TABLE IV

INFRARED SPECTRA OF $L_2M(X)CONRR'$ COMPLEXES

M	L^a	X	R	R′	Sample	ν_{CO}, cm^{-1}	Other
Pt	TPP	Cl	CH_3	CH_3	CH_2Cl_2	1566	Pt–Cl 264
					KBr	1572	
					Nujol	1570	
Pt	MDPP	Cl	CH_3	CH_3	CH_2Cl_2	1565	
					KBr	1570	
Pt	TPA	Cl	CH_3	CH_3	CH_2Cl_2	1585	
					Nujol	1580	
Pd	TPP	Cl	CH_3	CH_3	CH_2Cl_2	1605	
					KBr	1598	
Pd	TPP	Cl	H	CH_3	CH_2Cl_2	1628^b	ν(NH) 3458
Pt	TPP	I	CH_3	CH_3	CH_2Cl_2	1570	
					Nujol	1574	
Pt	TPP	NCO	CH_3	CH_3	Nujol	1580	NCO 2221
Pt	TPA	Cl	H	i-C_3H_7	KBr	1616^b	ν(NH) 3425
						1602^b	
Pt	TPP	Cl	H	C_2H_5	CH_2Cl_2	1601^b	ν(NH) 3422
Pt	TPP	Cl	H	CH_3	CH_2Cl_2	1600^b	
					Nujol	1618^b	
						1602^b	Pt–Cl 270
					Kel-F		ν(NH) 3400 ± 10

[a] Abbreviations are the same as in Table I. [b] δ(NH) and ν(CO) bands.

TABLE V

INFRARED SPECTRA OF $L_2M(X)CSN(CH_3)_2$ COMPLEXES

M	L^a	X	Sample	$CSN(CH_3)_2$ bands, cm^{-1}
Pd	TPP	Cl	Nujol	949, 1150, 1230, 1520
			KBr	960, 1145, 1240, 1525
Pd	TPP	Br	KBr	959, 1145, 1241, 1521
			CH_2Cl_2	957, 1144, 1238, 1520
Pd	TPP	I	KBr	954, 1140, 1235, 1515
			CH_2Cl_2	955, 1144, 1233, 1520
Pt	TPP	Cl	KBr	963, 1140, 1250, 1517
			CH_2Cl_2	964, 1131, 1246, 1510
Pt	TPP	I	KBr	960, 1140, 1250, 1522
			CH_2Cl_2	960, 1123, 1245, 1515
Pd	MDPP	Cl	CH_2Cl_2	963, 1137, 1239, 1515

[a] Abbreviations are the same as in Table I.

though there is extensive coupling of the other vibrations, the lowest frequency absorption appears to be due to a relatively pure C–S stretching vibration. In the thiocarboxamido complexes of Pt and Pd (Table V), we have also observed four bands in the region 900–1525 cm^{-1} which are associated with the thiocarboxamido ligand. These occur in approximately the same regions as their organic counterparts.

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Mechanisms of Substitution Reactions of Axially Blocked Palladium(II) Complexes in Different Solvents

BY RAYMOND ROULET AND HARRY B. GRAY*

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The rates of the reactions of halide ions with $Pd(Et_4dien)X^+$ ($Et_4dien = HN[C_2H_4N(C_2H_5)_2]_2$; $X^- = Cl^-, Br^-, I^-$) complexes have been investigated as a function of temperature in several different solvents. The activation parameters show that the reactions in protic solvents involve associative activation, whereas in aprotic solvents a dissociative mechanism with leaving-group solvation is probable.

