Kinetics of Substitution of Some Bis(pentafluorophenyl)platinum(II) Complexes by 2,2'-Bipyridine*

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The kinetics of the substitution reactions between the complexes *cis*-[Pt(C_6F_5)$_2$$L_2$] (L = Me_2SO, Et_2S or tetrahydrothiophene) and 2,2'-bipyridine (bipy) to give [Pt(C_6F_5)$_2$(bipy)] in toluene has been investigated. The results indicate that for the bis(sulfoxide) complex the reaction proceeds *via* a dissociative mechanism in which there is an initial dissociation of Me_2SO to form a three-co-ordinate intermediate, while an associative mechanism is operative for the bis(thioether) complexes. The role of electron density at the platinum atom and of ancillary ligands in determining the reaction pathway is discussed.

Kinetic studies have shown that substitution reactions of sulfur-bonded ligands L from *cis*-[PtR_2L_2] (R = Me or Ph, L = sulfoxide or thioether) by bidentate nucleophiles in apolar solvents occur through parallel associative and dissociative pathways.[1] The dissociative route yields a co-ordinatively unsaturated 14-electron [PtR_2L] intermediate.

In searching for factors promoting the dissociative mode of activation for these organometallic complexes it was thought that the main factor was the strong σ-donor power of the methyl and phenyl groups, which lengthens and weakens the platinum–sulfur bond.[1c] However, very recently it has been pointed out[2,3] that ground-state destabilization is not sufficient and that the electrophilicity of the metal centre plays a major role in determining the choice between associative and dissociative pathways.

It is well known that the pentafluorophenyl group withdraws electron density from platinum by a strong inductive effect.[4] Thus in order to gain further information concerning the importance of electron density at the metal in determining the reaction mechanism of such systems I decided to undertake a kinetic investigation in toluene of the reactions (1) [L =

$$cis\text{-}[\mathrm{Pt}(C_6F_5)_2L_2] + \text{bipy} \longrightarrow [\mathrm{Pt}(C_6F_5)_2(\text{bipy})] + 2L \quad (1)$$

Me_2SO, tetrahydrothiophene (tht) or Et_2S; bipy = 2,2'-bipyridine]. 2,2'-Bipyridine was chosen because the dissociative route is the dominant pathway in substitution reactions by nitrogen chelating ligands.[1]

Experimental

Materials and Instrumentation.—The complexes *cis*-[Pt(C_6F_5)$_2$(Et_2S)$_2$], *cis*- and *trans*-[Pt(C_6F_5)$_2$(tht)$_2$] were prepared according to published procedures.[5,6] Dimethyl sulfoxide was dried over 4 Å Linde molecular sieves and vacuum distilled, toluene was dried by distillation from sodium diphenylketyl. 2,2'-Bipyridine (from Aldrich) was reagent grade used without further purification. Infrared spectra were recorded as Nujol mulls between CsI plates on a Perkin Elmer FT 1720X instrument, ^1H NMR spectra on a Bruker 80Q or a Varian Gemini 300 instrument. Chemical shifts are in ppm downfield from internal tetramethylsilane.

Preparations.—cis-*Bis(dimethyl sulfoxide)bis(pentafluorophenyl)platinum*(II). The complex *cis*-[Pt(C_6F_5)$_2$(Et_2S)$_2$] (200 mg) was dissolved in Me_2SO (25 cm^3) at 80 °C and the solution was stirred overnight. Evaporation of the solvent under vacuum left a white solid. Crystallization from a dichloromethane–light petroleum (b.p. 40–60 °C) mixture gave white crystals of the product (yield 75%) (Found: C, 28.3; H, 1.65; F, 27.8; S, 9.2. $C_{16}H_{12}F_{10}O_2PtS_2$ requires C, 28.0; H, 1.75; F, 27.7; S, 9.35%).

trans-*Bis(dimethyl sulfoxide)bis(pentafluorophenyl)platinum*(II). This complex was prepared in a similar way starting from *trans*-[Pt(C_6F_5)$_2$(tht)$_2$]. The white crystalline residue was washed with diethyl ether and air-dried (yield 84%) (Found: C, 27.9; H, 1.75; F, 27.6; S, 9.2. $C_{16}H_{12}F_{10}O_2PtS_2$ requires C, 28.0; H, 1.75; F, 27.5; S, 9.35%).

