correspondence in the CT transition energies may be fortuitous because (1) there are no imidazoles in ligand Va, (2) the negative charge on [Fe(Va)]$^-$ has the effect of increasing the CT energy relative to one where the charge is neutral or positive (there is no suggestion that there is a negative charge on the iron site of Fe$_2$Lf or Fe$_2$Tf), (3) a similar ligand, Vb, forms an iron complex with a lower CT energy, and if this complex had been chosen, the correspondence would have fared no better than FeO$_3$N$_3$ types, and (4) carboxylates are not thought to be bound to Fe in Lf.

The single-crystal X-ray structure of [Fe(IIIa)(MeOH)$_2$]NO$_3$·MeOH has shown the nitrate group not to be directly coordinated to the iron atom but interacts with it via a hydrogen-bonding system involving bound and occluded MeOH molecules. As the nitrate ion is isoelectronic and isostructural with the bicarbonate ion, which is essential for the binding iron in Fe$_2$Lf (and Fe$_2$Tf), a possibility exists that in the natural protein the bicarbonate ion may not interact directly with iron but is hydrogen bonded to a water molecule attached to it.

While many complexes have EPR spectra characteristic of Fe(III) in a rhombic environment, the $g = 4.3$ signal occupies a very narrow range of values and does not appear to be sensitive to ligand types. The unique splitting of the $g = 4.3$ signal (due to the protein conformation) for the Fe$_2$Lf has not been mimicked in our small molecules. Mössbauer spectroscopy is more sensitive to the ligand environment, particularly to the degree of covalent binding in the complex. The complexes [Fe(IIIa)$_3$]·$1^1/_2$H$_2$O and Na[Fe(Va)]·4H$_2$O have Mössbauer parameters closest to those of Fe$_2$Tf, these being of the FeO$_3$N$_3$ and FeO$_2$N$_2$O'$_2$ types, respectively.

The evidence presented in this study would favor the ferric ion of Lf and Tf occupying a site of rhombic symmetry and bound to three tyrosyl and two cis histidyl residues, while the bicarbonate ion is not directly bound but is hydrogen bonded to a coordinated water molecule. A *mer*-type structure would be preferred.

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Registry No. Fe(Ia)$_3$, 14588-80-8; Fe(Ib)$_3$, 23683-82-1; Fe(Ic)$_3$, 23683-80-9; Fe(II)$_3$, 14283-77-3; Fe(IIIa)$_3$, 74877-73-9; [Fe(IIIa)$_2$(MeOH)$_2$]NO$_3$·MeOH, 74877-76-2; [Fe(IIIa)$_2$(MeOH)$_2$]NO$_3$, 74877-75-1; [Fe(IIIa)$_2$(Im)$_2$]NO$_3$, 74877-78-4; [Fe(IIIa)$_2$(tribenzylamine)$_2$]$^+$, 74877-79-5; [Fe(IIIa)$_2$(Me$_2$SO)$_2$]$^+$, 74877-69-3; [Fe(IIIa)$_2$(Me$_2$S)$_2$]$^+$, 74877-80-8; [Fe(IIIa)$_2$(Me$_2$PhPO)$_2$]$^+$, 74893-03-1; [Fe(IIIa)(MeOH)$_4$]$^{2+}$, 74877-81-9; Fe(IIIb)$_3$, 74877-82-0; Fe(IV)$_3$, 74877-83-1; Na[Fe(Va)], 16455-61-1; K[Fe(Vb)], 74877-84-2; K[Fe(VIa)$_2$], 74893-04-2; K[Fe(VIb)$_2$], 74877-85-3; [Fe(VIc)$_2$]PF$_6$, 74877-87-5; [Fe(VId)$_2$]PF$_6$, 74877-89-7; [Fe(VIIa)]PF$_6$, 60351-92-0; [Fe(VIIa)]NO$_3$, 67225-84-7; [Fe(VIIb)]PF$_6$, 74877-91-1; [Fe(VIIc)]PF$_6$, 74877-93-3; [Fe(VIIc)]I$_3$, 74877-94-4; [Fe(VIId)]PF$_6$, 74877-96-6; [Fe(VIII)]$^+$, 74877-97-7; [Fe(VIII)(Im)]$^+$, 74877-98-8; [Fe(VIII)(Im)$_2$]$^+$, 74877-99-9; [Fe(VIII)(N-MeIm)$_2$]$^+$, 74878-00-5.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

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Solvent Effect on the Rates of Uncatalyzed Isomerization and Ligand Substitution at a Square-Planar Platinum(II) Complex

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The rates of spontaneous cis–trans isomerization of the complex *cis*-[Pt(PEt$_3$)$_2$(m-MeC$_6$H$_4$)Cl] have been measured in a variety of hydroxylic solvents and in acetonitrile. Fairly good straight lines correlate these rates and some empirical parameters which measure the relative electrophilic character of the solvent such as the α values of the Taft HDB scale or the Dimroth–Reichardt E_T values. The role of the solvent is to promote the breaking of the Pt–Cl bond in the rate-determining step, and in this respect hydrogen-bonding interactions with the leaving chloride ion are the most important factors in determining the large differences in rate observed. By way of contrast, nucleophilic displacement of the chloride ion from the same complex either by the solvent or by thiourea is little influenced by the nature of the solvent, in keeping with an associative mode of activation with a small degree of Pt–Cl bond breaking.

