trans to *cis* Isomerisations of Platinum(II) Olefin Phosphine Complexes, $[PtX_2(ol)(PR_3)]$ (X = Cl or Br; ol = Ethene, Propene, or 1-Heptene; PR_3 = PBu_3 or PMe_2Ph)

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Isomerisation reactions of *trans*-$[PtX_2(ol)(PR_3)]$ (X = Cl or Br; ol = ethene, propene, or 1-heptene; PR_3 = PBu_3 or PMe_2Ph), formed by treating $[Pt_2X_4(PR_3)_2]$ with olefin, have been examined by ^{31}P n.m.r. spectroscopy in $CDCl_3$ solution with both excess and deficiency of olefin. The *trans* isomers readily lose olefin and equilibrate with the halide-bridged dimers. The positions of these equilibria are dependent upon incident light. The more stable *cis* isomers steadily form in these solutions, but whereas the rate of *trans* to *cis* isomerisation is markedly retarded by excess olefin when X = Cl, it is slightly increased when X = Br. Exchange of free and co-ordinated olefins is rapid with all the complexes compared to the isomerisation rate. The mechanisms of these reactions are discussed and it is concluded that, in addition to photochemical processes, more than one isomerisation pathway operates. A dissociative route predominates for the chloride compounds but an associative process is more important for the bromide complexes. Related studies have been performed on the dimethyl sulphoxide analogues, *cis*- and *trans*-$[PtX_2(dmso)(PR_3)]$, and broadly similar results were obtained, emphasising the similarity between the ligand properties of olefin and dmso at platinum.

Many compounds of the type *cis*-$[PtX_2(ol)(PR_3)]$ (X = Cl or Br, ol = olefin, R = alkyl or aryl) have been isolated.[1-9] The most common preparative route involves cleaving the halide bridges of $[Pt_2X_2(\mu\text{-}X)_2(PR_3)_2]$ by the olefin. By analogy to the cleavage of $[Pt_2X_2(\mu\text{-}X)_2(PR_3)_2]$ by carbon monoxide,[1] it has generally been assumed that the reactions produced first the *trans* compounds as transient species,[4] followed by a slower formation of the more stable *cis* complexes. It has been demonstrated by use of ^{31}P n.m.r. spectroscopy that this sequence indeed occurs in the reactions of these diplatinum compounds with 3-hydroxyalkenes,[6] vinyl and allyl acetates,[7] allene,[8] and 1,3-butadiene.[9]

The reactions of CO with $[Pt_2X_4(PR_3)_2]$ have recently been examined in detail, and the main isomerisation route of *trans*-$[PtX_2(CO)(PR_3)]$ to the *cis* complex was shown to be autocatalytic, dependent on CO eliminated from the *trans* isomer in solution, equation (1).[10] Here we report the results of

$$[Pt_2X_4(PR_3)_2] + 2\,CO \rightleftharpoons trans\text{-}[PtX_2(CO)(PR_3)] \xrightarrow{CO} cis\text{-}[PtX_2(CO)(PR_3)] \quad (1)$$

a similar study of olefin analogues and show that the formation and isomerisation of *cis*- and *trans*-$[PtX_2(ol)(PR_3)]$ (ol = ethene, propene, or 1-heptene; PR_3 = PBu_3 or PMe_2Ph) are more complicated than those of their carbonyl analogues.

Results and Discussion

Reactions of the appropriate halide-bridged diplatinum complexes with C_2H_4 or propene (C_3H_6) followed descriptions in previous reports, and white crystalline samples of *cis*-$[PtCl_2(C_2H_4)(PMe_2Ph)]$,[5] *cis*-$[PtCl_2(C_3H_6)(PMe_2Ph)]$, *cis*-$[PtBr_2(C_2H_4)(PMe_2Ph)]$, *cis*-$[PtCl_2(C_2H_4)(PBu_3)]$,[1] and *cis*-$[PtBr_2(C_2H_4)(PBu_3)]$ were readily isolated. Their ^{31}P n.m.r. parameters are listed in the Table.