Kinetics.—The kinetic data were obtained on a Perkin Elmer Lambda 5 spectrophotometer equipped with a constant-temperature cell holder. Absorbance readings were taken in the wavelength range 340–460 nm or at a selected wavelength (405 nm). The reactions were started by mixing a prethermostatted solution of the complex in toluene with an equal volume of a solution containing all the other reagents previously brought to the reaction temperature. The complex concentration ranged from 5×10^{-5} to 2×10^{-4} mol dm^{-3}. Runs were carried out under pseudo-first-order conditions and observed rate constants k_{obs} were calculated from the slopes of plots of $\ln(A_\infty - A_t)$ *versus* time. Such plots were linear for at least two to three half-lives of the reaction. Activation parameters were obtained from conventional Eyring plots of $\ln(k/T)$ *vs.* $1/T$. The values of k_{obs} have been deposited (see SUP 56929).

Results

The new complexes *cis*- and *trans*-[Pt(C_6F_5)$_2$(Me_2SO)$_2$] have been obtained by displacement reactions of bis(thioether) complexes with an excess of dimethyl sulfoxide. The synthesis of both isomers makes straightforward the assignment of the stereochemistry of the complexes by comparison of their spectroscopic properties. The IR spectrum of the *cis* compound shows two bands at 804 and 793 cm^{-1}, while the *trans* isomer has a single band at 784 cm^{-1}. These absorptions are attributable to 'X-sensitive' vibrations involving mainly Pt–C stretching and have already been used for structural elucidation.[6] Two strong

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* *Supplementary data available* (No. SUP 56929, 5 pp.): pseudo-first-order rate constants. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

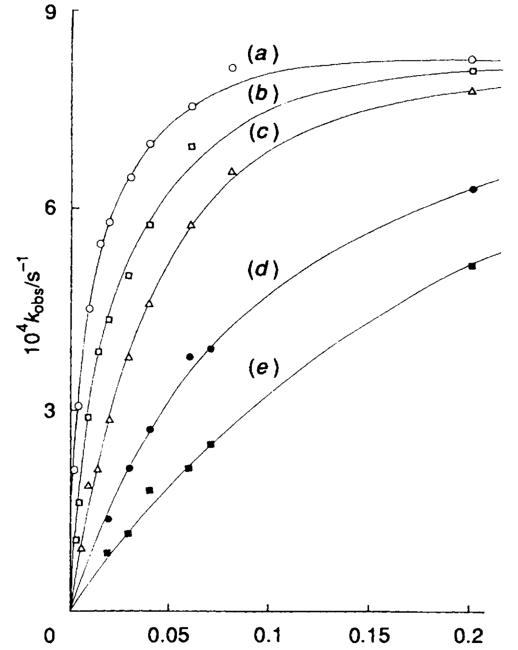

Fig. 1 Dependence of k_{obs} on [bipy] for the reaction of *cis*-$[Pt(C_6F_5)_2(Me_2SO)_2]$ with bipy in toluene at 303.2 K at various Me_2SO concentrations: (*a*) 0.0005, (*b*) 0.001, (*c*) 0.002, (*d*) 0.005 and (*e*) 0.01 mol dm^{-3}

ν(S=O) bands at 1138 and 1124 cm^{-1} and two ν(Pt–S) bands at 436 and 422 cm^{-1} are observed for the *cis* complex, while a single strong ν(S=O) band at 1150 cm^{-1} and a single ν(Pt–S) band at 424 cm^{-1} are observed for the *trans* isomer. The frequencies of the ν(S=O) bands are in the region expected for *S*-bonded dimethyl sulfoxide; the number of bands observed for each compound is consistent with the assigned geometry.[7]

The ^1H NMR spectra of *cis*-$[Pt(C_6F_5)_2(Me_2SO)_2]$ in $CDCl_3$ and *trans*-$[Pt(C_6F_5)_2(Me_2SO)_2]$ in $(CD_3)_2CO$ show a single peak δ(CH_3) at 3.14 [*J*(PtH) = 18.5] and at 3.22 [*J*(PtH) = 27.5 Hz] respectively. The chemical shift and the observed coupling to ^{195}Pt indicate that Me_2SO is co-ordinated through sulfur in solution. The values of the coupling constants agree with the greater *trans* influence of the C_6F_5 group compared with that of Me_2SO.