Introduction

Substitution reactions of 4-coordinate square-planar complexes, especially those of platinum(II), have been studied extensively, and nowadays the general mechanistic picture is reasonably clear.[1-5] The search for factors promoting the conversion of the normal associative mode of reaction into a dissociative process has then attracted much attention. It was thought to achieve this goal by one or both of the following methods: (i) prevent bond formation by using bulky ancillary ligands and/or (ii) promote bond weakening at the leaving group, usually a halide ion, by locating a strong σ donor group in trans position to it.

Increasing steric hindrance in Pd(II) and Au(III) substrates,[6] brought about by alkyl substitution on the terminal nitrogens of a coordinated ethylenetriamine ligand, leads to a large decrease of both k_1 and k_2, the nucleophile-independent and -dependent rate constants in the two-term rate law. In

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the so-called "pseudooctahedral" complexes $[M(Et_4dien)Cl]^+$ (M = Pt(II), Pd(II); Et_4dien = 1,1,7,7-tetraethyldiethylenetriamine) the k_2 term vanishes, leaving the rate of chloride displacement completely controlled by k_1.[7]

Early suggestions that Et_4dien is sufficiently crowded to completely inhibit the approach of a nucleophile to the reaction center are not in keeping with the increasing number of exceptions found to this unusual pattern of behavior. Indeed, reagent-dependent paths exist in water not only with OH^- (S_N1cB mechanism) or with $S_2O_3^{2-}$ (powerful nucleophile) but also with an extended range of nucleophiles reacting with $[Pd(Et_4dien)Cl]^+$ at a higher reagent concentration than that previously employed,[8] in the reactions of $[Pd(Et_4dien)Br]^+$ with certain ligands in $(CH_3)_2SO$ and CH_3CN as a solvent[9] and in the reactions of $[Pd(Et_4dien)X]^+$ with chloride ion in methanol (X = $SeCN^-$,[10] NO_2^-,[11] and N_3^-[11]).

Likewise, extensive electron transfer from the trans-activating group R to the metal atom and ground-state destabilization in complexes of the type *trans*-$[Pt(PEt_3)_2(R)Cl]$ (R = Cl, H, CH_3, C_2H_5, C_6H_5, *o*-tolyl, mesityl, *m*-FC_6H_4, *p*-$NO_2C_6H_4$, *m*-$CF_3C_6H_4$, C_6F_5)[12] lead to an increase of the k_1 term contribution, which dominates the rate of chloride displacement with a variety of "poor" nucleophiles.

While the predominance of the k_1 term in many cases in which steric, electronic, or other factors prevent bimolecular attack to the most common reagents has been interpreted in a satisfactory way with a mechanism involving a great extent of M–X bond breaking in the transition state, it falls short of providing direct evidence in favor of a dissociative mechanism involving a Pt(II) 3-coordinate intermediate.[13] There is little doubt that in many of these systems the k_1 term still relates to a bimolecular solvolysis, and the simplest way of envisaging its enhanced importance in the substitution is to consider the solvent as a more favored nucleophile than any other, with the normal ability of the substrate to discriminate between possible reagents being greatly reduced. Accordingly, recent measures of volumes of activation for solvolysis reactions of $[Pd(Et_4dien)X]^+$ in water,[14] of $[Pd(Et_4dien)I]^+$ in a variety of solvents,[14] and of *trans*-$[Pt(PEt_3)_2(2,4,6\text{-}Me_3C_6H_2)Br]$ in methanol[15] have been interpreted in terms of a basically associative mechanism.

More convincing evidence for the operation of a D mechanism comes not from substitution reactions but from uncatalyzed cis–trans isomerizations of complexes of the type *cis*-$[Pt(PEt_3)_2(R)X]$ (R = substituted aryl groups; X = halide ion).[16] This mechanism, which involves the dissociative loss of the X^- ligand and the conversion of two geometrically distinct T-shaped 3-coordinate intermediates, has been established by measuring the sensitivity of the rate of isomerization to structural changes influencing bond dissociation, viz., the nature of the halide ion and the amount of electronic density or of strain at the metal atom, brought about by substituents on the aromatic ring.

In this study we use solvent effects as a further criterion to distinguish between associative and dissociative reaction paths. The rates of isomerization, solvolysis, and nucleophilic substitution of the complex *cis*-$[Pt(PEt_3)_2(m\text{-}MeC_6H_4)Cl]$ have been measured in a series of alcohols. These processes represent three different ways of removing the chloride ion from the coordination sphere of the metal; the magnitude of the solvent effect is found to depend on the degree of charge separation occurring in the transition state.

