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Contribution from the Dipartimento di Chimica Inorganica e Struttura Molecolare,
Università di Messina, Vill. S. Agata, Salita Sperone 31, 98166 Messina, Italy

Competitive Uncatalyzed Geometrical Isomerization and β-Hydride Elimination of Alkyl Complexes of Platinum(II)

Giuseppe Alibrandi, Matteo Cusumano, Domenico Minniti,* Luigi Monsù Scolaro, and Raffaello Romeo*

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Rates and activation parameters for the spontaneous cis to trans isomerization of monoalkyl [Pt(PEt$_3$)$_2$(R)Cl] (R = CH_3, C_2H_5, C_2D_5, *n*-C_3H_7, *n*-C_4H_9, $CH_2Si(CH_3)_3$) complexes have been measured in 2-propanol. The reactions are inhibited by chloride ion, and for all systems the isomeric equilibrium lies well to the side of the trans form. As in the case of the related aryl complexes, the isomerization mechanism involves dissociative loss of chloride and interconversion of two T-shaped $[PtL_2(\text{alkyl})]^+$ 3-coordinate intermediates. An incipient interaction of the β-hydrogens of the alkyl group with the metal in the transition state leading to the first platinum cation intermediate accounts for the much higher reactivity of the complexes in which R = Et, *n*-Pr, and *n*-Bu with respect to that of complexes containing alkyl groups with no β-hydrogens. The *n*-propyl and *n*-butyl derivatives, in addition to spontaneous isomerization, undergo thermal decomposition through a concurrent pathway yielding *trans*-[Pt(PEt$_3$)$_2$(H)Cl] and olefins (propene and 1-butene, *cis*-2-butene, and *trans*-2-butene in the ratio 1:1:0.04, respectively). No alkanes are produced in these reactions that go to completion and are unaffected by the presence of excess of chloride ion in solution. The relative rate constants of the two competing processes either in the neat solvent or in solutions containing chloride have been calculated through kinetic, spectrophotometric, and GLC measurements. The most probable mechanism for the thermolysis involves a nondissociative pathway in which the loss of olefin after facile reversible β-hydride elimination is probably rate determining.

Introduction

Square-planar complexes of the type *cis*-[PtL$_2$(R)X](L = PEt$_3$; R = phenyl or substituted aryl groups; X = halide ions) are generally inert in apolar solvents, where their conversion to the corresponding trans isomers can be promoted by the presence of catalytic amounts of free ligand[1] or by photochemical activation,[2] as for [PtL$_2$X$_2$] complexes.[3] In protic solvents, cis to trans isomerization takes place spontaneously.[4] Detailed kinetic investigations of this latter process[4-7] have shown that in the generality of cases isomerization suffers mass law retardation by halide ion, and its rate is very much less than that at which halide is replaced by the solvent or other nucleophiles. The rate of isomerization is still particularly sensitive to factors controlling Pt–X bond dissociation as the nature of the halide ion,[5] electron donation or withdrawal by substituents on the cis aromatic ring,[5] and the electrophilic ability of the solvent.[6] Except for the case in which R = mesityl, large values of enthalpy of activation and positive entropies and volumes of activation[7] are associated with isomerization. The mechanism proposed for these uncatalyzed isomerizations involves the dissociative loss of the X ligand followed by the interconversion of two geometrically distinct 3-coordinate T-shaped intermediates. A recent study has shown that the same mechanism applies to the isomerization of *cis*-[Pt(PEt$_3$)$_2$(Ar)(S)]$^+$ (S = a series of hydroxylic solvents) complexes.[8]

Preliminary results for isomerization of the related alkyl complexes[9] have shown that *cis*-[Pt(PEt$_3$)$_2$(Me)Cl] in methanol isomerizes at a rate comparable to that of *cis*-[Pt(PEt$_3$)$_2$(Ph)Cl], confirming that the presence of an aromatic ring is not a prerequisite for the occurrence of the process. However, *cis*-[Pt(PEt$_3$)$_2$(Et)Cl] isomerizes at a much greater rate, virtually as soon as the solid compound is dissolved in methanol.

Since inductive or steric factors cannot account for this large difference of reactivity, we started a detailed kinetic study of the isomerization of complexes in which R comes from a series of linear or branched alkyl groups, with the aim of investigating the sensitivity of the process to the length of the chain and/or to the availability of β-hydrogens. The study has been carried out in 2-propanol as solvent, taking advantage of the minor effectiveness of this solvent with respect to methanol in promoting isomerization.[6] During this study we found that the *n*-propyl and *n*-butyl derivatives, in addition to spontaneous isomerization, undergo thermal decomposition through a concurrent pathway. A preliminary communication has appeared.[10]

Experimental Section

Dialkyl Substrates. Some of the complexes *cis*-[Pt(PEt$_3$)$_2$(R)$_2$] were prepared by literature methods. R group (reference number): methyl (1), ethyl (1), ethyl-d_5 (11), *n*-propyl (11).

The following are new.

***cis*-[Pt(PEt$_3$)$_2$(*n*-Bu)$_2$].** *cis*-[Pt(PEt$_3$)$_2$Cl$_2$] (1.5 g) suspended in diethyl ether was reacted at −78 °C with *n*-butyllithium (5 mL, 1.6 M) in *n*-hexane. After $^1/_2$ h of stirring at 0 °C the reaction mixture was cooled again at −78 °C and combined with water (3 mL) and methanol (0.3 mL). Evaporation of the organic layer gave a white oil that turned into a solid after crystallization from an ether–methanol mixture; mp 28–29 °C.

***cis*-[Pt(PEt$_3$)$_2$(Me$_3$SiCH$_2$)$_2$].** *cis*-[Pt(PEt$_3$)$_2$Cl$_2$] (1 g) suspended in dry benzene (10 mL) was treated with an ethereal solution of Me_3SiCH_2MgCl (2 mL, 3 M). After 1 h of stirring at room temperature, the mixture was hydrolyzed at 0 °C with a saturated aqueous solution of NH_4Cl. The pale yellow oil resulting from the dried organic layer was converted into a solid by washing with small amounts of ether and then crystallized from petroleum ether (bp 40–60 °C) as white needles, mp 89–90 °C.

