

The Isomerisation of *cis*-Bis-triethylphosphine-4-fluorophenyl-chloroplatinum(II): Solvent Effects and Mechanism

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Abstract

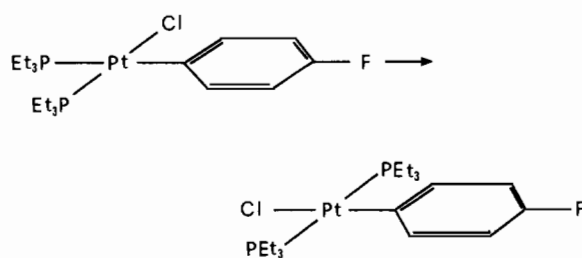
Rate constants are reported for isomerisation, solvolysis, and thiourea substitution of *cis*-[Pt(PEt₃)₂(4-FC₆H₄)Cl] in aqueous methanol and in aqueous ethanol. From these results and ancillary solubility measurements the observed effects of solvent on reactivity are analysed into initial state and transition state contributions, for isomerisation of this complex and for its reaction with thiourea. The initial state–transition state analysis for isomerisation is consistent with a dissociative mechanism, the reactivity trends being dominated by solvation of the leaving chloride ligand.

Introduction

There is overwhelming evidence that the majority of substitutions at square-planar d⁸ transition metal centres take place by associative mechanisms [1]. However, from time to time evidence has been presented which suggests the operation in certain cases of a dissociative mechanism [2]. Recent examples include ligand replacement in *cis*-[PtMe₂(SMe₂)₂] + *cis*- or *trans*-[PtCl₂(SMe₂)₂] [3], thermal and photochemical isomerisation of [Pt(Dialkyl Sulfoxide)₂Cl₂] complexes [4], and thermal decomposition of dialkyl and di(cycloalkyl)bis(phosphine)-platinum(II) complexes [5]. In the last few years evidence has accumulated that *cis* → *trans* isomerisation of complexes of the type [Pt(PEt₃)₂(XC₆H₄)Cl] is dissociative in character [6]. The determination of activation volumes failed to provide an unequivocal answer, since a pressure study of isomerisation of the extremely crowded *cis*-[Pt(PEt₃)₂(mesityl)Br] has led to a negative value of the activation volume (−12.0 ± 0.5 cm³ mol^{−1}) [7, 8] while for other complexes such as *cis*-[Pt(PEt₃)₂PhX] the activation volumes for isomerisation were found to be positive (X = Cl, Δ*V*[#] = +6.4 ± 0.4 cm³ mol^{−1};

X = Br, Δ*V*[#] = +7.7 ± 0.3 cm³ mol^{−1}; X = I, Δ*V*[#] = +7.2 ± 0.8 cm³ mol^{−1}) [8, 9]. Ambiguities of this sort in the observed Δ*V*[#] could well represent the balance between dissociative activation (positive contribution to Δ*V*[#]) and solvent electrostriction around the developing δ+ and δ− charges as the platinum–halide bond is extended (negative contribution to Δ*V*[#]). Analysis of solvent effects on isomerisation rate constants, with especial reference to transfer chemical potentials for leaving chloride, strongly favoured the dissociative mechanism [10]. This earlier analysis was less than completely satisfactory, as transfer chemical potential data for the complex were not available and because there were difficulties regarding the derivation of transfer chemical potentials for chloride ions between various alcohols on a consistent single ion assumption basis.

We now report the results of a full initial state–transition state analysis of solvent effects on the isomerisation



in methanol–water and ethanol–water solvent mixtures. We also report initial state–transition state analysis for the reaction of *cis*-[Pt(PEt₃)₂(4-FC₆H₄)Cl] with thiourea in methanol–water mixtures. The results are discussed in relation to a likely mechanism for the isomerisation and to the relative importance of solvation changes of the reactants and of the transition states for the thiourea substitution reaction.

TABLE I. Rate Constants for Isomerisation (k_i , s^{-1}), Solvolysis (k_1 , s^{-1}) and Nucleophilic Substitution by Thiourea (k_2 , $M^{-1} s^{-1}$) for the Complex *cis*-[Pt(PEt₃)₂(4-FC₆H₄)Cl] in Aqueous Methanol and Aqueous Ethanol at 298.2 K.