Experimental Section

The preparation of the complex *cis*-$[Pt(PEt_3)_2(m\text{-}MeC_6H_4)Cl]$ has been already reported.[16d] The trans derivative was prepared by reacting the cis compound (1.5 g) with silver nitrate (0.457 g) in methanol (40 mL). The mixture was stirred at room temperature for 2 h, then the precipitated silver chloride was filtered, and LiCl (0.12 g) was added to the filtrate. The crude product isolated after evaporation of the solvent was crystallized as white plates (1.32 g) from petroleum ether (40–70 °C). Anal. Calcd for $C_{19}H_{37}ClP_2Pt$: C, 40.90; H, 6.68. Found for the cis compound (mp 122–125 °C): C, 41.09; H, 6.77. Found for the trans compound (mp 82–84 °C): C, 40.83; H, 6.62. The stereochemistry of the compounds was established by IR and ^1H NMR spectra.[16d]

Methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-2-propanol, 2-methoxyethanol, and acetonitrile were purified and dried by standard methods.[17] All the other reagents were used without further purification.

Kinetics

In all the solvents examined the rate of cis to trans isomerization of the complex *cis*-$[Pt(PEt_3)_2(m\text{-}MeC_6H_4)Cl]$ was slow enough to be followed by conventional techniques. The reactions were carried out in a silica cell in the thermostated cell compartment of a double-beam OPTICA CF 4 spectrophotometer, where the temperature remained constant to ±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 sample of the 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 260 nm in each of the solvents used. Faster reactions were followed by recording the decrease in absorbance at 250 nm by means of a Beckman DU instrument, equipped with a Saitron 301 photometer and a Servogor S recording potentiometer.

Plots of log $(A_t - A_\infty)$ against time, where A_t and A_∞ are the absorbances at time t and at the end of the reaction, were linear for at least 90% completion of the reaction in each of the solvents employed, indicating the isomerization to be first order in *cis*-$[Pt(PEt_3)_2(m\text{-}MeC_6H_4)Cl]$. When the concentration of the starting material was varied over the range $(0.3–1.5) \times 10^{-4}$ M, no variations were observed in the observed rate constants k_i (s^{-1}). These latter were determined either from the gradients of the semilogarithm plots or from a nonlinear least-squares fit of experimental data to $A_t = A_\infty + (A_0 - A_\infty) \exp(-k_it)$ with A_0, A_∞, and k_i as the parameters to be optimized (A_0 = absorbance after mixing of the reagents).

The nucleophilic substitution reactions of *cis*-$[Pt(PEt_3)_2(m\text{-}MeC_6H_4)Cl]$ with I^- and thiourea were followed at 300 nm by means of a Durrum-Gibson D 110 stopped-flow spectrophotometer with a 20-mm observation cell. Absorbance changes with time were recorded on a Tektronics Model 564 storage oscilloscope fitted with a log converter. The exponential traces were photographed, and the values of the pseudo-first-order rate constants (k_{obsd} (s^{-1})) were evaluated either from gradients of plots of log $(A_t - A_\infty)$ against time, the absorbances being assigned arbitrary units, or by matching experimental traces with similar ones produced by an exponential generator[18] on the same oscilloscope. Each value of k_{obsd} is the average of at least three experiments. Isomerization of the starting complex was prevented

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Table I. Rate Constants for Some Reactions of *cis*-[Pt(PEt$_3$)$_2$(*m*-MeC$_6$H$_4$)Cl] in Various Solvents

solvent	$10^4 k_i$, s^{-1} [a]	k_1, s^{-1} [b]	k_2, M^{-1} s^{-1} [c]
methanol	186 ± 8	2.92 ± 0.06	13050 ± 140
ethanol	10.2 ± 0.24	1.93 ± 0.11	18900 ± 320
1-propanol	3.65 ± 0.18	1.54 ± 0.05	31350 ± 330
1-butanol	1.62 ± 0.08	1.60 ± 0.03	47140 ± 720
2-methoxyethanol	1.21 ± 0.10	0.456 ± 0.01	10200 ± 270
2-propanol	0.91 ± 0.006	0.658 ± 0.002	45100 ± 630
2-methyl-2-propanol	0.0204 ± 0.0014	0.115 ± 0.007	67700 ± 720
acetonitrile	0.042 ± 0.005	0.203 ± 0.018	4600 ± 160

[a] Rates of uncatalyzed isomerization at 40 °C. [b] Rates of solvolysis at 30 °C, obtained from the reagent-independent path 2 in Scheme I, by using I$^-$ as a nucleophile. [c] Rates of chloride displacement by thiourea at 30 °C, calculated from the slopes of linear plots of k_{obsd} (s^{-1}) vs. [thiourea].

by dissolving the substrate in 0.01 M tetrabutylammonium chloride. The kinetics were performed under pseudo-first-order conditions with the reagent (n-C$_4$H$_9$)$_4$NI or SC(NH$_2$)$_2$ in at least a 10-fold excess over the platinum complex concentration.