When the reactions were followed by ^{31}P n.m.r. spectroscopy in $CDCl_3$ solution, in each case the formation of the *cis* compounds was preceded by the appearance of resonances from another mononuclear platinum complex. We assign these signals to the *trans* isomers of $[PtX_2(ol)(PR_3)]$ (values in the Table), in view of their subsequent behaviour (see below) and by analogy to the few related compounds previously described.[6-9]

Table. ^{31}P N.m.r. parameters for olefin and dmso complexes, $[PtX_2(ol)(PR_3)]$ *

			cis Isomer		*trans* Isomer	
L	X	ol	δ/p.p.m.	J_{PPt}/Hz	δ/p.p.m.	J_{PPt}/Hz
PMe_2Ph	Cl	C_2H_4	−10.0	3 091		
			(−8.0)	(3 090)	(−10.0)	(3 467)
PMe_2Ph	Br	C_2H_4	−9.3	3 010		
			(−6.5)	(3 006)	(−12.2)	(3 343)
PBu_3	Cl	C_2H_4	5.0	3 041	5.8	3 440
			(7.2)	(3 054)	(6.0)	(3 383)
PBu_3	Cl	C_3H_6	4.1	3 088	5.3	3 459
					(5.2)	(3 399)
PBu_3	Cl	C_7H_{14}	3.6	3 089	4.7	3 468
					(5.2)	(3 364)
PBu_3	Br	C_2H_4	5.2	2 964	3.8	3 346
			(7.5)	(2 962)	(4.0)	(3 265)
PBu_3	Br	C_3H_6			(2.5)	(3 298)
PBu_3	Cl	dmso	9.8	3 411	2.9	3 121
PBu_3	Br	dmso	10.0	3 346	−0.5	3 012

* Recorded at ambient temperatures in $CDCl_3$ (values in parentheses recorded at −60 °C); external standard 85% H_3PO_4.

Reactions of the dimethylphenylphosphine complexes were always accompanied by precipitation of the *cis* olefin compounds. The reactions of the tributylphosphine complexes, on the other hand, were not accompanied by precipitation of any products from solution, so these were chosen for a more detailed investigation. Equilibria were established between the binuclear complexes and *trans*-$[PtX_2(ol)(PBu_3)]$, equation (2). These

$$[Pt_2X_4(PBu_3)_2] + 2\,ol \overset{K}{\rightleftharpoons} 2\,trans\text{-}[PtX_2(ol)(PBu_3)] \quad (2)$$

could be maintained at low temperature, and at −60 °C there was no tendency to form the *cis* isomer. Olefin loss from the *trans* products was a rapid and facile process. Bubbling nitrogen through the solutions completely removed the volatile olefins

ethene and propene in less than 1 min at room temperature, and in under 1 h at −60 °C. Attempts to isolate any of the *trans* complexes (including those of PMe_2Ph) by freeze-evaporation of benzene solutions failed, the olefins being lost at low pressure.

Comparisons with the analogous carbonyl compounds are interesting. Formation of *trans*-$[PtX_2(CO)(PR_3)]$ (X = Cl or Br) is essentially complete in solution, loss of CO from these compounds is slower, and they can (with some difficulty) be isolated.[10] This indicates that the *trans* olefin compounds are less stable than their CO analogues. That this is also the case for the *cis* isomers has already been reported.[1-3]

The equilibria of equation (2) are sensitive to temperature, the nature of the halide and olefin, and to light. As expected, lowering the temperatures markedly moves the equilibria to the right. The new positions are reached quite rapidly, being established in several minutes even at −60 °C. The effect of the halides is also as expected, the olefin complex being favoured by chloride over bromide. No iodide complexes were formed at all from the olefins studied [ethene, propene, and 1-heptene (C_7H_{14})], and this sequence follows the bridge-strength sequence of I > Br > Cl for the dimeric compounds.

For the chloride system the equilibria (2) were similar for ol = C_2H_4 and C_3H_6, K being greater for both than when ol = C_7H_{14}. With the bromide complexes, K for the ethene system was substantially larger than for ol = C_3H_6 or C_7H_{14}. Indeed, no *trans*-$[PtBr_2(ol)(PBu_3)]$ could be observed for these latter two olefins, at one atmosphere pressure of C_3H_6 or even a 20-fold excess of C_7H_{14}.

The effect of diffuse daylight on equilibria (2) is to displace them to the left. Observed at room temperature over several hours, the ratios of $[Pt_2Cl_4(PBu_3)_2]$ to *trans*-$[PtCl_2(ol)(PBu_3)]$ (ol = C_2H_4 or C_3H_6) were consistently greater in the light. Under these conditions *cis*-$[PtCl_2(ol)(PBu_3)]$ is steadily produced over *ca.* 24 h {at −60 °C, when formation of the *cis* isomer would be suppressed, the dimer/*trans*-$[PtCl_2(ol)(PBu_3)]$ equilibria were displaced too far for reliable measurement} but the attainment of the equilibria in question took only a few minutes and measurements seemed consistently reliable (see Figure). The changes in equilibria positions are most probably caused by light-induced eliminations of olefin from *trans*-$[PtCl_2(ol)(PBu_3)]$, which are yellow-green.