Monoalkyl Complexes. Some of the *cis*- and *trans*-[Pt(PEt$_3$)$_2$(R)Cl] complexes were prepared by literature methods. R group (reference number): cis methyl (11), trans methyl (1), trans ethyl (1).

The following are new.

***cis*-[Pt(PEt$_3$)$_2$(R)Cl] (R = Ethyl, Mp 71–73 °C; R = Ethyl-d_5, Mp 60–62 °C; R = *n*-Propyl, Mp 73–75 °C; R = *n*-Butyl, Mp 68–69 °C; R = Me$_3$SiCH$_2$, Mp 58–60 °C).** These compounds were prepared by using the general procedure described by Chatt and Shaw.[1] Thus, a weighed amount of the corresponding dialkyl complex in dry ether was treated

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with a stoichiometric quantity of dry HCl in diethyl ether. After evaporation of the solvent the residues were crystallized as white compounds from petroleum ether or from a benzene–petroleum ether mixture, as necessary.

***trans*-[Pt(PEt$_3$)$_2$(R)Cl] (R = *n*-Propyl, Mp 48–50 °C; R = *n*-Butyl, Mp 41–42 °C; R = Ethyl-*d*$_5$, Mp 51–53 °C).** These were prepared from the corresponding cis compounds under the catalytic effect of traces of free phosphine. In a typical preparative procedure, a weighed amount of the corresponding cis-monoalkyl compound suspended in *n*-hexane was combined with a small quantity of PEt$_3$ under nitrogen atmosphere. The reaction mixture was heated until complete dissolution of the starting material. After filtration and evaporation of the solvent, the residue was crystallized as a white compound from a methanol–water mixture.

***trans*-[Pt(PEt$_3$)$_2$(Me$_3$SiCH$_2$)Cl].** A 0.25-g amount of *cis*-[Pt(PEt$_3$)$_2$(Me$_3$SiCH$_2$)Cl] dissolved in MeOH (30 mL) was left overnight at room temperature. After evaporation of part of the solvent and addition of few drops of water, crystallization gave 0.21 g of the trans product, mp 41–43 °C.

Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 783 spectrophotometer equipped with a 3600 IR Data Station; ^{1}H NMR spectra were determined on a Hitachi Perkin-Elmer R 24 B spectrometer with CDCl$_3$ as the solvent and tetramethylsilane as an internal reference. ^{31}P{^{1}H} NMR spectra were recorded on a Bruker WP 80 spectrometer with [^{2}H$_6$] benzene as the solvent. ^{31}P chemical shifts, in parts per million, are relative to external phosphoric acid. Anhydrous methanol was obtained by distillation of the reagent grade solvent over Mg(OCH$_3$)$_2$. 2-Propanol was dried over magnesium ribbon and fractionally distilled in a 180-cm Dufton column. Diethyl ether was distilled under nitrogen from sodium benzophenone dianion. LiClO$_4$ "anhydrous" (99.8%) was purchased from K & K Fine and Rare Chemicals. Other compounds were the best available commercial materials and were used without further purification.

Kinetics. Isomerization reactions were followed spectrophotometrically by repetitive scanning of the spectrum at suitable times in the range 300–220 nm or at a fixed wavelength, where the difference of absorbance was largest. The reactions were carried out in a silica cell in the thermostated cell compartment of a Cary 219 spectrophotometer with a temperature accuracy of ±0.02 °C. Isomerizations were started by adding a weighed amount of a finely powdered sample of the cis complex to a prethermostated volume of solvent and shaking the solution rapidly. The values of the rate constants k_i, s^{-1}, were obtained graphically by means of the usual first-order plots, which, in the case of the *n*-propyl and *n*-butyl derivatives, showed some slight initial deviations from linearity; however, the extent of these deviations was not such to prevent a correct analysis of the plots and their origin was not further investigated.

The kinetics of decomposition of these latter compounds were followed in an analogous way, stopping the concurrent isomerization by addition of free chloride ion. At concentrations of chloride greater than 0.01 M the sole reaction is the decomposition of the starting material into *trans*-[Pt(PEt$_3$)$_2$(H)Cl], isolated in a quantitative yield and characterized by elemental analysis and UV, IR, and ^{1}H NMR spectra. The decomposition obeys a first-order rate law until well over 90% of the reaction, and the rate constants k_{obsd}, s^{-1}, were obtained either from graphs or from nonlinear least-squares fits of the experimental data to $A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{\text{obsd}}t)$ with A_0, A_∞, and k_{obsd} as the parameters to be optimized (A_0 = absorbance after mixing of reagents, A_∞ = absorbance at completion of reaction). Some kinetics of decomposition have been followed also by monitoring the increase of the Pt–H stretching frequency of the platinum-hydride product at 2216 cm^{-1}, with a barium fluoride cell and a computer-aided Perkin-Elmer infrared spectrophotometer. The same reactions were followed also by GLC, measuring the relative amounts of volatile products obtained after quenching with HCl samples taken at various times. In a typical kinetic procedure, weighted amounts of *cis*-[Pt(PEt$_3$)$_2$(*n*-Pr)Cl] (1 mg) were placed at the bottom of a series of cylindrical vessels (10 mL) sealed with a gastight rubber serum cap and immersed in a thermostated oil bath. Prethermostated anhydrous 2-propanol (2 mL) containing 0.1 M LiCl was added by means of a syringe and the solid rapidly dissolved by shaking. Alternatively, a solution of complex was prepared in a volumetric flask at low temperature and aliquots were transferred to the vessels placed in the thermostated bath. Quenching was carried out by removing at intervals a vessel, introducing concentrated hydrochloric acid (0.1 mL), and shaking the solution. Gas samples (less than 1% of the total volume) were taken and analyzed by gas chromatography. Since undecomposed starting material produces only propane on quenching and propene on thermal decomposition, it was possible to determine the extent of decomposition from the relative areas of the peaks due to propene and propane without need of an internal standard. The rate constants k_{obsd}, s^{-1}, were obtained from linear plots of ln (1–*F*) vs *t*, where *F* is the decomposition fraction. The same procedure applies for the *n*-butyl derivative. A Carlo Erba 5300 gas chromatograph was used with a 80-100 Carbopack/0.15% picric acid column for C$_4$ separation and with a 0.03–0.02-mm silica gel column for C$_3$ separation.

