Isomerisation Mechanisms of Square-Planar Complexes

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1 Introduction

Square-planar geometry is common amongst complexes of transition elements near the end of the transition series, and geometric isomers are known for many derivatives. These formally 16-electron complexes are readily converted into 18-electron or even 14-electron species by a variety of routes, making available many low-energy processes of great synthetic or catalytic value.[1,2] Considerable importance has thus been attached to mechanistic studies of such complexes.

The link between geometric isomerisation and nucleophilic ligand substitution reactions at these 4-co-ordinate complexes has long been recognised. Indeed the former process was generally thought to take place *via* consecutive operations of the latter.[3] A spate of recent activity has thrown new light on the isomerisation reaction, though it has created some confusion in its wake. Whilst several new mechanisms have been suggested, not all are universally accepted and different authors have used the same evidence to support radically different opinions. Moreover, the implications of these new isomerisation routes for other reactions of the complexes can be quite profound. The subject is therefore worthy of critical examination both in its own right and in relation to other important reactions of square-planar complexes.

2 Occurrence and Thermodynamic Stability of Geometric Isomers

Square-planar complexes of the d^8 ions Rh^I, Ir^I, Pd^{II}, Pt^{II}, and Au^{III} are legion, but detection of geometric isomers and subsequent isomerisation studies are so far limited almost exclusively to derivatives of palladium and platinum. This is almost certainly due to the ease of preparation (and identification) of the electroneutral complexes $[MX_2L_2]$, $[MXYL_2]$ and $[MX_2LL^1]$ of these elements, where X or Y are anionic ligands and L and L^1 are neutral ligands. These complexes may exist as *cis*- or *trans*-isomers. Other variations are known. For example with four different ligands, $[MXYLL^1]$, three isomers are possible, and multinuclear complexes with bridging ligands further expand the possibilities for geometric isomerism. In these cases also, examples are largely confined to compounds of palladium and platinum, but there is no evidence to suggest that the processes observed might not be applicable to 16-electron d^8 complexes of the other elements.

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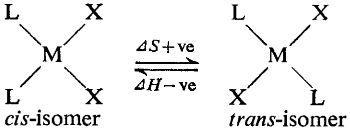
[1] C. A. Tolman, *Chem. Soc. Rev.*, 1972, **1**, 337.

[2] P. S. Braterman and R. J. Cross, *Chem. Soc. Rev.*, 1973, **2**, 271.

[3] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2nd edn., Wiley, New York, 1967.

Dealing first with the palladium and platinum complexes [MX_2L_2], the general rule is that the *cis*-isomers are enthalpy-favoured, but entropy changes in solution favour the *trans*-forms (equation 1). These factors are often finely balanced, allowing the observation of both geometries of many compounds in solution. Changes of metal, ligand, solvent, or temperature can substantially affect the equilibrium position, however, and it is apparent that many inter-related factors contribute to the stability of each isomer. Some useful generalisations can be made nevertheless.



(1)

Equilibria positions between *cis*- and *trans*-isomers have been measured by dipole-moment determinations,[4–7] i.r. spectrometry,[8] and n.m.r. spectrometry.[9–14] It is at once apparent that *trans*-geometry is more favoured by palladium complexes than platinum.[6,8–10] Indeed it was not until 1966 that *cis*-geometry was definitely established[12] for some compounds of Pd^{II}, and there is still doubt about the form in which some were isolated.[15] This trend continues up the group, and *cis*-square-planar complexes of nickel(II) are extremely rare without chelating ligands, though not unknown.[16]

The tendency towards more-stable *trans*-isomers increases along the series $Cl^- < Br^- < I^-$ for anionic ligands,[8,10] and $R_2S < R_2Se < R_2Te$ for neutral ligands.[9,10] Curiously, the heavier Group V donors tend towards *cis*-geometry, and R_3P complexes are more likely to be *trans* than R_3As and R_3Sb.[4–6] The effects of the organic groups R of the ligands R_2S and R_3P are quite marked, but follow no obvious pattern,[7–9,13] though it seems that aryl substituents promote the stabilisation of the *cis*-isomers to an extent.[12,13] Thus, for example, chloroform solutions of [$PdCl_2(PR_3)_2$] were found to be 100% *trans* when R_3 was Et_3, Pr_3, or Bu_3, but some *cis*-isomer was apparent when one or two of the R groups were Ph.[13]

A striking dependence on solvent was revealed by a study of [$PdCl_2(PMePh_2)_2$] and [$PdCl_2(PMe_2Ph)_2$] in eleven solvents.[14] *cis*-Isomers are strongly favoured by polar solvents.[12,14]

[4] J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 1952, 273.

[5] J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 1952, 4300.

[6] J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 1953, 70.

[7] J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 1956, 525.

[8] R. J. Goodfellow, J. G. Evans, P. L. Goggin, and D. A. Duddell, *J. Chem. Soc.* (*A*), 1968, 1604.

[9] R. Roulet and C. Barbey, *Helv. Chim. Acta*, 1973, **56**, 2179.

[10] R. J. Cross, T. H. Green, and R. Keat, *J.C.S. Dalton*, 1976, 382.

[11] J. H. Price, J. P. Birk, and B. B. Wayland, *Inorg. Chem.*, 1978, **17**, 2245.

[12] J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 770.

[13] S. O. Grim and R. L. Keiter, *Inorg. Chim. Acta*, 1970, **4**, 56.

[14] D. A. Redfield and J. H. Nelson, *Inorg. Chem.*, 1973, **12**, 15.

[15] J. J. MacDougal and J. H. Nelson, *Inorg. Nuclear Chem. Letters*, 1979, **15**, 315.

[16] R. A. Palmer, H. F. Giles, and D. R. Whitcomb, *J.C.S. Dalton*, 1978, 1671.

Thermodynamic parameters have been determined for several of these complexes in solution.[4,5,9,11,14,17–20] Typically, the *cis–trans*-conversion has an unfavourable enthalpy change, ΔH, of *ca.* $+ 20$ kJ mol^{-1}, but a favourable entropy change, ΔS, in the region of $+ 60$ J mol^{-1}K^{-1}. A useful compilation of the published data has been drawn up,[19] and this reveals a strong correlation to phosphine ligand basicity.

Both ΔH and ΔS will contain contributions from the solvation of the isomers. The entropy term is probably dominated by this effect with the non-polar *trans*-isomers having a smaller affinity for solvent molecules. ΔS will also involve changes in internal degrees of freedom. The enthalpy term will involve any change of internal bond energies. Their magnitudes are less easy to estimate, but where the bonding between M–L and M–X are dissimilar, internal bond energies will favour the *cis*-isomer. This configuration avoids placing two ligands of high bond-weakening *trans*-influence[21] opposite each other, and also prevents *trans*-arrangements of strongly π-bonding ligands, where they would compete for use of the same metal *d*-orbitals.

Thus di-organo-substituted complexes [MR_2L_2] tend to favour *cis*-geometry,[22] particularly for methyl derivatives (Me has a very high *trans*-influence[21]), where mono-organo-derivatives, [$MRXL_2$], prefer *trans*-geometry. The greater thermodynamic stability of *cis*-isomers for [$PtX_2L(PR_3)$] when L is carbon monoxide[23] or carbene[24] may be to avoid mutually *trans* π-bonding ligands, but the reasons for some preferences are not always clear and a number of other compounds with dissimilar neutral ligands also prefer *cis*-geometry.[25] Complexes [MX_2L_2] with particularly bulky L[26] are usually only found as *trans*-isomers.[27]

Finally, thermodynamic parameters are available for a few solid-state isomerisations. *cis–trans*-Conversion[28] of crystalline [$PtCl_2(NH_3)_2$] releases 13 kJ mol^{-1}, and similar isomerisation of *cis*-[$PtCl_2py_2$] (py = pyridine) has $\Delta H = - 20$ kJ mol^{-1}. Clearly no solvation effects can favour the *trans*-isomers, but changes in the crystal lattice energies could be considerable with these small, polar ligands. A solid-state *trans–cis*-isomerisation of [$PtCl_2(pms)_2$] (pms =

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[17] D. A. Redfield, J. H. Nelson, R. A. Henry, D. W. Moore, and H. B. Jonassen, *J. Amer. Chem. Soc.*, 1974, **96**, 6298.

[18] D. A. Redfield, L. W. Cary, and J. H. Nelson, *Inorg. Chem.*, 1975, **14**, 50.

[19] A. W. Verstuyft and J. H. Nelson, *Inorg. Chem.*, 1975, **14**, 1501.

[20] L. M. Knight and J. H. Nelson, *Inorg. Chem.*, 1977, **16**, 1317.

[21] (a) F. R. Hartley, *Chem. Soc. Rev.*, 1973, **2**, 63; (b) T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coordination Chem. Rev.*, 1973, **10**, 335.

[22] (a) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1959, 705; (b) *idem. ibid.*, 1959, 4020; (c) G. Calvin and G. E. Coates, *ibid.*, 1960, 2008.

[23] G. K. Anderson and R. J. Cross, *Inorg. Chim. Acta*, 1979, **38**, L21.

[24] B. Cetinkaya, E. Cetinkaya, and M. F. Lappert, *J.C.S. Dalton*, 1973, 906.

[25] (a) H. Motschi, P. S. Pregosin, and L. M. Venanzi, *Helv. Chim. Acta*, 1979, **62**, 667; (b) R. Ellis, T. A. Weil, and M. Orchin, *J. Amer. Chem. Soc.*, 1970, **92**, 1078.

[26] C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313.

[27] (a) A. J. Cheney, B. E. Mann, B. L. Shaw, and R. M. Slade, *J. Chem. Soc. (A)*, 1971, 3833; (b) E. C. Alyea, S. A. Dias, G. Ferguson, and P. J. Roberts, *J.C.S. Dalton*, 1979, 948.

[28] (a) I. I. Chernyaev, V. A. Palkin, R. A. Baranova, and N. N. Kuz'mina, *Russ. J. Inorg. Chem.*, 1960, **5**, 693; (b) G. Beech, G. Marr, and S. J. Ashcroft, *J. Chem. Soc. (A)*, 1970, 2903.

pentamethylenesulphide) was found to be exothermic but this was not typical of closely related compounds and may be due to ligand conformation and packing effects.[29]

3 Catalysed Isomerisations of Mono-nuclear Complexes

Although the distinction may be difficult to make in practice (*vide infra*), it is convenient to classify the isomerisations as either catalysed or spontaneous and to consider each type separately. It should be kept in mind, however, that in some cases at least this classification could represent a difference in rate rather than of reaction mechanism.

Both *cis*- and *trans*-$[PtCl_2(PEt_3)_2]$ remain unchanged indefinitely in benzene solution at ambient temperature unless a trace of free phosphine is added. This catalyses a rapid isomerisation to the equilibrium mixture.[4] By contrast, the palladium complex *cis*-$[PdCl_2(SbPr^n_3)_2]$ rapidly and spontaneously isomerises immediately upon dissolution.[6] This difference in isomerisation rate is quite typical, and it can profoundly affect the ease of isolation of the various isomers. Thus when isomerisation is slow, the less-soluble isomer crystallises from solution when a catalyst is present to maintain the equilibrium. *cis*-$[PtCl_2(PR_3)_2]$ can be obtained in this way. To obtain the more-soluble *trans*-isomer, the equilibrium must be frozen (preferably in a non-polar solvent to favour the *trans*-form) by removing the catalyst. This can be done by adding the halide-bridged material $[Pt_2Cl_4(PR_3)_2]$ to the solution.[30] When isomerisation is spontaneous, this choice is removed and generally only one isomer can be obtained.

A. The Consecutive Displacement Mechanism.—Of all the isomerisation routes suggested, this one is the best understood and best authenticated, involving as it does only stereospecific ligand substitution steps. Figure 1 shows a conventional reaction profile for the replacement of X by Y. The *trans*-ligand, T, and *cis*-ligands, C, retain their relationship and the reaction proceeds through a trigonal bipyramidal intermediate with T, X, and Y in the trigonal plane.[3] This is achieved through the *trans*-effect of T, which either weakens the bond M–X (a *trans*-influence) or stabilises the trigonal-bipyramidal intermediate by π-acceptor properties, or both.[21] The kinetics obey a two-term rate law (equation 2), where

$$\text{rate} = (k_1 + k_2[Y])[MXTC_2] \qquad (2)$$

k_2 relates to the direct associative attack of nucleophile Y, and k_1 applies to a similar solvent association route, where X is displaced by solvent (S), itself being subsequently displaced by Y.

Scheme 1 depicts the consecutive displacement isomerisation mechanism.[3] L can be any neutral ligand. It can be seen that two steps are needed to achieve isomerisation, as the substitutions at platinum are stereospecific. In the first step, L replaces a halide to form $[PtXL_3]^+X^-$. The second step involves attack of

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[29] E. A. Allen, N. P. Johnson, D. T. Rosevear, and W. Wilkinson, *Chem. Comm.*, 1971, 171.
[30] J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 1951, 2532.