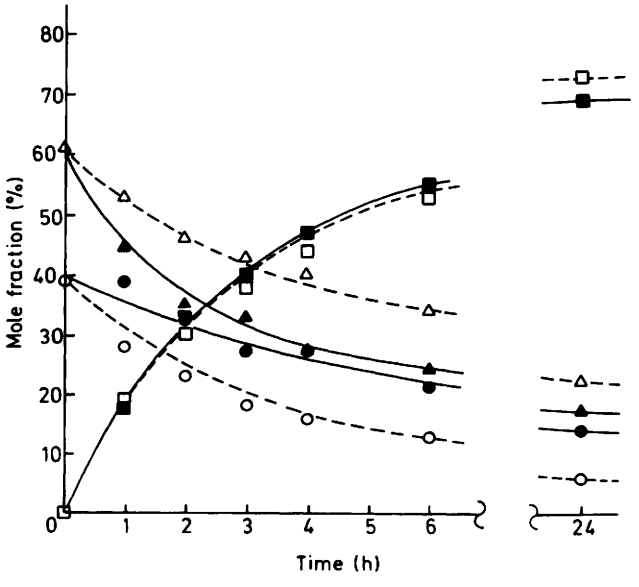


Figure. Products from the reaction between $[Pt_2Cl_4(PBu_3)_2]$ and propene in daylight (———) and darkness (– – –). (●) and (○), $[Pt_2Cl_4(PBu_3)_2]$; (▲) and (△), *trans*-$[PtCl_2(C_3H_6)(PBu_3)]$; (■) and (□), *cis*-$[PtCl_2(C_3H_6)(PBu_3)]$, in light and dark, respectively

The *trans* complexes readily undergo olefin-exchange reactions. Bubbling propene into $CDCl_3$ solutions of *trans*-$[PtCl_2(C_2H_4)(PBu_3)]$ for 2 min at −60 °C caused complete conversion to the propene compound, and the procedure could be reversed by treating the resultant propene complex with ethene, equation (3). It seems likely that these reactions are

$$\textit{trans}\text{-}[PtCl_2(C_2H_4)(PBu_3)] \underset{C_2H_4}{\overset{C_3H_6}{\rightleftharpoons}} \textit{trans}\text{-}[PtCl_2(C_3H_6)(PBu_3)] \quad (3)$$

associative. Although olefin loss from *trans* compounds to reform the diplatinum species could possibly be a dissociative process,* the time to remove all olefin from the samples by bubbling N_2 through the solutions is considerably longer under these conditions. Also, treatment of *trans*-$[PtBr_2(C_2H_4)(PBu_3)]$ by C_3H_6 resulted in formation of *trans*-$[PtBr_2(C_3H_6)(PBu_3)]$ (it subsequently lost C_3H_6). This compound could not be made by bubbling C_3H_6 through $[Pt_2Br_4(PBu_3)_2]$, so it seems improbable that these olefin-exchange reactions should proceed by elimination of one olefin followed by co-ordination of the next.

Interestingly, we also find that *cis*-$[PtCl_2(ol)(PBu_3)]$ complexes undergo equally rapid exchange reactions, equation (4),

$$\textit{cis}\text{-}[PtCl_2(C_2H_4)(PBu_3)] \underset{C_2H_4}{\overset{C_3H_6}{\rightleftharpoons}} \textit{cis}\text{-}[PtCl_2(C_3H_6)(PBu_3)] \quad (4)$$

again presumably by an associative route. This exchange reaction has been used preparatively in previous work.[2]