Table I. Elemental Analyses[a] and Spectral Characteristics of *cis*- and *trans*-[Pt(PEt$_3$)$_2$(R)Cl] Complexes

				^{31}P{^{1}H} NMR[b]		
R	geometry	% C	% H	δ, ppm	^1J(PtP), Hz	^2J(PP), Hz
CH$_3$	cis	(32.4)	(6.9)	8.28	4158	11.9
		32.6	6.8	15.36	1694	
	trans	32.5	7.0	15.12	2817	
CH$_2$CH$_3$	cis	(33.9)	(7.1)	9.01	4380	11.8
		33.5	7.0	14.82	1536	
	trans	33.9	7.2	15.12	2977	
CD$_2$CD$_3$	cis	(33.6)	(8.0)	8.90	4383	11.6
		33.4	8.2	14.89	1528	
	trans	33.4	7.9	15.18	2959	
CH$_2$CH$_2$CH$_3$	cis	(35.3)	(7.3)	8.70	4367	11.7
		35.0	7.2	15.01	1539	
	trans	35.6	7.4	15.18	2959	
CH$_2$(CH$_2$)$_2$CH$_3$	cis	(36.7)	(7.5)	8.64	4368	11.7
		36.7	7.4	15.00	1548	
	trans	36.4	7.1	15.00	2961	
CH$_2$Si(CH$_3$)$_3$	cis	(34.7)	(7.5)	7.27	4198	13.7
		34.8	7.7	14.72	1778	
	trans	34.4	7.3	12.26	2844	

[a] Theoretical values are given in parentheses. [b] [^{2}H$_6$]benzene.

Reactions of nucleophilic substitutions of *cis*-[Pt(PEt$_3$)$_2$(Me)Cl] with I$^-$ required the use of a Hi-Tech SF3 stopped-flow spectrophotometer equipped with a Gould 05100 oscilloscope and a Radiometer REC 61 potentiometric recorder. The analogous slower reactions of the silyl derivative were followed by conventional spectrophotometric techniques. Activation parameters were derived from a nonlinear fit of k/T vs T data according to the Eyring formalism.

Results

Cleavage of the first Pt–C σ bond by HCl in complexes of the type *cis*-[PtL$_2$R$_2$] gave monoalkyl *cis*-[PtL$_2$(R)Cl] compounds. These latter compounds were easily converted to their trans isomers by catalytic amounts of free phosphine in *n*-hexane or were converted spontaneously in protic solvents.

Satisfactory indications on the stereochemistry of both dialkyl and monoalkyl complexes came from their IR spectra that showed two Pt–P stretching frequencies for the cis compounds in the region between 410 and 440 cm^{-1} and only one for the trans derivatives.[12] A clear-cut confirmation of the geometry of the monoalkyl compounds arises from their ^{31}P{^{1}H} NMR spectra (Table I). The trans complexes show only one phosphorus resonance with a coupling constant to ^{195}Pt centered at 2939 ± 90 Hz whereas the cis derivatives show two ^{31}P resonances (^1J(PtP$_A$) = 4309 ± 100 Hz; ^1J(PtP$_B$) = 1603 ± 106 Hz). The low coupling constant ^1J(PtP$_B$) is typical of phosphorus atoms trans to carbon in platinum complexes, while the value of ^1J(PtP$_A$) of 4309 Hz is consistent with the presence of a weak trans donor ligand such as Cl$^-$.[13]

Although slower reactions can be effectively monitored by means of ^{31}P NMR spectroscopy, through the decrease of the signals due to the cis compound and the parallel matching increase of the signal of the trans compound, all isomerization reactions of [PtL$_2$(R)Cl] complexes were followed spectrophotometrically, by repetitive scanning of the spectrum in the UV region. When R = CH$_3$, C$_2$H$_5$, C$_2$D$_5$, and CH$_2$Si(CH$_3$)$_3$, the spectral changes show clean isosbestic points and the final spectra are identical with those of independently prepared solutions of trans isomers. The isomerization follows a first-order rate law. The specific rate constants, k_i, s^{-1}, at various temperatures are collected in Table II, and the associated activation parameters, in Table III. Upon addition of chloride ion to the solution, the nature of the observed changes remains the same but the rate of isomerization is greatly decreased. The effect of adding chloride was studied by keeping the ionic strength constant at 0.01 M with LiClO$_4$. The first-order

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Table II. Temperature Dependence of the Rate Constants for Uncatalyzed Cis to Trans Isomerization of $[Pt(PEt_3)_2(R)Cl]$ Complexes

R	T, K	10^3k_i, s^{-1}	R	T, K	10^3k_i, s^{-1}
CH_3[a,d]	293.16	0.21	$CH_2CH_2CH_3$[b,c]	288.16	0.976
	298.16	0.49		293.16	2.04
	303.16	1.27		298.16	3.27
	308.16	2.72		303.16	6.59
	313.16	6.05	$CH_2(CH_2)_2CH_3$[b,c]	288.16	2.21
CH_3[b]	303.16	0.009		293.16	4.08
	317.16	0.046		298.16	8.06
	327.16	0.188		303.16	14.2
CH_2CH_3[b]	293.16	4.44	$CH_2Si(CH_3)_3$[a]	288.16	1.95
	298.16	8.46		293.16	3.48
	303.16	16.0		298.16	6.34
	308.16	25.4		303.16	10.4
	313.16	48.9		308.16	17.2
CD_2CD_3[b]	293.16	3.94	$CH_2Si(CH_3)_3$[b]	298.16	0.03
	298.16	7.52		303.16	0.06
	303.16	14.2		308.16	0.10
	308.16	21.4		313.16	0.19
	313.16	46.1		318.16	0.36
				323.16	0.64

[a] In methanol. [b] In 2-propanol. [c] Calculated from the relationship $k_i = k_{obsd} - k_d$. [d] From ref 8.

