Preparation of the Complexes *trans*-[$PtX_2(CO)L$] and their Isomerisation to *cis* Isomers

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Treatment of halide-bridged dimers [{PtX_2L}$_2$] (X is halide; L is tertiary phosphine or arsine) by carbon monoxide gives solutions of the *trans* isomers of [$PtX_2(CO)L$], some of which can be isolated. These compounds readily lose CO and isomerise to *cis* derivatives. The *trans* to *cis* isomerisations are catalysed by free CO, phosphines, or halide ions, and the latter nucleophile operates even in the solid phase. Free CO exchanges with co-ordinated CO more rapidly with the *trans* isomer than the *cis*. The *trans* to *cis* isomerisations are accelerated by light or u.v. irradiation, and u.v. treatment of the thermodynamic *cis* isomers produces *trans–cis* mixtures. The mechanisms of all these processes are discussed.

MANY carbonyl complexes of platinum(II), [$PtX_2(CO)L$] (X is halide; L is PR_3 or AsR_3), have been isolated[1,2] and used in spectroscopic[3,4] or synthetic[5,6] studies. They are usually prepared by CO cleavage of the halide-bridged dimers *trans*-[{PtX_2L}$_2$]. The first report of their preparation suggested that a *trans* geometry for [$PtX_2(CO)L$] would be expected,[1] because of the high *trans* effect[7] of the tertiary phosphine or arsine ligands. In the event, the compounds isolated have always had the *cis* configuration,[1,2] and it has become accepted practice simply to generate and use them *in situ*,[6] confident of their geometry.

We report that the first products generated in solution by the action of CO on [{PtX_2L}$_2$] are in fact the *trans* isomers of [$PtX_2(CO)L$]. Although these complexes readily isomerise to the *cis* derivatives, under certain conditions they can exist for considerable times and some can be isolated as solids. A preliminary account has appeared.[8]

RESULTS AND DISCUSSION

(a) *Preparation and Spectroscopic Parameters.*—Bubbling carbon monoxide through suspensions of [{PtX_2L}$_2$] in chloroform, benzene, or toluene at room temperature produced solutions of *trans*-[$PtX_2(CO)L$] (X = Cl; L = PBu_3, PEt_3, PMe_2Ph, $PMePh_2$, PPh_3, $AsMePh_2$, or $AsPh_3$; X = Br; L = PMe_2Ph) [equation (1)]. Reactions were complete in *ca.* 20 min, though if

$$trans\text{-}[\{PtX_2L\}_2] \xrightarrow{CO} trans\text{-}[PtX_2(CO)L] \longrightarrow cis\text{-}[PtX_2(CO)L] \quad (1)$$

passage of CO was continued for 1—2 h, colourless crystals of *cis*-[$PtX_2(CO)L$] precipitated.[1,2] In the absence of an excess of CO, however, isomerisation is slow, taking 1—3 d at room temperature. Below *ca.* —30 °C, solutions of the *trans* isomers remain unchanged indefinitely in the dark, i.r. and ^{31}P n.m.r. investigations revealing no trace of the *cis* isomer after several days.

Attempts to isolate the *trans* complexes by crystallisation frequently led to *cis–trans* mixtures, or even to the pure *cis* isomer. Spectroscopically pure samples of the yellow solid complexes *trans*-[$PtCl_2(CO)(PMePh_2)$], *trans*-[$PtCl_2(CO)(PPh_3)$], and *trans*-[$PtCl_2(CO)(AsMePh_2)$] were obtained, however, by carefully removing benzene solvent from frozen solutions at —10 °C, or CH_2Cl_2 at —50 °C. These samples have been kept at —10 °C in the dark for several days, and when redissolved showed only the original *trans* isomers. Attempts to analyse the compounds for C and H by the usual combustion methods failed, however, resulting in loss of CO to regenerate [{$PtCl_2L$}$_2$] prior to combustion.