Interpretation of the formation of *cis*-$[PtX_2(ol)(PR_3)]$ from solutions containing the *trans* isomer is more difficult than in the cases of analogous carbonyl complexes for two reasons. First, because *trans*-$[PtX_2(ol)(PR_3)]$ equilibrate with $[Pt_2X_4(PR_3)_2]$, free olefin is always present and *trans* to *cis* isomerisations of $[PtX_2(ol)(PR_3)]$ cannot be examined in its absence. Secondly, *cis*-$[PtX_2(ol)(PR_3)]$ cannot be regarded as a final 'sink' for the olefin and platinum dimer in the way that *cis*-$[PtX_2(CO)(PR_3)]$ can in the carbonyl cases, since *cis*-$[PtX_2(ol)(PR_3)]$ can lose olefin in solution. Open $CDCl_3$ solutions of *cis*-$[PtBr_2(C_2H_4)(PBu_3)]$ largely reverted to $[Pt_2Br_4(PBu_3)_2]$ in 30 min, although the chloro analogue required 4 d. Similarly, bubbling N_2 through a suspension of *cis*-$[PtBr_2(C_2H_4)(PMe_2Ph)]$ for 1 h produced 60% of $[Pt_2Br_4(PMe_2Ph)_2]$: the chloro analogue was unaffected in this time interval.

Formation of the *cis* isomers was followed in $CDCl_3$ by ^{31}P n.m.r. spectroscopy for three systems: $[Pt_2Cl_4(PBu_3)_2]$ and C_2H_4, $[Pt_2Cl_4(PBu_3)_2]$ and C_3H_6, and $[Pt_2Br_4(PBu_3)_2]$ and C_2H_4. In each case the olefin was bubbled through the solution of platinum complex for 1 min at room temperature, and the solution was then divided between two sealed n.m.r. tubes. One part was kept dark, and the other was exposed to artificial light and daylight. Both were regularly monitored over 24 h at room temperature, after which most of the material was in the form of *cis*-$[PtX_2(ol)(PBu_3)]$. The Figure shows a typical result for the

* Though the majority of ligand replacement reactions at Pt^{II} are associative, some dissociative processes are known.[11] It should be kept in mind, however, that simply because olefin is eliminated, the mechanism does not have to be dissociative. A bimolecular reaction involving μ-Br formation *via* a bromine atom of one molecule interacting with another molecule is feasible. Also, even if the olefin is dissociatively eliminated from one *trans*-$[PtX_2(ol)(PR_3)]$, it is likely that the ensuing three-co-ordinate species would be very reactive (none has been observed), and would react associatively with the next *trans*-$[PtX_2(ol)(PR_3)]$.

reaction of $[Pt_2Cl_4(PBu_3)_2]$ with C_3H_6, that with C_2H_4 is broadly similar.

The most striking feature is that the rates of formation of the *cis* chloro complexes are much the same in the light as in the dark, despite the fact that the concentrations of the starting materials, equilibria (2), are different. One explanation is that the smaller concentration of *trans* complex in the light reactions isomerises more rapidly due to photochemical processes. Alternatively, there may be more than one reaction path leading to the *cis* compounds, and the rate effects of concentration changes cancel by coincidence.

Formation of the *cis* bromo complex is much faster than the chloro analogues. Indeed the concentration of the *trans*-$[PtBr_2(C_2H_4)(PBu_3)]$ remains too low for accurate measurement, and samples of *trans* bromo complexes could not be prepared in the absence of some *cis* isomer except at low temperatures (−60 °C). That *trans* bromo complexes convert to *cis* isomers at lower temperatures than do the analogous chloro derivatives has been reported previously,[6] and this seems to be a general phenomenon. *cis*-$[PtBr_2(C_2H_4)(PMe_2Ph)]$ also formed more rapidly than its chloro analogue, but precipitation of the complexes from solution prevented accurate comparison.

Additional information was obtained by observing the isomerisations with additional olefin present by maintaining a constant stream of the gas through the solution. The rate of formation of *cis*-$[PtCl_2(C_2H_4)(PBu_3)]$ was slowed by a factor of three, whereas the formation rate of *cis*-$[PtBr_2(C_2H_4)(PBu_3)]$ was slightly increased. [The position of equilibrium (2) lies well to the left in the bromo case, so additional olefin will have a less marked effect; there is always a large amount in solution.] These observations contrast markedly with the related carbonyl system, where excess CO catalysed *trans* to *cis* conversions in every case.[10] The reaction of $[Pt_2Cl_4(PBu_3)_2]$ with 1-heptene was also examined. Despite an unfavourable equilibrium in the formation of *trans*-$[PtCl_2(C_7H_{14})(PBu_3)]$, the *cis* isomer was formed slowly. With a 20-fold excess of olefin, however, formation of *cis*-$[PtCl_2(C_7H_{14})(PBu_3)]$ was exceedingly slow, requiring 5 d at room temperature to reach 70% completion. No reaction was observed between $[Pt_2Br_4(PBu_3)_2]$ and 1-heptene, even with a large excess of olefin.