Table III. Comparison of the Rate Constants at 303.16 K and Activation Parameters for Cis to Trans Isomerization of $[Pt(PEt_3)_2(R)Cl]$ Complexes in 2-Propanol

R	10^3k_i, s^{-1}	reactivity ratio	ΔH_i^*, kJ mol^{-1}	ΔS_i^*, J mol^{-1} K^{-1}
CH_3	0.009	1	101 ± 8	-9 ± 20
CH_2CH_3	16.0	1780	87 ± 2	+9 ± 8
CD_2CD_3	14.2	1580	88 ± 4	+11 ± 12
$CH_2CH_2CH_3$	6.59	730	87 ± 5	+2 ± 14
$CH_2(CH_2)_2CH_3$	14.2	1580	88 ± 2	+11 ± 6
$CH_2Si(CH_3)_3$	0.06	6	96 ± 3	-10 ± 5

Table IV. Effect of Lithium Chloride on the Rate Constant for Cis to Trans Isomerization of the Complexes $[Pt(PEt_3)_2(R)Cl]$[a]

R	$10^4 \times [Cl^-]$, M	10^4k_i, s^{-1}	R	$10^4 \times [Cl^-]$, M	10^4k_i, s^{-1}
CH_3[b,f]	0.0	15.4	$CH_2Si(CH_3)_3$[b,e]	0.0	65.9
	1.0	6.91		1.0	42.1
	2.0	4.63		2.0	28.3
	4.0	2.70		4.0	18.6
	10.0	1.20		6.0	12.7
	12.0	1.05		8.0	10.2
CH_3[c,g]	0.0	4.48		10.0	8.43
	1.0	0.781	$CH_2Si(CH_3)_3$[c,g]	0.0	31.8
	2.0	0.413		1.0	8.42
	4.0	0.221		2.0	4.88
	6.0	0.147		4.0	2.65
	8.0	0.113		6.0	1.88
CH_2CH_3[c,d]	0.0	321		8.0	1.40
	4.0	13.7			
	6.0	8.8			
	8.0	7.24			
	10.0	5.55			
	20.0	2.86			
	40.0	1.42			

[a] μ = 0.01 M ($LiClO_4$); [complex] = 0.75×10^{-4} M. [b] In methanol. [c] In 2-propanol. [d] At 293.16 K. [e] At 298.16 K. [f] At 303.16 K. [g] At 318.7 K.

rate constants are collected in Table IV. Plots of k_i^{-1} vs $[Cl^-]$ are linear for all systems, and the intercepts at $[Cl^-] = 0$ were identical with the k_i^{-1} values obtained in the absence of chloride ion; however, these values are still different from that obtained in the neat solvent, since the addition of inert salts to adjust the ionic strength increases the isomerization rate. This salt effect is particularly relevant in 2-propanol as solvent where the rate of isomerization in 0.01 M solution of $LiClO_4$ can be 10 times higher even than that in the neat solvent.

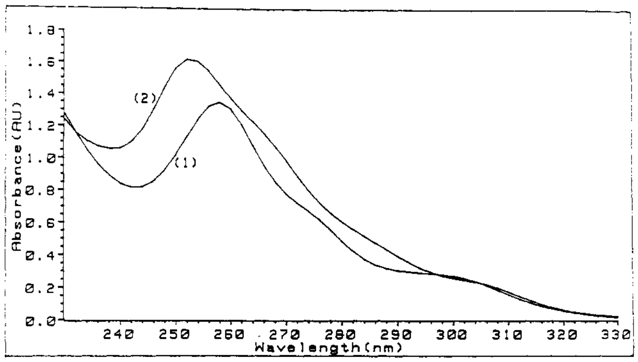

Figure 1. Electronic spectra of equimolar solutions of (1) *trans*-$[Pt(PEt_3)_2(n\text{-}Bu)Cl]$ and (2) *trans*-$[Pt(PEt_3)_2(H)Cl]$.

Table V. Temperature Effect on the Rates of Thermal Decomposition of *cis*-$[Pt(PEt_3)_2(R)Cl]$ (R = *n*-Propyl, *n*-Butyl) Complexes in 2-Propanol Containing 0.1 M LiCl

	10^3k_d, s^{-1}			10^3k_d, s^{-1}	
T, K	R = *n*-propyl[a]	*R* = *n*-butyl[b]	T, K	R = *n*-propyl[a]	*R* = *n*-butyl[b]
284.66	0.101	0.135	298.36	0.600	0.930
288.46	0.172	0.227	302.76	1.06	1.48
293.16	0.335	0.508			

[a] ΔH^* = 90 ± 1 kJ mol^{-1}; ΔS^* = -5 ± 6 J mol^{-1} K^{-1}. [b] ΔH^* = 94 ± 4 kJ mol^{-1}; ΔS^* = +11 ± 14 J mol^{-1} K^{-1}.

The kinetics of isomerization of the *n*-propyl and *n*-butyl complexes deviate from this simple pattern of behavior. The final spectrum corresponds roughly to that of the trans isomer (λ_{max} at 255 nm; λ_{min} at 240 nm) only for the kinetic runs carried out in 2-propanol or in 2-propanol containing inert salts. Addition of increasing amounts of LiCl produces as expected mass law retardation of the overall process, but the spectral changes are also influenced not as much in the shape as in the positions of λ_{max} and λ_{min}, which move toward lower wavelengths (see Figure 1). At concentrations of chloride higher than 0.01 M, the rate of reaction becomes independent of $[Cl^-]$ and the final spectrum has a λ_{max} at 250 nm and λ_{min} at 235 nm. It is possible to show that, under these circumstances, the sole reaction product is *trans*-$[Pt(PEt_3)_2(H)Cl]$, isolated in a quantitative yield and characterized by elemental analysis and UV, IR, ^1H, and ^{31}P NMR spectra.