Introduction

The principal pathway of the substitution reactions of the axially blocked, square-planar complexes $Pd(Et_4dien)X^+$ ($Et_4dien = HN[C_2H_4N(C_2H_5)_2]_2$; $X^- = Cl^-, Br^-$) with most nucleophilic reagents in aqueous solution involves a slow solvolysis step (eq 1), followed by rapid anation (eq 2).[1,2]

$$Pd(Et_4dien)X^+ + H_2O \xrightarrow[k_1]{\text{slow}} Pd(Et_4dien)H_2O^{2+} + X^- \quad (1)$$

$$Pd(Et_4dien)H_2O^{2+} + Y^{n-} \xrightarrow{\text{fast}} Pd(Et_4dien)Y^{(2-n)+} + H_2O \quad (2)$$

Little is known concerning the detailed role of the water molecule in the solvolysis step. For the reactions of unhindered square-planar substrates with a variety of solvent (sol) molecules, a mechanistic model has been developed which features strong associative activation, leading to a five-coordinate transition state containing a solvent molecule attached to the metal.[3,4]

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The fact that k_1 is considerably smaller in DMSO than in water for $Pd(Et_4dien)Br^+$ has been interpreted[5] in terms of the inability of the larger DMSO molecule to interact effectively with the Pd(II) in the axially blocked substrate. Particularly for relatively large solvent molecules, then, an attractive alternative to sol–$Pd(Et_4dien)X^+$ bond making is a dissociative mechanism in which transition-state stabilization is provided by solvation of the leaving group.

In order to shed light on the mechanistic issue, we have studied the rates of the substitution reactions of $Pd(Et_4dien)X^+$ ($X^- = Cl^-, Br^-, I^-$) as a function of temperature in several protic and aprotic solvents. We formulate in this paper the probable mechanisms of the rate-limiting solvolysis step in these reactions, based on the observed activation parameters and some additional information concerning ground-state Pd(II) solvation obtained from nmr data.

Experimental Section

Materials.—The complexes used in this study were prepared by literature methods[1,2] or slight modifications thereof. Satisfactory elemental analyses were obtained in all cases. Spectral grade methanol, ethanol, 2-propanol, dimethyl sulfoxide, and dimethylformamide were dried by standard procedures[6] and stored over 4A Linde molecular sieves.

Kinetics.—Reaction kinetics were followed using a Cary Model 14 spectrophotometer equipped with a water-jacketed cell compartment, at a uv wavelength where the spectral change for the reaction under consideration is large. All reactions were carried out under pseudo-first-order conditions; a constant ionic strength of 0.10 was maintained using $LiClO_4$. In water, Cl^-, Br^-, and I^- were introduced as Na^+ salts; in other solvents $[(C_2H_5)_4N]Cl$, $[(C_2H_5)_4N]Br$, and $[(n\text{-}C_4H_9)_4N]I$ were used. In all cases, good isosbestic points were obtained and the final uv spectra agreed well with the spectra of pure product complexes. The rate constants k_1 were calculated by a least-squares treatment of the data and are accurate to 5%. Each reaction was run at four or five different temperatures. The activation parameters were obtained from graphs of $\ln k_1/T$ *vs.* $1/T$ and $\Delta G^{\ddagger}$ *vs.* T.

Nuclear Magnetic Resonance Spectra.—Nmr spectra were recorded on a Varian A-60 spectrometer equipped with a variable-temperature probe (V-6058). A capillary tube containing benzene was used as an external reference. The temperature *in situ* was measured using a capillary filled with a mixture of water, methanol, and hydrochloric acid. This method[7] gives results to within ±0.2°.

Ground-State Solvation of the Substrates

Molecular models of $Pd(Et_4dien)X^+$ complexes show that each of the axial positions of the metal is occupied by two ethyl groups bound to the terminal nitrogen atoms of the ligand. The two axial positions are not equivalent, because one pair of ethyl groups is placed closer to the metal than the other pair. The steric requirements of the coordinated Et_4dien apparently prevent rapid interconversion of the two pairs of ethyl groups, as revealed by the proton nmr spectra of $Pd(Et_4dien)Cl^+$ shown in Figure 1.