With such a complex system, it is difficult to establish which mechanisms operate from the many plausible isomerisation pathways available to square-planar compounds.[12] The most straightforward route to the *cis* complexes would be by direct cleavage of the halide-bridged dimers, equation (5): this could

$$cis\text{-}[PtX_2(ol)(PR_3)] \underset{k}{\overset{\text{slow}}{\longleftarrow}} [Pt_2X_4(PR_3)_2] + 2\,ol \underset{\text{fast}}{\overset{K}{\rightleftharpoons}} 2\,trans\text{-}[PtX_2(ol)(PR_3)] \quad (5)$$

steadily compete with the faster but reversible formation of the *trans* isomers. The operation of such a route has previously been suggested for carbonyl reactions,[1] though it has subsequently been shown to be unimportant in that system.[10] Two observations from the olefin system are consistent with the operation of equation (5): the faster formation of *cis* bromo complexes and the inhibition of the isomerisation of *trans* chloro complexes by excess olefin. The smaller value of the equilibrium constant, K, when X = Br means that both concentrations of $[Pt_2X_4(PR_3)_2]$ and olefin are substantially increased. The inhibition by olefin arises because depletion of $[Pt_2X_4(PR_3)_2]$ by equilibrium K depends on $[ol]^2$, whereas the rate of formation of the *cis* isomer is first order in [ol];* thus overall the rate of formation of *cis*-$[PtX_2(ol)(PR_3)]$ varies inversely with [ol].

The effect of light is to reduce K (photochemical eliminations of olefins from *trans* and *cis* amine complexes are well known[14]), and if equation (5) is the only, or dominant, route to *cis*-$[PtX_2(ol)(PR_3)]$ the rates of the reactions should be increased. Since the rates are not appreciably affected it can be concluded at least that this route is not the only one operating. Also, the fact that $[Pt_2Br_4(PBu_3)_2]$ fails to react even with a 20-fold excess of 1-heptene could be taken as evidence against the operation of equation (5). Thus, on balance, the operation of this route must be regarded as not proven; though it could operate in some cases, it cannot be the only active pathway. The apparent lack of olefin inhibition of the isomerisation of *trans*-$[PtBr_2(C_2H_4)(PBu_3)]$ also casts doubt on the importance of reaction (5).

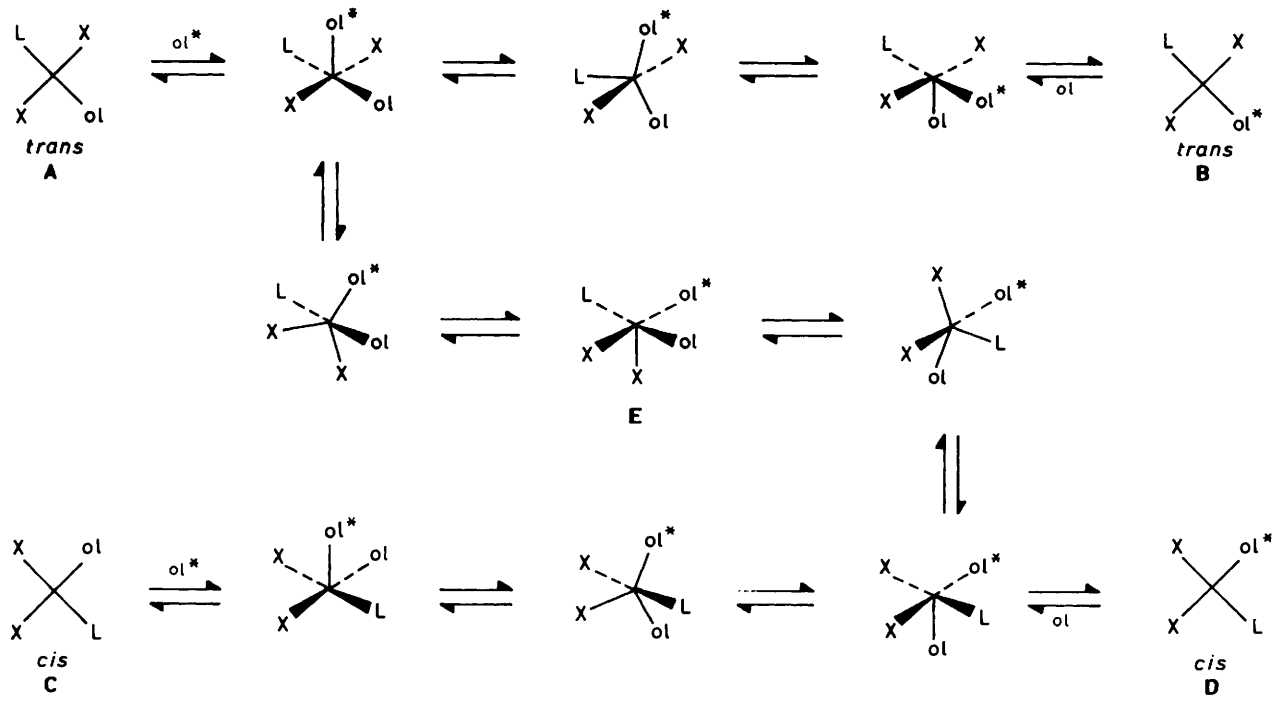
Non-dissociative photochemical isomerisation of square-planar complexes,[12] including olefin derivatives,[14a,c] is known and it is likely that some contribution from the isomerisation of *trans*- to *cis*-$[PtX_2(ol)(PR_3)]$ in the present case derives from such a route in daylight.

