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Substitution and Isomerisation Reactions at Platinum(II) involving Halide, Tertiary Phosphine, Carbonyl, and Isonitrile Ligands

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Carbon monoxide catalyses *trans* to *cis* isomerisations of $[PtCl_2L_2]$ (L = tertiary phosphine) in chloroform solution. The process involves formation of five-co-ordinate intermediates from which halide or tertiary phosphine can be eliminated, giving *trans*-$[PtCl(CO)L_2]^+$ or *cis*-$[PtCl_2(CO)L]$ respectively. Structure changes appear to be by pseudo-rotations rather than by consecutive displacements. A number of isonitrile complexes undergo similar reactions. Halide-bridged cations $[Pt_2(\mu\text{-}Cl)_2L_4]^{2+}$ formed by halide extraction from *cis*-$[PtCl_2L_2]$ by Ag^+ enter rapid (n.m.r. time-scale) exchange processes with the latter complexes at ambient temperatures. Halide elimination from *cis*-$[PtCl_2L_2]$ by solvent chloroform appears to initiate the process. The *trans* isomers do not participate in the exchange.

Square-planar platinum(II) or palladium(II) complexes react with nucleophiles by associative mechanisms, generally producing ligand substitutions,[1] geometric isomerisations,[2] or both. The nucleophile-catalysed isomerisations may proceed *via* consecutive ligand substitutions or by pseudo-rotation of the five-co-ordinate intermediates. These two routes can be regarded as extremes of a single associative pathway.[2] Reaction profiles for substitutions and isomerisations pass through both square-pyramidal and trigonal-bipyramidal intermediates. A few examples approaching both geometries have been isolated and characterised,[2-4] and there is evidence in some cases for strong associations in solution between cationic platinum complexes and halide anions, giving complexes which most likely have square-pyramidal geometry.[2,3,5,6]

Although the choice of which ligands remain attached to platinum or palladium after replacement and/or isomerisation processes is usually determined by thermodynamic factors,[2,7] stronger ligands can sometimes be replaced by weaker ones when the former are removed from the system. Examples include loss of volatile CO [8] [equation (1)] and removal of halide as its silver(I) salt [9] [equation (2), dppe = $Ph_2PC_2H_4PPh_2$].

$$2\ trans\text{-}[PtCl_2(CO)(PMePh_2)] \longrightarrow [Pt_2Cl_2(\mu\text{-}Cl)_2(PMePh_2)_2] + 2\ CO \quad (1)$$

$$2\ [PdCl_2(dppe)] + 2\ Ag^+ \longrightarrow [Pd_2(\mu\text{-}Cl)_2(dppe)_2]^{2+} + 2\ AgCl \quad (2)$$

A recent variation displaces strongly bonding tertiary phosphines by oxidation with sulphur during their temporary displacement by weak ligands [5] [equation (3)].

$$trans\text{-}[PtCl(Ph)(PPh_3)_2] + CO \xrightarrow{S_8} [PtCl(Ph)(CO)(PPh_3)] + PPh_3S \quad (3)$$

To further illuminate reactions of these types, and to explore the synthetic utility of processes like that shown in equation (3), we have examined a number of interactions of platinum(II) complexes involving halide, tertiary phosphine, carbonyl, and isonitrile ligands, with and without the presence of sulphur or silver salts. The reactions were followed by ^{31}P n.m.r. spectrometry in $CDCl_3$ solutions, and by i.r. spectrometry in $CHCl_3$. The reactants and products were of known type and were readily identified in solution by comparison of their spectroscopic parameters with those of authentic compounds. A variety of competing reaction paths were revealed.

