Dissociative Substitution in Four-co-ordinate Planar Platinium(II) Complexes. The Kinetics of Sulphoxide Exchange and its Displacement by Bidentate Ligands in the Reactions of *cis*-Di(aryl)bis(dimethyl sulphoxide)platinum(II) in Chloroform and Benzene

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A parallel flow ^{1}H n.m.r. and u.v. spectrophotometric study of the exchange of Me_2SO with $(CD_3)_2SO$, and the displacement of Me_2SO by L–L [L–L = 2,2′-bipyridine, 1,10-phenanthroline, and 1,2-bis(diphenylphosphino)ethane] from *cis*-$[Pt(Ph)_2(Me_2SO)_2]$ in $CDCl_3$ and benzene indicates that the main reaction path is dissociative with $[Pt(Ph)_2(Me_2SO)]$ as the reactive intermediate.

The normal mode of substitution in four-co-ordinate planar d^8 metal complexes is associative.[1] Attempts to induce a dissociative mode of activation by means of bond weakening[2] and/or steric hindrance[3] generally serve to reduce the nucleophilic discrimination to a point where the substitution takes place by way of solvolysis. The activation remains associative. Only in the case of the isomerisation of *cis*-$[Pt(PEt_3)_2(R)(X)]$ (R = alkyl or aryl; X = Cl, Br, *etc.*) is there good evidence for a rate-limiting dissociation[4] but, apart from the case where R = 2,4,6-$Me_3C_6H_2$, the dissociation leading to isomerisation is much slower than the associative substitution.

As part of our study of the mutual labilisation of two *cis*-sulphoxides,[5] it was our intention to investigate the effect of strong *trans* influence ligands. To this end we studied the reactions of *cis*-$[Pt(Ph)_2(Me_2SO)_2]$, in which it has been shown that the phenyl group exerts a significant *trans* influence on the Pt–S bond.[6] In $CDCl_3$ solution, a flow ^{1}H n.m.r. study shows that the complex exchanges co-ordinated-Me_2SO with $(CD_3)_2SO$ according to the rate law, Rate = $\{k_1 + k_2[Me_2SO]\}$[complex]. ^{1}H N.m.r. studies also show that, on addition of 2,2′-bipyridine (bipy) the complex is converted into $[PtPh_2(bipy)]$ without the build up of any significant concentrations of other Me_2SO-containing species. The rate of release of Me_2SO is consistent with the rate law, $d[Me_2SO]/dt = \{2k_1k_3[bipy]/(k_{-1}[Me_2SO] + k_3[bipy])\}$-$[Pt(Ph)_2(Me_2SO)_2]$, but the flow n.m.r. data are not sufficiently accurate to allow a precise determination of the rate constants.

$$cis\text{-}[Pt(Ph)_2(Me_2SO)_2] + L\text{–}L \rightarrow [Pt(Ph)_2(L\text{–}L)] + 2Me_2SO \quad (1)$$

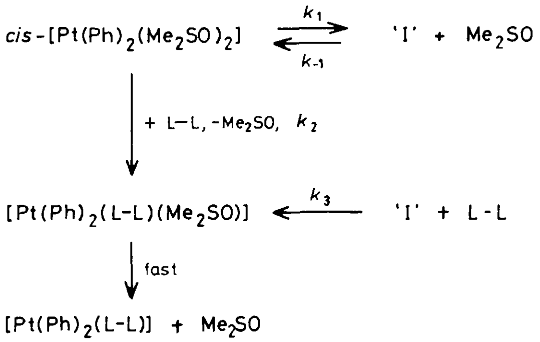
A spectrophotometric study of reaction (1), [L–L = bipy, 1,10-phenanthroline (phen), and 1,2-(diphenylphosphino)-ethane (dppe)] under first-order conditions {[L–L] and $[Me_2SO] \gg$ [complex]} in benzene solution confirmed the above rate law, but in the reaction with the strong nucleophile (dppe) there is an additional dependence on L–L, $\{+ k_2[L\text{–}L]\}$. The rate constants are collected in Table 1, where it will be seen that k_1 is nearly independent of the nature of the entering group whereas the ratio k_3/k_{-1} is very sensitive.

The rate law is consistent with the mechanism shown in Scheme 1, where species 'I' contains only one dimethyl

Table 1. Derived rate constants for the reaction: *cis*-$[PtR_2(Me_2SO)_2]$ + L–L → $[PtR_2(L\text{–}L)]$ + $2Me_2SO$.

R	L–L	k_1/s^{-1}	k_3/k_{-1}	$k_2/dm^3 mol^{-1} s^{-1}$
Ph	Me_2SO[a,b]	0.079		0.102
	bipy[a]	0.08 ± 0.02	0.06 ± 0.02	
	bipy[c]	0.014	0.049	0
	phen[c]	0.020	0.26	0
	dppe	0.020	5.6	10
$4\text{-}MeC_6H_4$	bipy[c]	0.015	0.044	0

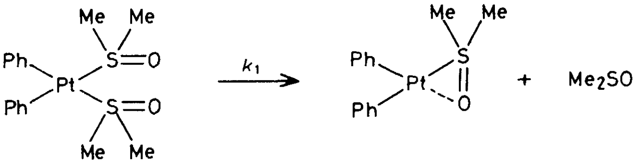
[a] In $CDCl_3$ at 300 K, by ^1H n.m.r. [b] Dimethyl sulphoxide exchange. [c] In benzene at 303.2 K, spectrophotometrically.



Scheme 1

sulphoxide and no L–L. Although this is the usual rate law for parallel associative solvolysis and direct substitution,[7] it is unlikely that chloroform or benzene, particularly the latter, is sufficiently nucleophilic to enter at a rate represented by the k_1 pathway and, indeed, insufficiently co-ordinating to occupy a site in the co-ordination shell of the platinum(II). Species 'I' is therefore $[Pt(Ph)_2(Me_2SO)]$. The experimental evidence points unequivocally to a dissociative mechanism, one of the first to be found in square-planar substitution that is not the result of the suppression of the normal associative pathway.

The intermediate possesses some discriminating ability (as measured by the dependence of k_3/k_{-1} on the nature of L–L), but a factor of only 10^2 on going from the weakish nitrogen donor of bipy to the strongly nucleophilic phosphine suggests that the discrimination is not large and indicates a highly reactive intermediate. It is likely that the dissociation is assisted by an anchimeric effect from the oxygen of the remaining sulphoxide, see Scheme 2. We suggest that the strong *trans* influence of the phenyl group is necessary in order to weaken and lengthen the Pt–S bond sufficiently to make the Pt···O interaction strong enough. Neither this explanation, nor the alternative, calling for assistance from a β-hydrogen,[8] can account for the possible occurrence of a similar mode of activation in the reaction between *cis*-$[Pt(Me)_2(Me_2S)_2]$ and the $[Pt(Me_2S)_2X_2]$ isomers in which a methyl group is transferred.[9]



Scheme 2

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