Kinetic Study of β-Hydride Elimination from Monoalkyl Solvento Complexes of Platinum(II)

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Electrophilic attack by a proton on *cis*-[Pt(PEt₃)₂(R)₂] (R = C_2H_5, C_2D_5, *n*-C_3H_7, *n*-C_4H_9) complexes in protic solvents and subsequent fast isomerization of the *cis*-alkyl(solvento) intermediates produce the solvento species *trans*-[Pt(PEt₃)₂(R)(S)]⁺ (S = solvent). These latter undergo a facile thermal decomposition, yielding *trans*-[Pt-(PEt₃)₂(H)(S)]⁺ and olefins under very mild conditions. The kinetics were followed by means of a variety of experimental techniques, including ¹H and ³¹P NMR, GLC, and conventional spectrophotometry. Results in methanol at 30 °C: R = C_2H_5, $k = 0.19 \times 10^{-3}$ s⁻¹, $\Delta H^* = 115 \pm 3$ kJ mol⁻¹, $\Delta S^* = +62 \pm 6$ J K⁻¹ mol⁻¹; R = C_2D_5, $k = 0.075 \times 10^{-3}$ s⁻¹, $\Delta H^* = 113 \pm 2$ kJ mol⁻¹, $\Delta S^* = +49 \pm 6$ J K⁻¹ mol⁻¹; R = *n*–C_3H_7, $k = 45 \times 10^{-3}$ s⁻¹, $\Delta H^* = 95 \pm 2$ kJ mol⁻¹, $\Delta S^* = +24 \pm 5$ J K⁻¹ mol⁻¹; R = *n*-C_4H_9, $k = 62 \times 10^{-3}$ s⁻¹, $\Delta H^* = 89 \pm 2$ kJ mol⁻¹, $\Delta S^* = +5 \pm 6$ J K⁻¹ mol⁻¹. Changes in the nature of the alcoholic solvents do not produce significant variations either in the rates or in the distribution of the olefin products. When chloride ion is added, the thermolysis is retarded because of the formation of the unreactive *trans*-[Pt(PEt₃)₂(R)Cl]. Values of the solvolytic equilibrium constants have been calculated from mass-law retardation plots. Other cationic species such as *trans*-[Pt(PEt₃)₂(R)(L)]⁺ (L = pyridine, amines, phosphines, etc.) were found to be unreactive. The mechanism is discussed within the framework of previous results on β-hydride elimination of trans and cis monoalkyl complexes or olefin insertion into trans hydride complexes. A unified picture can be drawn which involves the easy loss of the solvent molecule and the formation of 3-coordinate 14-electron species as key intermediates.

Introduction

Many years ago Chatt and Shaw[1] in their pioneer work showed that the thermolysis of *trans*-[Pt(PEt₃)₂(Et)Cl] (**1**), either as a melt or in solution at high temperature, leads to *trans*-[Pt(PEt₃)₂-(H)Cl] (**2**) and ethene in equilibrium with the starting material. Both sides of this reaction, β-hydride elimination and olefin insertion into the metal–hydrogen bond, are fundamental transformations that occur in a variety of organometallic systems[2] and are thought to be crucial steps in many catalytic cycles involving olefins. Evidently, β-hydride elimination[3] is closely related to cyclometalation[4] and also to intermolecular C–H bond activation.[5] Later, Brainard and Whitesides[6] studied in great detail the mechanistic aspects of the thermolysis of **1**, carried out in cyclohexane at 150 °C, and proposed that the lowest energy pathway involves fast and reversible addition of a C–H bond to

platinum in the square-planar 16-electron complex, yielding a 5-coordinate [PtL₂(H)(C₂H₄)Cl] intermediate. Thereby, rate-determining loss of olefin follows to yield the hydride product. This conclusion is in agreement with the original suggestion[7] that a similar 5-coordinate adduct is an intermediate in the reaction of C₂H₄ with *trans*-[PtL₂(H)Cl] yielding the ethyl complex. However, a theoretical analysis of the last reaction by Thorn and Hoffmann[8] showed that the 5-coordinate intermediate cannot easily reach a configuration with the hydride (in apical position) and ethylene upright (in the equatorial plane) as required for insertion. In contrast, the insertion becomes very much easier from a 4-coordinate intermediate where the olefin and the hydride occupy mutual cis positions. Extensive studies of the insertion of olefins into the Pt–H bond showed that the facility with which *trans*-[PtL₂(H)X] inserts olefins depends markedly on the lability of the X group,[9] the first step of the reaction being its replacement by C₂H₄ to yield a cationic hydrido olefin [PtL₂(H)(C₂H₄)]⁺ intermediate that has been intercepted in solution[9a] and isolated in the trans configuration as a tetraphenylborate salt.[10] A direct insertion from this species containing ethylene and hydride trans to each other seems unlikely,[8] and an exciting problem is to

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establish the sequence of steps that lead ethylene and hydride to occupy mutual cis positions in the coordination plane of the complex.