Results and Discussion

Ligand Replacement and Isomerisations.—Bubbling CO through chloroform solutions of *cis*-$[PtCl_2\{P(C_6H_4Me\text{-}p)_3\}_2]$ at room temperature caused no detectable change. When crystalline S_8 was added to the solution, however, a steady reaction took place over 90 min to produce equal amounts of $P(C_6H_4Me\text{-}p)_3S$ [$\delta(P)$ 42.4 p.p.m.] and *cis*-$[PtCl_2(CO)\{P(C_6H_4Me\text{-}p)_3\}]$ [$\delta(P)$ 8.2 p.p.m., ^1J (PtP) 3 043 Hz; $\nu(CO)$ 2 119 cm^{-1}]. We have found no evidence in this or previous [5] work that sulphur can displace phosphine from platinum(II) unaided in such solutions, so its effect is presumably to displace an equilibrium by reacting with liberated phosphine [equation (4), L = tertiary phosphine].

$$cis\text{-}[PtCl_2L_2] + CO \rightleftharpoons cis\text{-}[PtCl_2(CO)L] + L \xrightarrow{S_8} LS \quad (4)$$

Similar experiments on other platinum halide complexes produced evidence that the picture presented by equation (4) is misleadingly simple. The complex *trans*-$[PtCl_2(PEt_3)_2]$, when treated with CO for 30 min, isomerised almost completely to its *cis* form. No such isomerisation takes place in chloroform in the absence of CO or other nucleophiles. About 5% of *trans*-$[PtCl(CO)(PEt_3)_2]Cl$ [$\delta(P)$ 23.5 p.p.m., $^1J(PtP)$ 1 922 Hz, $\nu(CO)$ 2 103 cm^{-1}] was also produced. Attempts to isolate this salt led to loss of the carbon monoxide, but treatment of the solution by silver trifluoromethanesulphonate, $Ag[CF_3SO_3]$, removed the halide and indefinitely stabilised the compound as *trans*-$[PtCl(CO)(PEt_3)_2][CF_3SO_3]$. The cation now showed n.m.r. parameters of $\delta(P)$ 26.3 p.p.m. and $^1J(PtP)$ 1 846 Hz, suggesting that the chloride had been associating with the cation in solution.[5,6]

Prolonged treatment (6 h) of chloroform solutions of $[PtCl_2(PEt_3)_2]$ (either isomer, although material in solution would soon be largely *cis*) by CO in the presence of sulphur produced an intense $\nu(CO)$ band at 2 103 cm^{-1} suggesting complete reaction. Phosphorus-31 n.m.r. investigation of the solution revealed the presence of only 20% *cis*-$[PtCl_2(CO)(PEt_3)]$ [8] and PEt_3S; the major product was the salt *trans*-$[PtCl(CO)(PEt_3)_2]Cl$. This suggests that CO more readily displaces Cl^- than PEt_3 in this case. Any PEt_3 released would rapidly react with the sulphur.

Table. Some spectroscopic parameters of $[PtXYL_2][CF_3SO_3]$ complexes

Geometry	X	Y	L	$\delta(P)$/p.p.m.[a]	$^1J(PtP)$/Hz	$\nu(CO)$[b] or $\nu(CN)$/cm^{-1}
trans	Cl	CO	PEt_3	26.3	1 846	2 103
cis[c]	Cl	CO	PEt_3	18.1 (d)[d]	2 776	—
				17.2 (d)	2 919	
trans	Cl	CO	PMe_2Ph	−1.4	1 910	2 118
cis[c]	Cl	CO	PMe_2Ph	−9.5 (d)[e]	2 925	—
				−15.0 (d)	3 088	
trans	Br	CO	PMe_2Ph	−5.9	1 904	2 106
trans	Cl	CO	$PMePh_2$	9.1	1 983	2 118
cis[c]	Cl	CO	$PMePh_2$	3.6 (d)[f]	2 960	—
				−8.6 (d)	3 162	
trans	I	CO	PPh_3	18.8	2 019	—
trans	Cl	CO	$P(C_6H_4Me\text{-}p)_3$	17.8	1 959	2 115
trans	I	CO	$P(C_6F_5)_3$	−35.8	1 929	2 095
cis	Cl	CO	½(dppe)	49.3	*g*	2 116
				44.4	3 182	
trans	Cl	CNPh	PBu_3	14.4	1 967	2 203
trans	Cl	CNPh	$P(C_6H_{11})_3$	22.1	1 975	—
trans	Cl	CNPh	PMe_2Ph	−3.8	2 049	2 209
trans	Br	CNPh	PMe_2Ph	−8.2	2 060	—
trans	Cl	CNPh	$PMePh_2$	7.7	2 148	2 210
trans	Cl	CNMe	$PMePh_2$	6.9	2 143	2 256