Vol. % MeOH	30	40	50	60	70	80	90	100
$10^4 k_i$, s^{-1}	17.9 ± 0.8	14.3 ± 0.7	12.5 ± 0.5	8.34 ± 0.3	6.14 ± 0.2	4.02 ± 0.2	2.75 ± 0.1	2.09 ± 0.1
k_1 , s^{-1}		6.36 ± 0.3	5.67 ± 0.04	4.89 ± 0.1	4.13 ± 0.1	3.65 ± 0.1	2.54 ± 0.08	1.99 ± 0.02
$10^{-3} k_2$, $M^{-1} s^{-1}$		16.8 ± 0.6	12.7 ± 0.7	12.6 ± 0.3	13.4 ± 0.3	14.2 ± 0.2	16.2 ± 0.08	18.3 ± 0.3
Vol. % EtOH	30	40	50	60	70	80	90	100
$10^4 k_i$, s^{-1}		10.8 ± 0.5	7.29 ± 0.3	4.05 ± 0.2	2.80 ± 0.1	1.09 ± 0.04	0.413 ± 0.02	0.103 ± 0.003
k_1 , s^{-1}		5.46 ± 0.2	4.07 ± 0.2	3.44 ± 0.08	2.83 ± 0.04	2.38 ± 0.04	2.08 ± 0.07	1.19 ± 0.07
$10^{-3} k_2$, $M^{-1} s^{-1}$		16.5 ± 0.4	13.8 ± 0.5	14.9 ± 0.3	13.7 ± 0.6	15.9 ± 0.4	22.1 ± 0.1	53.9 ± 2.0

Experimental

Materials

Cis and *trans*-[Pt(PEt₃)₂(4-FC₆H₄)Cl] were prepared by the literature method [11, 12] and characterized through elemental analysis, i.r. and ¹H n.m.r. spectra. Methanol and ethanol were purified and dried by standard methods [13]. Other reagents were used without further purification.

Kinetics

The conversion of *cis*-[Pt(PEt₃)₂(4-FC₆H₄)Cl] into its *trans* isomer proceeds practically to completion in each of the solvent mixtures employed and is slow enough to be followed by conventional techniques. The reactions were carried out in a silica cell in the thermostatted cell compartment of a Cary 219 spectrophotometer, where the temperature remained constant within ±0.05 °C. The solvent was brought to reaction temperature in the spectrophotometer and the reaction was started by adding a weighed amount of a finely powdered complex and shaking the solution rapidly. The progress of the reaction was monitored by scanning the spectrum at suitable times over the range 320–220 nm, where the *cis* and *trans* compounds exhibit different spectra with an isosbestic point at 257 nm. For the mixtures with high water content, where the complex is less soluble and the conversion faster, the reaction was started by dissolving the complex rapidly in a known volume of pre-thermostatted alcohol, adding the required amount of water, and following the reaction at the selected wavelength.

The nucleophilic substitutions of *cis*-[Pt(PEt₃)₂(4-FC₆H₄)Cl] with thiourea and iodide ion were followed at 300 and 290 nm respectively, by means of a Durrum-Gibson D110 stopped-flow spectrophotometer, equipped with a photometric amplifier. Absorbances were displayed on a Gould 054100 storage oscilloscope, and traces were recorded on a Radiometer REC61 potentiometric recorder. Isomerisation of the starting complex was prevented by dissolving the substrate in the 0.01 M LiCl. The kinetics were performed under pseudo-first-order conditions with the reagent in at least a 10-fold excess over the platinum complex. The pseudo-first-order rate constants of the isomerisation (k_i/s^{-1}) and of the nucleophilic substitution (k_{obsd}/s^{-1}) were obtained either from the gradients of the plots of $\log(A_t - A_\infty)$ vs. time, (where A_t and A_∞ are the absorbances at time t and at the end of the reaction), or from a non-linear least-squares fit of experimental data to: $A_t = A_\infty + (A_0 - A_\infty)\exp(-kt)$ with A_0 , A_∞ and k as the parameters to be optimized (A_0 = absorbance after the mixing of the reagents). The rate constants (k_i/s^{-1}) listed in Table I were calculated as the mean of at least five kinetic runs for each solvent mixture.

TABLE II. Absorbances at 285 nm of Saturated Solutions of *cis*-[Pt(PEt₃)₂(4-XC₆H₄)Cl] in Aqueous Alcohols at 298.2 K in 0.01 M LiCl.