Thus, the *n*-propyl and *n*-butyl derivatives, in addition to spontaneous isomerization, undergo thermal decomposition through a concurrent pathway:

$$cis\text{-}[Pt(PEt_3)_2(R)Cl] \rightarrow trans\text{-}[Pt(PEt_3)_2(H)Cl] + \text{olefins} \quad (1)$$

For the *n*-propyl derivative the only volatile product was propene, while for the *n*-butyl derivative we observed the formation of 1-butene, *cis*-2-butene, and *trans*-2-butene in the ratio 1:1:0.04. The relative yields of the three butenes were independent of the extent of decomposition of the *n*-butyl complex and did not change appreciably with the temperature or the amount of Cl^- added in solution. No alkanes are produced in these reactions. The *trans*-$[Pt(PEt_3)_2(n\text{-alkyl})Cl]$ derivatives are stable under the same experimental conditions that promote the facile decomposition of the cis isomers.

The kinetics of decomposition in 2-propanol containing 0.1 M LiCl were followed by repetitive scanning of the spectrum in the UV region. Abstract factor analysis of these spectral changes[14] has shown the presence of only two independently absorbing species in solution, viz. the alkyl substrate and the hydride product. The kinetics obey a first-order rate law until well over 90% of the

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Table VI. Dependence of the Ratio k_i/k_d on Chloride Concentration in 2-Propanol at 298.16 K Calculated from Kinetic, Spectrophotometric, and GLC Data

[LiCl], M	10^3k_{obsd}, s^{-1}	10^3k_i, s^{-1}	k_i/k_d[a]	k_i/k_d[b]	k_i/k_d[c]
		R = *n*-Propyl			
0.000	128	127	213		
0.0001	10.9	10.3	17.1		17.1
0.0002	5.89	5.29	8.81	7.9	8.3
0.0004	3.14	2.54	4.23	4.1	4.0
0.0006	2.47	1.87	3.11	3.3	3.0
0.0008	1.68	1.08	1.79	2.2	2.0
0.0010	1.48	0.88	1.46	1.4	1.4
0.0020	1.12	0.52	0.86	0.80	0.80
0.100	0.602				
		R = *n*-Butyl			
0.000	116	115	130		
0.0001	12.5	11.6	13.2	12	14
0.0002	7.74	6.86	7.81	7.7	7.8
0.0004	4.04	3.14	3.57	4.1	3.7
0.0006	3.19	2.29	2.61	2.9	2.8
0.0008	2.68	1.80	2.05	2.4	2.4
0.0010	2.31	1.43	1.62	1.5	1.7
0.0020	1.60	0.72	0.8	0.8	0.9
0.100	0.878				

[a] From kinetic data. [b] From spectrophotometric data. [c] From GLC data.

reaction, are independent of the concentration of complex, and are unaffected by chloride in solution in the range of concentration examined (0.01–0.2 M). The specific rate constants k_d, s^{-1}, at various temperatures are listed in Table V together with the associated activation parameters. The kinetic results obtained by using different techniques (UV, IR, and GLC) were indistinguishable, within the experimental error.

Knowing the value of the rate constant for thermal decomposition (k_d) and its independence of the chloride concentration and the ionic strength, it was possible to derive the value of the rate constant for the concurrent isomerization process, at a given chloride concentration, by means of the relationship valid for parallel first-order reactions $k_{obsd} = k_d + k_i$. The observed rate constants in Table VI were calculated from the absorbance data taken at 232 nm, a wavelength at which the absorbances of the *trans*-haloalkyl and the *trans*-halo hydrido products are comparable. As expected, plots of the reciprocal of the derived isomerization rates against [Cl⁻] are linear. The final spectra of these reactions, in the range 240–300 nm, were compared with a best-fitting procedure with those of mixtures of standards *trans*-[Pt(PEt$_3$)$_2$(*n*-alkyl)Cl] (**1**) and *trans*-[Pt(PEt$_3$)$_2$(H)Cl] (**2**). The analysis was performed on a Hewlett-Packard 8452 A diode array spectrophotometer interfaced with a HP 9000 series 300 data station by means of the Quantitation II program. The concentration ratio [**1**]/[**2**] gave the rate constant ratio k_i/k_d.

A further independent control of these rate constants has been carried out by measuring the relative amounts of alkane and alkenes formed upon treatment of the reaction mixture with HCl, at the end of the reaction. To this purpose solutions of cis complex and lithium chloride in 2-propanol, prepared according to the procedure described above, were left to react until both isomerization and decomposition went to completion. Since the amount of alkane produced by protonolysis of the *trans*-chloroalkyl product measures the extent of isomerization and the amount of olefins the extent of decomposition, the relationship [alkane]/[alkene] = k_i/k_d applies. A comparison of the values of the ratios k_i/k_d, at various chloride concentrations, obtained with different techniques is made in the last three columns of Table VI.

Discussion

All the previous findings can be accommodated in Scheme I, which illustrates the most complicated case of the *n*-butyl complex.

Isomerization. As for the parent aryl compounds, isomerization of monoalkyl *cis*-[Pt(PEt$_3$)$_2$(R)Cl] complexes takes place spontaneously in the protic solvent 2-propanol. When R = CH$_3$ or CH$_2$Si(CH$_3$)$_3$, the only process that is observed is cis to trans isomerization, and this is still the case for R = C$_2$H$_5$ or C$_2$D$_5$, since the rate of isomerization is much faster than that of the concurrent β-hydride elimination. When R = *n*-propyl or *n*-butyl, the rate of isomerization can be dissected from that of the parallel β-hydride elimination, as we discussed above. In all the cases isomerization obeys the rate law $k_i = a/(b[Cl^-] + c)$. Thus, it is possible to assume that the isomerization of alkyl complexes may proceed according to the well-established mechanism that involves as the rate-determining step the dissociative loss of the chloride ligand followed by the interconversion of two geometrically distinct 3-coordinate [PtL$_2$R]$^+$ intermediates. For this simple reaction scheme the rate law takes the form $k_i = k_dk_T/(k_{-d}[Cl^-] + k_T)$ and does not include any retardation term due to the trapping of the first "cis-like" 3-coordinate intermediate by the solvent.[8] Under these circumstances, in the absence of added chloride ion, the rate of isomerization is directly related to Pt–Cl bond dissociation. Accordingly, the process is characterized by high values of enthalpy of activation and low, even positive, entropies of activation (Table III). As expected, the removal of the same chloride ion by the solvent in a bimolecular solvolytic pathway is much faster and the activation parameters are completely different (see Table VII).