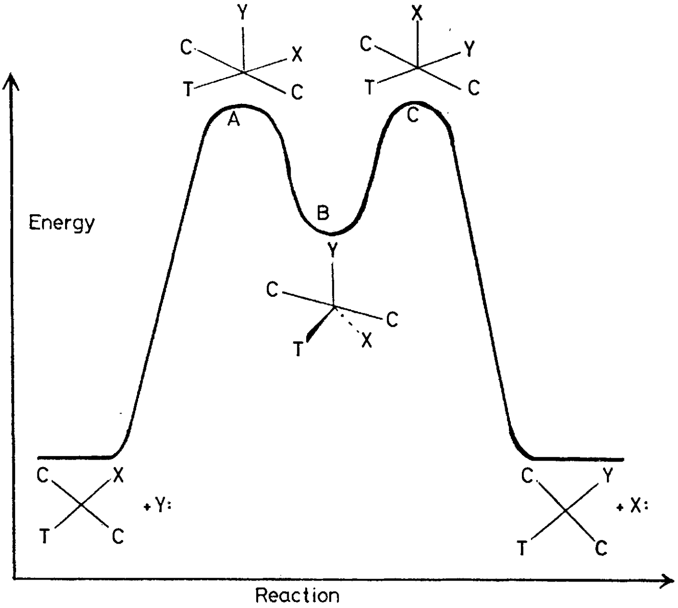
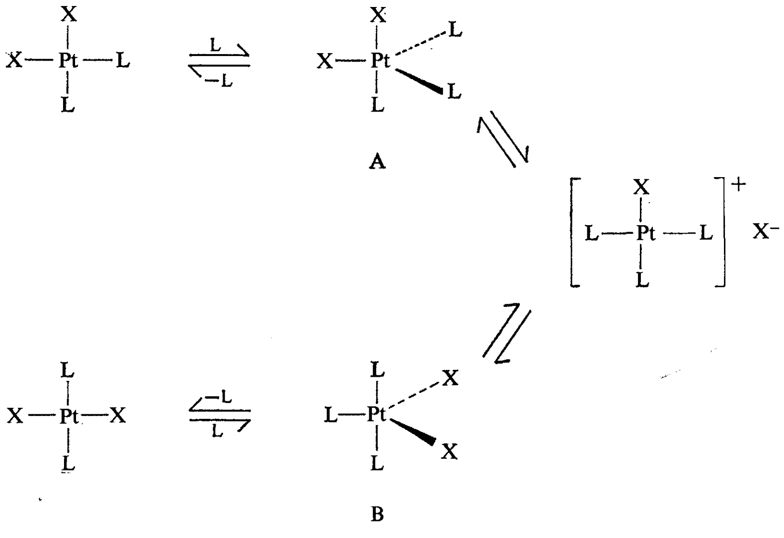


Figure 1 *Conventional reaction profile for the substitution of* X *in a square-planar complex by nucleophile* Y. *The activation energy is determined by transition state* A *or* C *depending on whether bond-making or bond-breaking dominates.*



Scheme 1

X^- on $[PtXL_3]^+$. If this goes through intermediate A the original isomer is reformed, but if intermediate B is produced the other isomer is generated.

This scheme satisfactorily accounted for all the catalysed isomerisations of platinum halides with phosphine, arsine, stibine, and sulphide ligands.[4,5,7,8,31] It also explained why mono-organo-derivatives *cis*-$[PtRX(PR'_3)_2]$ were isomerised in solution by free PR'_3, whereas the diorgano-derivatives of platinum and palladium were not.[22] Organoplatinum halides can produce the necessary ionic intermediates (equation 3).

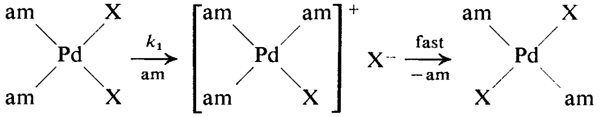
$$\textit{cis}\text{-}[PtRXL_2] \xrightleftharpoons[-L]{L} [PtRL_3]^+X^- \xrightleftharpoons[L]{-L} \textit{trans}\text{-}[PtRXL_2] \qquad (3)$$

Dialkyls and diaryls, on the other hand, have no convenient ionic leaving groups.

Although this mechanism was first tentatively put forward in 1934,[31] the first detailed mechanistic evidence in support of it was awaited until 1969,[32] and it came, somewhat surprisingly, from a study of some palladium compounds. Compounds of the type *cis*-$[PdX_2(am)_2]$ were prepared by the stereospecific displacement of the chelating disulphide ligand from $[PdX_2(PhSC_2H_4SPh)]$ by ammonia or pyridine derivatives (am).[32] Excess of amine catalysed the conversions into the thermodynamic isomers *trans*-$[PdX_2(am)_2]$. The kinetics obeyed the rate law (4), strongly suggesting that the rate-determining step is k_1 in

$$\text{rate} = k_1[\textit{cis}\text{-}PdX_2(am)_2]\,[am] \qquad (4)$$

equation 5. The faster second step is in keeping with the greater *trans*-effects for



(5)

X^- (N_3^-, Br^-, I^-, NCS^-) than (am) (NH_3 or py).[3,21] The rate of the reaction increased when the dielectric constant of the solvent was increased, thus assisting the intermediate anion formation. It was found that the effects of the leaving groups, X^-, followed the same sequence as in ligand replacement reactions at platinum.[3]

The isomerisation of both *cis*- and *trans*-isomers of $[PtCl_2(SMe_2)_2]$ catalysed by SMe_2, was followed in CH_2Cl_2 by Roulet and Barbey using n.m.r. techniques.[9] Both reactions were first-order in complex and free SMe_2. No intermediate species were detected in solution in the course of the isomerisations, but reactions carried out in the presence of silver salts led to the isolation of $[PtCl(SMe_2)_3]^+Z^-$ (where Z^- is a non-co-ordinating anion such as BF_4^- or ClO_4^-). Addition of Cl^- to this ionic complex rapidly formed *cis*-$[PtCl_2(SMe_2)_2]$, which proceeded to isomerise slowly. The fast and slow steps in the reaction sequence (6) are the

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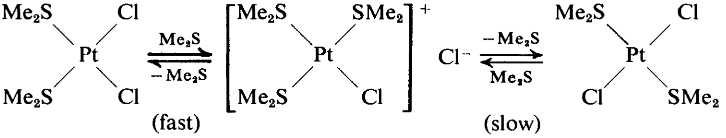
[31] H. D. K. Drew and G. H. Wyatt, *J. Chem. Soc.*, 1934, 56.

[32] L. Cattalini and M. Martelli, *J. Amer. Chem. Soc.*, 1969, **91**, 312.



(6)

reverse of those for the $[PdX_2(am)_2]$ system, in keeping with the *trans*-effect order $Me_2S > Cl^-$. Significantly, the rate constant for the formation of $[PtCl(SMe_2)_3]^+$ from the reaction of dimethyl sulphide and *trans*-$[PtCl_2(SMe_2)_2]$ in the presence of Ag^+ was the same as for the *trans* → *cis* isomerisation.[9]

Both the systems detailed above are relatively simple in that no appreciable amount of an intermediate complex was formed, and the catalysing ligands were the same as the neutral, co-ordinated ligands. Cooper and Powell[33] showed by ^1H n.m.r. spectroscopy that when up to one equivalent of PMe_2Ph was added to deuteriochloroform solutions of $[PtCl_2(PMe_2Ph)_2]$, no free ligand was detectable in solution and $[PtCl(PMe_2Ph)_3]^+Cl^-$ was formed instead. The same cationic species, with two tertiary phosphines *trans* to each other and a third *trans* to chloride, was present in methanol solution, and in the salt $[PtCl(PMe_2Ph)_3]PF_6$, which was isolated. At ambient temperatures the n.m.r. signals of the phosphines of $[PtCl(PMe_2Ph)_3]^+Cl^-$ coalesced, but the signals of $[PtCl(PMe_2Ph)_3]^+PF_6^-$ did not,[33] suggesting that phosphine exchange takes place *via* attack of Cl^- on the cation. Similarly, the phosphine signals of mixed $[PtCl(PMe_2Ph)_3]Cl$ and *cis*-$[PtCl_2(PMe_2Ph)_2]$ coalesced at ambient temperatures, whereas those of mixtures of $[PtCl(PMe_2Ph)_3]PF_6$ and *cis*-$[PtCl_2(PMe_2Ph)_2]$ did not (unless free Cl^- was present), again suggesting that intermolecular phosphine exchange is initiated by attack of Cl^- on the cation, releasing a tertiary phosphine. This is, of course, a critical step in the consecutive displacement isomerisation mechanism.

The salt $[PtCl(PMe_2Ph)_3]Cl$ may well exist as a contact ion-pair (the presence of only one Pt–Cl stretching frequency in its i.r. spectrum, identical to that in the PF_6^- salt, rules out all but a weak association of the Cl^- ion with the platinum of the cation), since the phosphine exchange rate was found to be insensitive to concentration. Addition of methanol solvated the ions, however, and suppressed the release (and exchange) of phosphine. The process was restored if additional Cl^- (as Ph_4AsCl) was added.[33]

The iodide complexes behaved similarly, and ligand exchange between *cis*-$[PtI_2(PMe_2Ph)_2]$ and $[PtI(PMe_2Ph)_3]I$ was found to be faster than those involving *trans*-$[PtI_2(PMe_2Ph)_2]$, and faster than *cis*–*trans*-isomerisation. All these observations are consistent with the *trans*-effect order of $R_3P > I^- > Cl^-$. The *trans* to *cis* catalysed isomerisation of $[PtI_2(PMe_2Ph)_2]$ in methanol followed a rate-law zero-order in platinum and second-order in added PMe_2Ph (after a 2 minute induction period) (equation 7). Since practically no free ligand would

$$\text{rate} = k_{\text{obs}}\,[L_0]^2 \qquad (7)$$

be present in solution, Cooper and Powell interpreted this as an initial slow reaction between *trans*-$[PtI_2(PMe_2Ph)_2]$ and PMe_2Ph to produce the methanol-

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[33] D. G. Cooper and J. Powell, *J. Amer. Chem. Soc.*, 1973, **95**, 1102.

solvated ions $[PtI(PMe_2Ph)_3]^+$ and I^- (the concentrations of each would equal $[L_0]$, the concentration of added ligand), followed by a reaction between these two species to produce first an ion-pair, then *cis*-$[PtI_2(PMe_2Ph)_2]$ (Scheme 2).

$$\begin{tikzcd}
\textit{cis}\text{-}[MX_2L_2] + L \arrow[r, shift left, "k_1"] & {[MXL_3]X} \arrow[l, shift left, "k_{-1}"] \arrow[r, shift left, "k_3"] & \textit{trans}\text{-}[MX_2L_2] + L \arrow[l, shift left, "k_{-3}"] \\
K_1 & \text{ion-pair} \arrow[d, shift left, "k_2\qquad K_2"] & K_3 \\
 & {[MXL_3]^+ + X^- \text{ solvated ions}} \arrow[u, shift left, "k_{-2}"] &
\end{tikzcd}$$

Scheme 2

The same authors interpreted[33] the discovery by Haake and Pfeiffer[34,35] of a rate-law first-order in both Pt and L for the catalysed *cis*- to *trans*-isomerisation of $[PtCl_2(PR_3)_2]$ in *cyclohexane* as being due to the poor solvating ability of that solvent, so appreciable concentrations of $[PtCl(PR_3)_3]^+Cl^-$ do not develop and the rate-law therefore resembles those already described[9,32] for thioether complexes of palladium or platinum. The addition of portions of polar solvent to the cyclohexane would solvate the ionic intermediate and thus inhibit the reaction.[36]

In a study of the catalysed isomerisations of palladium complexes $[PdCl_2\{PMe_2(o\text{-tol})\}_2]$[37] (the bulky *ortho*-tolyl substituents slow down the spontaneous isomerisation, allowing the effects of nucleophilic catalysts to be clearly discerned), Cooper and Powell found identical behaviour in $CDCl_3$ or methanol to the related $[PtX_2(PMe_2Ph)_2]$ systems described above. Followed in chloroform solution by u.v. spectroscopy, both *cis* to *trans* and *trans* to *cis* catalysed isomerisations conformed to rate law (7), where $[L_0]$ was the amount of phosphine added. N.m.r. data showed that equilibria between *cis*-$[PdCl_2L_2]$, $[PdClL_3]Cl$, and the ions $[PdClL_3]^+$ and Cl^- were rapidly established. Again the concentration of catalysing phosphine [L], approximated to zero, as it all reacted to form the solvated ions. Scheme 2 fits all the observed data and leads to rate laws (8) and (9), fitting the experimental observations. Moreover, in the presence of added

$$\text{Rate}_{(cis \to trans)} = \frac{k_3[PdClL_3^+][Cl^-]}{K_2} = k_{obs}[L_0]^2 \tag{8}$$

$$\text{Rate}_{(trans \to cis)} = \frac{k_{-1}k_{-2}[PdClL_3^+][Cl^-]}{k_{-1} + k_2 + k_3} = k'_{obs}[L_0]^2 \tag{9}$$

chloride, equation (9) simplifies to rate = $k''_{obs}[L_0][Cl^-]$, again fitting observed data.