We thought it worthwhile to investigate the reasons for the apparent contrast between the mechanistic picture found for thermal decomposition of the alkyl complex *trans*-[Pt(PEt₃)₂-(alkyl)Cl][6,7] and that proposed for olefin insertion into *trans*-[Pt(PEt₃)₂(H)(acetone)][+ 9a] or *trans*-[Pt(PEt₃)₂(H)(NO₃)].[9b] To this purpose, we studied the rates of β-hydride elimination of the solvento species *trans*-[Pt(PEt₃)₂(R)(S)]⁺ (S = hydroxylic solvent), formed "in situ" by protonolysis of *cis*-[Pt(PEt₃)₂(R)₂] (R = C₂H₅, C₂D₅, *n*-C₃H₇, *n*-C₄H₉) complexes in protic solvents. The results will be discussed within the framework of the known mechanistic patterns for these reactions. A unified mechanistic picture for β-hydride elimination and olefin insertion involves the formation of coordinatively unsaturated 3-coordinate 14-electron species as an alternative to the intermediacy of 4- and 5-coordinate species.

Experimental Section

All reactions were carried out under a dry, oxygen-free nitrogen atmosphere using standard Schlenk-tube techniques. Solvents were thoroughly dried over the appropriate reagents and freshly distilled prior to use. The dialkyl substrates *cis*-[Pt(PEt₃)₂(Et)₂],[11] *cis*-[Pt(PEt₃)₂(Et-*d*₅)₂],[12] *cis*-[Pt(PEt₃)₂(*n*-Pr)₂],[12] and *cis*-[Pt(PEt₃)₂(*n*-Bu)₂][13] were prepared by literature methods. The spectroscopic properties of the compounds obtained (UV spectra; IR stretching frequencies; ¹H, ¹³C, and ³¹P NMR resonances) were exactly the same as those reported in the literature. Elemental analyses were consistent with the theoretical formulas. Infrared spectra were taken on a Perkin-Elmer Model FT 1720 X instrument. ¹H, ¹³C, and ³¹P NMR spectra were recorded on a Bruker AMX R-300 spectrometer operating at 300.13, 75.5, and 121.49 MHz, respectively. ¹H NMR chemical shifts are reported in ppm (δ) from TMS as internal reference. ¹³C chemical shifts are relative to the solvent peak and are reported versus TMS. ³¹P chemical shifts, in parts per million, are relative to external phosphoric acid. Microanalyses were performed by Analytical Laboratories, Engelskirchen, RFG. Methanol, 1-propanol, 2-propanol, and 1-butanol were purified and dried by standard methods. All the other chemical products were reagent grade materials and were used without further purification.

Kinetics

The kinetics of decomposition of *trans*-[Pt(PEt₃)₂(R)(S)]⁺ (S = methanol, ethanol, 1-propanol, 2-propanol; R = ethyl, ethyl-*d*₅, *n*-propyl, *n*-butyl) complexes were followed spectrophotometrically by repetitive scanning of the spectrum at suitable times in the range 320–220 nm or at the fixed wavelength of 240 nm, where the difference of absorbance with the hydride product *trans*-[Pt(PEt₃)₂(H)(S)]⁺ is largest. The reactions were carried out in a silica cell in the thermostated cell compartment of a Cary 219 or of a rapid-scanning Hewlett-Packard Model 8452 A spectrophotometer with a temperature accuracy of ±0.02 °C. The reactions were initiated by adding with a syringe a prethermostated solution of *cis*-[Pt(PEt₃)₂(R)₂] to a thermostated solution of H⁺A⁻ (A⁻ = BF₄⁻, *p*-toluenesulfonate, CF₃SO₃⁻). In all cases, the concentration of acid was sufficient to produce a fast cleavage of the first Pt–R bond. All the reactions obeyed a first-order rate law until well over 90% of the reaction had occurred, and the rate constants k_{obsd} (s⁻¹) were obtained either by graphic means or from a nonlinear least-squares fit of the experimental data to $A_t = A_\infty + (A_0 - A_\infty) \exp(-k_{obsd}t)$ 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). Activation parameters were derived from a linear least-squares analysis of ln (k/T) vs T^{-1} data. Some reactions were also followed by GLC. The extent of decomposition was determined, without need for an internal standard, by measuring the relative areas of the peaks due to the alkenes produced on thermal decomposition and to the alkane produced after the addition of acid to the dialkyl at the beginning of the reaction. The rate