The rate sequence in Table III shows that from the methyl to the ethyl complex the rate increases by at least 3 orders of magnitude. This rate enhancement is seen also in the *n*-propyl and *n*-butyl derivatives, while, in the case of the silyl compound, the rate of isomerization drops again to a value comparable to that of the methyl complex. An incipient interaction of the β-

Scheme I

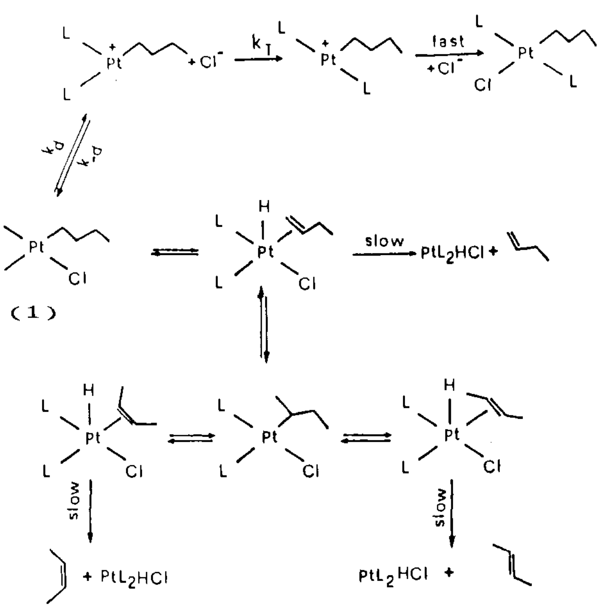

Table VII. Temperature Dependence of the Rate Constants for Solvolysis of *cis*-[Pt(PEt$_3$)$_2$(R)Cl] Complexes

R	solvent	*T*, K	k_s, s^{-1}
CH$_3$[a,d]	MeOH	285.16	4.47
		291.16	5.75
		303.16	12.6
		313.16	18.8
CH$_2$Si(CH$_3$)$_3$[b]	MeOH	286.16	0.0064
		293.16	0.0123
		303.16	0.0265
		312.16	0.0533
CH$_2$Si(CH$_3$)$_3$[c]	*i*-PrOH	286.16	0.00047
		293.16	0.00101
		303.16	0.00198
		313.16	0.00399

[a] $\Delta H^{\ddagger} = 38 \pm 3$ kJ mol^{-1}; $\Delta S^{\ddagger} = -100 \pm 8$ J K^{-1} mol^{-1}. [b] $\Delta H^{\ddagger} = 57 \pm 1$ kJ mol^{-1}; $\Delta S^{\ddagger} = -86 \pm 4$ J K^{-1} mol^{-1}. [c] $\Delta H^{\ddagger} = 55 \pm 3$ kJ mol^{-1}; $\Delta S^{\ddagger} = -114 \pm 12$ J K^{-1} mol^{-1}. [d] From ref 8.

hydrogens of the alkyl group with the metal in the transition state leading to the first platinum cation intermediate accounts for the much higher reactivity of the complexes in which R = C_2H_5, n-C_3H_7, and n-C_4H_9 with respect to that of complexes containing alkyl groups with no β-hydrogens (CH_3, $CH_2Si(CH_3)_3$). The low value of the kinetic isotope effect ($k_i(C_2H_5)/k_i(C_2D_5) = 1.12$) indicates that the participation of the β-hydrogens is not so extensive as required in a complete β-extraction process.[15] Thus, the platinum cation intermediate interconverts into a geometrically distinct "trans-like" T-shaped structure before a complete β-extraction can take place. This is in agreement with the low-energy barrier indicated for the fluxionality of coordinatively unsaturated reaction intermediates such as $H(PH_3)_2Pt^+$,[16] Me_3Au,[17] or $Et_2(PEt_3)Pt$.[18]

These results emphasize the role of ancillary ligands in assisting the formation and the stabilization of unsaturated 14-electron intermediates. As far as an aryl group is concerned, the fact that aryl and alkyl complexes with no β-hydrogens isomerize at comparable rates ($k_i(Me)/k_i(Ph) = 0.7$ in MeOH at 25 °C)[9] indicates that the participation of the aryl π-bonding system in the stabilization of the transition state is negligible. This supports the view that in these compounds the extent of aryl–platinum π interaction is small and is of secondary importance with respect to σ bonding.

Thermal Decomposition. The essential features of the β-hydride elimination of monoalkyl *cis*-[PtL_2(alkyl)Cl] complexes appear to differ markedly from those found in the decomposition of the strictly related dialkyl compounds.[19] The first process takes place under mild conditions; both the starting material and the final hydride product are stable enough to be isolated as pure compounds, and only alkenes are formed. The thermal decomposition of symmetrical and unsymmetrical *cis*-dialkylbis(phosphine)platinum(II) complexes in apolar solvents requires more drastic conditions leading to platinum(0) products and to disproportionation liberating alkane and alkene in a 1:1 ratio. Whitesides, Yamamoto, and others[11,20] have shown that the process most easily takes place when dissociation of the phosphine ligand produces an unstable coordinatively unsaturated T-shaped intermediate having a vacant coordination site for a facile β-hydride elimination. The transient four-coordinate platinum(II) hydride species formed on β-hydrogen abstraction of [PtL(alkyl)$_2$] subsequently undergoes reductive coupling of alkyl and hydride ligands and liberation of alkene. When an excess of phosphine ligand blocks the vacant coordination site at the metal, a higher energy β-elimination from the 16-electron starting complex becomes competitive with the dissociation route.

There are three conceivable pathways by which the process under study can take place: (i) that involving chloride loss and reversible β-hydride elimination through a [PtL_2(alkyl)]$^+$ intermediate; (ii) that involving phosphine dissociation and reversible β-hydride elimination through a [PtL(alkyl)Cl] intermediate; (iii) that involving β-hydride elimination from the four-coordinate starting material.

