

The Preparation and Isomerisation of *Trans*-[PtCl₂(CO)(PR₃)]

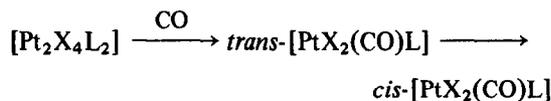
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A few Platinum carbonyl complexes [PtCl₂(CO)L] have been prepared in the *trans* configuration when L is a nitrogen or oxygen donor [1]. More commonly, when L is a tertiary phosphine or arsine, only *cis* complexes have been detected or isolated [2, 3], despite an early prediction that *trans* geometry might have been expected [2]. These *cis* phosphine or arsine carbonyls have found extensive use in spectroscopic [4, 5] and synthetic [6, 7] studies, and it has become accepted practice simply to generate them (by bridge-cleavage of [Pt₂X₄L₂] by CO) and use them *in situ* [7], confident of their geometry.

We have found that the first products generated in solution by the action of CO on [Pt₂X₄L₂] are in fact the *trans* isomers of [PtX₂(CO)L] (X = Cl; L = PBu₃, PEt₃, PMe₂Ph, PMePh₂, PPh₃, AsMePh₂, or AsPh₃; X = Br, L = PMe₂Ph), and these subsequently isomerise to the *cis* derivatives.



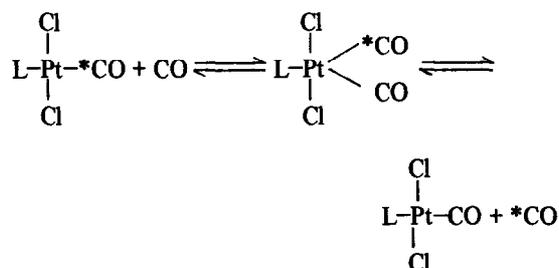
Under normal conditions, the isomerisations are quite rapid and can be complete in less than 1 h in the presence of carbon monoxide. If excess CO is removed, however, the conversion to the *cis* isomer takes from 1 to 3 days. The *trans* complexes can be isolated as solids by vacuum removal of the solvent at low temperatures immediately after generation. A sample of *trans*-[PtCl₂(CO)(PPh₃)] obtained in this way remained unchanged after being stored in the dark at -10 °C for several days.

The i.r. spectra of the *trans* isomers have $\nu(\text{CO})$ at ca. 2135 cm⁻¹, about 20–30 cm⁻¹ higher than their *cis* analogues. The ³¹P n.m.r. spectra of the phosphine derivatives reveal very similar δP and ¹J_{PtP} values to the *cis* materials. The ¹³C n.m.r. data for *trans*-[PtCl₂(¹³CO)(PMePh₂)], prepared from labelled carbon monoxide, revealed δC 168.3 ppm, ¹J_{PtC} 1221 Hz, and ²J_{PC} 171.7 Hz. This latter parameter is entirely typical of CO *trans* to a tertiary phosphine [5].

Some [Pt₂X₄L₂] is produced during the uncatalysed isomerisation of *trans*-[PtX₂(CO)L] in solution, and when a stream of N₂ was passed through a solution of *trans*-[PtCl₂(CO)(PMePh₂)], total loss of CO was observed after 5 h. In the same period an identical solution not swept by N₂ produced a 1:1 *cis/trans* mixture. *Cis*-[PtCl₂(CO)(PMePh₂)] does not lose CO in this way, and it appears that CO elimination is involved in the *trans* → *cis* isomerisation process. The rate of isomerisation shows no concentration dependence, but proceeds faster in benzene than in chloroform.

Excess carbon monoxide catalyses the isomerisation of *trans*-[PtX₂(CO)L] in solution. Addition of traces of L or X⁻ also enhances the rate of isomerisation, but the products are contaminated by [PtX₂L₂] or [PtX₃L]⁻, respectively, resulting from CO displacement. Treatment of a solution of *trans*-[PtCl₂(¹³CO)(PMePh₂)] by excess ¹²CO resulted in complete exchange of the coordinated carbon monoxide before isomerisation proceeded 50% (35 min).

Ligand substitution reactions at Pt^{II} almost always proceed *via* an associative mechanism [8] and the CO exchange may be depicted thus:



Nucleophile-catalysed isomerisations are also associative [8], and the same trigonal-bipyramidal intermediate is probably involved in the CO-catalysed *trans* → *cis* isomerisation. Other steps are necessary to change the geometry of the 5-coordinate species before *cis*-[PtCl₂(CO)L] can be produced. These could involve consecutive ligand displacement (of L and/or Cl⁻) [8] or pseudorotation [9]. We note that our conditions fit exactly those predicted by Redfield and Nelson [10] as most favourable to pseudorotation: namely small, weakly-nucleophilic ligands and non-polar solvents.

The uncatalysed isomerisation is unimolecular in Pt, and involves CO elimination from *trans*-[PtX₂(CO)L], either spontaneously or solvent assisted. It seems entirely plausible that the eliminated CO could catalyse the isomerisation of the remaining, undissociated *trans*-molecules (other routes are, of course, possible, including isomerisation of the 3-coordinate [11] (or solvated [12]) intermediate or even regener-

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ation of $[\text{Pt}_2\text{X}_4\text{L}_2]$ which might slowly but irreversibly build up the *cis*-carbonyl on CO cleavage [2]).

Whilst no other systems have been claimed to conform to such an autocatalytic mechanism, it seems highly probable that many others might. For example, tertiary phosphine is displaced by solvent from *trans*- $[\text{Pd}(\text{tet})_2(\text{PR}_3)_2]$ (tet = tetrazolate) [13], and free phosphine is known to catalyse the *trans* to *cis* isomerisation of this compound *via* the consecutive displacement route. Also, $[\text{PtCl}_2(\text{AsEt}_3)_2]$ isomerises spontaneously in benzene, but when $[\text{Pt}_2\text{Cl}_4(\text{AsEt}_3)_2]$ is added to the solution (which would remove free AsEt_3) the isomerisation reaction is quenched [14].

Finally, we note that the *trans* to *cis* isomerisations of $[\text{PtX}_2(\text{CO})\text{L}]$ are accelerated by visible and u.v. light, and that ultraviolet irradiation of solutions of *cis*- $[\text{PtX}_2(\text{CO})\text{L}]$ leads to the same mixture of the isomers. It is not yet clear whether the geometry changes result directly from the irradiation, or whether these reactions also proceed through CO elimination.

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