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[34] P. Haake and R. M. Pfeiffer, *Chem. Comm.*, 1969, 1330.

[35] P. Haake and R. M. Pfeiffer, *J. Amer. Chem. Soc.*, 1970, **92**, 4996.

[36] P. Haake and R. M. Pfeiffer, *J. Amer. Chem. Soc.*, 1970, **92**, 5243.

[37] D. G. Cooper and J. Powell, *Canad. J. Chem.*, 1973, **51**, 1634.

Cooper and Powell observed also that [$PdCl_2\{PMe_2(o\text{-tol})\}_2$] formed ionic complexes with PMe_2Ph, PBu_3, or $AsMe_2Ph$, but no ionic material could be detected with even a 4-fold excess of PPh_3, even though both ligand exchange and isomerisation were observed. Scheme 2 still described this situation, but this time $[L] \approx [L_0]$, and virtually none of the ionic material was present. Under these conditions, rate laws (10) and (11) operate, fitting observed data. They are

$$\text{Initial rate} = k_3K_1[cis\text{-}PdCl_2L_2][L'] = k_{obs}[\text{complex}][L'_0] \quad (cis \rightarrow trans) \tag{10}$$

$$\text{Initial rate} = k_{-3}[trans\text{-}PdCl_2L_2][L'] = k'_{obs}[\text{complex}][L'_0] \quad (trans \rightarrow cis) \tag{11}$$

identical to the rate laws found by Cattalini and Martelli,[32] and Roulet and Barbey,[9] where no appreciable amounts of ionic intermediates were detected either. The efficiency of catalysis be tertiary phosphines was found to decrease in the order $PMe_2Ph \sim PBu_3 \geqslant PMe_2(o\text{-tol}) \gg PMe(o\text{-tol})_2 > PPh_3$.[37]

These studies and several more, including for example examinations of ligand exchange, conductivity, and isomerisation reactions of palladium(II) tetrazolate complexes,[17] give a clear picture of the consecutive displacement mechanism. They suggest that it can operate under a variety of conditions, but that it can be somewhat more complicated than depicted in Scheme 1. An area of some contention is the formation and nature of the ion pairs of Scheme 2, and this is reflected in the next section.

B. The Pseudorotation Mechanism.—The 5-co-ordinate intermediates A and B of Scheme 1 are interconverted *via* the ionic species $[PtXL_3]^+X^-$ in the consecutive displacement mechanism. A pseudorotation mechanism could convert A into B directly and if such a process were faster than either or both of the steps linking A and B with the ionic intermediate, the isomerisation process would proceed by that route. Pseudorotation is a well-known low-energy process, particularly amongst 5-co-ordinate main-group element compounds, and including many with heavy metals.[38] A major problem in applying it in the present context, however, is that a geometry change of the intermediates would violate the highly stereospecific nature of substitution reactions at square-planar complexes.[3] Nevertheless such a mechanism, being inherently simpler than consecutive displacement in that it eliminates one step and an ionic intermediate (which is not always observable), has obvious attractions and has merited serious consideration for many years. Incontrovertible evidence for its operation has proved difficult to find, however, and many papers advocating this mechanism concentrated on highlighting problems of application or interpretation with the consecutive displacement route, thus favouring pseudorotation by default.

Into this category fall three papers by Haake and Pfeiffer.[34–36] The *cis–trans*-isomerisation of [$PtCl_2(PBu_3)_2$] catalysed by PBu_3 was shown to be first-order in both complex and phosphine in cyclohexane,[34] and is clearly an associative

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[38] J. S. Wood, *Progr. Inorg. Chem.*, 1972, **16**, 227.

process with $\Delta S^{\ddagger} = -154\ \text{J mol}^{-1}\ \text{K}^{-1}$. The fact that added amounts of polar solvent slow the reaction was taken as evidence against the formation of an ionic intermediate,[34,36] though as we have seen there are alternative explanations.[33] When a catalysing phosphine different from that in the complex was used, no incorporation of the catalyst into the product was observed.[35] It was concluded that isomerisation must proceed faster than ligand exchange, and pseudorotation was more likely than consecutive displacement, which must involve exchange of phosphines. It was subsequently shown, however, that phosphine exchange is faster than isomerisation under these conditions,[33,37] and that although the data were compatible with fluxional 5-co-ordinate reaction intermediates leading to isomerisation, they were also readily interpreted in terms of consecutive displacement. The incorporation or not of different phosphines into the product depends purely on the thermodynamics of the combinations possible.[33,39,40]

A similar argument on the failure of $[\text{PtCl}_2(\text{PEt}_3)_2]$ to take up the isomerisation catalyst PPh_3, whilst PEt_3 failed to displace triphenylphosphine from *cis*-$[\text{PtCl}_2(\text{PPh}_3)_2]$,[41] was explained[42] by the very low solubility of the latter complex and the operation of the dynamic equilibrium (12). In a

$$cis\text{-}[\text{PtCl}_2(\text{PPh}_3)_2] + 3\text{PEt}_3 \rightleftharpoons [\text{PtCl}(\text{PEt}_3)_3]\text{Cl} + 2\text{PPh}_3 \qquad (12)$$

similar vein, a claim that the reaction between $[\text{PtCl}(\text{PEt}_3)_3]^+$ and Cl^- to produce $[\text{PtCl}_2(\text{PEt}_3)_2]$ and PEt_3, a vital step in the consecutive displacement mechanism, was too slow to account for the observed isomerisation rate in this system[41] was countered by the argument that the methanol present in that experiment, but not the isomerisation, would so effectively solvate the ionic species as to make it thermodynamically more stable.[42]

Into this category also fall a number of papers describing catalysed isomerisation of some palladium complexes where no evidence could be found for ionic intermediates.[18–20] Although this need not rule out the operation of the consecutive displacement route (*vide supra*), the authors favour instead the formation of non-ionic 5-co-ordinate compounds as transition intermediates.

Perhaps the strongest support for the operation of a pseudorotation mechanism is that presented by Louw[43] from studies on the isomerisation reactions of $[\text{PtX}_2\text{L}_2]$ (X^- is halide, L is PEt_3 or PMe_2Ph) catalysed by either L or X^-. Addition of PMe_2Ph in CDCl_3 to the complexes led to the formation and isolation of $[\text{PtBr}_2\text{L}_3]$ and $[\text{PtI}_2\text{L}_3]$. Louw formulates these as non-ionic 5-co-ordinate species, although their n.m.r. characteristics are virtually identical with those of $[\text{PtXL}_3]^+\text{PF}_6^-$, and with those of $[\text{PtXL}_3]^+\text{X}^-$ obtained by Cooper and Powell.[33] At low temperatures only one isomer of $[\text{PtX}_2\text{L}_3]$ was apparent by n.m.r. spectroscopy.[43] The conclusion that compounds of type $[\text{PtX}_2\text{L}_3]$ are not

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[39] A. W. Verstuyft and J. H. Nelson, *Synthesis React. Inorg. Metal. Org. Chem.*, 1975, **5**, 69.

[40] A. W. Verstuyft, D. A. Redfield, L. W. Cary, and J. H. Nelson, *Inorg. Chem.*, 1976, **15**, 1128.

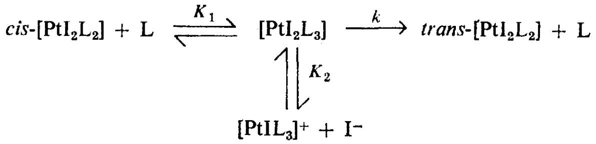
[41] W. J. Louw, *J.C.S. Chem. Comm.*, 1974, 353.

[42] J. Powell and D. G. Cooper, *J.C.S. Chem. Comm.*, 1974, 749.

[43] W. J. Louw, *Inorg. Chem.*, 1977, **16**, 2147.

ionic, nor even tightly-bound ion pairs, is based on u.v.–visible spectroscopy, which indicates that these species are quite different to those for which clearly-defined cations can be discerned, such as $[PtXL_3]PF_6$. Moreover, $[PdCl_2(PMe_2Ph)_3]$ has been isolated and structurally characterised,[44] and its u.v.–visible spectrum also differs from that of $[PdCl(PMe_2Ph)_3]^+$.

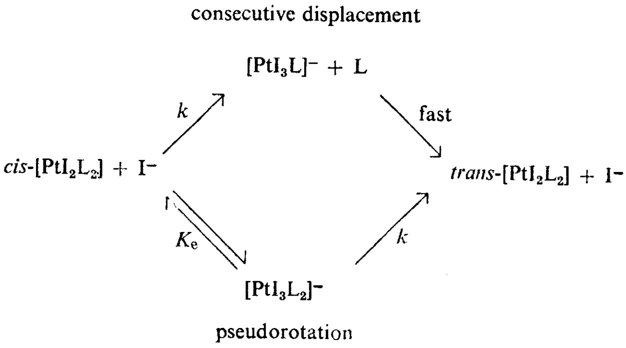
The argument for pseudorotation being the isomerisation mechanism is based on the assertions that isomerisation proceeds only when these 5-co-ordinate intermediates are formed, and that when stable, 4-co-ordinate ionic species are produced, no isomerisation results.[43] Louw therefore suggested Scheme 3 to account for the phosphine-catalysed *cis–trans*-isomerisation of $[PtI_2(PMe_2Ph)_2]$. The similarity to Scheme 2 for consecutive displacement established by Cooper and Powell[33,37] is obvious (the only difference is that a 5-co-ordinate intermediate replaces the ion-pairs) and similar kinetic rate laws are to be expected and were, indeed, found.[43] Louw concluded, reasonably, that kinetic studies alone could not differentiate between these mechanisms.



$L = PMe_2Ph$

Scheme 3

A somewhat different situation was claimed for the iodide-catalysed *cis–trans*-isomerisations, however.[43] Scheme 4 outlines the two most probable reaction



$L = PEt_3$

Scheme 4

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[44] W. J. Louw, D. J. A. de Waal, and G. J. Kruger, *J.C.S. Dalton*, 1976, 2364.

routes: consecutive displacement and pseudorotation. The rate-law derived from the pseudorotation mechanism, equation 13, fits well with the experimentally observed law. In this case it does not also fit the consecutive displacement mechanism, unless there is a build-up of $[PtI_3(PEt_3)_2]^-$ prior to formation of $[PtI_3(PEt_3)]^-$ and PEt_3. Moreover, the phosphine released by consecutive displacement would be available to catalyse isomerisations itself, and this does not appear to happen.[43] (The iodide-catalysed isomerisation is slower than the phosphine-catalysed reaction, so effects of liberated I^- from a consecutive displacement reaction catalysed by phosphine would go unnoticed.[33] Many of the phosphine-catalysed reactions were examined in the presence of an excess of ionic iodide in any case.[43]) Whilst there is no precedent for 5-co-ordinate intermediates of the type $[PtI_3(PEt_3)_2]^-$, a colour change on the addition of I^- to $[PdI_2(PMe_2Ph)_2]$ has been interpreted[12] as being due to the formation of $[PdI_3(PMe_3Ph)_2]^-$. Whether the iodide-catalysed isomerisation proceeds *via* pseudorotation, as claimed,[43] or not, it should be emphasised that it is so far the only well-documented case of catalysis of this type by anions.

$$k_{\text{obs}} = \frac{kK_e[I^-]}{1 + K_e[I^-]} \tag{13}$$

Louw[43] explained that the problem of the stereospecific nature of substitution reactions at Pt^{II} and Pd^{II} could be overcome by considering the relative reaction rates, and pointed out that most substitution reactions on square-planar phosphine complexes have been carried out in polar solvents, in which a 5-co-ordinate intermediate would have a very short lifetime. If the 5-co-ordinate intermediate had an appreciable lifetime, however, pseudorotation might then occur. The problem is thus reduced to whether or when such species might be produced.