Since the thermal decomposition, unlike the parallel isomerization process, is unaffected by the presence of excess chloride ion, a mechanism involving a rate-determining chloride dissociation from the starting material can be ruled out. Thus, the two reactions, isomerization and β-hydride elimination, do not proceed through a common intermediate of reduced coordination number.

Addition of phosphine to the solutions of the cis monoalkyl complexes produces a very fast catalyzed pathway for isomerization, which predominates over decomposition. Thus, a proper study of the effect of the phosphine on the thermal decomposition is prevented by its role as catalyst for isomerization. However, dissociation of phosphine as a prerequisite for β-hydride elimination can be ruled out for two reasons: (i) free phosphine should promote a ready autocatalytic cis to trans isomerization; (ii) its place in the coordination sphere of the metal should be taken by the excess chloride ion (0.1 M) or by a molecule of the donor solvent. No loss of ^{195}Pt coupling to phosphine ligands can be noted when the thermolysis is followed by ^{31}P NMR spectroscopy.

We would suggest that β-hydride elimination involves a fast and reversible addition of a C–H bond to platinum in the square-planar complex yielding a 5-coordinate [PtL_2(H)(olefin)Cl] intermediate. Fast olefin insertion in this latter complex leads to the formation of different olefin isomers. The rate-determining pathway is the olefin loss from the 5-coordinate intermediate. The main points of evidence are as follows: (i) The facile reversible β-hydride elimination and olefin insertion in the pre-rate-determining step accounts for the facile skeletal isomerization of linear to branched alkyl groups. (ii) The value of the entropy of activation is consistent with a process in which two particles are being formed from one. Indeed, isomerization and β-elimination have comparable values of entropy of activation. (iii) A further support for olefin loss as the rate-determining step is found in the sequence of the rates of thermolysis $L_2Pt(Et)Cl \ll L_2Pt(n\text{-}Pr)Cl \sim L_2Pt(n\text{-}Bu)Cl$. If the comparison is restricted to the rate data in Table V it would appear that the rate of β-hydride elimination is almost unaffected by the nature of the alkyl group. However, it must be kept in mind that in the case of the ethyl complex a slower thermal decomposition is hidden by the high rate of its cis to trans isomerization.[21] The reactivity sequence reflects the ease of olefin liberation from the 5-coordinate intermediate, ethylene ≪ propylene ~ butene. Similar reasonings have been applied to explain the sequence of reactivity of dialkylphosphine complexes when the thermolysis is carried out in the presence of excess phosphine, and a similar mechanism is thought to take place.[20c] In this context it is worth mentioning that at high concentrations of added phosphine the rate of decomposition of *cis*-[Pt(PEt_3)$_2$(n-Pr)$_2$] is approximately 12 times faster than that of the ethyl analogue.[11]

These results would suggest that β-elimination from the 16-electron starting *cis*-[PtL_2(R)Cl] complexes has a much lower energy barrier with respect to a similar process taking place from the strictly related *cis*-[PtL_2R_2] species. The substitution of the ancillary alkyl group with a chloride ion should lead to an increase in the electrophilic character of the metal center and might provide the driving force for the facile β-elimination. In this connection it is worth mentioning that the presence of a methoxo group in [Pt(DPPE)(CH_2CH_3)(OCH_3)] (DPPE = 1,2-bis(diphenylphosphino)ethane) makes the decomposition of this substrate very much easier than that of [Pt(DPPE)(CH_2CH_3)$_2$].[22]

Finally, we already mentioned that the complexes *trans*-[Pt(PEt_3)$_2$(R)Cl] (R = Et, n-Pr, n-Bu) are stable under the same conditions that promote a facile decomposition of the corresponding cis isomers. Brainard and Whitesides[23] have carried out a very detailed study of the thermal decomposition of *trans*-[Pt(PEt_3)$_2$(Et)Cl], which takes place in cyclohexane at 150 °C. The most probable rate-limiting step for this reaction is assumed to be dissociation of ethylene from a 5-coordinate 18-electron platinum(II) [$PtL_2(C_2H_4)$(H)Cl] intermediate. It is possible that the great difference of reactivity between the two monoalkyl isomers stems from the different Pt–C(alkyl) energy bond in the

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(21) Preliminary results in apolar solvents, where cis to trans isomerization is blocked, have shown that thermal decomposition of *cis*-[Pt(PEt_3)$_2$(Et)Cl] is at least 10 times slower than that of the n-Pr and n-Bu analogues.

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starting 16-electron square-planar complexes, as dictated by the trans-activating chloride or phosphine ligands. In other words, the development of a carbanionic character in Pt–C could help β-elimination.

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Registry No. *cis*-[$Pt(PEt_3)_2(CH_3)Cl$], 22289-46-9; *trans*-[$Pt(PEt_3)_2(CH_3)Cl$], 13964-96-0; *cis*-[$Pt(PEt_3)_2(CH_2CH_3)Cl$], 61009-44-7; *trans*-[$Pt(PEt_3)_2(CH_2CH_3)Cl$], 54657-72-6; *cis*-[$Pt(PEt_3)_2(CD_2CD_3)Cl$], 117605-15-9; *trans*-[$Pt(PEt_3)_2(CD_2CD_3)Cl$], 97548-99-7; *cis*-[$Pt(PEt_3)_2(CH_2CH_2CH_3)Cl$], 89362-98-1; *trans*-[$Pt(PEt_3)_2(CH_2CH_2CH_3)Cl$], 17764-68-0; *cis*-[$Pt(PEt_3)_2(CH_2(CH_2)_2CH_3)Cl$], 89308-86-1; *trans*-[$Pt(PEt_3)_2(CH_2(CH_2)_2CH_3)Cl$], 90581-22-9; *cis*-[$Pt(PEt_3)_2(CH_2Si(CH_3)_3)Cl$], 33937-93-8; *trans*-[$Pt(PEt_3)_2(CH_2Si(CH_3)_3)Cl$], 117605-16-0; *cis*-[$Pt(PEt_3)_2(CH_2(CH_2)_2)CH_3)_2$], 117559-19-0; *cis*-[$Pt(PEt_3)_2(CH_2Si(CH_3)_3)_2$], 33937-88-1; *cis*-[$Pt(PEt_3)_2Cl_2$], 15692-07-6; Me_3SiCH_2MgCl, 13170-43-9; *cis*-[$Pt(PEt_3)_2(CH_2CH_3)_2$], 75847-39-1; *cis*-[$Pt(PEt_3)_2(CD_2CD_3)_2$], 117605-17-1; *cis*-[$Pt(PEt_3)_2(CH_2CH_2CH_3)_2$], 17764-65-7.