When *cis*-$[Pt(C_6F_5)_2(Me_2SO)_2]$ (10^{-2} mol dm^{-3}) is treated with pyridine (py) (10^{-1} mol dm^{-3}) in $CDCl_3$ the proton NMR spectra show that the displacement of Me_2SO occurs in two consecutive steps, the first being faster. The signal of free Me_2SO is observed at δ 2.61 (6 H) and the resonances of the monosulfoxide complex *cis*-$[Pt(C_6F_5)_2(Me_2SO)(py)]$ are assigned as follows: δ 3.00 [6 H, s, *J*(PtH) 19.5, CH_3], 7.44 (2 H, m, $H^{3,5}$), 7.82 (1 H, m, H^4) and 8.78 [2 H, m, *J*(PtH) 27 Hz, $H^{2,6}$]. The final product, *cis*-$[Pt(C_6F_5)_2(py)_2]$, separated as white crystals from the reaction mixture and was isolated and characterized by elemental analysis and from the ^1H NMR spectrum in $(CD_3)_2CO$ which was in agreement with reported data.[8]

When the complex *cis*-$[Pt(C_6F_5)_2(Me_2SO)_2]$ was treated with an equimolar amount or an excess of bipy in $CDCl_3$ the signal of co-ordinated Me_2SO changed with time to the singlet of the free ligand, while yellow crystals separated. There is no evidence of formation in solution of any monosulfoxide species. The same behaviour is observed in C_6D_6. In this solvent the resonances of co-ordinated and free Me_2SO are observed at δ 2.18 [*J*(PtH) = 18.5 Hz] and 1.69 respectively. The yellow crystals precipitated during the reaction were isolated and analytically and spectroscopically identified as $[Pt(C_6F_5)_2(bipy)]$.[9]

The reaction of the compound *cis*-$[Pt(C_6F_5)_2(Et_2S)_2]$ with an excess of pyridine in $CDCl_3$ was slow. After 20 h at room temperature the proton NMR spectrum showed signals assigned to co-ordinated Et_2S of unreacted starting substrate (a multiplet at δ 2.67 and a triplet at 1.40), free Et_2S (a quartet at δ 2.54 and a triplet at 1.26) and co-ordinated Et_2S of a mono(thioether) species (multiplet obscured, triplet at δ 1.36) in the ratio of *ca.* 2 : 1 : 1.

When *cis*-$[Pt(C_6F_5)_2(Et_2S)_2]$ is treated with an excess of bipy in $CDCl_3$ there is no evidence of build-up of any mono(thioether) species and $[Pt(C_6F_5)_2(bipy)]$ separated slowly from the reaction mixture.

The kinetics of the reactions (1) was followed spectrophotometrically in toluene under pseudo-first-order conditions in the presence of a sufficient excess of bipy and leaving ligand L. The reactions go to completion; the final spectra are identical with those of independently prepared solutions of $[Pt(C_6F_5)_2(bipy)]$. According to the NMR results, there is no spectral evidence of the presence of any monosubstituted intermediate. Proton NMR and electronic spectra clearly indicate that the reaction of *cis*-$[Pt(C_6F_5)_2L_2]$ with bipy occurs in a single observable step, ring closing being faster than the displacement of the first ligand L.

For the system *cis*-$[Pt(C_6F_5)_2(Me_2SO)_2]$–bipy the displacement of Me_2SO by bipy is retarded by addition of free leaving group, with the pseudo-first-order rate constants (SUP 56929) tending towards a limiting value at high concentration of entering nucleophile (Fig. 1). At constant $[Me_2SO]$, good linear plots of $1/k_{obs}$ *vs.* 1/[bipy] are obtained, the slopes of which are linearly dependent on dimethyl sulfoxide concentration. The intercept is independent of $[Me_2SO]$. These results indicate a rate equation of the form (2).

$$k_{obs} = a[\text{bipy}]/(b[Me_2SO] + [\text{bipy}]) \qquad (2)$$

For the thioether complexes *cis*-$[Pt(C_6F_5)_2(tht)_2]$ and *cis*-$[Pt(C_6F_5)_2(Et_2S)_2]$, the k_{obs} values are linearly correlated [equation (3)] to the nucleophile concentration and are

$$k_{obs} = k_2[\text{bipy}] \qquad (3)$$

independent of the concentration of added free leaving group (SUP 56929). The linear plots pass through the origin within the limits of experimental error.