[a] In $CDCl_3$ relative to 85% H_3PO_4 (positive is downfield), d = doublet. [b] Solutions (0.02 mol dm^{-3}) in $CHCl_3$ at 20 °C in 0.5 mm NaCl cells. [c] Recorded at −60 °C. [d] $^2J(PP)$ 18.2 Hz. [e] $^2J(PP)$ 21.3 Hz. [f] $^2J(PP)$ 19.5 Hz. [g] Not resolved.

Similar ^{31}P n.m.r. and i.r. investigations were made on a number of related reactions using different platinum complexes. From the carbonylations of *cis*-$[PtCl_2(PMe_2Ph)_2]$ and *cis*-$[PtCl_2(PMePh_2)_2]$ small amounts of the salts *trans*-$[PtCl(CO)L_2]Cl$ were formed. In the presence of sulphur, some *cis*-$[PtCl_2(CO)L]$[8] and LS were also slowly formed. With $Ag[CF_3SO_3]$ present, however, complete conversion to the trifluoromethanesulphonate salts resulted [equation (5)]. Spectroscopic parameters for these ionic platinum compounds are listed in the Table.

$$cis\text{-}[PtCl_2L_2] + CO + Ag[CF_3SO_3] \longrightarrow trans\text{-}[PtCl(CO)L_2][CF_3SO_3] + AgCl \quad (5)$$

The formation of *trans*-$[PtCl(CO)L_2]Cl$ from *cis* dihalide complexes even in the presence of sulphur suggests that phosphine is not eliminated as part of this sequence, or it would presumably be trapped by the S_8. The reverse step also seems not to involve release of L, though the geometry of these ligands changes from *trans* to *cis*. Thus when *trans*-$[PtCl(CO)L_2][CF_3SO_3]$ [L = PEt_3, PMe_2Ph, $PMePh_2$, or $P(C_6H_4Me\text{-}p)_3$] were treated with Cl^- (as NEt_4Cl), *cis*-$[PtCl_2L_2]$ complexes were obtained every time. No *cis*-$[PtCl_2(CO)L]$ was obtained, even in the presence of S_8 (when L = $PMePh_2$ or PMe_2Ph) again suggesting no L displacement, and only small amounts of LS and $[PtCl_2(CO)L]$ were produced in the case of the other phosphines. This strongly suggests an isomerisation mechanism more akin to pseudo-rotation than to consecutive displacement. The Scheme depicts such a sequence. It resembles that proposed to account for *trans* to *cis* isomerisations of $[PtCl_2(CO)L]$.[8]

Halide Abstraction.—Also shown in the Scheme are the compounds arising from halide loss from *cis*-$[PtCl_2L_2]$. These complexes react in chloroform with $Ag[CF_3SO_3]$ at −60 °C, eliminating AgCl to form $[Pt_2(\mu\text{-}Cl)_2L_4][CF_3SO_3]_2$. These react with CO at −60 °C to produce *cis*-$[PtCl(CO)L_2][CF_3SO_3]$, which isomerise to the *trans* form at +30 °C [equation (6)].

$$\begin{tikzcd} {[Pt_2(\mu\text{-}Cl)_2L_4]^{2+} + CO} \arrow[r, "-60\ ^\circ C"] & {cis\text{-}[PtCl(CO)L_2]^+} \arrow[d, "30^\circ C"] \\ & {trans\text{-}[PtCl(CO)L_2]^+} \end{tikzcd} \quad (6)$$