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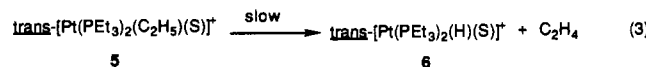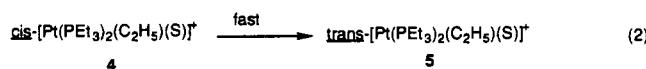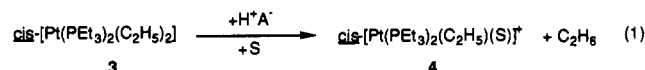
constants k_{obsd} (s⁻¹) were obtained from linear plots of ln(1 − *F*) vs *t*, where *F* is the decomposition fraction.

Results

The ³¹P{¹H} NMR spectrum of *cis*-[Pt(PEt₃)₂(Et)₂] at 298 K in CD₃OD shows one phosphorus resonance at δ = +8.90 ppm (¹J_{Pt-P} = 1836 Hz). The value of the coupling constant is within the range typical of a phosphorus atom trans to a carbon in platinum complexes.[14] Upon addition of the stoichiometric amount of an ethereal solution of HBF₄, there is an immediate and sharp change of the spectrum, which still shows only one ³¹P resonance, but at δ = +25.06 ppm (¹J_{Pt-P} = 3012 Hz), due to two equivalent phosphorus nuclei. Thus, the cis configuration is not retained as a result of the Pt–C bond breaking and the product of the protonolysis is *trans*-[Pt(PEt₃)₂(Et)(MeOH)]⁺. This was confirmed by the fact that, upon addition of solid LiCl to a portion of the above solution, the ³¹P {¹H} NMR spectrum changed to that of *trans*-[Pt(PEt₃)₂(Et)Cl] (δ = +17.15 ppm (¹J_{Pt-P} = 2977 Hz)). The solvento complex readily decomposes to *trans*-[Pt(PEt₃)₂(H)(MeOH)]⁺, and the process can be monitored through the decrease in the signal associated with the trans monoalkyl complex and the parallel and matching increase in the signal of the corresponding trans hydrido, which appears at δ = +29.36 ppm (¹J_{Pt-P} = 2704 Hz). At the end of the reaction, the molecule of solvent is readily replaced by chloride to yield *trans*-[Pt(PEt₃)₂-(H)Cl] (δ = +24.54 ppm (¹J_{Pt-P} = 2697 Hz)). When the same experiment is carried out in an NMR tube sealed with a gastight rubber serum cap in order to prevent olefin loss, at the end of the reaction the final hydride [Pt(PEt₃)₂(H)(MeOH)]⁺ is found in equilibrium with the starting monoalkyl complex and, if the temperature is lowered below 273 K, a third signal appears in the ³¹P spectrum at δ = +13.82 ppm (¹J_{Pt-P} = 2354 Hz). This peak disappears when the temperature is increased to 308 K, and it appears again on cooling. The proton NMR spectrum of this labile intermediate in the hydridic hydrogen region exhibits characteristics identical to those found for *trans*-[Pt(PEt₃)₂(H)-(C₂H₄)]⁺ (δ = −6.70 ppm (¹J_{Pt-H} = 905 Hz; ²J_{P-H} = 12 Hz)). There is evidence also for coordinated ethylene (δ = +3.64 ppm (¹J_{Pt-H} = 36 Hz); ¹³C δ = +69.8 ppm (²J_{Pt-C} = 27 Hz)), and therefore we assume that the labile species in equilibrium with the starting alkyl complex and the hydride solvento product at low temperature is a hydrido–olefin cationic complex identical to that isolated and characterized by Deeming et al.[10] The hydridic peak for *trans*-[Pt(PEt₃)₂(H)(MeOH)]⁺ is found at δ = −26.07 ppm (¹J_{Pt-H} = 1493 Hz; ²J_{P-H} = 14 Hz). The large value of the ¹J_{Pt-H} coupling constant indicates that the MeOH molecule is very weakly bound to the metal[15] and can readily dissociate or be replaced by other ligands.