Catalytic isomerisation *via* nucleophilic attack is the most common route found in square-planar complexes.[12] Reactions proceed either by associative consecutive ligand displacement, or by pseudorotation of the five-co-ordinate intermediate, descriptions which can be regarded as extremes of a single process.[11,12] This appears to be the most important isomerisation route of *trans*-$[PtX_2(CO)(PR_3)]$, and with additional CO as catalyst, the pseudorotation process seems the most likely mechanism.[10] The operation of such a mechanism in the present work is an attractive possibility, since both *trans*- and *cis*-$[PtX_2(ol)(PR_3)]$ undergo rapid associative olefin exchange. In the Scheme, the direct pathways from **A** to **B** and from **C** to **D** represent the conventional stereoretentive associative ligand exchanges at *trans*- and *cis*-$[PtX_2(ol)(PR_3)]$, respectively. It can be seen that pseudorotation of the five-co-ordinate intermediates *via* species **E** can lead to isomerisation. (Loss of X^- from **E** followed by subsequent reattack would convert the process to consecutive displacement, with the same overall result.)

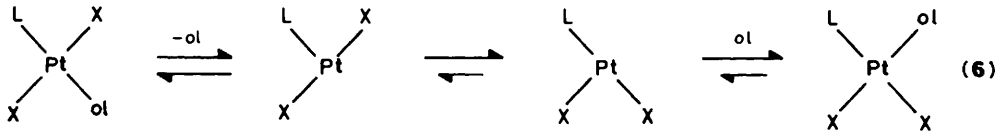
Attractive though this mechanism is, the inhibition by excess olefin of the *trans* to *cis* isomerisations of the chloro complexes indicates against the operations of this route. Thus, whilst its involvement cannot be completely discounted, the case cannot be made that it is of major importance in these olefin complexes.

One further possibility needs to be considered. Dissociation of a ligand from a square-planar complex to form a three-co-ordinate T-shaped intermediate which can change shape prior to the rejoining of the lost ligand has proved to be one of the most controversial isomerisation pathways proposed.[12] Recently, however, the importance of solvation, of the leaving group as well as the three-co-ordinate species, has been demonstrated,[11,15] and evidence for the operation of dissociative pathways in ligand exchange has continued to grow. Examples include the loss of weakly bonding ligands, usually from opposite ligands of high *trans* influence.[16] This can clearly apply to the present situation, with readily replaceable olefin *trans* to a tertiary phosphine. At the very least 'spontaneous' loss of olefin from *trans*-$[PtX_2(ol)(PR_3)]$ might initiate reformation of the dimer, equation (2), and a geometry change could lead directly to the observed isomerisation, equation (6). This mechanism fits the observed retardation by excess olefin of the isomerisation of the chloro complexes. The faster reactions of the bromo complexes are not so easy to explain, however, as they would require a marked *cis* effect to speed the initial olefin loss, or a faster (and rate-determining) geometry change of the T-shaped intermediate. Neither possibility seems wholely convincing; therefore, as with the other routes discussed, this mechanism, though plausible, cannot claim dominance.