There can be little doubt that such compounds are attainable. Several phosphine halide complexes of platinum and palladium with the relevant stoicheiometry $[MX_2L_3]$ have been described,[44,45] and the geomety of those elucidated lies close to square-pyramidal or trigonal-bipyramidal. This would seem to be ideal for fluxional motion of the Berry type, but little is known about their behaviour and many tend to lose a ligand (X^- or L) in solution. Indeed it is not yet clear just which factors stabilise such 5-co-ordinate compounds.[38] Thus, for example, whilst a few 5-co-ordinate compounds of platinum(II) involve chelating ligands,[46] the presence of such groups does not always ensure a higher-than-

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[45] (a) J. W. Collier, F. G. Mann, D. G. Watson, and H. R. Watson, *J. Chem. Soc.*, 1964, 1803; (b) D. W. Allen, I. T. Millar, and F. G. Mann, *J. Chem. Soc.* (*A*), 1969, 1101; (c) *idem.*, *Chem. and Ind.* (*London*), 1966, 2096; (d) J. W. Collier, F. G. Mann, and I. T. Millar, *J. Chem. Soc.* (*C*), 1971, 3937; (e) R. L. Bennett, M. I. Bruce, and F. G. A. Stone, *J. Organometallic Chem.*, 1972, **38**, 325; (f) K. M. Chui and H. M. Powell, *J.C.S. Dalton*, 1974, 2117; (g) R. G. Pearson, W. J. Louw, and J. Rajaram, *Inorg. Chim. Acta*, 1974, **9**, 251; (h) K. M. Chui and H. M. Powell, *J.C.S. Dalton*, 1974, 1879; (i) C. A. McAuliffe, I. E. Niven, and R. V. Parish, *Inorg. Chim. Acta*, 1975, **15**, 67.

[46] (a) H. C. Clark and L. E. Manzer, *J. Amer. Chem. Soc.*, 1973, **95**, 3813; (b) J. D. Oliver and N. Rice, *Inorg. Chem.*, 1976, **15**, 2741; (c) M. K. Cooper, D. W. Yaniuk, and M. McPartlin, *J. Organometallic Chem.*, 1979, **166**, 241.

usual co-ordination number,[47] and they may simply enhance a pseudo-intermolecular ligand site-exchange.[48]

There is good evidence that nickel forms more 5-co-ordinate complexes than palladium or platinum, and intramolecular rearrangements are faster for that element also.[49] The equilibrium (14) lies to the right when M is Ni, but to the

$$[MH(PEt_3)_3]^+ + PEt_3 \rightleftharpoons [MH(PEt_3)_4]^+ \qquad (14)$$

left when M is Pt. Also, intramolecular rearrangement is faster than the dissociative process in the nickel system, where the reverse is true for platinum with the processes being of similar rate for the palladium complex.[50] As well as the dissociative process (14), three distinct routes have been postulated to account for fluxional behaviour in the many 5-co-ordinate nickel complexes known.[51] These include a 'tetrahedral jump' (whereby H^+ of $[MHL_4]^+$ moves from face to face of the ML_4 tetrahedron), Berry pseudorotation (for trigonal bipyramidal complexes such as $[Ni(PR_3)_5]^{2+}$ and $[Ni(CN)_2(PR_3)_3]$), and an associative route *via* a 6-co-ordinate species (for complexes like $[NiXL_4]^+X^-$).

(*i*) *The relationship between consecutive displacement and pseudorotation.* These mechanisms may best be viewed as two extreme situations of a single type of process. The fact that the structures of some 5-co-ordinate adducts approach square-pyramidal indicates that this configuration could be regarded as a reaction intermediate rather than as a transition state as depicted in Figure 1. This is not unreasonable when it is borne in mind that the vacant (octahedrally disposed) sites of square-planes and square-pyramids will almost certainly be solvated,[33,37,43] whereas trigonal-bipyramids may not, at some cost in energy. The reaction profile for catalysed isomerisations therefore most probably resembles one of those in Figure 2. Polar solvents favour ionic intermediates (and *cis*-isomers) whereas non-polar media lead to 5-co-ordinate intermediates. Between these, ion-pairs may be the most stable intermediate configuration. The reaction between carbon monoxide and $[PtXPhL_2]$ produces either ionic $[PtPhL_2(CO)]^+X^-$ or 5-co-ordinate $[PtXPhL_2(CO)]$, depending on the polarity of the solvent, in an exactly analogous manner.[52]

The reaction path followed, A, B, or C of Figure 2, will depend on the natures of M, X, and L, and on the temperature and solvent. The situation may be complicated in that the energy differences between the possible intermediates may not be great, and both ionic and 5-co-ordinate intermediates might co-exist and

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[47] W. Levason, C. A. McAuliffe, and S. G. Murray, *J. Organometallic Chem.*, 1975, **101**, C29.

[48] (a) R. J. Cross and N. H. Tennent, *J.C.S. Dalton*, 1974, 1444; (b) C. D. Tau and D. W. Meek, *J. Organometallic Chem.*, 1977, **139**, C83; (c) K. R. Dixon, *Inorg. Chem.*, 1977, **16**, 2618.

[49] E. C. Alyea and D. W. Meek, *Inorg. Chem.*, 1972, **11**, 1029.

[50] A. D. English, P. Meaking, and J. P. Jesson, *J. Amer. Chem. Soc.*, 1976, **98**, 422.

[51] (a) E. A. Jeffery, *Austral. J. Chem.*, 1973, **26**, 219; (b) E. J. Lukosius and K. J. Coskran, *Inorg. Chem.*, 1975, **14**, 1922; (c) *idem, ibid.*, 1975, **14**, 1926; (d) P. Meakin, R. A. Schunn, and J. P. Jesson, *J. Amer. Chem. Soc.*, 1974, **96**, 277; (e) P. Meakin and J. P. Jesson, *J. Amer. Chem. Soc.*, 1974, **96**, 5751, 5760; (f) P. Meier, A. E. Merbach, M. Dartiguenave, and Y. Dartiguenave, *J.C.S. Chem. Comm.*, 1979, 49.

[52] G. K. Anderson and R. J. Cross, *J.C.S. Dalton*, in the press.

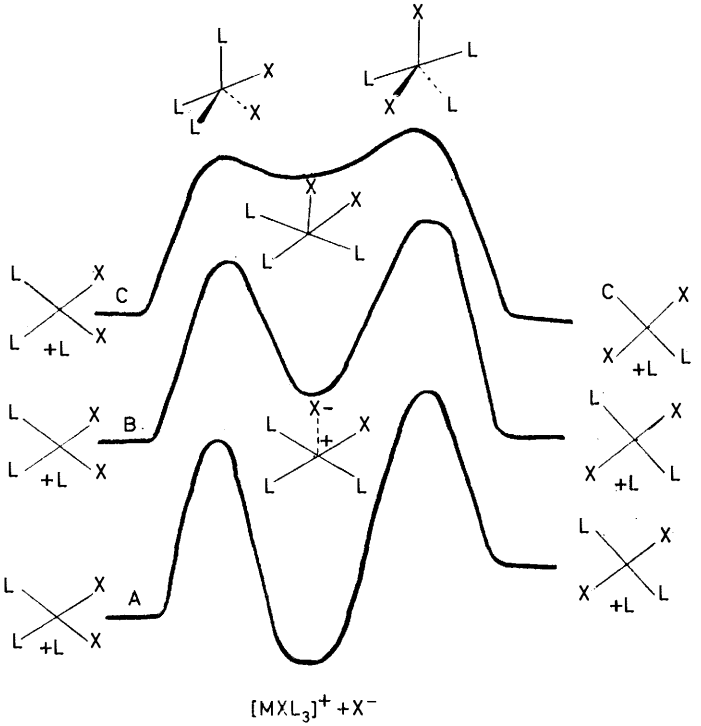

Figure 2 *Reaction profiles for* L-*catalysed* cis–trans-*isomerisations of* [MX$_2$L$_2$].[33] A: *polar solvent, favouring the formation of ionic intermediates.* B: *intermediate polarity solvent, allowing ion-pair formation.* C: *non-polar solvent with 5-co-ordinate intermediate. Profile* A *represents consecutive displacement, whereas* C *proceeds by pseudorotation.*

interchange rapidly[43] (15). The true nature of the intermediates in these catalysed

$$[PtCl(PMe_2Ph)_3]^+ + Cl^- \rightleftharpoons [PtCl_2(PMe_2Ph)_3] \qquad (15)$$

isomerisations is thus very difficult to determine in some cases.

It is significant that the configurations so far determined for complexes [MX$_2$L$_3$] (M is Pd or Pt) is that shown in Figure 2C.[44,45a,f,h] The other two square-pyramidal configurations of [MX$_2$L$_3$] are presumably of higher energy. They will be involved, along with the trigonal-bipyramidal species, in ligand-exchange processes as well as isomerisations. Figure 3 shows the relationship between all the intermediates.

Much still remains to be explained concerning the relationship of consecutive displacement and pseudorotation. It is not possible to predict which might operate, although it has been suggested that strong ligands of small steric demand favour 5-co-ordination,[53] and might thus promote pseudorotations. It is not

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[53] A. W. Verstuyft, L. W. Cary, and J. H. Nelson, *Inorg. Chem.*, 1976, **15**, 3161.

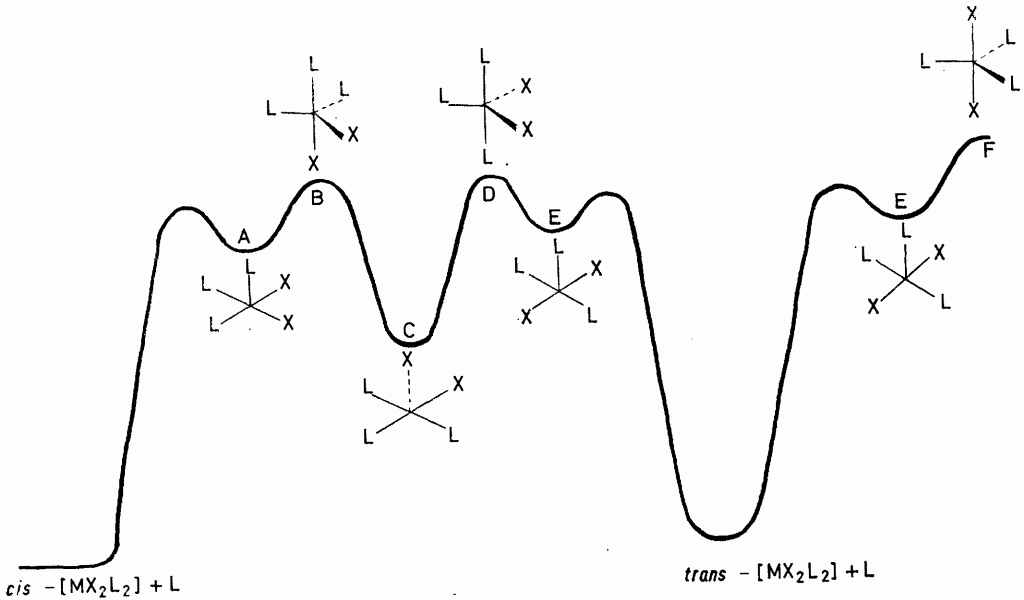

Figure 3 *Relationship between isomerisation and exchange of* L. *No significance should be attached to the relative energies of intermediates or transition states, except that* C *is probably of lower energy than the others. The nature of* C *depends on conditions (see Fig. 2).* L *exchange with the* cis-*isomer involves* A *and* B, *and* L *exchange with the* trans-*isomer proceeds through* E *and* F. *In principle, all the species* A *to* F *can be interconverted by pseudorotation. In practice this probably only occurs if no deep potential wells are encountered.*

even possible to predict if either catalysed route may operate. For example, the failure of $[MMe_2L_2]^{22}$ to isomerise *via* consecutive displacement when treated with free L is easy enough to understand, but why do they not undergo pseudorotation? Louw[43] explains this failure in terms of the complex being too soft to form stable 5-co-ordinate intermediates, but this seems unlikely in view of the isolation of several metal–metal-bonded species with very soft ligands.[54] Perhaps the best rationalisation to date is that put forward by Redfield and Nelson.[55] The consecutive displacement of anions X^- should dominate when X^- is poorly co-ordinating and the neutral ligands and catalysing nucleophiles are strong bases. Pseudorotation should dominate in non-polar solvents, and when X and L are of similar basicity and small.

(*ii*) *Implications to other reactions*. The most obvious consequence is that ligand substitution reactions at square-planar complexes should not be regarded as invariably stereospecific. Whilst this could lead to complications in interpreting such reactions, the other side of the coin is that there could be synthetic advantages essentially to carrying out ligand replacement and isomerisation at one step. It would obviously be of value if examples of non-specific substitution could be found, but whereas modern spectroscopic instruments would make the detection of such processes easy, the interpretation could prove difficult. Nucleophilic agents would necessarily be present and these could lead to isomerisation independent of replacement. If the leaving nucleophile could be removed from the system, this may alleviate the problem.