Vol. % MeOH:	30	40	50	55	60	67	70	80
X=F	0.20	0.55	0.93	1.21	2.12	2.7	3.0	6.8
X=H	0.062	0.170	0.92		2.43			
Vol.% EtOH:	30	36	40	50	60	67		
X=F	0.156	0.26	0.29	0.63	1.46	2.20		
X=CF ₃	0.17	0.24	0.34					

TABLE III. Initial State–Transition State Analysis of Reactivity Trends for Isomerisation of *cis*-[Pt(PEt₃)₂(4-FC₆H₄)Cl] in Aqueous Methanol at 298.2 K, molar scale, kJ mol⁻¹. All transfers are from 30% methanol.

% Methanol (volume)	40	50	60	70	80
$\delta_m \mu^\circ$ (<i>cis</i> -Pt(PEt ₃) ₂ (4-FC ₆ H ₄)Cl) ^a	-2.4	-3.8	-5.8	-6.7	-8.7
$\delta_m \Delta G^\ddagger$ ^b	+0.6	+0.9	+1.9	+2.7	+3.7
$\therefore \delta_m \mu^\ddagger$ [#]	-1.8	-2.9	-3.9	-4.0	-5.0
$\delta_m \mu^\circ$ (Cl ⁻) ^c	+0.4	+1.0	+2.3	+3.7	+5.6
$\therefore \delta_m \mu^\circ$ (Pt(PEt ₃) ₂ (4-FC ₆ H ₄)) [#]	-2.2	-3.9	-6.2	-7.7	-10.6

^aFrom Table II solubilities. ^bFrom Table I rate constants. ^cFrom ref. 14.

The reaction with thiourea obeys a two-term rate law: $k_{\text{obsd}} = k_1 + k_2 [\text{thiourea}]$, the contribution from the nucleophile-independent term k_1 being small even at the lowest reagent concentrations. The second-

order rate constants k_2 were calculated by linear regression analysis of plots of k_{obsd} vs. [thiourea] and are listed together with k_1 in Table I. In the reactions with I⁻ as entering group the contribution

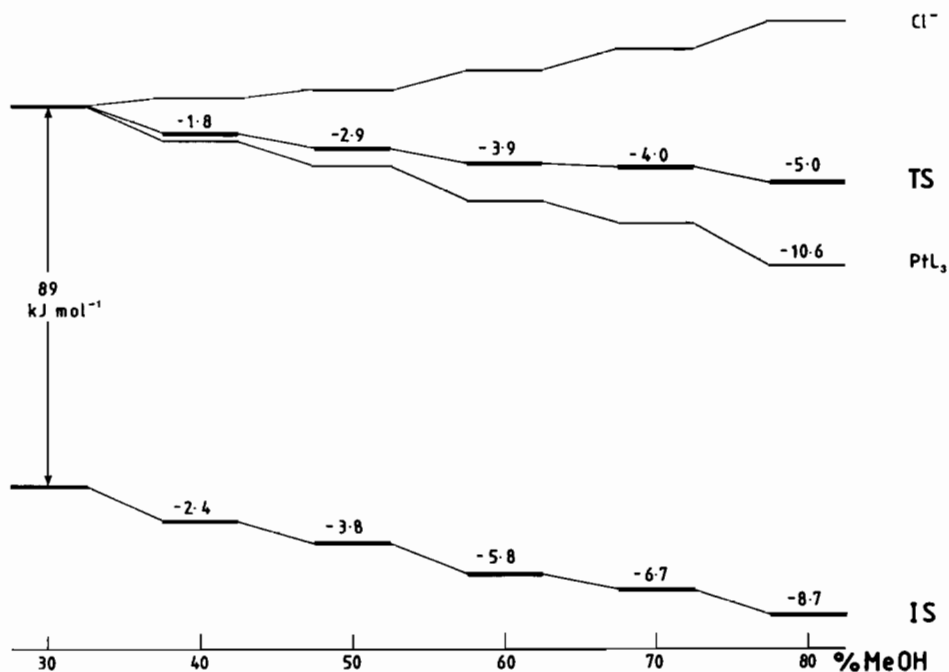


Fig. 1. Initial state–transition state analysis of solvent effects on reactivity for isomerisation of *cis*-[Pt(PEt₃)₂(4-FC₆H₄)Cl] in methanol–water mixtures.

TABLE IV. Initial State–Transition State Analysis of Reactivity Trends for Isomerisation of *cis*-[Pt(PEt₃)₂(4-FC₆H₄)Cl] in Aqueous Ethanol at 298.2 K, molar scale, kJ mol⁻¹. All transfers are from 40% ethanol.