Contribution from the Department of Chemistry, University of Florence, via Maragliano 75/77, 50144 Florence, Italy,
and Department of Inorganic Chemistry, Facultad de Ciencias Quimicas,
University of Valencia, Dr. Moliner 50, 46100 Burjassot, Valencia, Spain

Thermodynamic Study of the Formation in Aqueous Solution of Cadmium(II) Complexes with Polyazacycloalkanes. Synthesis and Crystal Structure of the Dicadmium(II) Complex $Na[Cd_2(L)Cl_2](ClO_4)_3$ (L = 1,4,7,10,13,16,19,22,25,28-Decaazacyclotriacontane)

Andrea Bencini,*[1a] Antonio Bianchi,*[1a] Manuel Castelló,*[1b] Massimo Di Vaira,*[1a] Juan Faus,*[1b]
Enrique Garcia-España,*[1b] Mauro Micheloni,*[1a] and Piero Paoletti*[1a]

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Potentiometric and calorimetric studies on the equilibria between cadmium(II) and large polyazacycloalkanes of the series $[3k]aneN_k$ ($k = 6–11$) have been carried out at 25 °C in 0.15 mol dm^{-3} $NaClO_4$ as ionic medium. Both mononuclear ($k = 6–8$) and dinuclear ($k = 8–11$) complexes are formed. The stability of these mononuclear complexes is compared with that, previously reported, of complexes formed by smaller macrocycles. Results indicate that the stability of the mononuclear complexes increases on going from the smallest macrocycle $[9]aneN_3$ to the pentadentate $[15]aneN_5$, then slightly decreases for $[18]aneN_6$ ($\log k = 18.80$ (1)) and $[21]aneN_7$ ($\log k = 18.10$ (1)), and finally sharply decreases for $[24]aneN_8$ ($\log k = 14.52$ (7)). Ligand strain and formation of large, unstable chelate rings are invoked to explain this trend. The formation enthalpies of $[Cd[18]aneN_6]^{2+}$ ($\Delta H^\circ = -15.3$ (1) kcal mol^{-1}) and $[Cd[21]aneN_7]^{2+}$ ($\Delta H^\circ = -16.1$ kcal mol^{-1}) have been determined by microcalorimetry. Larger macrocycles of the series form stable dinuclear complexes: $[Cd_2[24]aneN_8]^{4+}$ ($\log k = 18.21$ (7)); $[Cd_2[27]aneN_9]^{4+}$ ($\log k = 20.75$ (1)); $[Cd_2[30]aneN_{10}]^{4+}$ ($\log k = 23.21$ (1)); $[Cd_2[33]aneN_{11}]^{4+}$ ($\log k = 23.63$ (2)). Many protonated species are formed, whose equilibrium constants have been measured, but no hydroxo species have been detected. The molecular structure of the dinuclear complex $Na[Cd_2(L)Cl_2](ClO_4)_3$ (L = 1,4,7,10,13,16,19,22,25,28-decaazacyclotriacontane ($[30]aneN_{10}$)) has been determined by single-crystal X-ray analysis. The compound crystallizes in the *Pbna* space group with $a = 29.626$ (7) Å, $b = 13.790$ (3) Å, $c = 9.307$ (3) Å, and $Z = 4$. Refinement of the atomic parameters by least squares gave a final R factor of 0.068 ($R_w = 0.077$) for 1428 unique reflections having $I > 3\sigma(I)$. The structure consists of dimetallic $[Cd_2(L)Cl_2]^{2+}$ and Na^+ cations and of ClO_4^- anions. Both cadmium(II) ions are six-coordinated but with different environments: Cd(1) is surrounded by two chlorine atoms and by four nitrogen atoms of the macrocyclic ligand, whereas Cd(2) is coordinated by the other six ligand nitrogen atoms. The environment of Cd(2) is somewhat unusual, due to the constraints imposed by the intrachelate angles of 73–77°, and can be visualized as a distorted trigonal prism whose three lateral edges are spanned by the $-NHCH_2CH_2NH-$ chains of the macrocycle. The same kind of environment may be present in other six-coordinated cadmium(II) macrocyclic complexes in solution.

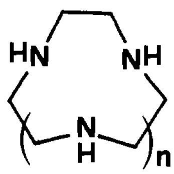
Introduction

During the last few years much interest has been attracted by the metabolism of important non-iron elements such as copper and zinc, as well as of nonessential metals such as mercury and cadmium.

The substitution of zinc(II) by cadmium(II) in zinc(II)-containing metalloenzymes offers the opportunity to use the experimental technique of ^{113}Cd NMR in the study of enzymatic systems. It has been shown,[2] for instance, that the affinity of the alkaline phosphatase for cadmium(II) depends on the pH value and the presence of phosphate. At pH 6.5 two cadmium(II) ions are tightly bound whereas at higher pH values or in the presence of phosphate up to six cadmium(II) ions can be bound.

Polyazacycloalkanes, which produce polynuclear complexes with a number of metal ions in solution, can be a helpful tool in understanding some simple mechanisms occurring in biological systems. The polyammonium species formed by these ligands can efficiently and selectively bind nucleotide anions, catalyzing their dephosphorylation.[3] The implication of metal ions in these processes can alter the reaction pathway, providing positive or negative catalytic effects.[4]

We are presently looking for macrocyclic ligands able to produce metal complexes that may act as solution catalysts. In the present paper we report the results of a thermodynamic and structural study on the equilibria between cadmium(II) and the polyazacycloalkanes of the series $[3k]aneN_k$ ($k = 6–11$).



$k = n+2$

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