The second consequence is that 5-co-ordinate complexes of the platinum metals must be regarded as fluxional. This is particularly important for Rh^I and Ir^I, where many such complexes are known,[2] and it should be kept in mind that geometries other than the ground-state may be readily attainable even under mild conditions.

Finally, consecutive displacement does operate for at least some cases in solvents such as chloroform, and probably in even less-polar media. This means that ionic species may be produced from complexes of the same type in other reactions, including catalytic sequences, where their presence may not be suspected.

C. Isomerisation of π-Allyl Complexes.—Many η^3-allyls of Rh^I, Ir^I, Pd^{II}, and Pt^{II} can be considered to have square-planar geometry. With different ligands, L and L′, the different ends of the allyl group are identifiable (A and C of

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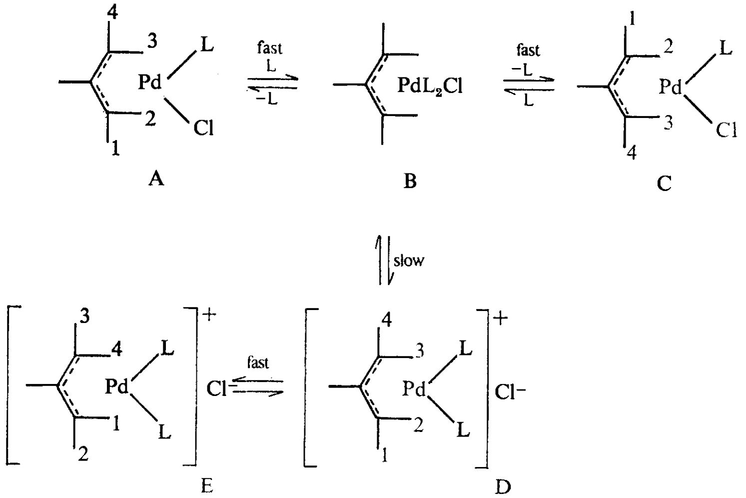
[54] (a) R. G. Vranka, L. F. Dahl, P. Chini, and J. Chatt, *J. Amer. Chem. Soc.*, 1969, **91**, 1574; (b) M. I. Bruce, G. Shaw, and F. G. A. Stone, *Chem. Comm.*, 1971, 1288; (c) *idem.*, *ibid.*, 1972, 1781; (d) V. D. Estes and D. J. Hodgson, *Inorg. Chem.*, 1973, **12**, 2932; (e) A. Modinos and P. Woodward, *J.C.S. Dalton*, 1975, 1534; (f) A. Albinaty, G. Carturan, and A. Musco, *Inorg. Chim. Acta*, 1976, **16**, L3; (g) D. C. Moody and R. R. Ryan, *Inorg. Chem.*, 1977, **16**, 1052; (h) A. Albinati, *Inorg. Chim. Acta*, 1977, **22**, L31; (i) M. Green, J. A. K. Howard, M. Murray, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 1509; (j) R. D. Cramer, R. V. Lindsey, C. J. Prewitt, and U. G. Stolberg, *J. Amer. Chem. Soc.*, 1965, **87**, 658.

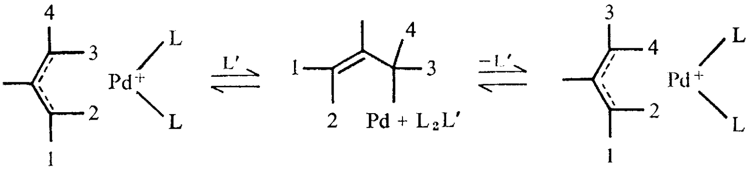
[55] D. A. Redfield and J. H. Nelson, *J. Amer. Chem. Soc.*, 1974, **96**, 6219.



Scheme 5

Scheme 5), and numerous processes are known to lead to site exchange.[56,57] With asymmetrically substituted allyls, these processes could potentially achieve *cis–trans*-isomerisation.

Some mechanisms will be discussed later, but most involve catalysis by a nucleophile and resemble consecutive displacement or pseudorotation, and they are discussed here. The general processes are outlined in Scheme 5 for palladium complexes. The 5-co-ordinate B and ionic D and E resemble the intermediates in pseudorotation or consecutive displacement, and they appear to have a similar relationship. The complexes $Pt(C_3H_5)X(PPh_3)_2$ are covalent 5-co-ordinate in chloroform, but ionic and 4-co-ordinate in nitromethane.[58] Site exchange can also be brought about *via* $\pi \rightarrow \sigma \rightarrow \pi$ bonding changes in these allylic complexes (D to E in Scheme 5),[56,57,59] and these are usually from 5-co-ordinate complexes. Equation 16 shows such a process.[57] It resembles consecutive displacement, where an olefin acts as leaving group rather than an ionic halide.



(16)

[56] K. Vrieze, H. C. Volger, and P. W. N. M. van Leeuwen, *Inorg. Chim. Acta Rev.*, 1969, **3**, 109.

[57] P. M. Maitlis, "The Organic Chemistry of Palladium", Academic Press, London, 1971.

[58] M. C. Baird and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 1278.

[59] G. Carturan, A. Scrivanti, U. Belluco, and F. Morandini, *Inorg. Chim. Acta*, 1978, **26**, 1.

D. Ligand Exchange.—Whilst noting that phosphine exchange sometimes accompanied *cis–trans*-isomerisation of $[MX_2(PR_3)_2]$ by phosphine catalysis,[55] Redfield and Nelson suggested this as an alternative mechanism for some catalysed isomerisations (17). Unless accompanied by pseudorotation, however,

$$\textit{cis}\text{-}[MX_2L_2] + L' \rightleftharpoons \underset{A}{MX_2L_2L'} \rightleftharpoons MX_2LL' + L \rightleftharpoons \underset{B}{MX_2L_2L'}$$

$$\rightleftharpoons \textit{trans}\text{-}[MX_2L_2] + L' \qquad (17)$$

such ligand replacements are stereospecific.[3] They have often been observed to accompany isomerisations,[17–20,33,37] but without a geometry change at *A* or *B* above, this process alone cannot lead to *cis–trans*-isomerisations. Many examples of neutral ligand exchange or replacement are known which are not involved with a geometry change of the compounds.[9,39,40,53,60,61] The well-known metathetical replacement of anionic ligands likewise generally proceeds stereospecifically[3] and does not in itself produce isomerisation.

E. Oxidative Addition/Reductive Elimination.—Reductive elimination of two ligands is usually a concerted process and involves the loss of two mutually-*cis* groups.[62] If this process is preceded by *trans* oxidative addition to a square-planar complex, an overall geometry change can result. *trans-Concerted* oxidative addition is a symmetry-forbidden reaction,[2] but the oxidative addition process is often more complicated and can proceed through polar and ionic transition states leading to an overall *trans*-addition.[63]

As an isomerisation route, this system is less convenient and less predictable than the free-ligand catalysed methods, but examples of its operation are known. *cis-* or *trans*-$[PtCl_4(PPr^n_3)_2]$ can be made stereospecifically by the *trans*-addition of Cl_2 to *cis-* or *trans*-$[PtCl_2(PPr^n_3)_2]$, respectively.[64] Both platinum(IV) complexes lose chlorine on heating and revert to the platinum(II) complexes (accompanied by some unspecified decomposition) as a mixture of *cis-* and *trans*-isomers.

4 Spontaneous Isomerisations

These can be conveniently divided into three groups: those which in reality are catalysed but for which the catalyst has not been identified; reactions involving a straightforward change of geometry; and reactions involving ligand loss and rearrangement of a 3-co-ordinate intermediate. The border-line between these categories is somewhat blurred, and not surprisingly it is impossible to classify some of the reactions encountered.

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[60] A. W. Verstuyft, D. A. Redfield, L. W. Cary, and J. H. Nelson, *Inorg. Chem.*, 1977, **16**, 2776.

[61] R. J. Cross, T. H. Green, R. Keat, and J. F. Patterson, *J.C.S. Dalton*, 1976, 1486.

[62] P. S. Braterman, R. J. Cross, and G. B. Young, *J.C.S. Dalton*, 1976, 1306, 1310; 1977, 1892.

[63] (a) J. K. Jawad and R. J. Puddephatt, *J. Organometallic Chem.*, 1976, **117**, 297; (b) R. Osso and J. V. Rund, *J. Coord. Chem.*, 1978, **8**, 169; (c) R. J. Mureinik, M. Weitzberg, and J. Blum, *Inorg. Chem.*, 1979, **18**, 915.

[64] J. Chatt, *J. Chem. Soc.*, 1950, 2301.

A. Solvent-Catalysed and Autocatalysed Reactions.—Since the addition of bases identical or similar to those co-ordinated to the metal promotes isomerisation *via* an associative pathway, it is only to be expected that basic solvents, particularly those with similar characteristics to the ligands, might do the same. Indeed it is possible (though by no means proven) that all the spontaneous isomerisations of palladium compounds $[PdX_2L_2]$ could proceed *via* solvent association.

The effects of the solvents pyridine and dmso on the azido-palladium complexes $[Pd(N_3)_2(PMe_2Ph)_2]$ and $[Pd(N_3)_2(PMePh_2)_2]$ are identical with those of added phosphines or phosphites, promoting rapid isomerisation and ligand exchange.[18] Less basic solvents did not have these effects on these complexes. This suggests that a 5-co-ordinate intermediate $[Pd(N_3)_2(S)L_2]$ is formed, which isomerises either directly or *via* eliminations.

An examination by n.m.r. spectroscopy of $[PdCl_2L_2]$ (L = PMe_2Ph or $PMePh_2$) in eleven solvents[14] found a similar solvent dependence to *linkage* isomerism processes of palladium thiocyanates and selenocyanates,[65] reactions believed to proceed *via* dissociation of the ligands.[12] The solvents examined range from benzene and toluene, through various chlorocarbons, to acetone and nitrobenzene, and it seems quite possible, therefore, that *all* these solvents can act in the same way as pyridine or dmso in causing isomerisation through association. Further evidence for a similar, associative, role for catalysing tertiary phosphines and solvents was obtained from studies on $[PdX_2L_2]$ (where X is N_3 or Cl; L is PMe_2Ar or $PMeAr_2$, where Ar is *para*-substituted phenyl).[19] A comparison of the rates of phosphine (L) exchange and isomerisation in a series of complexes $[PdX_2L_2]$ found the same rate dependence on X [X = CN (instantaneous) > Cl (seconds) > N_3 (minutes) > NCO (hours) > tetrazolates (hours)].[20] It was concluded, therefore, that both phosphine exchange and *cis–trans*-isomerisation proceed through penta-co-ordinate intermediates.

Finally, it has been noted that these spontaneous isomerisations of square-planar palladium complexes are slowed when bulky ligands are employed,[37,60] a finding consistent with associative processes.

Cooper and Powell[37] noted that *trans*-$[PdCl_2(PMe_2\{o\text{-tol}\})_2]$ isomerises to the *cis*-isomer much more rapidly in methanol than in chloroform. A new species, shown to be $[PdCl(MeOH)(PMe_2\{o\text{-tol}\})_2]^+Cl^-$, was generated at a rate similar to that for the isomerisation, so it seems clear in this case that isomerisation is by solvent catalysis, and chloride ion displacement by the solvent is the rate-determining step. In none of the other cases discussed above was any evidence for ionic intermediates found, so a pseudorotation mechanism cannot be ruled out.

A variation on these solvent-association catalysed isomerisations arises from the possible elimination by solvent of a ligand such as tertiary phosphine. Since these are known to catalyse isomerisations themselves, any appreciable concentration of them caused by solvent attack on the metal should in turn catalyse

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[65] (a) J. L. Burmeister, R. L. Hassell, and R. J. Phelan, *Inorg. Chem.*, 1971, **10**, 2032; (b) J. L. Burmeister, *Coord. Chem. Rev.*, 1968, **3**, 225; K. A. Johnson, J. C. Lim, and J. L. Burmeister, *Inorg. Chem.*, 1973, **12**, 124.

isomerisations at other molecules. As the catalysing group in such cases originates from the same molecular species, the term autocatalysis is appropriate. The likelihood of ligand elimination following solvent association has already been noted.[14,18–20] Moreover the formation of mixed ligand complexes from solutions of symmetrical palladium[39,40,66] and platinum[67] derivatives may well proceed through release of phosphine by solvent (* equation 18).

$$[MX_2(R^1{}_3P)_2] + [MX_2(R^2{}_3P)_2] \rightleftharpoons 2[MX_2(PR^1{}_3)(PR^2{}_3)] \qquad (18)$$

One of the best-proven cases of autocatalytic isomerisation is also one of the earliest. The platinum arsine and stibine complexes, $[PtCl_2(AsEt_3)_2]$ and $[PtCl_2(SbEt_3)_2]$, isomerise spontaneously in benzene solution. If the halide-bridged complex $[Pt_2Cl_4(AsEt_3)_2]$ is added to the solutions to scavenge any free ligand, however, the isomerisation of the former complex is completely quenched, and of the latter slowed.[5] Clearly ligand is freed from the complexes in solution, and catalyses isomerisation at other molecules.