The preceding observations are in agreement with reactions in Scheme I. The rate of protonolysis of the first Pt–C bond (eq 1) is controlled by the amount of acid added, but it takes place so easily that the reaction goes to completion soon after the mixing of the reagents even when the dialkyl reacts only with the stoichiometric amount of acid. The subsequent cis–trans isomer-

Scheme I

cis-[Pt(PEt₃)₂(C₂H₅)₂] $\xrightarrow[+\text{S}]{+\text{H}^+\text{A}^-}$ cis-[Pt(PEt₃)₂(C₂H₅)(S)]⁺ + C₂H₆   (1)
3   **4**

cis-[Pt(PEt₃)₂(C₂H₅)(S)]⁺ $\xrightarrow{\text{fast}}$ trans-[Pt(PEt₃)₂(C₂H₅)(S)]⁺   (2)
4   **5**

trans-[Pt(PEt₃)₂(C₂H₅)(S)]⁺ $\xrightarrow{\text{slow}}$ trans-[Pt(PEt₃)₂(H)(S)]⁺ + C₂H₄   (3)
5   **6**

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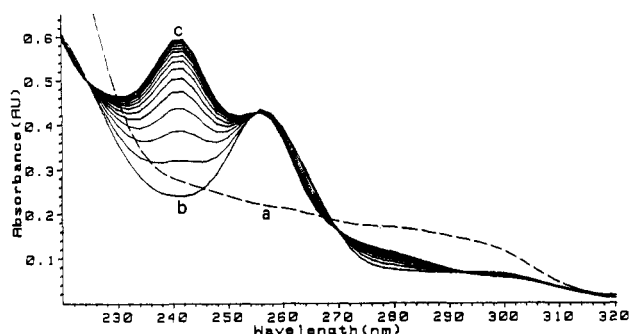
Figure 1. Electronic spectrum (a) of cis-[Pt(PEt₃)₂(C₂H₅)₂] in methanol at 313.16 K and spectral changes (b→c) associated with β-hydride elimination of trans-[Pt(PEt₃)₂(C₂H₅)(MeOH)]⁺ generated in situ. Scanning time = 8 min.

ization (eq 2) is very fast, and as a consequence the only product derived from the protonolysis of the starting dialkyl is a *trans*-alkyl(solvento) complex. The latter eventually undergoes a slow β-hydride elimination to yield **6**. The *n*-propyl and *n*-butyl derivatives behave in exactly the same way.

Although the reactions, as we have seen above, can be effectively monitored by means of ³¹P{¹H} NMR, the kinetics of all of the β-hydride eliminations were followed by conventional spectrophotometry (Figure 1). The spectral changes observed in the UV region after the protonolysis are consistent with a smooth conversion of the alkyl compound into the hydride product. All reactions go to completion. Under the experimental conditions adopted, there is no evidence for the buildup of any intermediate species in solution, as confirmed by abstract factor analysis of the spectral changes.[16] For the ethyl and the *n*-propyl derivatives, the only volatile products were ethene and propene, respectively. For the *n*-butyl derivatives, we observed the formation of *cis*-2-butene, 1-butene, and *trans*-2-butene in the ratio 1:0.80:0.08. In all cases, 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 upon chloride addition to the solution. No alkanes were detected in these reactions, except those produced upon the initial proton attack. The kinetics obey a first-order rate law until well over 90% completion of the reaction, are independent of the concentration of the complex, and are unaffected by the amount of acid in solution. The specific rate constants at various temperatures for the β-hydride elimination of the *trans*-[Pt(PEt₃)₂(R)-(MeOH)]⁺ (R = ethyl, ethyl-d₅, *n*-propyl, *n*-butyl) complexes are listed in Table I together with the associated activation parameters. The pseudo-first-order rate constants for the decomposition of *trans*-[Pt(PEt₃)₂(*n*-Bu)(S)]⁺ (S = a series of hydroxylic solvents at 30 °C) are listed in Table II, and those for the thermal decomposition of *trans*-[Pt(PEt₃)₂(R)(MeOH)]⁺ in the presence of varying amounts of chloride ion are listed in Table III.