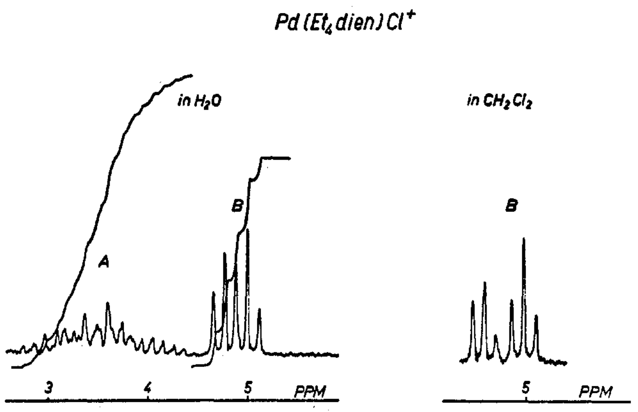

Figure 1.—Proton nmr spectra of $Pd(Et_4dien)Cl^+$ showing the resonances of the methylene protons (A) and the methyl protons (B) of the complex in H_2O and CH_2Cl_2. Shifts are in parts per million on the high-field side of benzene (external reference).

The chemical shifts of the methyl protons of the complex $Pd(Et_4dien)Cl^+$ in various solvents at 20.0° are given in Table I. These shifts are in parts per million relative to benzene. Since an external reference was used, the shifts have been corrected for the diamagnetic susceptibilities of the solvents (equation 3), where

$$\delta_{corr} = \delta_{obsd} + 2\pi/3(\chi^{v}_{benzene} - \chi^{v}_{sol}) \qquad (3)$$

TABLE I

CHEMICAL SHIFTS OF THE METHYL PROTONS OF THE COMPLEX $Pd(Et_4dien)Cl^+$ IN VARIOUS SOLVENTS AT 20°

Solvent	$\delta(-CH_3)$,[a] ppm	$\delta(-CH_3)$,[b] ppm	$\Delta\delta$, ppm
CH_2Cl_2	+5.22	+4.83	0.39
DMSO-d_6			0.34
C_2D_5OD			0.33
CH_3OH	+5.22	+4.92	0.30
H_2O	+5.23	+4.99	0.24

[a] The two equivalent methyl groups placed furthest from the metal; shifts are in parts per million on the high-field side of benzene (external reference). [b] The two equivalent methyl groups placed closest to the metal atom.

δ_{obsd} is the mean value of the shifts observed at 19.0 ± 0.2 and 21.0 ± 0.2°, and $\chi^{v}_{benzene}$ and χ^{v}_{sol} are respectively the diamagnetic volume susceptibilities of benzene and the solvent used as given in Emsley, Feeney, and Sutcliffe[8] for 20.0°.

Table I shows that the chemical shifts of the low-field signals corresponding to the two methyl groups placed closest to the metal atom vary with the solvent used, whereas the chemical shifts of the high-field signals corresponding to the two other methyl groups are practically constant. From these data we conclude that the ability of the solvent to interact with the Pd(II) atom and partially displace the ethyl groups decreases in the order $H_2O > CH_3OH > C_2H_5OH \sim$ DMSO $> CH_2Cl_2$. By increasing the temperature to 80°, the $\Delta\delta$'s in water and DMSO become smaller but do not cancel. The same pattern is observed in the case of the complex $Pd(Et_4dien)I^+$. It appears that the smaller solvent molecules are able to interact with the Pd(II) better than the larger ones, and the advantage in coordination through sulfur–M bonding that DMSO has over C_2H_5OH, CH_3OH, and H_2O in non-axially blocked complexes is lost here.

Rates, Activation Parameters, and Mechanisms

The rates and activation parameters for the substitution reactions of $Pd(Et_4dien)X^+$ with halide ions in various solvents are summarized in Table II. The rates are first order in all cases. In protic solvents, the reactivity of $Pd(Et_4dien)X^+$ decreases as X is varied

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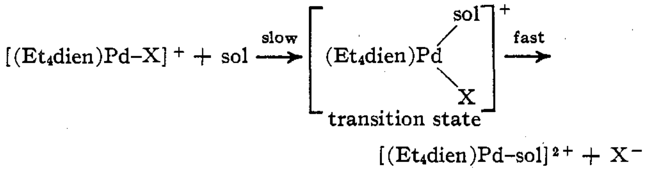
TABLE II