Discussion

The rate equation (2) is consistent with a mechanism consisting of two or more reaction steps, one involving competition for an intermediate by Me_2SO and bipy. According to all the experimental evidence the mechanism given in equations (4)–(6)

$$cis\text{-}[Pt(C_6F_5)_2(Me_2SO)_2] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Pt(C_6F_5)_2(Me_2SO)] + Me_2SO \qquad (4)$$

$$[Pt(C_6F_5)_2(Me_2SO)] + \text{bipy} \xrightarrow{k_3} [Pt(C_6F_5)_2(\text{bipy})(Me_2SO)] \qquad (5)$$

$$[Pt(C_6F_5)_2(\text{bipy})(Me_2SO)] \xrightarrow{\text{fast}} [Pt(C_6F_5)_2(\text{bipy})] + Me_2SO \qquad (6)$$

is proposed. Equation (4) represents the initial dissociation of one dimethyl sulfoxide to give a three-co-ordinated intermediate and the second step leads to the formation of an open-ring monosulfoxide species. A rapid ring closing gives the observed product. If the intermediate $[Pt(C_6F_5)_2(Me_2SO)]$ is assumed to be formed under steady-state conditions, the rate equation (7) is obtained, of the same form as the empirical

Table 1 Derived rate constants and activation parameters for the reactions *cis*-[Pt(C_6F_5)$_2$L$_2$] + bipy $\longrightarrow$ [Pt(C_6F_5)$_2$(bipy)] + 2L in toluene

L	$10^3k_1/s^{-1}$	k_3/k_{-1}	10^3k_2/dm^3 mol^{-1} s^{-1}
Me_2SO^a	0.480 ± 0.018	0.037 ± 0.008	0
Me_2SO^b	0.886 ± 0.011	0.055 ± 0.003	0
Me_2SO^c	1.41 ± 0.02	0.029 ± 0.001	0
Me_2SO^d	2.27 ± 0.02	0.034 ± 0.003	0
Me_2SO^e	3.61 ± 0.02	0.029 ± 0.001	0
tht^b	0		0.026 5 ± 0.001 1
tht^d	0		0.059 1 ± 0.000 1
tht^e	0		0.089 2 ± 0.001 1
Et_2S	0		0.002 93 ± 0.000 10

$\Delta H_1^\ddagger = 76 \pm 2$ kJ mol^{-1}, $\Delta S_1^\ddagger = -53 \pm 6$ J K^{-1} mol^{-1};
$\Delta H_2^\ddagger = 62 \pm 1$ kJ mol^{-1}, $\Delta S_2^\ddagger = -128 \pm 4$ J K^{-1} mol^{-1}

[a] 298.2 K. [b] 303.2 K. [c] 308.2 K. [d] 313.2 K. [e] 318.2 K.

$$k_{obs} = k_1[\text{bipy}]/\{(k_{-1}/k_3)[\text{Me}_2\text{SO}] + [\text{bipy}]\} \quad (7)$$

equation (2). The values of k_1 (= *a*) and k_{-1}/k_3 (= *b*), calculated by multiple non-linear regression of k_{obs} *vs.* [bipy] and [Me_2SO] dependencies, are presented in Table 1. The rate equation (7) is identical to that found for the substitution of Me_2SO from *cis*-[PtPh$_2$(Me_2SO)$_2$] by 2,2′-bipyridine in benzene.[1b]