The palladium complexes $[PdX_2L_2]$ (X is azide, 5-methyltetrazolate, or 5-trifluoromethyltetrazolate; L is PMe_2Ph or $PMePh_2$) also seem excellent candidates for the autocatalysis mechanism of isomerisation.[17,18] Isomerisation is catalysed by free phosphine in each case, but also proceeds spontaneously in a number of solvents. The solvents are known to displace phosphine ligands, however. It seems plausible that the displaced phosphines should also act as catalysts.

A further example where autocatalysis may well be implicated is the *trans–cis*-isomerisation of $[PtCl_2(CO)L]$.[23] The reactions proceed spontaneously in several solvents of the weakly-co-ordinating type, and elimination of carbon monoxide is involved. Addition of carbon monoxide to *trans*-$[PtCl_2(CO)L]$ catalyses the isomerisation, however, *via* an associative mechanism. Once again it seems likely that CO released from one molecule would catalyse the isomerisation of another (19 and 20). The formation of mixed neutral-ligand *trans*-complexes $[MCl_2LA]$ (M is palladium or platinum) from the bridge-splitting by A of symmetrical, halide-bridged dimers seems to be a general process,[25,68] and not confined to A = CO. The facts that many of these *trans*-isomers convert to *cis*-geometry,[25] and that some of them have been shown to eliminate ligands A in solution,[25,40] may indicate that the autocatalytic process is indeed quite common.

$$trans\text{-}[PtCl_2(CO)L] \xrightarrow{\text{solvent}} [PtCl_2(S)L] + CO \qquad (19)$$

$$trans\text{-}[PtCl_2(CO)L] \xrightarrow{CO} cis\text{-}[PtCl_2(CO)L] \qquad (20)$$

It is worth noting at this stage that ligand eliminations such as these may not

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*Other mechanisms are, of course, possible, including ligand transfer *via* transient bridges, but the presence in solution of free ligand has consistently been found to lead to exchange.

[66] R. J. Goodfellow, *Chem. Comm.*, 1968, 114.

[67] W. McFarlane, *J.C.S. Dalton*, 1974, 324.

[68] J. Chatt, *J. Chem. Soc.*, 1951, 652.

result from associative attack by solvent in every case. Elimination could be a spontaneous dissociative step, followed by solvation of the 3-co-ordinate fragment. This possibility might be particularly favourable in complexes such as *trans*-[$PtCl_2(CO)(PR_3)$], where two π-bonding ligands of high *trans*-effect[21] lie opposite one another. Other reactions which might fall into this category are discussed separately later, as the possibility of geometry change at the 3-co-ordinate intermediate adds another dimension to the problem.

Whilst intuitively it seems likely that very many geometrical isomerisation reactions will fall into the categories of solvent catalysis or autocatalysis, there are relatively few proven cases. For example, the thermal isomerisation of *cis*-[$PtCl_2(PBu_3)_2$] in solution appears to operate at a rate and in conditions not dissimilar to phosphine- or carbonyl-catalysed reactions,[69] but mechanistic data are not available. Nevertheless the importance of these reaction types is obvious. The degree of solvation and the ability of even weakly co-ordinating solvents to displace strong ligands from transition metals can have an important effect on catalytic reactions. The loss of Ph_3P from Wilkinson's catalyst, [$RhCl(PPh_3)_3$], is a critical step,[70] and such eliminations may be more common than generally believed amongst square-planar compounds of Rh^I, Ir^I, Pd^{II}, and Pt^{II}. The operation of autocatalytic isomerisation has scarcely been recognised previously, and other reactions of eliminated ligands could also prove to be of great importance. It is obvious that many compounds of palladium(II) and rhodium(I), and some also of platinum(II) and iridium(I), do not retain their molecular integrity in solution.

B. Direct Geometry Change: Photochemical Isomerisations.—This is perhaps the most obvious and conceptually simplest of the possible isomerisation routes of square-planar complexes. The intermediary of a tetrahedral complex would secure a route to change geometry (Scheme 6). Despite this there is little agreement about the likelihood of its application, and practically no experimental evidence concerning its operation, except photochemically.

Dealing first with thermal reactions, a paper by Eaton[71] considered the problem using Woodward–Hoffmann type symmetry correlations, and concluded that square-planar to tetrahedral transitions should be allowed, but *cis–trans*-isomerisations were not. Whitesides[72] pointed out that these conclusions were contradictory and, refining the arguments by considering a tetragonal transition state between square-plane and tetrahedron, reached the conclusion that both transitions between tetrahedra and square-planes and *cis–trans*-isomerisation of square-planes were thermally disallowed. He also pointed out some serious limitations inherent in applying this treatment to transition-metal complexes. Whereas for carbon atoms the energy differences between "allowed" and

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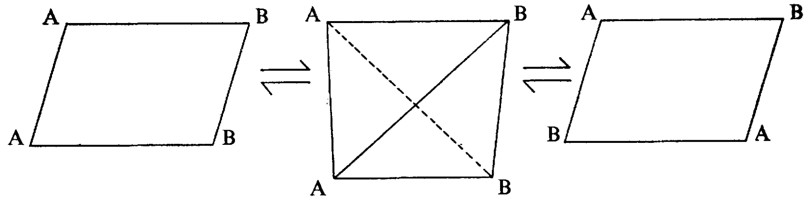
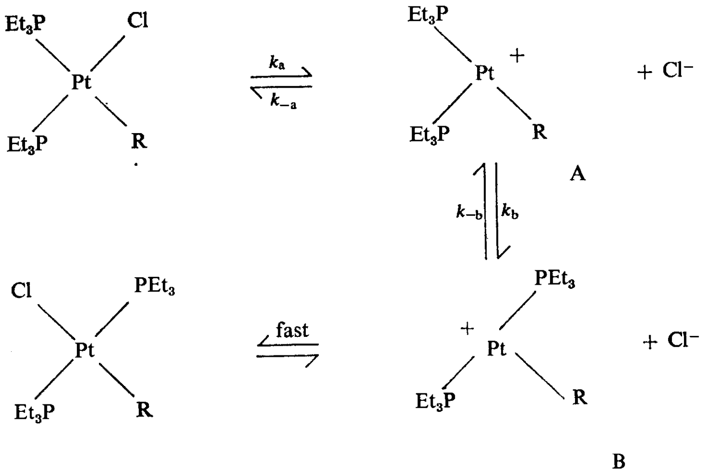
[69] (a) G. B. Kauffman and L. A. Teter, *Inorg. Synth.*, 1963, **7**, 245; (b) R. M. Pfeiffer, *Synth. React. Inorg. Metal-Org. Chem.*, 1976, **6**, 55.

[70] C. A. Tolman, P. Z. Meakin, D. L. Lindner, and J. P. Jesson, *J. Amer. Chem. Soc.*, 1974, **96**, 2762.

[71] D. R. Eaton, *J. Amer. Chem., Soc*, 1968, **90**, 4272.

[72] T. W. Whitesides, *J. Amer. Chem. Soc.*, 1969, **91**, 2395.





Scheme 6

"disallowed" pathways are probably large, for transition elements the energy contributions from orbital symmetry conservation alone might be small compared with other contributions (ligand-field stabilisation, bond energy changes, *etc.*) to the alternative pathways under consideration.

Experimentally, tetrahedral to square-planar conversions have been followed by n.m.r. spectroscopy for a number of nickel(II) complexes [$NiX_2(PR_3)_2$].[73] The effect of the substituents on the rate of interchange, X = I > Cl > Br, and R = Et > Bu^n > Pr^n > Me, are not understood. Whilst this route makes possible *cis–trans*-isomerisation of such complexes, only the *trans*-isomers have been detected for these nickel complexes thus far, so this isomerisation route remains theoretical.

The relatively high energy of the triplet tetrahedral configuration of palladium(II) and platinum(II) complexes makes it unlikely that they would be reached as thermal reaction intermediates. It has been suggested, however, as a possible mechanism in the high-temperature conversion of *trans*-[$PtCl_2$(CO)

[73] (a) G. N. LaMar and E. O. Sherman, *J. Amer. Chem. Soc.*, 1970, **92**, 269; (b) L. H. Pignolet, W. De W. Horrocks, and R. H. Holm, *J. Amer. Chem. Soc.*, 1970, **92**, 1855; (c) L. Que and L. H. Pignolet, *Inorg. Chem.*, 1973, **12**, 156.

(+-$NH_2CHMePh$)] into its *cis*-isomer in the liquid state.[25] The authors argue that any mechanism involving free CO or amine is unlikely, as these would be lost at the high temperatures involved. The isomerisations of *cis*-[$PtCl(C_6F_5)(PEt_3)_2$] and *cis*-[$Pt(C_6F_5)_2(PPh_3)_2$] may well be related cases.[74]

There is agreement in principle that photochemical excitation of square-planar complexes could lead to isomerisation *via* an intermediate close to tetrahedral symmetry.[71,72] The photochemical perturbation of [$NiCl_2(Ph_2PC_3H_6PPh_2)$] to tetrahedral geometry has been reported,[75] for example. It is less easy in practice to determine if a photochemically induced isomerisation does indeed proceed by such a route. The glycinate complex *cis*-[$Pt(gly)_2$] isomerises with a quantum yield, ϕ, of 0·13 when the $d \rightarrow d$ bands are irradiated, and this does appear to be a truly intramolecular process.[76] A twist mechanism to a tetrahedral intermediate probably also operates during u.v. irradiation of [$PtCl_2(PEt_3)_2$].[77] The equilibrium *cis–trans*-ratio is not the same as for thermal reactions, and the equilibrium constant varies linearly with the solvent dielectric constants.[77a] There are complications, however. The *trans–cis*-conversion is irreversible and ϕ is reduced from 1 to 0·13 in the presence of oxygen.

A number of other isomerisations are known to be promoted by u.v. irradiation. These include *cis*-[$Pd(N_3)_2(PMe_2Ph)_2$],[60] *cis*-[$PtCl_2(Pr^n_2SO)_2$],[11] *cis*-[$Pt(NH_3)_2(OH_2)_2$]$^{2+}$,[78] and *cis*- and *trans*-[$PtCl_2(CO)L$].[23] Photochemical routes have been employed synthetically for *trans*-[$PtCl_2(PPh_3)_2$] and *trans*-[$PtCl_2py_2$].[79]

An important point is that many of the complexes discussed are coloured, so the possibility of even diffuse light causing isomerisations should be borne in mind. The consequences for isomerisation studies, and related reactions, could be quite profound.

C. The Dissociation Mechanism.—Bearing in mind the tradition of associative reactions at square-planar complexes, the concept of a straightforward ligand loss being the initiating step of a reaction sequence is somewhat revolutionary. Like the associative isomerisation mechanisms discussed previously, this one also is inextricably linked with mechanisms of ligand substitution. The current situation is also somewhat analogous to the arguments concerning consecutive displacement *versus* pseudorotation: similar kinetic data have been interpreted both in favour of and against the operation of dissociative reaction paths.