RATES AND ACTIVATION PARAMETERS FOR SUBSTITUTION REACTIONS OF $Pd(Et_4dien)X^+$ IN DIFFERENT SOLVENTS[a]

Substrate	Solvent	Entering group	10^5k_1, sec^{-1} (T, °C)	ΔT, °C	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
$Pd(Et_4dien)Cl^+$	H_2O	I^-	420 (32.7)	25–40	16.5 ± 0.5	−16 ± 2
		Br^-	430 (32.7)	25–40	16.5 ± 0.5	−16 ± 2
	C_2H_5OH	I^-	8.0 (45.4)	37–55	18.0 ± 0.5	−21 ± 2
		Br^-	8.1 (45.4)	37–55	18.6 ± 1.0	−19 ± 3
	i-C_3H_7OH	I^-	6.4 (51.4)	50–65	18.9 ± 1.0	−18 ± 3
$Pd(Et_4dien)Br^+$	H_2O	I^-	550 (40.2)	25–40	17.6 ± 0.5	−13 ± 2
	DMSO	Cl^-	43 (41.6)	31–48	20.4 ± 1.0	−7 ± 2
	CH_3OH	I^-	14.8 (45.6)	38–52	19.2 ± 1.0	−16 ± 2
	C_2H_5OH	I^-	7.9 (45.6)	45–60	19.6 ± 0.5	−16 ± 2
	i-C_3H_7OH	I^-	4.4 (51.6)	48–65	19.8 ± 0.5	−18 ± 2
$Pd(Et_4dien)I^+$	H_2O	Br^-	140 (40.0)	29–40	18.4 ± 0.5	−13 ± 2
		Cl^-	140 (40.0)	29–40	18.6 ± 0.5	−13 ± 2
	DMSO	Cl^-[b]	96 (41.6)	31–48	19.6 ± 0.5	−10 ± 2
	DMF	Cl^-[b]	89 (41.6)	31–48	19.4 ± 0.5	−11 ± 2
	CH_3OH	Br^-[c]	7.2 (45.0)	45–57	19.9 ± 0.5	−15 ± 2
	C_2H_5OH	Br^-[c]	5.5 (55.0)	50–66	20.4 ± 0.5	−16 ± 2

[a] For $\mu = 0.10$ ($LiClO_4$). [b] Reaction with Br^- gives the same k_1. [c] Reaction with Cl^- gives the same k_1.

in the order Cl > Br > I. Our results confirm that this reactivity order is due to a corresponding increase in $\Delta H^{\ddagger}$ along the halo series. The $\Delta S^{\ddagger}$ values in aqueous and alcohol solutions suggest an associative mechanism for the solvent substitution path



Solvation and dissociation of the leaving group apparently are of much less importance than sol–Pd(II) bond formation in the transition state, because the $\Delta S^{\ddagger}$ values are negative and not very sensitive to the nature of X. For example, the equal, negative $\Delta S^{\ddagger}$ values for the aqueous solution reactions of the bromo and iodo substrates are incompatible with a mechanism in which considerable Pd–X bond breaking must occur to reach the transition state. In particular, $\Delta S^{\ddagger}$ would be expected to be much more positive than observed for an iodide leaving group.

Data showing the influence of ionic strength (μ) on the rate constants of the substitution reactions of $Pd(Et_4dien)X^+$ in aqueous solution are presented in Table III. An increase in μ by a factor of 10 in each case produces a small decrease in rate. Rate reductions by factors of 1.4, 1.2, and 1.2, respectively, are observed for chloro, bromo, and iodo complexes. These results provide additional support for a mechanism involving associative activation to give a five-coordinate $[Pd(Et_4dien)(X)(sol)]^+$ transition state.