% Ethanol (volume)	50	60	70
$\delta_m\mu^\circ$ (<i>cis</i> -Pt(PEt ₃) ₂ (4-FC ₆ H ₄)Cl) ^a	-2.9	-5.3	-7.5 ^b
$\delta_m\Delta G^\ddagger$ ^c	+1.0	+2.4	+3.4
$\therefore\delta_m\mu^\ddagger$	-1.9	-2.9	-4.1
$\delta_m\mu^\circ$ (Cl ⁻) ^d	+1.0	+1.9	+2.8
$\therefore\delta_m\mu^\circ$ (Pt(PEt ₃) ₂ (4-FC ₆ H ₄)) [#]	-2.9	-4.8	-6.9

^aFrom Table II solubilities.^bExtrapolated.^cFrom Table I rate constants.^dFrom ref. 15.

of the k_2 term was statistically insignificant in the 0.001–0.02 M Γ^- concentration range. The solvolytic rate constants (k_1/s^{-1}), listed in Table I together with their standard deviations, were calculated as the mean of a number of runs carried out at different iodide concentrations.

Solubilities were determined by thermostating an excess of compound with the appropriate solvent, with repeated agitation, for several hours in the dark. Spontaneous isomerisation was prevented by adding LiCl. Aliquots of the saturated solutions were removed, appropriately diluted, and concentrations determined spectrophotometrically (Unicam SP8-100 spectrophotometer).

Results

The rate constants determined in the course of this investigation are reported in Table I; solubilities are reported in Table II.

Discussion

Tables III and IV show analyses of solvent effects on isomerisation rate constants for *cis*-[Pt(PEt₃)₂(4-FC₆H₄)Cl] into initial state and transition state components. These Tables also show a breakdown of the solvent effects on the transition state into contributions from chloride and from the Pt(PEt₃)₂(4-FC₆H₄)⁺ moiety assuming a limiting dissociative (S_N1 lim or D) mechanism. The patterns established in the Tables III and IV analyses are depicted in Figs. 1 and 2, for aqueous methanol and aqueous ethanol respectively. The two diagrams are directly comparable in respect to the initial state and transition state trends, as these species are uncharged. They are approximately compatible in respect to the transition state component trends. The single ion assumption used in obtaining $\delta_m\mu^\circ$ (Cl⁻) values in aqueous methanol is $\delta_m\mu^\circ$ (Ph₄As⁺) = $\delta_m\mu^\circ$ (Ph₄P⁺) = $\delta_m\mu^\circ$ (BPh₄⁻) [14]; the single ion assumption used in obtaining $\delta_m\mu^\circ$ (Cl⁻) values in aqueous ethanol is $\delta_m\mu^\circ$ (Am₃BuN⁺) = $\delta_m\mu^\circ$ (BPh₄⁻) [15]. This latter

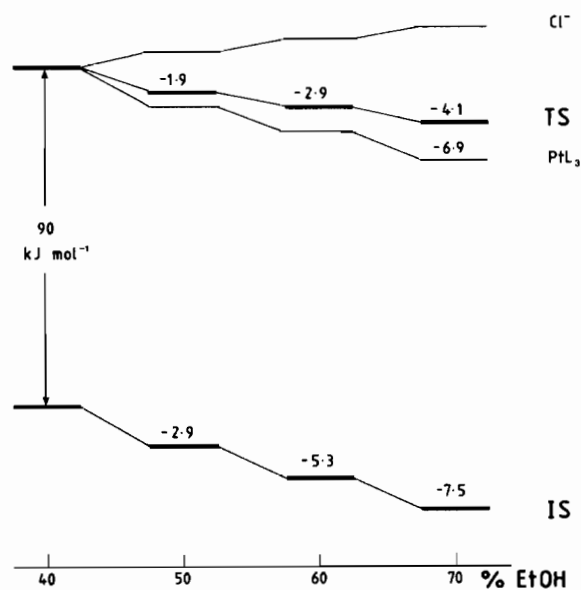


Fig. 2. Initial state–transition state analysis of solvent effects on reactivity for isomerisation of *cis*-[Pt(PEt₃)₂(4-FC₆H₄)Cl] in ethanol–water mixtures.

assumption is roughly equivalent to the former, but it is possible that there may be a discrepancy of 3 or 4 kJ mol⁻¹ in $\delta_m\mu^\circ$ (Cl⁻) values derived by the two methods, particularly in mixed solvents in the region of 50%. The analyses in Tables III and IV (Figs. 1 and 2) are restricted to the middle composition range by technical difficulties in water-rich and methanol-rich mixtures. In water and water-rich mixtures the platinum complex is too sparingly soluble for accurate kinetic and solubility results to be obtained; in methanol and methanol-rich mixtures the complex is so soluble that again accurate solubility determinations are impossible.