* Attack of the first nucleophile in bridge-cleavage reactions of this type is usually rate-determining,[13] though in general such reactions are faster than related ligand replacements of mononuclear complexes.



Scheme. L = PR_3, X = halide, ol = olefin



In summary, none of the recognised isomerisation routes for square-planar complexes can be said to dominate the *trans* to *cis* conversions of $[PtX_2(ol)(PR_3)]$. A photochemical dissociative pathway is clearly involved, and an accompanying non-dissociative photochemical route cannot be excluded. Amongst the non-photochemical processes, direct dimer cleavage to the *cis* compound and/or dissociative isomerisation best fit the evidence for the chloro complexes, whereas associative olefin-catalysed isomerisation seems more appropriate for the bromo compounds. Since there is not a significant change in the nature of the compounds involved, this difference is more likely to reflect a change in relative rates of competing pathways, so the best conclusion that can be drawn is that more than one of the pathways discussed operate.

Dimethyl Sulphoxide Complexes.—Dimethyl sulphoxide (dmso) has a low nucleophilicity and relatively high *trans* effect when bonded to platinum,[17] a combination which resembles ethene.[18] In the hope of further elucidating the olefin system, we have examined the reactions of dmso with $[Pt_2Cl_4(PBu_3)_2]$ and $[Pt_2Br_4(PBu_3)_2]$, using both deficiency and excess of dmso, in light and dark. The reaction of less than two equivalents of dmso with $[Pt_2Cl_4(PBu_3)_2]$ has already been described as producing first *trans*-$[PtCl_2(dmso)(PBu_3)]$, then *cis*-$[PtCl_2(dmso)(PBu_3)]$ which has been fully characterised.[19] The reaction of dmso with the phosphine complex $[Pt_2Cl_4\{P(C_6H_{11})_3\}_2]$ has also recently been described, and is likewise reported as producing first *trans*-$[PtCl_2(dmso)\{P(C_6H_{11})_3\}]$, which then isomerises to the *cis* form.[20]

The reactions of dmso with both $[Pt_2Cl_4(PBu_3)_2]$ and $[Pt_2Br_4(PBu_3)_2]$ were essentially complete: no dimer remained except when a deficiency of dmso was employed. The conversion of the *trans* isomers to the *cis* complexes was followed in $CDCl_3$ by ^{31}P n.m.r. spectroscopy. The formation of *cis*-$[PtCl_2(dmso)(PBu_3)]$ was faster in diffuse light than in the dark, and was inhibited by excess dmso. Conversion was complete in *ca.* 24 h.

For the bromo complexes, no appreciable difference between the light and dark reaction rates could be detected, the isomerisation proceeding much more quickly than for the chloro complexes, and excess dmso speeded the reaction. About 7% of *trans*-$[PtBr_2(dmso)(PBu_3)]$ remained in equilibrium with the *cis* complex at the completion of the reaction. This equilibrium is dependent on [dmso], being displaced towards *cis*-$[PtBr_2(dmso)(PBu_3)]$ as [dmso] increases. {The persistent presence of $[Pt_2Br_4(PBu_3)_2]$ in the olefin studies prevented detection of any such equilibria in those systems.}

Clearly the dmso reactions broadly resemble those of the olefins, with the same intriguing change in behaviour to excess ligand between the chloro and bromo complexes. Once again the most likely explanation is that two or more reaction paths compete (excluding additional photochemical pathways), with a dissociative pathway dominating the chloro complex whilst an associative route is more important for the bromide. A recent careful study of *trans* to *cis* isomerisation of $[PtCl_2(dmso)_2]$ found a dissociative equilibrium with dmso and $[Pt_2Cl_4(dmso)_2]$, and the dmso released catalysed the isomerisation associatively,[21] a result which is closer to that found for the bromo complexes in the present work.

Experimental

Phosphorus-31 n.m.r. spectra were recorded on a Varian XL-100 spectrometer operating in the Fourier-transform mode. I.r.

spectra were recorded as KBr discs on a Perkin-Elmer PE 580 instrument. The complexes $[Pt_2Cl_4(PBu_3)_2]$,[22] *cis*-$[PtCl_2(C_2H_4)(PBu_3)]$,[1] *cis*-$[PtCl_2(C_2H_4)(PMe_2Ph)]$,[5] and *cis*-$[PtCl_2(dmso)(PBu_3)]$[19] were prepared by the literature methods.