Phosphorus-31 n.m.r. spectroscopic parameters and ν(CO) from the i.r. spectra of the complexes are presented in the Table. Values of δ(P) and ^1J(Pt–P) are quite similar in both isomers, and although ^1J(Pt–P) is consistently larger in the *trans* isomers, values are too close for this to be a reliable diagnostic test for geometry. Values of ν(CO), on the other hand, are always 20—30 cm^{-1} higher in the *trans* isomers, and the characteristic values of *ca.* 2 137 cm^{-1} are clearly diagnostic of *trans* compounds. Samples of *trans*-[$PtCl_2(CO)(PEt_3)$] labelled with ^{13}CO [$\delta(^{13}C)$, 169.9 p.p.m.; ^1J(Pt–C) 1 164 Hz; ^2J(P–C) 159.6 Hz] and *trans*-[$PtCl_2(CO)(PMePh_2)$][$\delta(^{13}C)$, 168.3 p.p.m.; ^1J(P–C) 1 221 Hz; ^2J(P–C) 171.7 Hz] were prepared in the usual way. The most striking features of their ^{13}C n.m.r. spectra are the high values of ^2J(P–C). These are entirely typical of the few values reported for CO *trans* to PR_3 at platinum,[5] values for *cis* isomers being typically only 5—10 Hz.

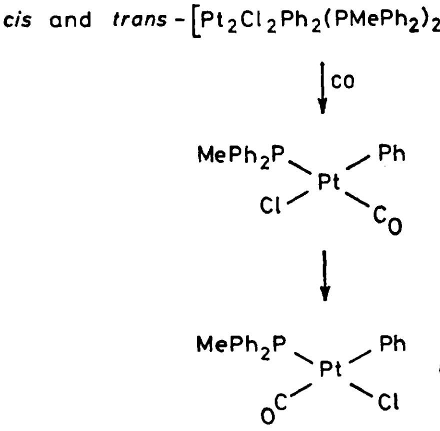
Two interesting comparisons emerge at this stage. Firstly, a few *trans* platinum carbonyls, [$PtCl_2(CO)L$], have been prepared previously, generally by replacing C_2H_4 in *trans*-[$PtCl_2(C_2H_4)L$] by CO (L is substituted pyridine, pyridine *N*-oxide, or aniline).[9] Although these compounds can be readily isolated, and appear more stable with respect to CO loss (see below) or isomerisation than the phosphine or arsine analogues described here, related amine derivatives do nevertheless isomerise on heating.[10] Secondly, the generation of *trans* complexes as the first products of bridge-cleavage reactions of *trans*-[$M_2X_4(PR_3)_2$] (M = Pd or Pt) by a variety of nucleophiles (now including CO) is well known and seems to be a general process.[11] It is a reasonable supposition that the high *trans* effect of PR_3 is responsible, but this kinetic phenomenon may be more subtle than that. The dinuclear complex $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$ exists in solution as similar amounts of both *cis* and *trans* isomers,[6,12] but carbonylation produces 98% of the isomer of $[PtClPh(CO)(PMePh_2)]$ with CO *trans* to phosphorus [13] [which in turn isomerises to other forms,[5] equation (2)]. Clearly some rearrangement must take place at the intermediate stages to avoid producing more of the thermodynamic isomer.

Phosphorus-31 n.m.r.[a] and i.r.[b] spectroscopic characteristics for *cis*- and *trans*-$[PtX_2(CO)L]$

		cis Isomers			*trans* Isomers		
X	L	δ(P)/p.p.m.	^1J(Pt–P)/Hz	ν(CO)/cm^{-1}	δ(P)/p.p.m.	^1J(Pt–P)/Hz	ν(CO)/cm^{-1}
Cl	PEt_3	22.3	2 793	2 106	11.6	2 885	2 135
Cl	PMe_2Ph	−10.4	2 855	2 112	−11.0	2 933	2 138
Cl	$PMePh_2$	−0.2	2 946	2 115 [c]	0.6	3 000	2 139 [d]
Cl	PPh_3	9.8	3 061	2 115	15.1	3 077	2 139
Cl	PBu_3	14.3	2 783	2 106	3.9	2 865	2 135
Cl	$AsMePh_2$			2 109			2 133
Cl	$AsPh_3$			2 110			2 134
Br	PMe_2Ph	−11.2	2 822	2 107	−15.9	2 825	2 132
I	PMe_2Ph	−14.7	2 748	2 096			
Cl	$P(C_6H_{11})_3$	36.4	2 850	2 099			
Cl	$P(o\text{-tolyl})_3$	5.6	3 010	2 110			

[a] At 25 °C in $CDCl_3$: chemical shifts measured downfield of external H_3PO_4. [b] At 20 °C in $CDCl_3$. [c] ν(^{13}CO) 2 065 cm^{-1}. [d] ν(^{13}CO) 2 090 cm^{-1}.

