_{\mathrm{Pd}}{}^{*}$ for LF states, $\pi_{\mathrm{P}} \longrightarrow \sigma_{\mathrm{Pd}}{}^{*}$ and $\pi_{\mathrm{X}} \longrightarrow \sigma_{\mathrm{Pd}}{}^{*}$ for the CTTM states, is suggestive of ligand lability owing to weakening of metal–ligand (PPr$^n_3$, X$^-$) bonds. However, a direct correlation between bond weakening and ligand lability is implicit only for a dissociative mechanism. The absence of any effect of X$^-$ and free PPr$^n_3$ on the quantum yields, ^{31}P n.m.r. and conductometric results are inconsistent with a consecutive dissociative mechanism for the *trans* ⟶ *cis* isomerization. If a dissociative mechanism is inoperable, possible distortion of the CTTM (P ⟶ Pd) excited states away from square-planar geometry would explain the higher quantum yield observed for 254-nm irradiation. Evidence that the distortions relate to the conformations around phosphorus comes from the crystal structure [12] of the *cis* form, (1b).

The structural results show in fact that the major steric effect is on the P–Pd–P angle, which is increased to 105° 76′ from the 90° of the square-planar geometry. There is also a considerable increase in one Pd–P–C angle on each phosphorus to not less than 121°. These results and the facts that *trans*-to-*cis* photoisomerization of (1a) occurs with high efficiency but the corresponding *cis*-to-*trans* photoprocess does not occur suggest that the thermally equilibrated excited state responsible for isomerization is ' *cisoid* '. That is, although the lowest energy configuration of the excited state could have a tetrahedral-like configuration,[4] it is distorted toward the *cis* geometry. Non-radiative deactivation of the ' *cisoid* excited state ' would give a *cisoid* vibrationally excited ground state that relaxes to the *cis* isomer.

From the data of Table 2 it can be seen that the quantum yields of the *trans–cis* isomerization decrease along the series Cl$^-$ to I$^-$. This decrease may be attributed to an enhanced stability of the Pd–P bonds as the halogen increases in atomic number.[23] A comparison of the force constants of the Pd–P bond in the complexes [PdL$_2$X$_2$] (L = tertiary phosphines, X = Cl$^-$, Br$^-$, or I$^-$) shows that the Pd–P bond strength increases in the series [PdL$_2$I$_2$] > [PdL$_2$Br$_2$] > [PdL$_2$Cl$_2$]. The occurrence of this behaviour may be taken as further evidence for an excited state with a distorted configuration around the P atom.

The remaining source of kinetic information on isomerization of the halogeno-phosphine complexes of Pd$^{\text{II}}$ is the lack of influence on the quantum yields of either X$^-$ or PPr$^n_3$. This means that the photochemical isomerization suffers no mass law retardation. Additionally, it was observed that in all cases the conductivity of the irradiated solutions never reached that of a 1 : 1 electrolyte even when an excess of PPr$^n_3$ was added. The results of conductometric studies and the independence of the quantum yields of added X$^-$ and PPr$^n_3$ are therefore complementary and both indicate the absence of an ionic pathway for the photoinduced isomerization.

Another important result is that the amount of the *cis* isomer, (1b), increases as the dipole moment of the solvent increases (Table 3). The results of Table 3 show that if

TABLE 3

Isomerization of *trans*-[$Pd(PPr^n_3)_2Cl_2$] in various solvents (20 °C), $\lambda_{irr.}$ = 313 nm

Solvent	μ [a]/D	Percent of *cis* isomer [b]
Nitromethane	4.39	72
Dimethylformamide	3.85	64
Acetone	3.11	56
1,2-Dichloroethane	2.94	48
Dichloromethane	1.80	32
Chloroform	1.10	18
Deuteriochloroform	1.01	16
Ethanol	2.89	45
Methanol	2.87	40
Propan-1-ol	1.66	25

[a] Dipole moment (Debye units; 1 D ≈ 3.336×10^{-30} C m): A. L. McClellan, 'Tables of Experimental Dipole Moments,' W. H. Freeman and Co., San Francisco, 1963. [b] Estimated from signal height of ^{31}P n.m.r. resonance. Irradiation time 2 h. Concentration of *trans* isomer 5×10^{-2} mol dm^{-3}.

the solvents are ordered according to dipole moment into three separate groups (hydroxylic solvents; chlorinated hydrocarbons; nitromethane, acetone, and dimethylformamide) three distinct linear regions are evident where the amount of (1b) generally increases as the solvent dipole moment increases. That the solvents used have separate correlation lines is not surprising in view of a probable difference in nature of the complex–solvent interaction.[8] Thus it appears that the solvent dipole moment is the most important factor in determining the yield of the *cis* isomer (1b), but also that during the course of the isomerization process the solvent achieves intimate contacts with the *cis* forms of palladium(II) complexes. This is in agreement with previous arguments regarding some platinum(II) phosphine complexes for which it was suggested that solvent interaction is greater for the *cis* complexes than for the *trans* isomers.[24]

The *cis*-[$Pd(PPr^n_3)_2Cl_2$] complex (1b) undergoes thermal isomerization [10] to the *trans* complex; the rate of reversion of *cis* to *trans* followed by ^{31}P n.m.r. spectroscopy is extremely temperature-sensitive, with a very large energy requirement to achieve the transition state.[10] However the *cis* complex (1b) undergoes wavelength-dependent photodecomposition when irradiated. The photoprocess is associated with low-wavelength photolysis (λ 313 nm), and apparently the principal reaction involves dissociation of a Pd–PPr^n_3 bond. The photodissociative process was confirmed both by direct observation of free PPr^n_3 in ^{31}P n.m.r. measurements in the first stages of photolysis and by the more quantitative method of isolation of [$Pd_2(PPr^n_3)_2Cl_4$]. The lability of PPr^n_3 in a P→Pd charge-transfer state, but not the ground state of the *cis* complex (1b), can be explained on the basis of excited-state geometry. Interpretation of both the observed wavelength dependence for the photolysis of (1b) and the crystal-structure analysis leads to the conclusion that the P–Pd excited states could be considerably distorted toward a tetrahedral-like geometry. In such a configuration, π backbonding from Pd^{II} to PPr^n_3 should be reduced compared to that in the square-planar geometry, a perturbation leading to greater ligand lability of the PPr^n_3 ligand.

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