The arguments centre around the mono-organoplatinum complexes [$PtRCl(PEt_3)_2$] and their bromo-analogues. Substitutions of the halide by various nucleophiles Y in polar solvents such as methanol or dmso follows the usual

[74] D. T. Rosevear and F. G. A. Stone, *J. Chem. Soc.*, 1965, 5275.
[75] J. J. McGarvey and J. Wilson, *J. Amer. Chem. Soc.*, 1975, **97**, 2531.
[76] (a) V. Balzani, V. Carassiti, L. Moggi, and F. Scandola, *Inorg. Chem.*, 1965, **4**, 1243; (b) F. Scandola, O. Traverso, V. Balzani, G. L. Zucchini, and V. Carassiti, *Inorg. Chim. Acta*, 1967, **1**, 76; (c) V. Balzani and V. Carassiti, *J. Phys. Chem.*, 1968, **72**, 383.
[77] (a) P. Haake and T. A. Hylton, *J. Amer. Chem. Soc.*, 1962, **84**, 3774; (b) S. H. Goh and C. Y. Mok, *J. Inorg. Nuclear Chem.*, 1977, **39**, 531.
[78] J. R. Perumareddi and A. W. Adamson, *J. Phys. Chem.*, 1968, **72**, 414.
[79] S. H. Mostin and P. Haake, *Chem. Comm.*, 1970, 202.

two-term rate-law (Equation 2) where k_1 refers to solvolysis and k_2 to direct attack by Y[80] (Equation 21). The k_1 term often dominates except when Y is a

$$\begin{tikzcd}
{[PtRCl(PEt_3)_2]} \arrow[r, shift left, "k_1\ \text{solvent}"] \arrow[d, "k_2"', "Y"] & {[PtR(S)(PEt_3)_2]^+ + Cl^-} \arrow[l, shift left, "k_{-1}"] \arrow[dl, "Y\ \text{(fast)}"] \\
{[PtRY(PEt_3)_2]^+ + Cl^-} &
\end{tikzcd} \qquad (21)$$

very strong nucleophile like CN^-, SCN^-, or $SC(NH_2)_2$. Similar, associative, solvent and nucleophile attack routes have been found even in analogous nickel compounds with sterically hindering R groups.[81] It was a comparison of the k_1 terms in methanol and dmso for substitution at the sterically hindered platinum complexes where R = *o*-tolyl or mesityl (2,4,6-trimethylphenyl) which first led to the idea that the solvolytic step might be dissociatively controlled.[82]

Romeo and his co-workers embarked on an investigation of possible dissociative reactions at platinum(II) with a comparison of the rates of isomerisation of *cis*-$[Pt(o\text{-tol})Cl(PEt_3)_2]$ in MeOH or EtOH with the rates of halide substitutions.[82c] The rate-constant for the isomerisation, k_i, was found to be 100 times smaller than the solvolytic part of the substitution process, k_1. Moreover, the solvolysis step in methanol had an entropy of activation, $\Delta S^\ddagger$, of -136 J K^{-1} mol^{-1}, in keeping with an associative process, whereas $\Delta S^\ddagger$ for the isomerisation was positive. The isomerisation was retarded by an excess of Cl^- in solution, and k_i varied inversely with $[Cl^-]$. It was thus concluded that, for the *ortho*-tolyl complex, both the solvolytic and direct nucleophile substitution processes were associative in nature, but the *cis–trans*-isomerisation, on the other hand, was a dissociative process. Scheme 7 was put forward to account for the isomerisation. The "*cis*-like" and "*trans*-like" 3-co-ordinate intermediates, A and B, are essential features of the mechanism.

In a similar comparative study of the bromo-complexes in methanol, the effects of increasing steric hindrance by R were examined.[83] With increasing bulk, particularly in the *ortho*-positions (R = Ph, *p*-tol, *o*-tol, *o*-EtC_6H_4, mesityl), the rates of attack by MeOH (k_1 of the substitution process) were dramatically reduced, but the rates of isomerisation of *cis*-$[PtRBr(PEt_3)_2]$, k_i, were little changed (though they all displayed mass-law retardation by Br^-). For the very hindered complex *cis*-$[Pt(mesityl)Br(PEt_3)_2]$, $k_1 = k_i$ with $\Delta H^\ddagger = 77$ $kJmol^{-1}$ and $\Delta S^\ddagger = -94$ $JK^{-1}mol^{-1}$. It was concluded that for the mesityl complex only, the solvolysis as well as the isomerisation steps proceeded by ligand loss to a 3-co-ordinate species, the *ortho*-substituents on the phenyl ring effectively preventing the usual associative attack by solvent. The negative entropy of activation remained to be explained, however, as did the significant k_2 term in the

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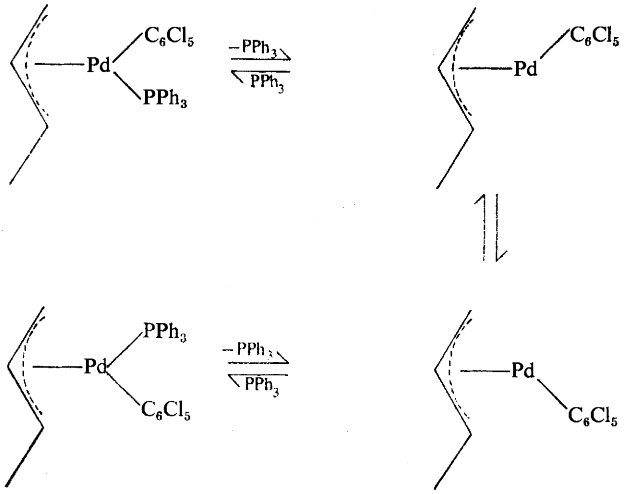
[80] M. Cusumano, P. Marricchi, R. Romeo, V. Ricevuto, and U. Belluco, *Inorg. Chim. Acta*, 1979, **34**, 169.

[81] M. Cusumano and V. Ricevuto, *J.C.S. Dalton*, 1978, 1682.

[82] (a) G. Faraone, V. Ricevuto, R. Romeo, and M. Trozzi, *Inorg. Chem.*, 1969, **8**, 2207; (b) *idem*, *ibid.*, 1970, **9**, 1525; (c) *idem*, *J. Chem. Soc.* (*A*), 1971, 1877.

[83] R. Romeo, D. Minniti, and M. Trozzi, *Inorg. Chem.*, 1976, **15**, 1134.



Scheme 7

substitution reaction between *cis*-[Pt(mesityl)Br(PEt_3)$_2$] and CN^- or SCN^-. The low sensitivity of k_1 to steric crowding was explained in that the immediate 3-co-ordinate "T"-shaped intermediate, A, (Scheme 7) does not relax its geometry on elimination of Br^-. (The interconverting "T"-shaped intermediates are necessary to explain the observed mass-law retardation and stereospecificity of substitution.)

Later work by Romeo and his co-workers[84a] suggests that the methyl and ethyl derivatives *cis*-[PtRCl(PEt_3)$_2$] also isomerise spontaneously in alcohols *via* the dissociative pathway. In summarising evidence for this dissociative mechanism and the occurrence of 3-co-ordinate platinum complexes in general, Romeo[84] also pointed out that the addition of Ag^+ ions to *cis*-organoplatinum halides accelerated their isomerisation,[85] in keeping with this reaction path (Equation 22). Addition of free PEt_3 to solutions of this *o*-tolyl complex did not catalyse the isomerisation.

$$cis\text{-}[Pt(o\text{-tol})Cl(PEt_3)_2] + AgNO_3 \rightarrow trans\text{-}[Pt(o\text{-tol})(NO_3)(PEt_3)_2] + AgCl \qquad (22)$$

A 3-co-ordinate intermediate which changes geometry (this time from *trans*-like to *cis*-like) has also been suggested as the isomerisation route for *trans*-[$PtCl_2L_2$], where L is Me_2SO(dmso), Et_2SO, or Pr_2SO.[11] Sulphoxide substitution at either isomer is stereospecific, and isomerisation is *retarded* by an excess of sulphoxide in solution—quite the reverse of what might be expected

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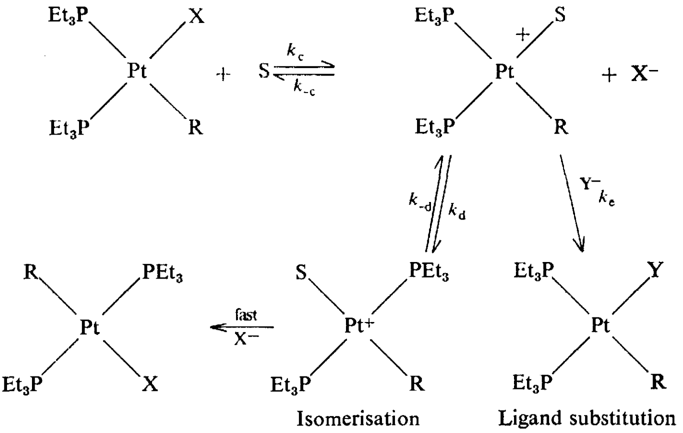
[84] (a) R. Romeo, D. Minniti, and S. Lanza, *Inorg. Chim. Acta*, 1976, **18**, L15; (b) R. Romeo, *Inorg. Chem.*, 1978, **17**, 2040.

[85] F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson, and B. L. Shaw, *J. Chem. Soc.* (*A*), 1961, 2207.

for a nucleophile catalysed process—leading to the suggestion that a dissociative process most likely operates. Similarly, the *cis–trans*-isomerisation of the π-allylpalladium complex [Pd(η^3-crotyl) (C_6Cl_5) (PPh_3)] was found to be retarded by PPh_3 addition. Scheme 8, involving 3-co-ordinate species, was suggested.[86]



Scheme 8

Finally, dissociation of Ph_3P from $[AuMe_2Et(PPh_3)]$ to give a "T"-shaped intermediate which changes geometry has been suggested as the mechanism of isomerisation of that complex.[87] Calculations suggest that the "T"-shaped intermediates would readily interconvert *via* "Y"-shaped species.

The case against kinetic support for such dissociative mechanisms is put in a well-argued paper by van Eldik, Palmer, and Kelm.[88] Concentrating on the triethylphosphine–organoplatinum halides, they point out that the rate-law obtained from steady-state treatment of the dissociative mechanism (Scheme 7), Equation 23, is identical in form with that for the isomerisation part of Scheme

$$k_{obs} = \frac{k_a k_b}{(k_{-a}[Cl^-] + k_b)} \tag{23}$$

9, in which the halide is released *via* the usual associative attack of solvent (usually MeOH) (24). The reverse steps (k_{-b} and k_{-d}) are negligible in both

$$k_{obs} = \frac{k_c k_d}{(k_{-c}[X] + k_d)} \tag{24}$$

cases. The solvolysis step is, of course, identical with that of the first step of ligand displacement (Scheme 9). The differences in the values obtained for k_c and

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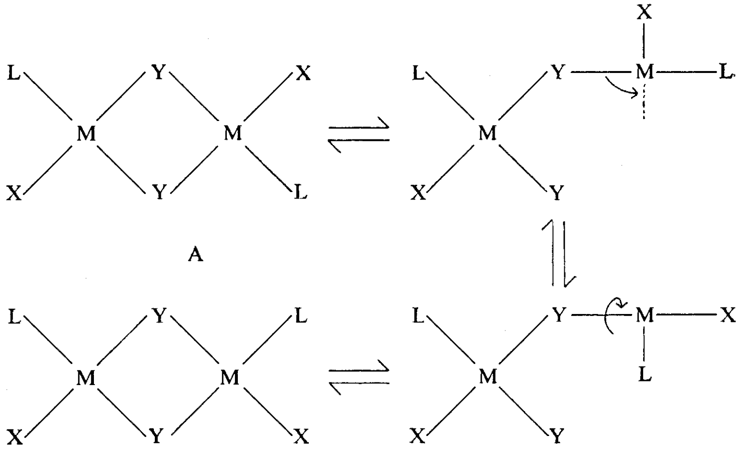
[86] H. Kurosawa and S. Numata, *J. Organometallic Chem.*, 1979, **175**, 143.

[87] S. Komiya, T. A. Albright, R. Hoffmann, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1976, **98**, 7255.

[88] R. van Eldik, D. A. Palmer, and H. Kelm, *Inorg. Chem.*, 1979, **18**, 572.

k_a (except when R = mesityl) were mainly responsible for the suggestion by Romeo *et al.* that isomerisation proceeded *via* Scheme 7.[82–84] Kelm and his co-workers suggest instead that the isomerisation reactions follow Scheme 9 (solvent association, displacing X^-), but the solvolysis step is so fast that it can be considered as a pre-equilibrium to isomerisation. The rate expression is now given by Equation 25. The measured rate constants in the absence of $[X^-]$



Scheme 9

$$k_{obs} = \frac{k_d K_c}{[X^-] + K_c} \qquad (25)$$

would refer to k_d, not k_c, explaining the differences observed between isomerisation and solvolysis. The negative values obtained for $\Delta S^\ddagger$ by this treatment are in accord with associative processes, and the insensitivity of k_i to R is explained. When R = mesityl, however, k_c and k_{-c} are no longer much greater than k_d, due to steric hindrance, so the pre-equilibrium treatment is no longer valid. The steady-state treatment must be used, this time leading to $k_{obs} = k_c$. Thus with the mesityl complex, the identity of k_i and k_1 found by Romeo *et al.*[83] can be explained as both reactions involving a common, *associative*, solvolysis step, instead of both proceeding *via* the same halide *dissociation*. Kelm and his co-workers also measured volumes of activation for the reactions, and interpreted these, too, as favouring associative processes.[88]

For the time being the controversy over the operation of dissociative processes at some square-planar complexes remains.[89] Considering on the one hand the wealth of evidence in favour of associative processes, and the importance of solvation of even 4-co-ordinate species (*vide supra*), compelling and unambiguous evidence should be required before the formation of 3-co-ordinate intermediates

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[89] R. Romeo, D. Minniti, and S. Lanza, *Inorg. Chem.*, 1979, **18**, 2362.

is accepted. On the other hand, it must be kept in mind that several different complexes have now been postulated to isomerise dissociatively, and several other reactions of elements in this part of the Periodic Table have been postulated to proceed *via* such 3-co-ordinate species.