Results

The conversion of *cis*-[Pt(PEt$_3$)$_2$(*m*-MeC$_6$H$_4$)Cl] to its trans isomer proceeds practically to completion in each of solvents employed, as shown by qualitative paper chromatography tests and by the identity of the UV spectrum of the reaction mixture after 10 half-lives with that of a freshly prepared solution of trans isomer. A good isosbestic point is maintained at 260 nm, indicating that the two isomers are the only absorbing species in solution. The isomerization follows simple first-order kinetics for at least 3 half-lives. 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.

Reaction 1 (R = m-MeC$_6$H$_4$; Y = I$^-$ and SC(NH$_2$)$_2$) at 30

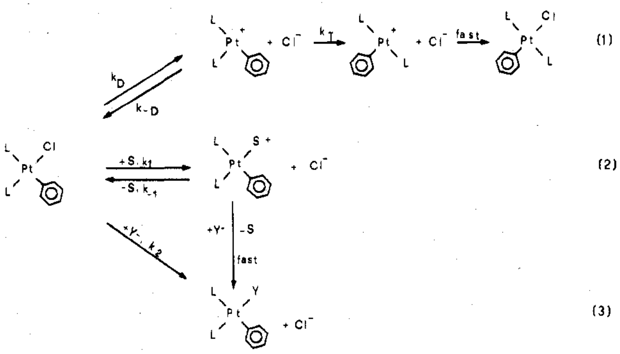
$$cis\text{-}[\mathrm{Pt(PEt_3)_2(R)Cl}] + \mathrm{Y} \rightarrow cis\text{-}[\mathrm{Pt(PEt_3)_2(R)Y}] + \mathrm{Cl} \tag{1}$$

°C and under pseudo-first-order conditions (excess of reagent) proceeds to completion, obeying the two-term rate law as shown in eq 2. In the reactions with I$^-$ as entering group, the

$$k_{obsd} = k_1 + k_2[\mathrm{Y}] \tag{2}$$

contribution of the k_2 term was statistically insignificant in the 0.001–0.1 M I$^-$ 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. In 2-propanol and 2-methyl-2-propanol, however, the rate of chloride displacement exhibits a definite dependence on the concentration of (n-C$_4$H$_9$)$_4$NI salt. On plotting the rates of reaction k_{obsd} (s^{-1}) as a function of the initial concentration of the I$^-$ salt, one obtains straight lines with a nonzero intercept. It is well documented that the low values of the dielectric constant of these solvents favor ion association. The value of the ion-pair association constant for n-Bu$_4$N$^+$I$^-$ in the solvent 2-propanol[19] is K_a = 1.3 × 10^3 at 25 °C, and that in the solvent 2-methyl-2-propanol, K_a = 8.3 × 10^4 at 25 °C, can be estimated by extrapolating to (1/10.9) a linear plot of log K_a vs. 1/D for various hydroxylic solvents.[20] The reagent n-Bu$_4$NI, therefore, reacts as the ion pair n-Bu$_4$N$^+$I$^-$ even at the lowest reagent concentrations in 2-methyl-2-propanol, the rate constant being k_p = 34.4 ± 0.65 M^{-1} s^{-1}; in 2-propanol as solvent it reacts either as a free ion I$^-$ or as an ion pair, the two reactivities being comparable in magnitude, as shown by the linearity of the plot of k_{obsd} vs. [salt] ($k_p \simeq k_I$ = 2.93 ± 0.04 M^{-1} s^{-1}). The small amount of other data for ion pairs reacting at a Pt(II) center[21] and the limited knowledge of their structure in the above solvents make it difficult to discuss the reactivities of such reagent species.

Scheme I



In the reactions with thiourea the contribution from the nucleophile independent term k_1 was small even at the lowest reagent concentration. The second-order rate constants k_2 were calculated by linear regression analysis of plots of k_{obsd} vs. [thiourea] (in the 0.001–0.01 M concentration range) and are listed in Table I.