TABLE III

INFLUENCE OF IONIC STRENGTH ON THE RATES OF SUBSTITUTION REACTIONS OF $Pd(Et_4dien)X^+$ COMPLEXES IN AQUEOUS SOLUTION

Substrate	Entering ligand (T, °C)	$\mu(LiClO_4)$	10^4k_1, sec^{-1}
$Pd(Et_4dien)Cl^+$	I^- (25)	0.10	19.0
		1.00	14.0
$Pd(Et_4dien)Br^+$	I^- (30)	0.10	21.0
		0.50	18.0
		1.00	17.0
$Pd(Et_4dien)I^+$	Br^- (35)	0.10	8.5
		0.50	7.7
		1.00	7.1

In the protic solvents the variations of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for a given $Pd(Et_4dien)X^+$ substrate are readily interpreted on the basis of associative activation. All the solvents under consideration utilize oxygen-donor atoms in binding to Pd(II). Increasing the size of the solvent molecule results in an increase in $\Delta H^{\ddagger}$ and a more negative value of $\Delta S^{\ddagger}$. As the nmr data show less ground-state solvation of Pd(II) by the larger protic solvent molecules, a greater expenditure of activation energy and also considerably more ordering of the entering solvent molecule are required to reach the five-coordinate transition state in these cases.

In the aprotic solvents DMSO and DMF, the reactivity of $Pd(Et_4dien)X^+$ decreases as X is varied in the order I > Br > Cl. Goddard and Basolo showed[5] that this rate order in DMSO and CH_3CN solutions parallels the order of instabilities of these complexes. The relative instability of the $Pd(Et_4dien)I^+$ complex is presumably due to a combination of Pd–I bond weakening through severe steric interactions and the stabilization of uncoordinated I^- by solvation in DMSO.

In view of the activation parameters for solvent substitution in DMSO and DMF, a dissociative interchange pathway accompanied by solvation of the leaving group is attractive.

$$[(Et_4dien)Pd\text{-}X]^+ + sol \xrightarrow{\text{slow}} \underset{\text{transition state}}{[(Et_4dien)Pd\cdots X\cdot]^+\cdots sol} \xrightarrow{\text{fast}} [(Et_4dien)Pd\text{-}sol]^{2+} + X^-$$

The $\Delta S^{\ddagger}$ values are much less negative than in protic solvents. The substitution reaction of $Pd(Et_4dien)Br^+$ in DMSO, for example, has a $\Delta S^{\ddagger}$ some 10 eu more positive than reactions in the alcohols which show comparable ground-state solvation of Pd(II). Steric considerations indicate that the ground-state interaction is $(CH_3)_2S{=}O\rightarrow Pd^{II}$ and that it is not possible to reach the sulfur-bonded configuration preferred by Pd(II) undergoing associative activation. Thus the substrate chooses a reaction pathway in which Pd–X bond breaking and leaving-group solvation assume much more importance. The fact that the $\Delta S^{\ddagger}$ value is more negative for the iodo than for the bromo complex in DMSO is reasonable, because more solvent ordering in the transition state is expected in the former case.

In summary, our results indicate that both associative and dissociative activation processes operate in the solvolysis reactions of $Pd(Et_4dien)X^+$ substrates. Apparently the steric requirements for effective associative activation are so severe that only small solvent molecules (or ligands) with accessible donor atoms qualify. This conclusion is consistent with the observation[1] that in aqueous solution only the powerful nucleophilic ligand $S_2O_3^{2-}$, which possesses an exposed sulfur donor atom ($-S^-$), is able to utilize effectively a direct associative pathway. For all other entering groups the substitution rates are controlled by the associative solvolysis path to give an aquo intermediate.

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Polyamine Substitution Reactions of Tris(2-aminoethyl)aminecopper(II)[1]

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The rates of the ligand-exchange reactions of dien, trien, and tetren with Cu(tren) are measured using stopped-flow spectrophotometry. The pH dependence of the reaction rate is analyzed and two unprotonated nitrogen donor atoms on the incoming ligand are sufficient for the displacement of tren. The rate constants for the attack of the unprotonated polyamine on Cu(tren) are 106 × 10³, 85.2 × 10³, and 54.1 × 10³ for dien, trien, and tetren, respectively, at 25° and 0.1 *M* ionic strength. A mechanism is proposed wherein one nitrogen on the incoming ligand is bonded prior to the rate-determining step.