Table III and Fig. 1 show that the decrease in rate on increasing the methanol content of the solvent mixtures is due to a somewhat greater stabilisation of the initial state than of the transition state. This seems reasonable in view of the charge separation

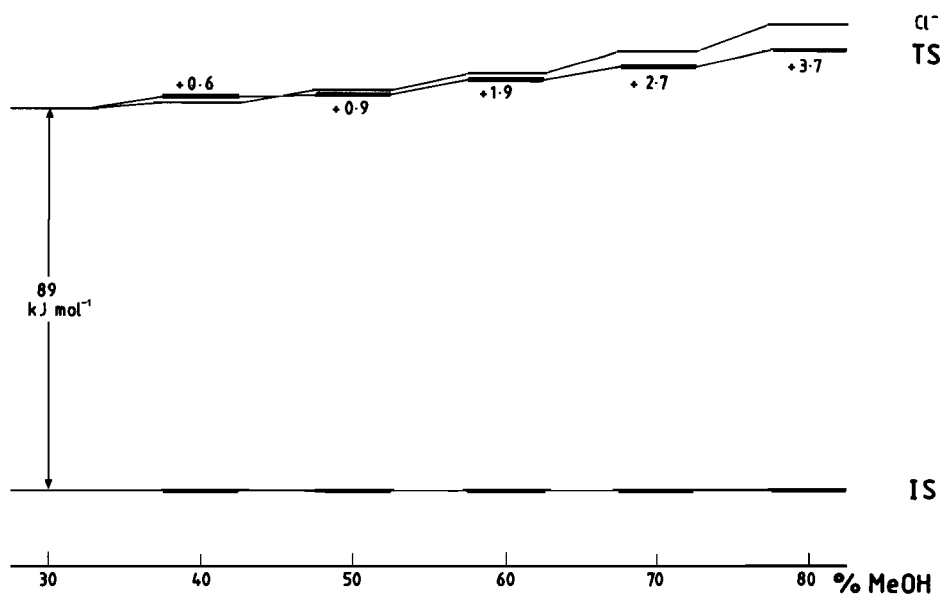


Fig. 3. Initial state-transition state analysis of solvent effects on reactivity for isomerisation of *cis*-[Pt(PEt₃)₂(4-FC₆H₄)Cl] in methanol-water mixtures, assuming that the reactivity trend is determined solely by solvation of the leaving chloride (cf. text and ref. 10).

TABLE V. Initial State-Transition State Analysis of Reactivity Trends for Reaction of *cis*-[Pt(PEt₃)₂(4-FC₆H₄)Cl] with Thiourea in Aqueous Methanol at 298.2 K, molar scale, kJ mol⁻¹. All transfers are from 50% methanol.

% Methanol (volume)	60	70	80
$\delta_m \mu^\circ$ (<i>cis</i> -Pt(PEt ₃) ₂ (4-FC ₆ H ₄)Cl)	-2.0	-2.9	-4.9
$\delta_m \mu^\circ$ (thiourea) ^a	0	+0.1	+0.3
$\therefore \delta_m \mu^\circ$ (initial state)	-2.0	-2.8	-4.6
$\delta_m \Delta G^\ddagger$	0	-0.1	-0.3
$\therefore \delta_m \mu^\ddagger$	-2.0	-2.9	-4.9

^a Interpolated from M. J. Blandamer, J. Burgess and S. J. Hamshere, *J. Chem. Soc. Dalton Trans.*, 1539 (1979) and unpublished solubility data kindly supplied by S. Balt.

which would be involved in generating a Pt^{δ+}...Cl^{δ-} transition state. The hydrophilic nature of such a dipole would to some extent counteract the hydrophobic nature of the complex in its initial (ground) state. Table IV and Fig. 2 show parallel behaviour and patterns in ethanol-water mixtures.