Discussion

The aim in preparing *cis*-[Pt(PEt₃)₂(R)₂] complexes was to have suitable precursors for the formation of *trans*-alkyl(solvento) species in methanol and so to avoid the usual method of extracting the halide ion from halide complexes by making use of silver salts, which can interfere strongly with the subsequent processes. We knew from previous studies that the cleavage of the first alkyl group by the proton is a fast process ($k_H = 75 \times 10^3$ M⁻¹ s⁻¹ for *cis*-[Pt(PEt₃)₂(Me)₂] at 303.2 K in methanol) but the subsequent cis–trans isomerization of the cationic solvento species [Pt(PEt₃)₂-

(Me)(MeOH)]⁺ was relatively slow.[17] However, kinetic studies of the spontaneous isomerization of monoalkyl complexes of the type *cis*-[Pt(PEt₃)₂(R)Cl][13] (R = a series of linear and branched alkyls) have shown that the presence of β-hydrogens on the alkyl group (as for ethyl, *n*-propyl, and *n*-butyl ligands) has the effect of producing a significant enhancement of the rate of isomerization (at least 3 orders of magnitude) with respect to that of complexes containing alkyl groups with no β-hydrogens (CH₃, CH₂Si-(CH₃)₃). Thus, we were not surprised by the high rate of geometrical conversion of the *cis*-[Pt(PEt₃)₂(R)(MeOH)]⁺ (R = C₂H₅, *n*-C₃H₇, *n*-C₄H₉) species obtained upon protonolysis of the dialkyls and by the fact that we were not able to detect their presence in solution. Isomerization is thought to involve dissociative loss of a ligand (MeOH or Cl⁻) and interconversion of two T-shaped [PtL₂(alkyl)]⁺ 3-coordinate intermediates.[18] The enhancement of the rate of isomerization in these particular bis-(phosphine) monoalkyl Pt(II) complexes is accounted for by 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. The possible structure of this transient species, depicted as **B** in Chart I, is similar to that of the [Pt-(P-P)C₂H₅]⁺ (P-P = (*t*-Bu)₂P(CH₂)₃P(*t*-Bu)₂) platinum cation (**A**), recently isolated and structurally characterized by Spencer et al.[19] as a very interesting example of β-agostic interaction.

Chart I
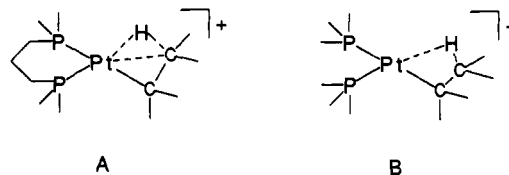
The main difference between the two structures probably consists in the extent of interaction of the β-hydrogens of the alkyl group with the metal, which in **B** should be not so extensive as in **A**. The latter species exhibits a well defined 3-center 2-electron Pt–H–C bond, and isomerization is prevented by the presence of the chelating ligand. In contrast, the platinum cation intermediate **B** interconverts very easily into a geometrically distinct "trans-like" T-shaped structure, in agreement with the low-energy barrier indicated by theoretical calculations for the fluxionality of coordinatively unsaturated 3-coordinated species of this type.[8,20] Besides the use of chelating ligands, blocking the vacant coordination site with a 2-electron-donor molecule (X) can delay or completely prevent ready isomerization of species like **B**. Under these circumstances the species *cis*-[Pt(PEt₃)₂-(alkyl)X] becomes unstable toward β-elimination, which takes place through a nondissociative pathway by fast and reversible addition of a C–H bond to the metal in the square planar 16-electron complex.[21]

The final result of the protonolysis of the dialkyl substrates in methanol is then the generation "in situ" of *trans*-bis(phosphine)-alkyl(solvento) species that undergo a facile β-hydride elimination, yielding *trans*-[Pt(PEt₃)₂(H)(S)]⁺ and olefins. Under the experimental conditions adopted, all reactions go to completion. The kinetic data in Table I give the following sequence of lability

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Table I. Temperature Dependence of the Rate Constants for Thermal Decomposition of *trans*-[Pt(PEt₃)₂(R)(MeOH)]⁺ Complexes in Methanol[a]

	$10^4 k_d/s^{-1}$			
T/K	R = Et	R = [²H₅]Et	R = n-Pr	R = n-Bu
288.16			5.93	8.60
293.16	0.349	0.141	11.9	18.4
298.16	0.824	0.321	21.5	35.6
303.16	1.87	0.748	45.6	61.5
308.16	3.96	1.60	82.2	109
313.16	7.43	2.85	152	186
318.16	16.0	6.12		
323.16		12.0		
	$\Delta H^* = 115 \pm 3$	$\Delta H^* = 113 \pm 2$	$\Delta H^* = 95 \pm 2$	$\Delta H^* = 89 \pm 2$
	$\Delta S^* = +62 \pm 6$	$\Delta S^* = +49 \pm 6$	$\Delta S^* = +24 \pm 5$	$\Delta S^* = +5 \pm 6$

[a] ΔH^* in kJ mol⁻¹; ΔS^* in J K⁻¹ mol⁻¹.