(b) *Isomerisations of* trans-$[PtX_2(CO)L]$.—Solutions of *trans*-$[PtCl_2(CO)L]$ changed entirely to the *cis* isomer after standing from 1—3 d at ambient temperatures. The bromide complex *trans*-$[PtBr_2(CO)(PMe_2Ph)]$ converted faster, and only *cis*-$[PtI_2(CO)(PMe_2Ph)]$ could be detected after passing CO through chloroform suspensions of the sparingly soluble $[Pt_2I_4(PMe_2Ph)_2]$. This probably reflects an even faster conversion of a *trans* isomer to the *cis*, but the possibility cannot be ruled out that the *trans* isomer may not be formed at all with this halide.



(2)

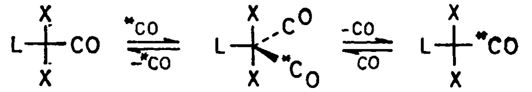
All the *trans* complexes tended to lose carbon monoxide from solution, and their isomerisations were often accompanied by the production of 5—20% of $[\{PtX_2L\}_2]$. When a stream of nitrogen gas was passed through a benzene solution of *trans*-$[PtCl_2(CO)(PMePh_2)]$, total loss of CO had occurred after 5 h. An identical solution not treated by N_2 contained a 1 : 1 mixture of *cis*- and *trans*-$[PtCl_2(CO)(PMePh_2)]$ after the same time. Carbon monoxide is therefore released during the *trans* to *cis* conversion. Solutions of *cis*-$[PtCl_2(CO)L]$ showed no tendency to lose CO when treated in this way.

The isomerisation is independent of concentration. Chloroform solutions of *trans*-$[PtBr_2(CO)(PMe_2Ph)]$ at four concentrations ranging from 0.025 to 0.0125 mol dm^{-3} were periodically examined by i.r. spectroscopy. After each time interval, all four solutions showed identical isomer ratios. On the other hand, samples of *trans*-$[PtCl_2(CO)(PMePh_2)]$ in benzene isomerised twice as fast as solutions of similar concentration in chloroform. This suggests a faster isomerisation in non-polar solvents, but difficulties in observing i.r. spectra in other solvents have so far prevented substantiation of this point.

The *trans* to *cis* isomerisations are dramatically catalysed by free carbon monoxide. A 0.1 mol dm^{-3} solution of *trans*-$[PtCl_2(CO)(PMePh_2)]$ was completely converted to the *cis* isomer in only 35 min with passage of CO through the solution, whilst an identical, untreated solution was virtually unchanged in this time interval. A sample of *trans*-$[PtCl_2(^{13}CO)(PMePh_2)]$ was similarly treated with ^{12}CO. After 15 min similar amounts of both *trans*-$[PtCl_2(^{13}CO)(PMePh_2)]$ and *trans*-$[PtCl_2(^{12}CO)(PMePh_2)]$ were apparent in solution, whilst after 25 min the major species was *trans*-$[PtCl_2(^{12}CO)(PMePh_2)]$. Quantities of the two *cis* isomers were by then also apparent. Again, an untreated solution of *trans*-$[PtCl_2(^{13}CO)(PMePh_2)]$ remained unchanged after this time interval. When ^{12}CO was passed through a chloroform solution of *cis*-$[PtCl_2(^{13}CO)(PMePh_2)]$, exchange of CO was considerably slower than for the *trans* isomer, requiring *ca.* 1 h for 30% exchange. No *trans* complex was detected during this experiment.

Other nucleophiles also catalyse these *trans* to *cis* isomerisations. The addition of 0.1 molar equivalents of $PMePh_2$ to solutions of *trans*-$[PtCl_2(CO)(PMePh_2)]$ caused complete conversion to the *cis* isomer in 30 min. Likewise, small amounts of $[NEt_4]Cl$, $[NBu_4]Br$, or $[NBu_4]I$ promoted complete *trans* to *cis* conversions in 1 h. Partial loss of CO was evident, presumably due to the formation of some $[PtCl_2(PMePh_2)_2]$ and $[PtCl_2X(PMePh_2)]^-$, respectively, by CO displacement. It seemed possible that the displaced carbon monoxide might be the true catalyst in these experiments, but this was discounted by the following experiment. To two of three identical 0.01 mol dm^{-3} chloroform solutions of *trans*-[$PtCl_2(CO)(PPh_3)$] were added 0.5 mg of PPh_3 and [NEt_4]Cl, respectively, and a fast stream of N_2 was passed through all three samples for 15 min. Infrared examination then revealed complete conversion to the *cis* isomers in the samples treated by PPh_3 or Cl^-, but *ca.* 25% CO loss with no isomerisation in the untreated sample. Thus, while exchange of free and co-ordinated CO is faster than the CO-catalysed isomerisation, replacement of CO by PR_3 or X^- is slower than isomerisation catalysed by these nucleophiles. The halide-catalysed interconversion at least also operates in the solid phase. Grinding samples of *trans*-[$PtCl_2(CO)L$] (L = PPh_3 or $AsMePh_2$) with KBr caused substantial isomerisation. After the mixtures were compressed into a disc for i.r. measurements, the isomerisation continued. Grinding the complexes alone had no effect: redissolution in chloroform showed that no isomerisation had occurred.