Figure 3 shows an analysis based on the assumption used in our previous paper [10], namely that the rate constant trend is entirely determined by the solvation of the leaving chloride. In methanol-water, as in the range of alcohols discussed earlier, this assumption appears to work rather well. Indeed the slightly lower effect of solvent composition change on the transition state compared with free chloride could be held to indicate that the

Pt-Cl bond was 80 or 90% of the way to actual rupture in the transition state, but Figs. 1 and 2 now show that it is inadmissible to ignore the solvation of the rest of the complex. Indeed, the initial complex is more affected by change in solvent than is chloride. Also the transition state is *stabilised* on adding methanol, since the stabilisation of the hydrophobic Pt(PEt₃)₂(4-FC₆H₄)⁺ moiety outweighs the destabilisation of the leaving chloride, in this fully dissociative model. The destabilisation of the leaving chloride remains the major factor in determining the differences in rates observed, since we find a fairly good correlation between the stabilisation of the Pt(PEt₃)₂(4-FC₆H₄)⁺ moiety and of the initial complex. In summary, we must now say that the initial state-transition state analysis needs to be more complicated than assumed earlier, but our earlier assumption that solvation changes at the initial complex and at the Pt(PEt₃)₂(XC₆H₄)⁺ moiety are very similar is now found to be a reasonable approximation.

It is interesting to compare this reaction with the Fe(bipy)₃²⁺ plus cyanide reaction, where it was similarly found that the reactivity trends were dominated by $\delta_m \mu^\circ$ (CN⁻), for $\delta_m \mu^\circ$ (Fe(bipy)₃²⁺) and $\delta_m \mu^\ddagger$, though large, were nearly equal [16].

An initial state-transition state analysis of the solvent effect on reactivity for associative substitution at *cis*-[Pt(PEt₃)₂(4-FC₆H₄)Cl] by thiourea, in methanol-water mixtures, is detailed in Table V and the results are depicted in Fig. 4. As for the other reactions, the platinum(II) complex is successively stabilised as the proportion of methanol

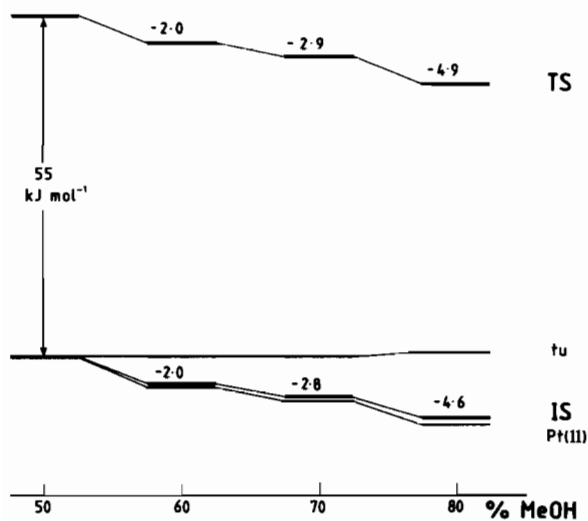


Fig. 4. Initial state-transition state analysis of solvent effects on reactivity for nucleophilic attack of thiourea on *cis*-[Pt(PEt₃)₂(4-FC₆H₄)Cl] in methanol-water mixtures.

increases. The chemical potential of the thiourea changes only very little over the composition range covered here, so $\delta_m\mu^\circ$ (initial state) is essentially the same as the transfer chemical potential of the platinum(II) complex. Moreover, as the rate constant for the reaction varies only slightly, the transfer chemical potential of the transition state is almost the same as that of the initial state, *i.e.* the platinum(II) complex. As the transition state is expected to look very like the initial state – the strong affinity of thiourea for platinum(II) means that the platinum(II) to leaving chloride bond is extended only slightly in the transition state – this similarity of chemical potential trends seems eminently reasonable.

An initial state-transition state analysis of reactivity trends for solvolysis is precluded by two factors. One is that we do not know the relative importance of water and methanol as incoming ligands in mixed solvents, the second is that we do not know the mechanism (which indeed may change on going from water to methanol-rich mixtures). Even if these two problems could be overcome, there remains the difficulty of deciding on the appropriate reference states for the solvents methanol and water. In the analysis of solubilities, kinetics, and transfer parameters, the reference states for the solutes are the ideal solutions in the appropriate solvents, pure and mixtures – *cf.* Henry's Law. In reviewing the thermodynamic properties of either component in a binary mixture of methanol and water, the obvious reference states are the pure components – *cf.* Raoult's Law. However in comparing the reactivity patterns of solutes in these mixtures when the com-

ponents are potential reactants, using the pure solvents as references for the components of the solvent mixture does not seem helpful. The problems are closely related to those encountered in analysis [17] of kinetic solvent isotope effects for S_N2 solvolytic reactions. A number of possible approaches to this analytical problem are currently under review, but as indicated above, other obstacles are expected to prevent an initial state-transition state analysis of solvolysis of *cis*-[Pt(PEt₃)₂(4-FC₆H₄)Cl].

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