Table II. Effect of Solvent on the Rate of Thermal Decomposition of *trans*-[Pt(PEt₃)₂(n-Bu)(solvent)]⁺ and on the Distribution of the Olefin products[a]

		% product		
solvent	$10^4 k_d/s^{-1}$	1-butene	*cis*-2-butene	*trans*-2-butene
methanol	35.6	42.4	53.3	4.3
ethanol	45.4	47.8	50.5	1.6
1-propanol	57.2	49.5	49.0	1.5
2-propanol	50.7	53.0	45.2	1.8

[a] At 298.16 K.

Table III. Effect of Adding Lithium Chloride on the Rates of Thermal Decomposition of *trans*-[Pt(PEt₃)₂(R)(MeOH)]⁺ Complexes in Methanol[a]

	$10^4 k_d/s^{-1}$		
10^4[LiCl]/M	R = Et	R = n-Pr	R = n-Bu
0.0	7.43	152	186
1.0	0.108	10.9	21.7
1.5	0.067	3.33	3.84
2.0	0.0521	2.27	2.86
3.0	0.0368	1.78	1.85
4.0	0.0267	1.22	1.60
6.0	0.0174	0.897	1.43
8.0		0.637	0.990
10.0		0.459	0.676
		0.370	0.510
			0.410

[a] At 313.16 K; μ = 0.005 M (LiClO₄); [complex] = (0.1–0.8) × 10⁻⁴ M.

for thermal decomposition of *trans*-[Pt(PEt₃)₂(alkyl)(MeOH)]⁺ complexes: Et ≪ n-Pr < n-Bu (at 298.16 K, $10^4 k_d$ = 0.824, 21.5, and 35.6, respectively). The activation parameters are as follows: R = C₂H₅, ΔH^* = 115 ± 3 kJ mol⁻¹, ΔS^* = +62 ± 6 J K⁻¹ mol⁻¹; R = n-C₃H₇, ΔH^* = 95 ± 2 kJ mol⁻¹, ΔS^* = +24 ± 5 J K⁻¹ mol⁻¹; R = n-C₄H₉, ΔH^* = 89 ± 2 kJ mol⁻¹, ΔS^* = +5 ± 5 J K⁻¹ mol⁻¹. The rate of β-hydride elimination increases with increasing length of the chain as a result of a decrease in the enthalpy of activation which outweights a decrease in the entropy of activation. A fairly good straight line (R = 0.997) correlates these enthalpy and entropy data, but the limited number of points available does not allow any speculation to be made on the reliability or significance of such a relationship which, as many other isokinetic plots, could well be due only to compensation effects.[22] However the greater reactivity of n-propyl and n-butyl complexes compared to that of the ethyl analogue deserves some comment. It would appear that the statistical prevalence for β-hydride extraction from a primary carbon atom is outweighed by a much higher lability of the hydrogens bound to a secondary carbon atom. Bercaw et al.[23] have explained the increase in the

rate of β-hydrogen elimination on substitution of hydrogen at the β-carbon by alkyl groups (CH₃ or C₂H₅) in a series of permethylscandocene complexes Cp*₂ScCH₂CH₂R with a tight 4-center transition state, where positive charge is developed at the β-carbon and hydrogen is transferred to the metal as hydride. The negative values of the entropies of activation were consistent with the idea of restricted rotation around Sc–C, C–C, and C–H bonds, and for the ethyl derivative there was kinetic evidence for stabilization of the ground state by agostic interaction. We are inclined to think that a similar explanation does not apply to the system under study for at least three reasons: (i) the reactions are characterized by largely positive values of the entropy of activation, suggesting an overall gain of molecular freedom upon approaching the most energetic transition state and are consistent with a process in which two particles are being formed from one; (ii) the simultaneous formation of three olefin isomers, 1-butene, *cis*-2-butene, and *trans*-2-butene, in the decomposition of the n-butyl complex is a straightforward indication that the release of the organic products must be preceded by a pre-equilibrium in which fast and reversible β-hydride elimination and olefin insertion lead to a facile skeletal isomerization of linear to branched alkyl groups; (iii) the value of the kinetic isotope effect for the solvento ethyl complex (k^H_{obs}/k^D_{obs} = 2.55 at 298.16 K) is very similar to that found by Brainard and Whitesides[6] for the thermal decomposition of the corresponding chloride *trans*-[Pt(PEt₃)₂(Et)Cl] (k^H_{obs}/k^D_{obs} = 2.5 ± 0.2 at 431 K), which was interpreted as an equilibrium isotope effect reflecting mainly conversion of a C–H(D) bond to a Pt–H(D) bond in the pre-equilibrium which precedes the rate-determining step. The same reasoning applies for the thermal decomposition of *cis*-[Pt(PEt₃)₂(alkyl)X] complexes,[21] where fast and reversible β-hydride elimination and olefin insertion from an alkene–hydride 5-coordinate intermediate precedes the release of organic products and the reactivity sequence ethene ≪ propene < butene is thought to be due to the extent of this pre-equilibrium and/or to the relative ease of olefin liberation from the intermediate. Therefore, we can conclude that, as for most similar processes,[24] there is no evidence in the system studied for a progressive synchronous transfer of hydrogen from the β-carbon to the metal and of a direct involvement of the C–H bond breaking in the rate-determining step.