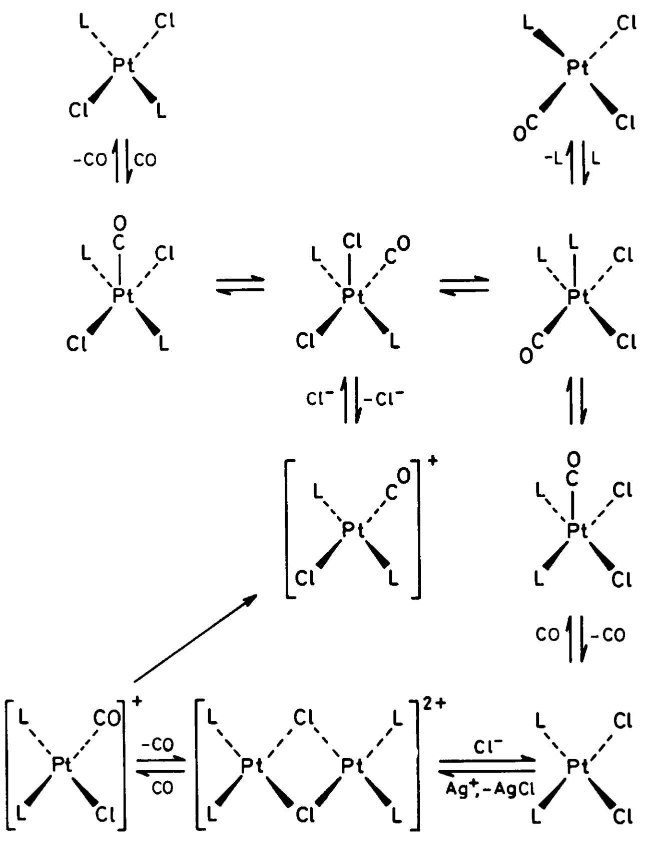
This isomerisation could be solvent assisted,[2] or autocatalysed by CO loss.[8] The carbonyl salt of the chelating diphosphine dppe readily lost CO in solution, and the very low solubility of this chloride-bridged product made the reverse carbonylation unfavourable [equation (7)].

$$[Pt_2(\mu\text{-}Cl)_2(dppe)_2]^{2+} \underset{-CO}{\overset{CO}{\rightleftharpoons}} 2\ [PtCl(CO)(dppe)]^+ \quad (7)$$

Treatment of $[PtCl(CO)(dppe)][CF_3SO_3]$ with NEt_4Cl regenerated $[PtCl_2(dppe)]$ by CO elimination. Removal of halide by silver salts has been described by Hartley and co-workers[9] for a variety of platinum(II) and palladium(II) dichlorides. An equilibrium is established [equation (8)] which depends on the donor ability of the solvent (S).

$$[PdCl(S)L_2]^+ \underset{S}{\overset{-S}{\rightleftharpoons}} [Pd_2(\mu\text{-}Cl)_2L_4]^{2+} \quad (8)$$

The mechanism of halide abstraction by silver (I) is of considerable interest. Obviously any halide eliminated by solvent would be removed from the system but the fact that even poor donors (such as benzene[9]) can promote the abstraction might indicate the operation of a direct approach of Ag^+ to the co-ordinated halide instead. Whilst this latter explanation is attractive, we have found that ^{31}P n.m.r. spectra of mixtures of $[Pt_2(\mu\text{-}Cl)_2L_4]^{2+}$ and *cis*-$[PtCl_2L_2]$ in $CDCl_3$ are broad at ambient temperatures (L = PEt_3 or $PMePh_2$), although sharp at −60 °C, suggestive of a fast exchange process. The complexes *trans*-$[PtCl_2L_2]$ take no part in the exchange, their spectra remaining sharp when those of the *cis* complex and dimer in the same solution broaden. This situation resembles that reported from ^1H n.m.r. spectroscopic observations on the rapid exchange of tertiary phos-



Scheme. L = tertiary phosphine. Interconversion of five-co-ordinate intermediates involves trigonal-bipyramidal transition states which are not shown. The position of CO can be taken by RNC

phine between [PtCl(PMe$_2$Ph)$_3$]Cl and *cis*-[PtCl$_2$(PMe$_2$Ph)$_2$].[10] Chloride ion releases PMe$_2$Ph from the cation, which in turn attacks the *cis* complex to release another Cl$^-$ [equation (9)]. The less reactive *trans* isomer takes no part in the exchange. Similar findings from ^{31}P n.m.r. spectra of related systems have recently been reported.[3] Our results can be similarly interpreted by halide displacement from *cis*-[PtCl$_2$L$_2$] by solvent. The chloride is then available to cleave the bridges of [Pt$_2$(μ-Cl)$_2$L$_4$]$^{2+}$ [equation (10)]. The attack of even neutral ligands on neutral halide-bridged dimers is known to be very rapid.[11] Release of halide from the *trans* complexes is less favourable,[10] hence they take no part in the rapid exchange process. The importance of even poorly co-ordinating solvents in isomerisations and displacements has been emphasised.[2]