Discussion

Data in Table I refer to the effect of changing the solvent on the rates of spontaneous isomerization, solvolysis, and chloride displacement by thiourea in *cis*-[Pt(PEt$_3$)$_2$(*m*-MeC$_6$H$_4$)Cl]. We recall that many experimental findings are consistent with a dissociative rate-determining step in the isomerization of *cis*-[Pt(PEt$_3$)$_2$(R)Cl] complexes,[16] namely, (i) the large values of enthalpy of activation and positive entropies of activation associated with isomerization, (ii) the great mass-law retardation produced by small amounts of free Cl$^-$ ions, and (iii) the large sensitivity of the rates to factors controlling bond dissociation such as changes of electron density at the metal brought about by electron-donating or -withdrawing substituents on the aromatic ring or changes in the nature of the coordinated halide ions. Strain effects are of little importance, since the formation of a T-shaped 14-electron platinum(II) cation in the transition state does not require a great distortion of the coordinated ancillary ligands.[16c]

Summing up, the experimental evidence available seems to rule out alternative mechanisms such as the more traditional process of thermal stereochemical rearrangements which require a sequence of associative displacement reactions or a preequilibrium mechanism. On the assumption, therefore, that isomerization involves ionization to a cationic intermediate, the three processes in Scheme I represent three different ways for the release of Cl$^-$ from the coordination sphere of the metal. The magnitude of the solvent effect will reflect the degree of charge separation occurring during the activation steps.

Isomerization. The range of solvents amenable to this study was restricted either by the general reluctance of the process to occur in apolar aprotic solvents or by the ultraviolet cutoff of the most ionizing dipolar aprotic solvents. However, the spontaneous cis–trans isomerization of [Pt(PEt$_3$)$_2$(*m*-MeC$_6$H$_4$)Cl] occurs readily in the solvents employed and appears extremely sensitive to changes in their nature. Indeed, data in Table I show a decrease in the rate of 4 orders of magnitude on going from methanol to 2-methyl-2-propanol.

In the absence of specific solvent–solute interactions, Kirkwood's equation[22] from transition-state theory predicts

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a linear relationship between the logarithm of the rate constant and a solvent parameter $f(D) = (D - 1)/(D + 2)$, where D is the dielectric constant of the medium. The dielectric approach has been widely used to interpret the results of several kinetic investigations; however, its limits are clearly shown in Panasyuk's studies of aquations of Pt(II) and Pd(II) complexes[23] in which dispersion of lines of log k vs. $f(D)$ plots and, above all, inversions[24] in their direction are obtained on changing of the composition of the solvent system. Although in the system under study the general trend for the rate constants is to decrease with decreasing of the dielectric constant of the medium, the circumstance that the rate in methanol ($D = 32.6$ at 25 °C) exceeds by a factor of 4×10^3 that in acetonitrile ($D = 37.5$ at 25 °C) emphasizes the inadequacy of the dielectric constant to be used as the only measure of the "ionizing-power" of the solvents.

The effect of the variation of the solvent on the rates of some unimolecular reactions may be correlated by eq 3[25] where k

$$\log (k/k_0) = mP \qquad (3)$$

and k_0 are rate constants for the reaction in question in a particular solvent and in a standard solvent, respectively. The parameter m is taken to be a measure of the susceptibility of the substrate to changes in P, a parameter characteristic of the solvent. Many different suggestions for the parameter P have been made in the literature. Those usually chosen are rate constants or spectral properties associated with a process in which a weakly solvated species AB generates or is generated by a species A^+B^- which interacts strongly with solvent molecules.[26] The solvent effect is to stabilize the separation of charge so that the associated parameter P is often somewhat loosely described as "the ionizing power" of the solvent.

It is of interest to discuss the rate variations in terms of Grunwald–Winstein solvent Y values which are based on kinetic data for *tert*-butyl chloride as a typical compound undergoing solvolysis by a dissociative (D) mechanism.[27] For this reference system the slope of the correlation plot (m) is 1.00. Values of the gradient much lower than this (in the range 0.2–0.4) were said to indicate a dissociative mechanism for aquations of octahedral aminochlorocobalt(III) complexes[28] and aminochlororuthenium(III) complexes,[29] while the observation of still lower gradients for iron(II) ($m = 0.1$–0.2)[30] and chromium(III) ($m = 0.12$)[31] complexes was thought to reflect an appreciable contribution of associative character in their substitution reactions. Linear free-energy relationships of the Grunwald–Winstein type have also been applied successfully to substitution reactions on square-planar Pd(II) complexes. In particular, a well-established associative process such as the direct replacement of iodide with Cl^- in $[Pd(dien)I]^+$ (dien = diethylentriamine)[32] was shown to be more sensitive to solvent variations ($m = 0.63$) than either the solvolytic path ($m = 0.33$) or the palladium(II)–chloride bond breaking in the solvolysis of the pseudooctahedral $[Pd(Et_4dien)Cl]^+$ cation ($m = 0.4$).[32,33] Curvatures of the mY plots were observed for aquation of $[PtCl_4]^{2-}$ [34] and of *cis*-$[Pt(NH_3)_2Cl_2]$,[23c] while the *trans*-$[Pt(NH_3)_2Cl_2]$plot[23d] approximates to linearity and has a slope, m, of 0.4. In any case, the associative cleavage of the Pt–Cl bond is largely less sensitive to solvent change than the organic reference substrate.