The essential features of the β-hydride process do not change on changing the nature of the hydroxylic solvent. The data in Table II show that both the rate of thermal decomposition and the distribution ratio of the three butenes obtained from decomposition of the butyl complex are almost insensitive to the nature of the alcoholic solvent used. In contrast, addition of strong neutral nucleophiles (L) such as pyridines, amines, phosphines, and thioureas to the *trans*-alkyl(solvento) species has the effect of blocking the process of β-elimination. Thus, the cationic *trans*-[Pt(PEt₃)₂(alkyl)(L)]⁺ species are stable toward thermal decomposition, at least under the same experimental

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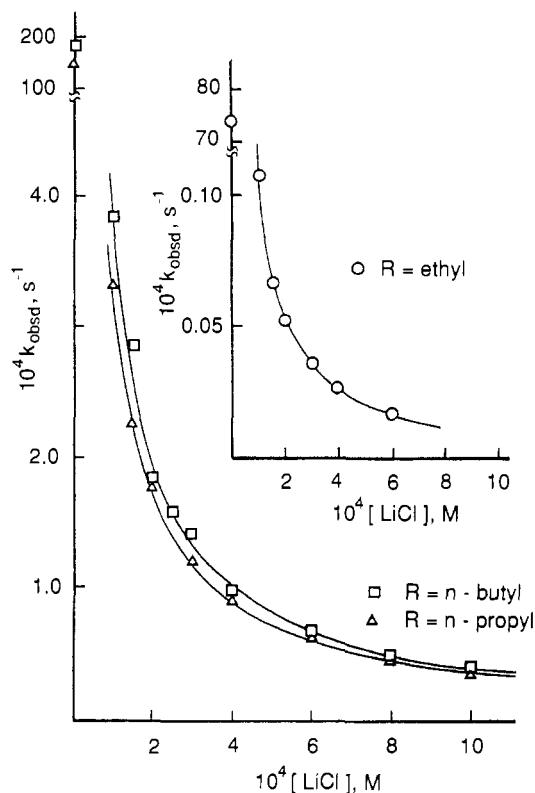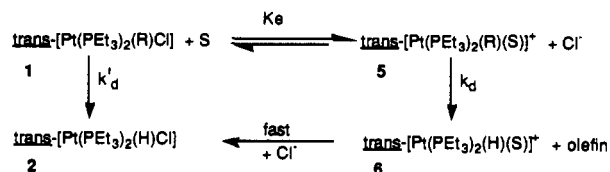
Figure 2. Dependence of the pseudo-first-order rate constants k_{obs} (s^{-1}) on the concentration of lithium chloride for the thermal decomposition of *trans*-[Pt(PEt$_3$)$_2$(R)(MeOH)]$^+$ complexes in methanol at 313.16 K: (O) R = ethyl; ($\triangle$) R = *n*-propyl; ($\square$) R = *n*-butyl.
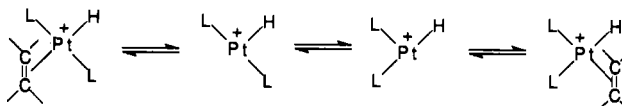
conditions that promote a facile β-elimination of **5**, and this is a straightforward indication that the lability of the monoalkyl solvento species is due not to the overall charge of the complex but rather to the facility of vacating a coordination site. Strong support for this comes from some experiments carried out in dichloromethane solution. The rate of thermal decomposition of cation **5** becomes so fast as to require the use of a stopped-flow apparatus to follow the reaction. The high instability of this trans monoalkyl species toward β-elimination in weakly coordinating solvents stands in contrast to the great stability of the analogous complex *trans*-[Pt(PMe$_3$)$_2$(*neo*-Pe)(SO$_3$CF$_3$)] (*neo*-Pe = neopentyl), containing no β-hydrogens, which, at high temperature, is able to activate the benzene-d_6 C–D bonds, giving *trans*-[Pt(PMe$_3$)$_2$(*neo*-Pe)(C$_6$D$_5$)].[25]

