

Substitution of a Platinum(II) Complex without Retention of Stereochemistry; Direct Evidence for Pseudorotation of a Five-co-ordinate Platinum(II) Cationic Complex containing Chelating Phosphine Ligands

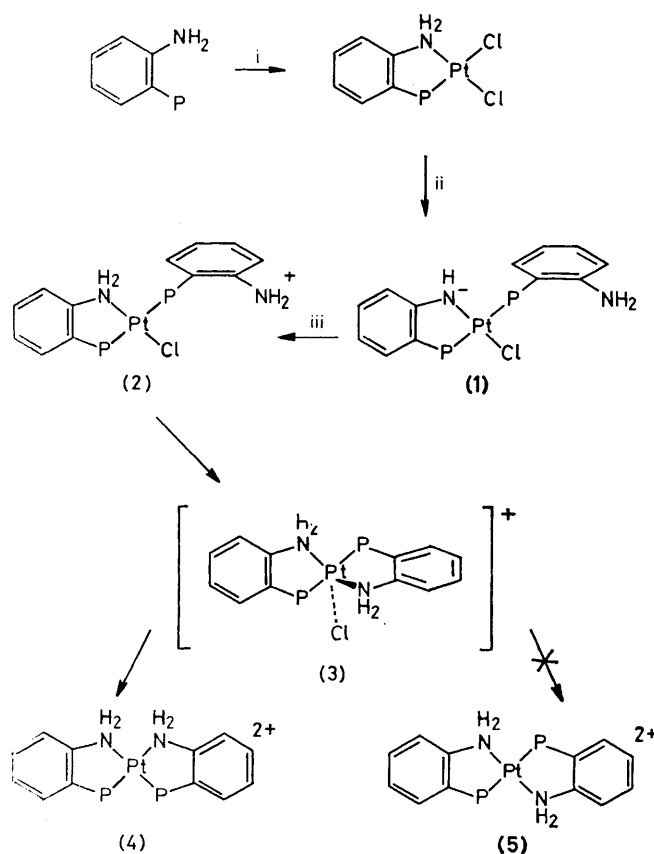
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Summary Ring closure of *trans*-[Pt(PNH₂)(PNH₂)Cl]⁺ (**2**) [PNH₂ = (*o*-aminophenyl)diphenylphosphine; PNH₂ denotes monodentate co-ordination through the phosphorus] proceeds without retention of stereochemistry; this is the first direct evidence for pseudorotation of a five-co-ordinate platinum(II) complex.

THE mechanism of *cis-trans* isomerisation of square-planar complexes has aroused considerable controversy and a comprehensive review of the topic has recently appeared.¹ Two mechanisms have been proposed, consecutive displacement and pseudorotation, but to date incontrovertible evidence for the existence of the latter process has not been forthcoming for complexes of platinum(II).¹

We have recently reported that the complex cation *trans*-[Pt(PNH₂)₂]²⁺ (**5**)[†] is isomerised to its *cis*-isomer (**4**) by co-ordinating anions.² We now report that compound (**4**) is also produced by chloride elimination from *trans*-[Pt(PNH₂)(PNH₂)Cl]⁺ (**2**) without the intermediacy of cation (**5**), an unprecedented example of change in stereochemistry during substitution at platinum(II), which is explained by the pseudorotation of the five-co-ordinate reaction intermediate (**3**).

The synthesis of cation (**2**), which undergoes rapid ring closure at 25 °C and has so far not been isolated, is shown in the Scheme. The precursor, *trans*-[Pt(PNH⁻)(PNH₂)Cl] (**1**) {³¹P n.m.r. (chloroform) δ 29.6 [*J*(Pt,P) 2833 Hz, P] and 14.0 [*J*(Pt,P) 2501 and ²*J*(P,P) 422 Hz, P]; i.r. ν(mull) 327 cm⁻¹ (Pt-Cl); satisfactory C, H, N, and P analyses}, is a bright yellow crystalline solid which has a high kinetic stability with respect to ring closure. This is the result of the extremely low *trans*-effect of the amido-group, a finding which will be discussed elsewhere. Colourless solutions of cation (**2**), stable for at least two days at -60 °C, are obtained by protonation of the amido-group of complex (**1**) {³¹P n.m.r. (chloroform) δ 34.8 [*J*(Pt,P) 2573 Hz, P] and 14.4 [*J*(Pt,P) 2276 and ²*J*(P,P) 413 Hz, P]}.



SCHEME. For clarity, Ph groups on the phosphorus have been omitted. Reagents: i, 1 equiv. platinum(II) chloride in dimethylformamide, 130 °C; ii, triethylamine + PNH₂ in chloroform; iii, 1 equiv. trifluoroacetic acid in chloroform, -60 °C.

[†] PNH₂ = (*o*-aminophenyl)diphenylphosphine, PNH⁻ = conjugate base of PNH₂, PNH₂ denotes monodentate co-ordination through the phosphorus.

Warming solutions of cation (2) to $-20\text{ }^{\circ}\text{C}$ allows the ring closure to occur at a conveniently observable rate. The reaction, monitored by ^{31}P n.m.r. spectroscopy, is first-order in platinum complex and yields exclusively *cis*- $[\text{Pt}(\text{PNH}_2)_2]^{2+}$ (4) rather than the expected *trans*-isomer (5).

It might be envisaged that the *cis*-product results from the initial formation of the *trans*-isomer (5) and its subsequent isomerisation. This possibility is ruled out by the observation that isomer (5) is stable under the reaction conditions as it may be added to the reaction mixture and isolated quantitatively at its completion; the change in the configuration of the phosphines from *trans* to *cis* clearly occurs before elimination of the chloride. This is to our knowledge the first example of substitution at platinum(II) without retention of configuration.

According to the currently accepted theory of square-planar substitution reactions,³ the first step in the ring closure and chloride displacement reaction of cation (2) is the formation of the trigonal-bipyramidal intermediate (3) in which the entering (amino-) and leaving (chloride) ligands

occupy the trigonal plane. The second step would normally be the loss of chloride to give the *trans*-complex (5) and the configuration about the platinum would be retained. Since no plausible *dissociative* reaction pathway of intermediate (3) can explain the observed change in configuration about the platinum we conclude that intermediate (3) reacts by pseudorotation.

The occurrence of a pseudorotation mechanism requires that the five-coordinate intermediate be sufficiently stable for intramolecular rearrangement to be a faster process than ligand dissociation.¹ The relative stability of the five-coordinate intermediate (3), for which pseudorotation is in fact faster than dissociation, is most likely due to a combination of positive charge on the complex and the presence of chelating ligands. Indeed, we have found that iodide associates with *cis*- $[\text{Pt}(\text{PNH}_2)_2]^{2+}$ to form a stable five-coordinate complex cation in chloroform and in nitromethane.⁴

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⁴ J. M. Downes, Ph.D. thesis, University of Sydney, 1978.