The magnitude of the gradient which we obtain when logarithms of rate constants for isomerization of *cis*-$[Pt(PEt_3)_2(m\text{-}MeC_6H_4)Cl]$ are plotted against the Grunwald–Winstein parameters Y ($m = 1.82$) is the highest found so far for coordination compounds and should indicate beyond all doubt a reaction taking place via a cationic intermediate as shown in Scheme I. It seems also that these reactions are significantly more sensitive to the solvent than those of carbon chloride solvolyses.

However, we do not wish to rely only on the magnitude of m for our assumption of a dissociative mode of activation, since the above examples have made clear the danger of considering the value of m as a direct measure of the degree of M–X bond breaking in the transition state, if one compares systems of vastly different properties. In fact the absolute value of m may be governed inter alia by various factors such as the "ionicity" of the M–X bond, the composition of the solvent mixture, the nature and the charge of the substrates, and the relative solvation of the ground state and the transition state. We believe that a much more diagnostic tool is the comparison of the extent of solvent effects on the three processes which involve the removal of the *same* chloride ion from the *same* substrate in the *same* environment. Rates of solvolysis and nucleophilic displacement (paths 2 and 3 in Scheme I) are little influenced by solvent changes and by no means can be related to the Y parameters, in keeping with the essentially associative nature of the activation processes which do not require large changes of polarity or charge formation; isomerization is much more strongly influenced by the solvent, and this is a straightforward indication that ionic charges are formed during passage through the transition state.

In physical organic chemistry efforts have been made to take account of all the possible modes of solvent interaction influencing a given physicochemical quantity. These eventually can be restricted, especially for rates of solvolysis of organic substrates, to two factors of overriding importance: solvent "electrophilicity" and solvent "nucleophilicity". These terms refer to the ability of the solvent to act as electrophile or nucleophile to heterolyze a covalent bond. Several scales of solvent acceptor properties (A) and solvent donor properties (D) have been proposed.[35] Reaction rates, equilibria, and electrochemical and spectroscopic properties have been correlated[36] through a two-parameter equation (see eq 4), where

$$Q = Q_0 + \alpha(\mathrm{A}) + \beta(\mathrm{D}) \qquad (4)$$

Q stands for a solvent-dependent physicochemical parameter, Q_0 is the corresponding parameter in the gas phase or in an inert solvent, and α and β are regression coefficients that measure the relative importance of solvent electrophilicity and nucleophilicity on Q, respectively. The use of multiparameter regressions, introducing contributions of "polarity" and "polarizability" to take better account of the multiplicity of the substrate–solvent interactions, sometimes resulted in a better fit to the experimental data.[37]

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Table II. Correlation of the Rate Constants k_i (s^{-1}) for the Isomerization of *cis*-[$Pt(PEt_3)_2(m\text{-}MeC_6H_4)Cl$] with Some Empirical Parameters of the Ionizing Power of Solvents

solvent parameter P^a	m^b	n^c	R^d
Grunwald-Winstein's Y^e	1.82	7	0.977
Koppel-Palm's Y'^f	0.879	7	0.999
Taft's α^f	7.03	6^g	0.997
Brownstein's S	24.4	7	0.993
Dimroth-Reichardt's E_T	0.354	7	0.993
Kosower's Z	0.307	7	0.996

[a] From ref 26, except where cited. [b] Slopes of linear plots of log k_i (s^{-1}) in Table I vs. P values. [c] Number of data points, excluding 2-methoxyethanol. [d] Correlation coefficients of the plots. [e] Data points for 1-propanol, 1-butanol, and acetonitrile were estimated from E_T values (cf. text). [f] From ref 39. [g] Data points for 2-methoxyethanol and acetonitrile excluded from the calculation.

We find fairly good linear free-energy relationships (LFER) on plotting the logarithms of the rate constants for the isomerization of *cis*-[$Pt(PEt_3)_2(m\text{-}MeC_6H_4)Cl$] (data in Table I) against some popular empirical P parameters of solvent polarity such as Grunwald–Winstein's Y, Koppel–Palm's Y', Brownstein's S, Dimroth–Reichardt's E_T, Kosower's Z, and Taft's α. These scales of solvent polarity have been obtained by determining the effect of solvent variation on rates constants (Y and Y') or absorption maxima of solvatochromic dyes (E_T, Z, and α) and are known to describe chiefly the electrophilicity or Lewis acidity of the solvents.[38] A least-squares regression analysis of the rate data was performed according to eq 3, and the results are collected in Table II. Close correlations between the P scales used, at least in the restricted range of protic solvents, have long been known.[38]

On the other hand, we cannot find any meaningful relationship between the rates of isomerization and the solvent donor properties, whether these are measured by the few existing values of Guttman's donor numbers (DN) or by the set of solvolytic rate constants k_1 (s^{-1}) in Table I. This fact, coupled with the excellent LFER's of the isomerization rates with the anion solvating properties, as measured by the P scales of the solvents, justifies the use of a single parameter treatment, indicating too that a single type of solvent interaction is involved either in the isomerization or in the process from which the correlating parameter P is derived. Hydrogen-bonding contributions in HBD (hydrogen-bonding donor) solvents to some of the solvent polarity scales in Table II have been recently evaluated by using a solvatochromic comparison method.[39] The results have revealed that these scales, as far as protic solvents are concerned, are more a measure of hydrogen-bonding ability than polarity. In addition, an α scale of solvent HBD acidities was established which correlates well with isomerization rates (see Figure 1). Summing up, uncatalyzed isomerization in protic solvents involves a rate-determining ionization to a cationic intermediate with no detectable nucleophilic participation by the solvent. Electrophilic solvation of the leaving chloride ion through hydrogen bonding is the major factor in determining the large differences in rates observed, the contribution of nonspecific solvent–solute interactions being negligible or constant.