For example, key intermediates in the process of olefin insertion into the Pt–H bond,[84,90] and its reverse, the β-elimination step,[91] are believed to be 3-co-ordinate. So also are intermediates in the CO insertion into the Pt–R bond,[92] and its reverse,[93] and 3-co-ordinate species may be involved in cleavage reactions of Pt–R by HX.[94] All these species would be formally 14-electron compounds, and might be expected to be very reactive. It can be kept in mind, however, that some 14-electron species have even been isolated and structurally investigated,[95] including $[Rh(PPh_3)_3]^+$, which has a geometry near "T" shaped.[96] As a counter-example, however, $[PtI\{C_6H_3Me(CH_2NMe_2)_2\}]BF_4$ can be quoted, in which Pt binds to a "saturated" aromatic carbon atom rather than remain co-ordinatively unsaturated.[97] The rhodium complex cited above also has a close approach of a phenyl group at its "vacant site".[96]

Many of the reactions thought to involve 3-co-ordinate "T"-shaped intermediates were performed in methanol, a powerfully co-ordinating solvent, known to promote isomerisation by chloride ion displacement in at least one case,[37] though the suggestion[43] that solvent-eliminated halide might displace a neutral ligand and thus lead to isomerisation does not agree with the evidence.[84b] The preferred geometry for the "T"-shaped intermediates is unclear. "*cis*-Like" is converted readily into "*trans*-like" in the isomerisations studied by Romeo *et al.*, but the equilibrium must lie at the other extreme in the cases of olefin insertion into Pt–H.[84]

Perhaps the final comment should be that if the isomerisations described in this section do not proceed by 3-co-ordinate intermediates, their mechanism remains unknown. For example the isomerisation step in Scheme 9 (k_d/k_{-d}) suggested by Kelm *et al.* is completely uninformative as to how the geometry change comes about. Whilst there are plenty of possibilities previously discussed, most of them involving solvation or nucleophile attack, it can equally be said that many other as yet unexplained isomerisations could conceivably proceed by

[90] (a) H. C. Clark and C. J. Jablonski, *Inorg. Chem.*, 1974, **13**, 2213; (b) H. C. Clark and C. S. Wong, *J. Amer. Chem. Soc.*, 1974, **96**, 7213.

[91] G. M. Whitesides, J. F. Gaash, and E. R. Stedronski, *J Amer. Chem. Soc.*, 1972, **94**, 5258.

[92] (a) G. K. Anderson and R. J. Cross, *J.C.S. Dalton*, 1979, 1246; (b) C. J. Wilson, M. Green, and R. J. Mawby, *J.C.S. Dalton*, 1974, 1293; (c) R. W. Glyde and R. J. Mawby, *Inorg. Chem.*, 1971, **10**, 854.

[93] M. Kubota, R. K. Rothcock, and J. Geibel, *J.C.S. Dalton*, 1973, 1267.

[94] (a) R. Romeo, D. Minniti, S. Lanza, P. Uguagliati, and U. Belluco, *Inorg. Chem.*, 1978, **17**, 2813; (b) R. Romeo, D. Minniti, and S. Lanza, *J. Organometallic Chem.*, 1979, **165**, C36.

[95] (a) W. Kuran and A. Musco, *Inorg. Chim. Acta*, 1975, **12**, 187; (b) M. Matsumoto, Y. Yoshioka, K. Nakatsu, T. Yoshida, and S. Otsuka, *J. Amer. Chem. Soc.*, 1974, **96**, 3322; (c) M. Green, J. K. Howard, J. L. Spencer, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1975, 3.

[96] Y. W. Yared, S. L. Miles, R. Bau, and C. A. Reed, *J. Amer. Chem. Soc.*, 1977, **99**, 7076.

[97] G. van Koten, K. Timmer, J. G. Noltes, and A. L. Spec, *J.C.S.Chem. Comm.*, 1978, 250.

the 3-co-ordinate route. Possible candidates are certain platinum carbonyl derivatives,[23,92a] and binuclear complexes (*vide infra*). The best conclusion to this section may be that whilst it appears unnecessary to invoke the dissociative mechanism to explain many isomerisation processes at present, its operation under certain conditions cannot be ruled out and it should be kept in mind as a viable possibility.

5 Binuclear Compounds

We refer to complexes with bridging ligands of the type A in Scheme 10, rather than derivatives with metal–metal bonds. The metal–metal bonds of the latter can be regarded as normal covalent links, and each metal centre can then be regarded in the same way as mononuclear complexes. For the bridged-ligand compounds, however, whilst it is likely that the same mechanisms and factors affecting mononuclear derivatives will apply to them too, additional reaction paths *via* bridge-opening could be available.

For platinum derivatives with bridging halides (A, Scheme 10, M = Pt; Y = halide; L = tertiary phosphine or arsine), there is a tendency to exist in solution as *cis*- and *trans*-isomers which readily interconvert at a rate commensurate with the n.m.r. timescale.[98] With halide terminal groups (X), the *trans*-isomers predominate,[99,100] with mixtures when X is aryl or acyl[98,101] and *cis*-isomers are to the fore with X = Me.[102] Stronger bridging groups such as thio (RS) and phosphido (R_2P) slow the rate of isomerisation and *cis*- and *trans*-isomers can sometimes be isolated.[99] Palladium complexes appear to favour *trans*-geometry, though data are sparse as compared with platinum derivatives. With complexes less symmetrical than A, (differing bridge ligands, *etc.*)[99] data are too limited for meaningful generalisations to be made.

Nucleophilic attack on bridged complexes $[Pt_2X_4L_2]$ follows the same two-term rate-law as ligand-displacement reactions of mononuclear derivatives,[103] and there is no reason to suspect a mechanism other than the usual associative one involving solvent and/or nucleophile. It is therefore not surprising that traces of tertiary phosphine (L) catalyse the *cis–trans*-interconversion of the thiolate-bridged complexes $[Pt_2Cl_2(\mu\text{-SR})_2L_2]$,[99] presumably *via* the usual associative pathways of consecutive displacement or pseudorotation.

Pearson and Muir[103] reported that bridge-opening reactions are much faster than substitution reactions at mononuclear derivatives, and this is no doubt responsible for the rapid spontaneous isomerisation of many of these derivatives.[98] It seems probable that such reactions will be solvent-catalysed, though a spontaneous single-bridge opening followed by a geometry-change at the

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[98] G. K. Anderson, R. J. Cross, L. Manojlovic-Muir, K. W. Muir, and T. Solomun, *J. Organometallic Chem.*, 1979, **170**, 385.

[99] J. Chatt and J. M. Davidson, *J. Chem Soc.*, 1964, 2433.

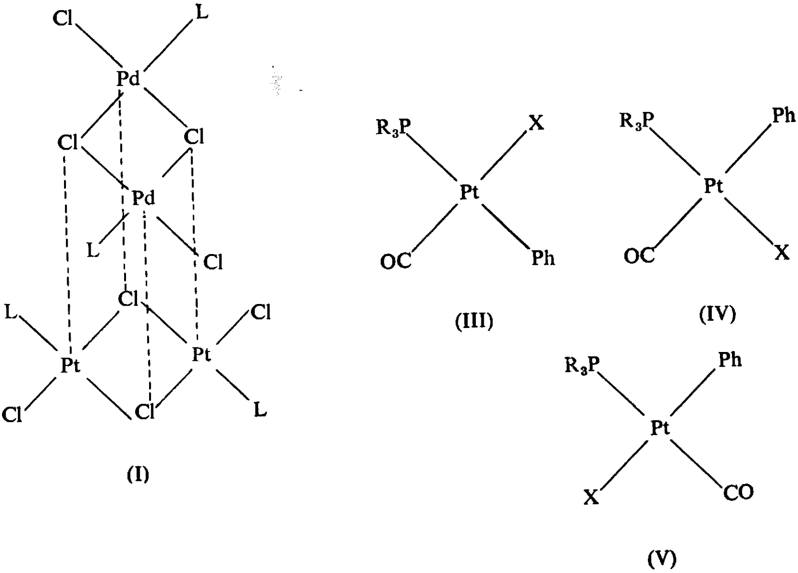
[100] (a) C. Crocker and P. L. Goggin, *J. Chem. Research*, 1978, S93; M1274. (b) R. G. Goel and R. G. Montemayor, *J. Coord. Chem.*, 1978, **8**, 1.

[101] C. Eaborn, K. J. Odell, and A. Pidcock, *J.C.S. Dalton*, 1978, 1288.

[102] R. J. Puddephatt and P. J. Thompson, *J.C.S. Dalton*, 1977, 1219.

[103] R. G. Pearson and M. M. Muir, *J. Amer. Chem. Soc.*, 1966, **88**, 2163.

"T"-co-ordinated platinum (analogous to Romeo's suggested dissociative route) is possible. If this route operates at all, it is likely to apply to these complexes, where the longer, weaker, bridge bonds[98,103] will be more likely both to open spontaneously, and change bond-sites spontaneously. Scheme 10 depicts such a route. Isomerisations of halide-bridged, dimeric π-allylpalladium compounds have been reported, sometimes following ligand dissociations,[104] and single bridge openings may well be involved.[105]



(I)

(III)

(IV)

(V)

Scheme 10

Another alternative mechanism is suggested by the work of Masters and his co-workers.[106] Equimolar solutions of $[Pt_2Cl_4L_2]$ and $[Pd_2Cl_4L'_2]$ react to form some of the mixed complex $[PdPtCl_4LL']$, and all three exist together in dynamic equilibrium. Kinetic studies indicate that a possible route for this reaction is *via* a dimer–dimer association of type (I), and such an association could clearly lead to *cis–trans*-isomerisation in either single or mixed complexes. (Similar tetranuclear intermediates have been suggested to account for some dynamic processes in allylpalladium dimers.[106]) No neutral-ligand (tertiary phosphine) dissociation accompanies this reaction,[107] ruling out auto-catalysis and other isomerisation routes involving ligand transfer from one metal to another. Such

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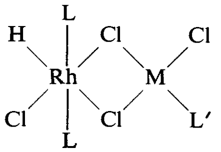
[104] J. W. Faller and M. J. Mattina, *Inorg. Chem.*, 1972, **11**, 1296.

[105] K. Vrieze, P. Cossee, A. P. Praat, and C. W. Hilbers, *J. Organometallic Chem.*, 1968, **11**, 353.

[106] D. L. Tibbetts and T. L. Brown, *J. Amer. Chem. Soc.*, 1969, **91**, 1108.

[107] A. A. Kiffen, C. Masters, and J. P. Visser, *J.C.S. Dalton*, 1975, 1311.

routes cannot altogether be dismissed, however, as phosphine transfer has been observed to accompany the decomposition of the asymmetrical complexes, (II) (Equation 26).[108] Ligand exchange *via* transient bridge-formation (eletrophilic attack) is also an observed mechanism at square-planar complexes,[102,109] and could conceivably lead to isomerisation *via* one of the routes discussed.



(II)

$\rightarrow$ $[MCl_2LL']$ (26)

M = Pd or Pt

Finally, the ready isomerisation of halide-bridged square-planar complexes means that the production of these species as intermediates might afford an isomerisation pathway for other complex types. Such appears to be the case for the three isomers (III—V). Their isomerisation involves reversible loss of CO or R_3P,[52,92a] and interconverting *cis*- and *trans*-binuclear complexes seem likely intermediates.

6 Conclusions

The isomerisation reactions of square-planar compounds have become a rewarding field of study, revealing many mechanistic variations. Whilst these may be as fundamentally diverse as associative or dissociative processes, it is still quite possible that the majority of them may ultimately be recognised as conforming to one basic associative route. In either case, the processes are much more subtle than was once thought and, as indicated throughout, the implications to other reactions can be very profound, and threaten the security of even the most basic concepts in the mechanistic chemistry of these complexes.

Pervading the entire review, a major, yet often neglected, consideration has been the effects of solvation on the square-planar complexes. Solvents co-ordinate to the metals and in many cases are known to cause geometry changes or displace ligands. The groups displaced range from strongly-bonded tertiary phosphines to halide ions, and even non-polar solvents like benzene may not be innocent in this respect. The species so produced may be in low concentration but can be highly reactive and could be responsible for some reactions. It has been shown also that the eliminated groups themselves are free to catalyse reactions elsewhere.

It is apparent, too, that visible light could have an effect on some isomerisations, and therefore on other reactions related to them. Like solvent effects, this is frequently neglected during studies on square-planar complexes. Obviously such details should be kept in mind or important information could be overlooked.

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[108] R. Huis and C. Masters, *J.C.S. Dalton*, 1976, 1796.

[109] (a) J. P. Visser, W. W. Jager, and C. Masters, *Rec. Trav. Chim.*, 1975, **94**, 70; (b) R. J. Puddephatt and P. J. Thompson, *J. Organometallic Chem.*, 1979, **166**, 251; (c) *idem*, *J.C.S. Dalton*, 1975, 1810; (d) *idem*, *ibid.*, 1976, 2091.