$$[\mathrm{PtCl(PMe_2Ph)_3]Cl} \underset{\mathrm{PMe_2Ph}}{\overset{-\mathrm{PMe_2Ph}}{\rightleftharpoons}} cis\text{-}[\mathrm{PtCl_2(PMe_2Ph)_2}] \quad (9)$$

$$[\mathrm{Pt_2(\mu\text{-}Cl)_2L_4}]^{2+} \underset{-2\mathrm{Cl}^-}{\overset{2\mathrm{Cl}^-}{\rightleftharpoons}} 2\ cis\text{-}[\mathrm{PtCl_2L_2}] \quad (10)$$

Synthetic Studies.—A number of factors limit the synthetic utility of replacing tertiary phosphines by CO in the presence of sulphur. As well as the obvious complications from the halide-eliminating side reactions described above, separation of the tertiary phosphine sulphide from the carbonyl product can be difficult, and in some cases CO was eliminated from Pt by LS during work up. Thus after a large-scale reaction of [PtCl$_2$(PBu$_3$)$_2$] with CO and S$_8$, only 20% of *cis*-[PtCl$_2$(CO)(PBu$_3$)] was obtained after chromatographic separation; the remaining oily material could not be purified, and was tentatively identified as *cis*-[PtCl$_2$(PBu$_3$S)(PBu$_3$)] [δ(P) −4.3, ^1J(PPt) 3 556; δ(P) 72.3 p.p.m., ^2J(PPt) 125; ^3J(PP) 16.0 Hz]. Also, suspensions of *trans*-[PtCl$_2${P(C$_6$H$_4$Me-*o*)$_3$}$_2$], *trans*-[PtCl$_2${P(C$_6$F$_5$)$_3$}$_2$], [PtCl$_2$(dppe)], and [PtCl$_2$(dppm)] (dppm = Ph$_2$PCH$_2$PPh$_2$) failed to react with CO and S$_8$ in chloroform over 2 h. This no doubt reflects to a large extent the very limited solubility of these materials, but the great degree of steric hindrance in the P(C$_6$H$_4$Me-*o*)$_3$ complex,[12] and the reluctance of P(C$_6$F$_5$)$_3$ to react with sulphur[13] may contribute to the unreactivity of the first two.

Isonitrile Complexes.—These studies were extended to some related reactions with isonitriles, and several features in common with the CO derivatives were revealed. The best leaving group in the isonitrile systems was undoubtedly the halide ions, since salt formation proved to be a process of greater relative importance than in the carbonyl systems. Thus reactions between *cis*-[PtCl$_2$(CNR)L] and L, or *cis*-[PtCl$_2$L$_2$] and RNC (R = Me or Ph; L = PMe$_2$Ph or PMePh$_2$), form ionic compounds more rapidly and completely than their CO anaogues [equations (11) and (12)]. Spectroscopic parameters for these isonitrile salts, stabilised as their CF$_3$SO$_3$ salts, are listed in the Table.

$$cis\text{-}[\mathrm{PtCl_2L_2}] + \mathrm{RNC} \rightleftharpoons trans\text{-}[\mathrm{PtCl(CNR)L_2]Cl} \quad (11)$$

$$cis\text{-}[\mathrm{PtCl_2(CNR)L}] + \mathrm{L} \rightleftharpoons trans\text{-}[\mathrm{PtCl(CNR)L_2]Cl} \quad (12)$$

Chloride is able to displace both RNC and L from *trans*-[PtCl(CNR)L$_2$]$^+$. Thus when *trans*-[PtCl(CNPh)L$_2$]Cl is left in solution at ambient temperatures for several days, *cis*-[PtCl$_2$L$_2$] is generated as freed PhNC slowly polymerises and is removed from the system. If sulphur is added to the ionic salt solutions on the other hand, tertiary phosphine sulphide is rapidly formed generating *cis*-[PtCl$_2$(CNPh)L]. Neither of these reactions occurs with the CF$_3$SO$_3$ salt unless extra Cl$^-$ is added to the solutions.