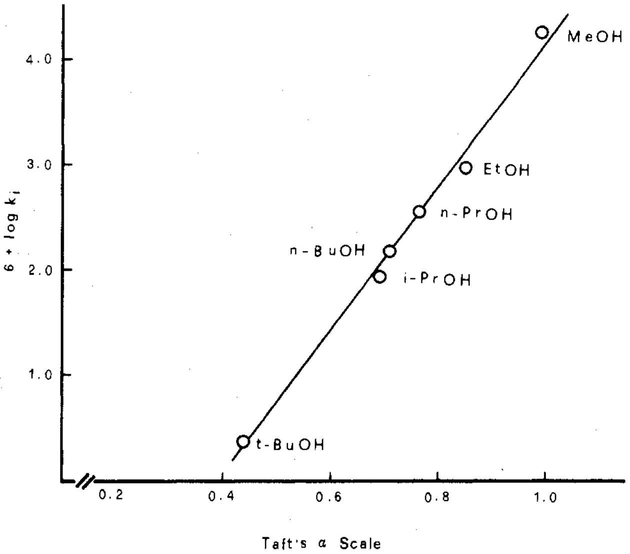

Figure 1. Correlation plot of the rates of uncatalyzed isomerization of *cis*-[$Pt(PEt_3)_2(m\text{-}MeC_6H_4)Cl$] with the hydrogen-bonding donor (HBD) properties of the solvents.

Table III. Steric Effects of Hydroxylic Solvents ROH Reacting with *cis*-[$Pt(PEt_3)_2(m\text{-}MeC_6H_4)Cl$]

R	3 + log k_S (M^{-1} s^{-1})^a	$\Sigma\sigma^{*\,b}$	$E_s{}^c$
methyl	2.07	0.49	0.00
ethyl	2.05	0.39	−0.02
n-propyl	2.07	0.37	0.00
n-butyl	2.16	0.36	+0.09
isopropyl	1.70	0.30	−0.38
2-methoxyethyl	1.55		−0.52
tert-butyl	1.04	0.19	−1.03

[a] $k_S = k_1/[\text{solvent}]$ (see text); at 30 °C. [b] Sum of the Taft σ^* values.[40a] [c] $E_s = \log (k_S/k_S{}^\circ)$, where $k_S{}^\circ = k_S$ for methanol.

Solvolytic Pathway. The pseudo-first-order rate constants k_1 (s^{-1}) in Table I are ascribed to the rate-determining replacement of Cl^- from *cis*-[$Pt(PEt_3)_2(m\text{-}MeC_6H_4)Cl$] by a molecule of solvent (path 2 in Scheme I). For all the solvents employed, these rates are of many orders of magnitude greater than the rates of isomerization. This large difference of reactivity, already observed and discussed in methanol,[16c,d] confirms that a bimolecular solvolysis is not the initial step of the isomerization and rules out the possibility of a common intermediate for either solvolysis or isomerization. Since solvent effects are complicated due to the solvent acting as a nucleophile and k_1 is negligibly small in most cases, the discussion of it in the literature has been usually neglected.

Second-order rate constants k_S (M^{-1} s^{-1}) for the solvolysis reactions can be calculated by dividing k_1 (s^{-1}) by the molal concentration of the solvent (Table III). The values obtained, which reflect the nucleophilic power of the solvents, do not vary markedly along the series examined. It is reasonable to attempt to correlate these rate data with the sum of Taft values,[40] which measure inductive effects of the individual groups attached to the oxygen of the solvent. On doing this, a completely random plot is obtained with a trend opposite to that expected.

Indeed, the rates of solvolysis remain essentially constant with increasing chain length and decrease with branching of the alkyl groups. Clearly inductive effects are not the dominant factor in the observed rates.

The variations of k_S can be reasonably assigned to steric strain produced by alkyl groups on the oxygen donor atom.