Introduction

The ligand-exchange reactions of tris(2-aminoethyl)aminecopper(II) (abbreviated Cu(tren) or CuTr)[2]

$$\text{Cu(tren)} + 2\text{dien} \longrightarrow \text{Cu(dien)}_2 + \text{tren} \quad (1)$$

$$\text{Cu(tren)} + \text{trien} \longrightarrow \text{Cu(trien)} + \text{tren} \quad (2)$$

$$\text{Cu(tren)} + \text{tetren} \longrightarrow \text{Cu(tetren)} + \text{tren} \quad (3)$$

with dien, trien, and tetren have been investigated. The Cu(tren) complex can exist in solution at high pH with a hydroxide ion coordinated to the copper ion in a ternary complex (abbreviated Cu(OH)tren). Cu(tren) has been reported to be a *cis*-diaquo octahedral[3a] structure while Cu(OH)tren exists as a trigonal-bipyramidal complex.[3b,c] Cu(trien), characterized as *trans*-diaquo octahedral,[4,5] is thermodynamically more stable than Cu(tren) due to the tetragonal distortion of the latter complex induced by the ligand structure. A planar arrangement of dentates is preferred by copper(II) to any nonplanar geometry. Reactions 1–3 are therefore favored to completion in the 6–12 pH range. Reactions 1–3 are rapid and are monitored by stopped-flow spectrophotometry. Many multidentate ligand replacement reactions have been reported in the literature but ligand-exchange kinetics of all-polyamine multidentate ligand systems have not been reported previously.

Experimental Section

A standard copper nitrate solution was prepared from pure metal and was standardized electrogravimetrically. This standard solution was used to standardize tren and tetren spectrophotometrically and to prepare Cu(tren). Cu(tren) was prepared by the addition of a slight excess of copper nitrate to a known quantity of ligand followed by precipitation of the excess as the metal hydroxide.

tren was obtained commercially from Jefferson Chemical Co. The liquid, gas chromatographically pure by the observation of only a single peak (20% SE-30 on silanized Chromosorb W, 190°, flow rate 20 ml/min), was dissolved in water and standardized by a mole ratio plot with the standard copper. trien was commercially obtained as the sulfate salt and was recrystallized according to the procedure of Reilley.[6] dien was recrystallized as the hydrochloride salt from a commercially obtained liquid.[7] tetren was precipitated as the sulfate salt from the impure commercial material obtained from Aldrich Chemical Co. and recrystallized according to the procedure of Reilley.[6]

A 0.01 *M* potassium borate–boric acid buffer system was used to control the pH of the solution. The large excess of free attacking ligand also served to buffer the solution. Solution pH was measured immediately after each kinetic run. Potassium nitrate was used to control the ionic strength at a value of 0.10 *M*. See Table I for reaction conditions.

Reactions 1–3 were followed spectrophotometrically in a 2-cm cell on a Durrum–Gibson stop-flow apparatus thermostated at 25 ± 0.01°. The photomultiplier signal was amplified and opposed by a voltage from a mercury battery source so that a selected portion of the per cent transmittance could be observed on a Tektronix 564 storage oscilloscope. (The 80–100% transmittance range was used for all the studies.) The stored image was photographed on Polaroid film. Reaction 2 was followed at the maximum absorption of Cu(trien) at 575 mμ (ε 150), under a variety of concentration ratios and levels including equal initial concentrations and with 10- and 20-fold excesses of trien to give pseudo-first-order reactions. All of these conditions were used to establish the pH profile (Figure 2) from pH 6.90 to 11.50. The excellent agreement of the rate constants observed

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[1] This paper was presented in part at the Midwest Regional Meeting of the American Chemical Society, Kansas City, Mo., Nov 1969, and was abstracted from the thesis presented by J. V. to the University of Nebraska for the Ph.D. degree.

[2] The following abbreviations are used throughout this paper: tren, tris(2-aminoethyl)amine (Tr); trien, triethylenetetramine (T); tetren, tetraethylenepentamine (Te); dien, diethylenetriamine (D). All charges have been left out for convenience.

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