

Thermally Reversible Photoisomerization of a Square-planar *trans*-Diphosphinedichloropalladium(II) Complex to Yield its Elusive *cis*-Isomer

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Summary U.v. irradiation of *trans*-bis(tri-*n*-propylphosphine)dichloropalladium(II) in solution yields a photo-stationary *trans*-*cis* mixture which reverts quantitatively to the *trans*-form in the dark with an exceptionally high activation energy; the hitherto elusive *cis*-form has been characterised by u.v., i.r., and ^{31}P n.m.r. spectroscopy and is relatively stable in solution ($t_{1/2}$ 10^3 h) at 273 K.

MUCH interest attaches to the isomerization of square-planar transition metal complexes both from the preparative and the mechanistic aspects,¹ particularly in view of the catalytic potentialities of these materials.² The occurrence of *cis*-*trans* isomerism in bis(phosphine)palladium(II) complexes is well established,³ and in some cases either form reverts rapidly to an equilibrium mixture;^{1c,4} however, in other cases, e.g. that of $[(\text{R}_3\text{P})_2\text{PdCl}_2]$ (R = Me, Et, Prⁿ, or Buⁿ) only the *trans*-form appears to exist either in the solid state or in solution.⁵ We demonstrate here the potential of photoirradiation as a means of preparing unstable isomeric forms at ambient temperature from the following experiments with *trans*- $[(\text{Pr}^n)_2\text{P}_2\text{PdCl}_2]$ (**1**).

(i) Photolysis ($\lambda = 254, 313,$ and 405 nm) of methanolic (**1**) induces a u.v. spectral transformation with a clearly defined isosbestic point at 288 nm and with a final spectrum exhibiting the features for established *cis*-bis(phosphine)-dichloropalladium(II) complexes.⁶ Interruption of irradiation leads to a quantitative return to (**1**) except after very long irradiation when a dimer is produced (see below).

(ii) Photolysis (bare 200 W Xe arc) of (**1**) in CDCl_3 (5×10^{-2} mol dm^{-3}) for 10 h leads to gradual loss of the ^{31}P resonance of (**1**) (-9.05 p.p.m. relative to P_2O_5) and emergence of a new peak at -23.4 p.p.m. Such a down-field shift is entirely typical of the *cis*-isomer of established *cis*-*trans* pairs in this series.^{1c,5} In the dark, the new material decays with strictly first-order kinetics to reform quantitatively the -9.05 p.p.m. peak of (**1**); such an uncatalysed intramolecular thermal isomerization is a comparative rarity.¹

(iii) Photolysed solutions of (**1**) in CHCl_3 exhibit new i.r. peaks at 298 cm^{-1} (m) and 280 cm^{-1} (s) which compare with those⁵ for $\nu(\text{Pd}-\text{Cl})$ for *cis*- $[(\text{PhMe}_2\text{P})_2\text{PdCl}_2]$ of 306 and 284 cm^{-1} .

Attempts to isolate the *cis*-isomer have, so far, led only to (**1**).

Two other features of these studies deserve mention.

(i) The rate of reversion of *cis*-to-*trans*-(**1**) (followed by ^{31}P n.m.r. spectroscopy) is extremely temperature sensitive (Table) and these data lead to Arrhenius parameters,

TABLE

T/K	271.0	284.0	293.9	307.0	320.8
$10^7 k_{\text{iso}}/\text{s}^{-1}$	1.54	42.4	378	1 230	10 820

$\log A = 17.4 \pm 1.9$, $E_a = 124.4 \pm 11.5$ kJ mol^{-1} (i.e. with $\Delta H^\ddagger = 122.0 \pm 11.5$ kJ mol^{-1} and $\Delta S^\ddagger = 79.8 \pm 36.4$ $\text{J K}^{-1} \text{mol}^{-1}$), indicating a very large energy requirement to achieve the transition state, which is offset by a large positive entropy, suggesting perhaps a dissociative mechanism.

(ii) Prolonged photolysis of the *cis-trans* mixture leads to a new isosbestic point (236 nm) and production of the (known)⁷ symmetric chloro-bridged $[(Pr^{n_3}P)_2Pd_2Cl_4]$, identified by i.r. spectrum, elemental analysis, and m.p. It is not yet clear whether the dimerisation results from a reaction of the *cis*-isomer or a secondary photoreaction of the *trans*-form, but studies to clarify this are in progress.

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