A decrease in the value of k_1 on changing from phenyl to perfluorophenyl (14.0 × 10^{-3} to 0.886 × 10^{-3} s^{-1} at 303.2 K) is observed, as a result of an increase in the value of $\Delta H_1^\ddagger$ associated with a less negative $\Delta S_1^\ddagger$. Dissociative processes have been characterized by high $\Delta H^\ddagger$ and positive $\Delta S^\ddagger$ values {*e.g.* $\Delta H_1^\ddagger = 100.7 \pm 3$ kJ mol^{-1} and $\Delta S_1^\ddagger = 42 \pm 8$ J K^{-1} mol^{-1} for the system *cis*-[Pt(C_6H_5)$_2$(Me_2S)$_2$]–bipy}. The smaller $\Delta H_1^\ddagger = 64 \pm 2$ kJ mol^{-1} and the negative value of $\Delta S_1^\ddagger = -67 \pm 8$ J K^{-1} mol^{-1} found for *cis*-[PtPh$_2$(Me_2SO)$_2$] suggested the possibility of an anchimeric assistance of the oxygen atom of the ambidentate dimethyl sulfoxide in the intermediate [PtPh$_2$(Me_2SO)]. This chelation will compensate partially for bond breaking between Pt and leaving Me_2SO; $\Delta H^\ddagger$ is smaller and $\Delta S^\ddagger$ negative due to the loss of rotational freedom. Such a hypothesis is still consistent with the activation parameters found for the complex *cis*-[Pt(C_6F_5)$_2$(Me_2SO)$_2$] (see Table 1).

The reactions between *cis*-[Pt(C_6F_5)$_2$(thioether)$_2$] and bipy obey the rate equation (3). Addition of free thioether does not produce any mass-law retardation. The most convincing interpretation of (3) is the operation of an associative mechanism, in line with the large negative entropy of activation found for the displacement of tht from *cis*-[Pt(C_6F_5)$_2$(tht)$_2$] by bipy ($\Delta S_2^\ddagger = -128 \pm 4$ J K^{-1} mol^{-1}, see Table 1). A solvolytic contribution, as typically found for ligand substitution in square planar platinum(II) complexes,[10] is not observed. However, a zero intercept is to be expected when the dissociative pathway is suppressed, since the possibility of formation of a solvento intermediate in poor co-ordinating solvents, is ruled out.

A salient feature of this kinetic study is the demonstration that the introduction of pentafluorophenyl in place of the phenyl group for complexes of the type *cis*-[PtR$_2$(thioether)$_2$] makes the dissociative pathway non-operative in spite of the fact that the concurrent associative pathway is made energetically unfavourable by steric strain produced by the *o*-fluoro substituents on the aromatic ring.[11]

X-Ray diffraction data for the complexes *cis*-[Pt(PEt$_3$)$_2$(*p*-MeC$_6$H$_4$)Cl] and *cis*-[Pt(PEt$_3$)$_2$(C_6F_5)Cl] show no significant difference in the Pt–C bond lengths [2.05(3) and 2.08(2) Å respectively] and in the Pt–P bond lengths *trans* to aryl group [2.320(9) and 2.326(7) Å respectively].[12] It was concluded that both *p*-tolyl and pentafluorophenyl groups exert a strong *trans* influence and that no significant π-bonding contribution is detectable by X-ray measurement in perfluoro complexes having *trans* P atoms. Indeed, the Pt–C bond lengths of most phenyl- and pentafluorophenyl-platinum(II) complexes are comparable, *e.g.* 2.0477(25) Å for *cis*-[Pt(C_6F_5)$_2$(PhC≡CPh)$_2$],[13] 2.056(6) and 2.045(7) Å for *cis*-[Pt(C_6F_5)$_2$-{SC(S)P(C_6H_{11})$_3$}(CO)],[14] and 2.043(5) and 2.049(6) Å for *cis*-[PtPh$_2$(Me_2SO)$_2$].[15]

Thus the observed suppression of the dissociative pathway for the substitution reactions of *cis*-[Pt(C_6F_5)$_2$(thioether)$_2$] is hardly only a ground-state effect. This result may be attributed to the reduced capacity of the C_6F_5 group to release electron density so that the three-co-ordinate intermediate is destabilized. This is not the case of the intermediate [Pt(C_6F_5)$_2$(Me_2SO)], where the electron deficiency is partly satisfied by the oxygen of Me_2SO, and the dissociative process therefore needs less inductive assistance from the aromatic ring. It can be concluded that, for complexes of the type *cis*-[PtR$_2$L$_2$], the change from phenyl to pentafluorophenyl withdraws electron density from platinum in such a way that dissociation is suppressed except when an anchimeric assistance of an ancillary ligand is possible.

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