(c) *Isomerisation Mechanism.*—Ligand substitution reactions at platinum usually proceed stereospecifically by an associative mechanism,[14] and CO exchange probably follows this route [equation (3)]. Nucleophile-catalysed isomerisations are also associative,[15] and the same five-co-ordinate intermediate is probably involved in the CO-catalysed process. The geometry change can come about either through pseudorotation, or consecutive displacement of L and/or X. These can be regarded as two extremes of one basic process.[15] We note that our conditions fit exactly those predicted by Redfield and Nelson [16] as most favourable to pseudorotation, and that L and X^- (either or both of which would have to be eliminated during consecutive displacement reactions) themselves catalyse the isomerisations.



(3)

The Scheme represents some possible routes. Trigonal-bipyramidal intermediates rather than square-pyrimidal intermediates are depicted for clarity (both may be encountered during isomerisation sequences). No inference concerning the relative energies of these five-co-ordinate species should be drawn.[13,15]

Intermediates A and C (Scheme) must be involved in the stereospecific exchange of CO with the *trans* and *cis* isomers, respectively, so it is tempting to suggest that the isomerisation proceeds from A through B to C. The other routes cannot, however, be ruled out. Similar schemes can be drawn for the phosphine- and halide-catalysed reactions.

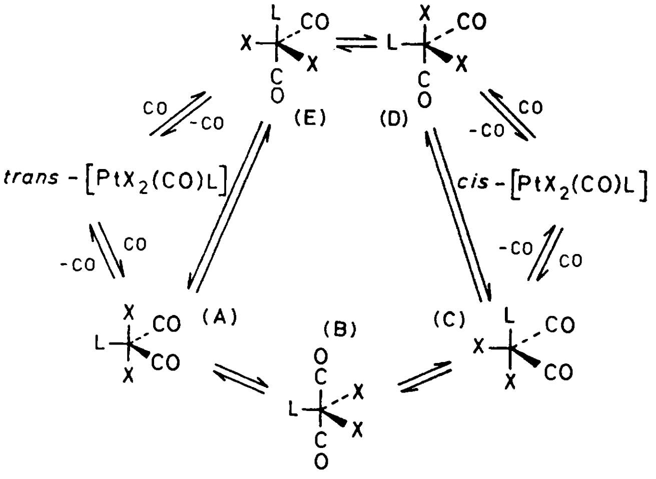
The uncatalysed isomerisation is first order in Pt and involves CO loss from the *trans* isomer, either spontaneously or solvent assisted. In view of the ready catalysis by CO of this isomerisation, it seems very likely that the eliminated CO would catalyse the conversion of the remaining, undissociated, *trans* molecules [equations (4) and (5)]. Such a process is essentially

$$trans\text{-}[PtX_2(CO)L] \rightleftharpoons [PtX_2L] + CO \qquad (4)$$

$$trans\text{-}[PtX_2(CO)L] \xrightarrow{CO} cis\text{-}[PtX_2(CO)L] \qquad (5)$$

autocatalytic. Whilst no other systems have been claimed to conform to such a mechanism, there is good evidence that many other isomerisations of square-planar complexes may be similar.[15]

A number of alternative mechanisms must be considered, all of them involving CO loss. A strong contender is the possibility of regenerating the dimeric [$\{PtX_2L\}_2$], which might slowly but irreversibly build up the *cis* isomer on CO cleavage [equation (6)]. This was



SCHEME

$$cis\text{-}[PtX_2(CO)L] \xleftarrow[\text{slow}]{CO} [\{PtX_2L\}_2] \underset{-CO}{\overset{CO}{\rightleftharpoons}} trans\text{-}[PtX_2(CO)L] \qquad (6)$$

originally suggested to explain the apparent non-appearance of the *trans* isomer.[1] Mechanisms of this type have also been shown to be involved in isomerisations of the complexes [$PtXPh(CO)L$].[5,13] Interestingly, isomerisations of these latter complexes are inhibited, not catalysed, by CO, and treatment by L or X has no effect other than to displace CO from the molecules.