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On the assumption that inductive effects are negligible, the effect of increasing alkyl substitution on the attacking atom in the entering nucleophile may be calculated by using the Taft steric parameter[40] E_s (see Table III), defined as $E_s = \log (k/k_0)$, where k_0 is a reference rate constant for the least sterically hindered member of the series (MeOH, $k_0 = 2.92$ s^{-1}). In coordination chemistry, this approach has been used by Rorabacher and co-workers[41] to measure steric effects of alkyl substituted mono- and diamines reacting with Ni(II) and more recently by Jones et al.[42] in the kinetics of the square-planar complex $[Pd(dien)OH_2]^+$ (dien = diethylentriamine) with an extended series of dialkyl sulfides. A rough straight line can be obtained on plotting the values of E_s in Table III against that reported by Jones (slope = 0.37, $r = 0.969$). While it seems clear that steric crowding produced during the formation of a five-coordinate transition state by two alkyl groups in the thioethers R_2S exceeds that produced by the only one in ROH, a good deal more data for other systems are required to test thoroughly the validity of such comparisons.

Nucleophile-Dependent Pathway. A definite second-order contribution k_2 (M^{-1} s^{-1}) arises from the direct displacement of Cl^- from *cis*-$[Pt(PEt_3)_2(m\text{-}MeC_6H_4)Cl]$ by the strong nucleophile thiourea. This reagent is known to possess good π-acceptor properties and to stabilize the 5-coordinate transition state in reactions with Pt(II) substrates via electron delocalization. This capacity is usually enhanced by strong σ donation of the coordinated ligands to the metal atom in the ground state.[12] The intimate mechanism of the reaction can be described as a two-step addition–elimination process, in which the rate-determining step is the formation of a 5-coordinate transition state having both the incoming and the leaving group firmly bonded to the metal, followed by a rapid conversion into the square-planar product. A clear example of this pattern of behavior can be found in a study of solvent effects on the halide displacement by thiourea from the complexes *trans*-$[Pt(PEt_3)_2(R)X]$ (R = CH_3, C_6H_5, *m*-FC_6H_4; X = Cl, Br, I, N_3, NO_2).[43] The ease of replacement of Br^-, N_3^-, and NO_2^- relative to chloride, assumed as reference, was found to be essentially the same in methanol and dimethyl sulfoxide, suggesting a small degree of Pt–X bond breaking in the transition state which makes solvation of the leaving group kinetically unimportant.

Accordingly, we observe that the solvent effect in the reactions with thiourea (see Table I) is very small compared to that found in the isomerization and it goes in the opposite direction, confirming that the Pt–Cl bond remains essentially intact during the formation of the 5-coordinate transition state.

Although HDB interactions of the protic solvents with nitrogens of the reagent $SC(NH_2)_2$ could account for the trend observed in the reactivity along the examined series, a discussion of these small effects at this stage risks being only speculative in nature. A fuller understanding of the problem could involve measures of volumes of activation[44] or dissection of the solvent effects into initial-state and transition-state components, by the use of appropriate thermodynamic parameters for the reactants. An analysis of this type has been performed successfully by Burgess and co-workers, who studied the kinetics of the reaction of 2,2′-bipyridyldichloroplatinum(II)[45a] and of *cis*-dichlorobis(4-cyanopyridine)platinum(II)[45b] with thiourea in binary aqueous solvent mixtures, showing that the solvation of the initial complex is the most important factor controlling reaction rates.

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Registry No. *cis*-$[Pt(PEt_3)_2(m\text{-}MeC_6H_4)Cl]$, 70445-93-1; *trans*-$[Pt(PEt_3)_2(m\text{-}MeC_6H_4)Cl]$, 74824-29-6; I^-, 20461-54-5; $SC(NH_2)_2$, 62-56-6.

Supplementary Material Available: Listings of observed rate constants for isomerization of *cis*-$[Pt(PEt_3)_2(m\text{-}MeC_6H_4)Cl]$ and chloride displacement by I^- and $SC(NH_2)_2$ (5 pages). Ordering information is given on any current masthead page.

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Formation of Polynuclear Cupric Halides in Cationic Reversed Micelles

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The structure of cupric chloride and bromide complexes cosolubilized in cationic reversed micelles has been investigated by means of electronic absorption and electron paramagnetic resonance spectroscopy. At low water concentrations (0.3 M or less), the principal amount of water is bound to surfactants and does not go into solvation equilibrium with the copper. Under the circumstances, cupric chloride cosolubilized in the micelles showed absorption bands at 408 and ~1150 nm, and it was EPR negative. The structure has been elucidated as a distorted-tetrahedral configuration of polymeric form. It converts to a monomeric distorted tetrahedron with the increase in water concentration, leading eventually to a distorted octahedron normally observable in an aqueous medium. Cupric bromide behaved in a similar manner. The origin of these unique solution structures of cupric halides is discussed in conjunction with the microenvironment surrounding the cupric ion in a restricted field provided by cationic reversed micelles.

Introduction

Reversed micelles, aggregates between surfactants and polar solutes formed in apolar media, certainly provide a specific and restricted field.[2,3] Depending on the concentrations of surfactant and water, the tightness of surfactant–water interaction,[4] the size of water pool, and the microscopic viscosity[5]