Di-μ-bromo-dibromobis(tributylphosphine)diplatinum(II).—Excess potassium bromide (5 g) was added to an acetone (70 cm^3) solution of $[Pt_2Cl_4(PBu_3)_2]$ (2 g) and the mixture was refluxed for 2 h then filtered hot. Solvent was removed, and the resultant solid was extracted into chloroform to remove potassium salts. Evaporation of the chloroform and recrystallisation from methanol yielded pure $[Pt_2Br_4(PBu_3)_2]$ as orange crystals (1.63 g, 68%), m.p. 154—155 °C (Found: C, 25.8; H, 4.8; P, 5.4. $C_{24}H_{54}Br_4P_2Pt_2$ requires C, 25.9; H, 4.9; P, 5.6%). ^{31}P N.m.r.: δ 1.78 p.p.m. ($^1J_{PPt}$ 3 679, $^3J_{PPt}$ −25.4, $^4J_{PP}$ 3.4, $^2J_{PtPt}$ 230.0 Hz).

Di-μ-iodo-di-iodobis(tributylphosphine)diplatinum(II).—The ^{31}P n.m.r. spectrum of this compound has been described,[23] but no preparative or physical details were given. It was prepared by an analogous route to that above, using LiI instead of KBr, as red crystals, m.p. 156—157 °C (Found: C, 22.0; H, 4.1; P, 5.0. $C_{24}H_{54}I_4P_2Pt_2$ requires C, 22.1; H, 4.2; P, 4.8%).

cis-*Dibromo(dimethylphenylphosphine)(ethene)platinum*(II).—Ethene was slowly bubbled through a $CHCl_3$ solution (3 cm^3) of $[Pt_2Br_4(PMe_2Ph)_2]$ (200 mg, 0.2 mmol) at room temperature for 2 h. Crystals of *cis*-$[PtBr_2(C_2H_4)(PMe_2Ph)]$ (136 mg, 65%; decomp. > 120 °C) grew in solution and were isolated by filtration (Found: C, 22.7; H, 2.5; Br, 31.2; P, 6.2. $C_{10}H_{15}Br_2PPt$ requires C, 23.05; H, 2.9; Br, 30.7; P, 6.2%).

cis-*Dichloro(dimethylphenylphosphine)(propene)platinum*(II).—This was prepared similarly as colourless crystals. Yield 95%, m.p. 160—171 °C (decomp.) (Found: C, 29.6; H, 3.8; Cl, 15.2. $C_{11}H_{17}Cl_2PPt$ requires C, 29.6; H, 3.8; Cl, 15.9%). I.r.: ν(C=C) at 1 505, ν(Pt–Cl) at 278, 325 cm^{-1}.

cis-*Dibromo(ethene)(tributylphosphine)platinum*(II).—This was prepared similarly as colourless crystals, m.p. 95—100 °C (decomp.) (Found: C, 28.55; H, 5.3; Br, 27.5. $C_{14}H_{40}Br_2PPt$ requires C, 29.1; H, 4.2; Br, 27.6%). I.r.: ν(C=C) at 1 515 cm^{-1}. ^1H N.m.r.: δ 4.39 p.p.m. ($^2J_{HPt}$ 61 Hz, C_2H_4).

cis-*Dibromo(dimethyl sulphoxide)(tributylphosphine)platinum*(II).—The solutions from four n.m.r.-scale isomerisations of $[PtBr_2(dmso)(PBu_3)]$ were collected and the $CDCl_3$ solvent slowly evaporated until yellow crystals of *cis*-$[PtBr_2(dmso)(PBu_3)]$ were formed. Yield 34%, m.p. 117—118 °C (Found: C, 26.65; H, 5.30; Br, 23.0. $C_{14}H_{33}Br_2OPPtS$ requires C, 26.45; H, 5.25; Br, 25.15%).

Isomerisation Reactions.—These were all performed on a small scale and followed by ^{31}P n.m.r. spectroscopy. A typical example is given below.

Isomerisation of $[PtCl_2(C_2H_4)(PBu_3)]$. Through a solution of $[Pt_2Cl_4(PBu_3)_2]$ (20 mg) in $CDCl_3$ (0.5 cm^3) was passed C_2H_4 gas for 1 min at room temperature. The solution was transferred quantitatively into an n.m.r. tube and sealed. The isomerisation was followed by regular monitoring of the sample by ^{31}P n.m.r. spectroscopy.

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