Finally, in the presence of sulphur, PhNC readily replaces L of *cis*-[PtX$_2$L$_2$] to form *cis*-[PtX$_2$(CNPh)L] and LS [X = Cl, L = PBu$_3$, PMe$_2$Ph, PMePh$_2$, or P(C$_6$H$_4$Me-*p*)$_3$; X = Br, L = PMe$_2$Ph]. Whilst the reactions proceed more readily and with fewer complicating by-products than do the analogous CO reactions, the separation problems of LS remain and limit the synthetic utility of this process also. All the above isonitrile sequences fit into the proposed reaction scheme simply by replacing CO by RNC.

Experimental

The ^{31}P-{^{1}H} n.m.r. spectra were recorded as CDCl$_3$ solutions on a Varian HX100 spectrometer operating in the Fourier transform mode. Infrared spectra were recorded on a Perkin-Elmer 577 instrument. The complexes *cis*- and *trans*-[PtCl$_2$L$_2$], *cis*-[PtCl$_2$(CO)L], *cis*-[PtCl$_2$(CNR)L], and *trans*-[PtCl(CO)L$_2$]$^+$Z$^-$ were prepared by standard methods.[14] All complexes encountered were known types and were identified in solution by their spectroscopic parameters (refs. 5, 8, 9, 11 and the Table herein). Reaction mixtures (0.04 mol dm^{-3}) were transferred to n.m.r. tubes after mixing and being monitored regularly. Typical procedures for isonitrile salts are described below.

cis-*Carbonylchlorobis(methyldiphenylphosphine)platinum Trifluoromethanesulphonate.*—The complex *cis*-[PtCl$_2$(PMePh$_2$)$_2$] (36.1 mg) was dissolved in CDCl$_3$ (0.5 cm^3) and cooled to −60 °C; Ag[CF$_3$SO$_3$] (15 mg) was added and ^{31}P n.m.r.

examination after a few minutes revealed the presence of $[Pt_2(\mu\text{-}Cl)_2(PMePh_2)_4][CF_3SO_3]_2$ in solution [δ(P) 0.7 p.p.m., ${}^1J$(PPt) 3 795 Hz]. After removal of AgCl by filtration, CO was bubbled through the solution for 35 min, maintaining the temperature at −60 °C. Phosphorus-31 n.m.r. spectroscopic examination now revealed only *cis*-$[PtCl(CO)(PMePh_2)_2][CF_3SO_3]$ in solution. Allowing the solution to warm to +30 °C for 10 min caused complete conversion to the *trans* isomer.

trans-*Chlorobis(methyldiphenylphosphine)(phenylisocyanide) platinum Chloride.*—The complex *cis*-$[PtCl_2(CNPh)(PMePh_2)]$ (30 mg, 5.3 mmol) was dissolved in $CDCl_3$ (0.5 cm)^3 and $PMePh_2$ (10.5 mg, 5.3 mmol) was added by syringe. N.m.r. examination revealed the presence of *trans*-$[PtCl(CNPh)(PMePh_2)_2]Cl$ in solution. When this solution was allowed to stand for 24 h, it turned brown, and examination revealed only *cis*-$[PtCl_2(CNPh)(PMePh_2)]$ in solution.

Attempts to isolate *trans*-$[PtCl(CNPh)(PMePh_2)_2]Cl$ from a larger (300 mg) scale preparation led only to brown oils. Treatment of the salt with $Ag[CF_3SO_3]$ to convert it to *trans*-$[PtCl(CNPh)(PMePh_2)_2][CF_3SO_3]$ also led only to oils on attempted crystallisation from a wide range of solvents. Methyl isocyanide derivatives behaved similarly. Behaviour of this type has been reported previously for cationic isonitrile complexes.[15]

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