

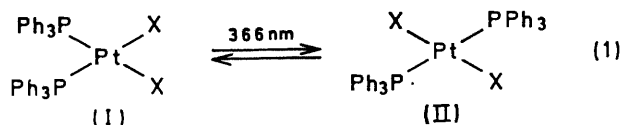
Synthesis of *trans*-Platinum(II) Complexes by Photochemical Isomerization

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Summary The *trans*-isomers of dihalogenobis(triphenylphosphine)platinum(II) complexes, difficult to obtain by other methods, are readily synthesized by photochemical isomerization of the *cis*-complexes: this method can also be applied to other platinum(II) complexes.

CONVENTIONAL methods of synthesis of dihalogenobis(R_3P)-platinum(II) complexes yield only the *cis*-isomer in the case of $R = Ph$.¹ A recently published preparation of a *trans*-isomer (II; $X = Cl$) involves a laborious route which, in our hands, gives a poor yield.² We now report a very simple method of preparation of (II; $X = Cl$ or Br) by photochemical isomerization³ (equation 1) of the readily available¹ *cis*-complexes, (I).



cis-Pt(Ph_3P)₂Cl₂, prepared by a modified version of the method of Grinberg and Razumova,^{3,4} was irradiated in CHCl₃ with a 200 w Hanovia Type S lamp at 366 nm for 4 hr. The resulting bright yellow solution was, by electronic absorption spectroscopy, approximately 60% *trans*-(II) and 40% *cis*-(I). Vacuum evaporation gave a residue

which was extracted with benzene producing a yellow solution and a white solid. Evaporation of the yellow solution followed by addition of methanol gave a precipitate which was crystallized from benzene to yield *trans*-Pt-(Ph_3P)₂Cl₂, (42%), m.p. 306—309° (lit.² 307—310°), with far-i.r. and Raman bands characteristic of $\nu(Pt-Cl)$ in a *trans*-dichloroplatinum(II) complex.^{4,5}

T.l.c. demonstrated that the same method could be used to prepare (II; $X = Br$). The comparison sample of (II; $X = Br$) was prepared by treatment of (II; $X = Cl$) with a solution of LiBr.

Irradiation of *cis*-Pt(pyridine)₂Cl₂ yielded the *trans*-isomer in ca. 80% yield, and when *cis*-Pt(isoquinoline)₂Cl₂ was irradiated, the previously unknown *trans*-Pt(isoquinoline)₂Cl₂ was identified as the photoproduct by spectral methods.

The solvent and the wavelength of irradiation are critical factors in this method. The photochemical steady state for (I) \rightleftharpoons (II) is highly dependent on solvent.^{4,6} Non-polar solvents favour formation of the *trans*-isomer. If unfiltered light is used for irradiation, higher energy wavelengths cause decomposition of the *cis*-complex.^{4,6} Use of the 366 nm line in the mercury emission spectrum eliminates side reactions and pure isomerization has been demonstrated.⁴

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