Other routes for the isomerisations include a geometry change of the three-co-ordinate (or solvated) intermediate, following CO elimination. All these mechanisms have recently been compared and discussed.[15]

(d) *Photochemical Reactions.*—Ultraviolet irradiation not only accelerated the *trans* to *cis* conversions, but promoted the conversions of *cis*-[$PtCl_2(CO)L$] into mixtures of the isomers. Prolonged irradiation at 0 °C of deuteriochloroform solutions of pure *cis*- or *trans*-[$PtCl_2(CO)(PMePh_2)$] resulted, after *ca.* 5 h, in the same equilibrium point at 68% *trans*. It is possible that a direct geometry change *via* a pseudotetrahedral intermediate is responsible for the conversions,[15] but a photochemical elimination of CO is an alternative route.

Formation of some of the dimers, $[\{PtX_2L\}_2]$, accompanies the conversions. Some support for the latter hypothesis may be drawn from an experiment in which mixed solutions of *cis*-$[PtCl_2(CO)(PMePh_2)]$ (39 mg) and $[Pt_2Cl_4(PMe_2Ph)_2]$ (32 mg) were irradiated. The experiment was interrupted before equilibrium was reached, when *cis*-$[PtCl_2(CO)(PMePh_2)]$ was still the major CO-containing component. More than twice as much *trans*-$[PtCl_2(CO)(PMe_2Ph)]$ was present in solution than *trans*-$[PtCl_2(CO)(PMePh_2)]$ (from ^{31}P n.m.r. measurements). A small amount of *cis*-$[PtCl_2(CO)(PMe_2Ph)]$, and some of the dimers $[Pt_2Cl_4(PMePh_2)_2]$ and $[Pt_2Cl_4(PMePh_2)(PMe_2Ph)]$ had also been formed. Since the *trans*-carbonyl complexes readily lose CO, even without irradiation, this experiment cannot be taken as proof of a light-induced CO elimination as the mechanism, but the product ratios are suggestive. No reaction took place between *cis*-$[PtCl_2(CO)(PMePh_2)]$ and $[Pt_2Cl_4(PMe_2Ph)_2]$ in the dark at 0 °C.

Interestingly, the conversions of the yellow *trans*-$[PtCl_2(CO)L]$ to the colourless *cis* isomers are accelerated by daylight. Though the effect is quite small in the absence of direct sunlight, it necessitates storing the *trans* complexes in the dark.

EXPERIMENTAL

Solution i.r. spectra were recorded on a Perkin-Elmer 577 spectrophotometer, using 0.5-mm path length NaCl solution cells. ^{31}P and ^{13}C n.m.r. spectra were recorded in $CDCl_3$ on a Varian XL-100 spectrometer operating in the F.T. mode. Ultraviolet irradiations were performed in Pyrex apparatus using a Hanovia medium-pressure mercury lamp. Carbon-13 monoxide (90%) was obtained from Merke, Sharp and Dohm.

Most samples were prepared in solution (see text) and their identity and purity checked by spectroscopic methods (Table). A few were isolated as pure solids. The preparation below is typical.

trans-$[PtCl_2(CO)(AsMePh_2)]$.—The compound $[Pt_2Cl_4(AsMePh_2)_2]$ (0.121 g) was dissolved in CH_2Cl_2 (10 cm^3) and the solution was cooled to −40 °C. Carbon monoxide gas was bubbled through the solution for 5 min. An aliquot of the solution was monitored by i.r. spectroscopy, which revealed the presence of the *trans* isomer only of $[PtCl_2(CO)(AsMePh_2)]$ [ν(CO) *ca.* 2 130 cm^{-1}]. The remaining solution was cooled to −50 °C, and the solvent was removed by evacuating at this temperature. Yellow, solid, *trans*-$[PtCl_2(CO)(AsMePh_2)]$ resulted [ν(CO) in $CHCl_3$ was 2 134 cm^{-1}].

After keeping the sample for 21 d. at −10 °C, no decomposition or isomerisation was detected. Several attempts at C and H analysis produced results in consistently good agreement with $[Pt_2Cl_4(AsMePh_2)_2]$.

The authors thank Johnson, Matthey and Co. Ltd. for a loan of platinum salts, and the S.R.C. for a maintenance award (to G. K. A.).

[9/2031 *Received, 31st December*, 1979]

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