As expected, the thermal decomposition of the *trans*-alkyl-(solvento) species is also blocked by the addition of negatively charged nucleophiles such as Cl$^-$, Br$^-$, I$^-$, SCN$^-$, etc. Taking advantage of the possibility of creating "in situ" the solvento complex and of controlling exactly the amount of halide added, we decided to measure the rates of β-elimination at different concentrations of halide in order to make a comparative measure of the reactivity of the cationic solvento and neutral halide species. Table III lists the kinetic data obtained using chloride ion at 313.16 K in methanol. The overall pattern of behavior is illustrated in Figure 2, where it is possible to see that at sufficiently low concentrations of chloride the thermolysis is retarded and there is a curvilinear dependence of the rate on [Cl$^-$]. A plausible reaction mechanism (Scheme II) involves a solvolytic equilibrium (K_e) between the chloro **1** and the solvento species **5** and the possibility for both of them to undergo thermal decomposition, yielding **2** and **6** with rate constants k'_d and k_d, respectively. The attack of Cl$^-$ on **6** to yield **2** is assumed to be fast. The kinetic data were fitted by nonlinear regression analysis to the rate equation $k_{obsd} = (k_d K_e + k'_d[Cl^-])/(K_e + [Cl^-])$, and the values

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Scheme II

Scheme III

of the constants obtained are as follows: for R = C$_2$H$_5$, K_e = 1.45 × 10^{-6}, k'_d < 0.001 × 10^{-4} s^{-1}, k_d = 7.4 × 10^{-4} s^{-1}; for R = C$_3$H$_7$, K_e = 2.79 × 10^{-6}, k'_d < 0.07 × 10^{-4} M^{-1} s^{-1}, k_d = 152 × 10^{-4} s^{-1}; for R = C$_4$H$_9$, K_e = 2.14 × 10^{-6}, k'_d < 0.02 × 10^{-4} M^{-1} s^{-1}, k_d = 186 × 10^{-4} s^{-1}. Thus, the reaction proceeds almost completely through the solvento complex *trans*-[PtL$_2$(R)(S)]$^+$. This is confirmed by the fact that in all kinetic runs of the butyl complex the distribution of the olefinic products was constant, irrespective of the amount of chloride ion added to the solution.

All the available experimental evidence indicates that β-hydride elimination and olefin extrusion from *trans*-[Pt(PEt$_3$)$_2$(alkyl)X] complexes take place easily when X is a labile group and coordinative unsaturation is facile. This reflects what has been already demonstrated by Clark et al.[9] for the inverse process, namely olefin insertion into the Pt–H bond. Under particular conditions, studying the reaction of the ethyl system from both sides, an intermediate of the type [Pt(PEt$_3$)$_2$(H)(C$_2$H$_4$)]$^+$ has been isolated and demonstrated to have the trans geometry. It has been argued[8,9a,b] that insertion takes place most easily when the hydride and the olefin occupy mutual cis positions and then the isomerization of the hydride–olefin intermediate becomes a key step in the reaction pathway. Attempts have been made to explain how this geometrical change comes about. According to our findings on the uncatalyzed isomerization,[18,26] we already suggested[27] that this may occur through interconversion of asymmetric 3-coordinate species (see Scheme III).

It is possible now to draw a unified picture of the behavior of monoalkylplatinum(II) complexes toward isomerization, β-hydride elimination, and olefin insertion (Scheme IV). For the sake of simplicity, we avoid including in Scheme IV any solvento species, considering X a labile leaving group, whose departure from the metal yields a 3-coordinate species.

A prerequisite for a facile route to the thermal decomposition of **1** or to olefin insertion into the Pt–H bond of **2** is the presence of a vacant coordination site on both species. The loss of X from **1** gives a T-shaped "trans-like" [PtL$_2$(C$_2$H$_5$)]$^+$ 3-coordinate species **7**, which can form one of the two geometrical isomers of [PtL$_2$-(H)(C$_2$H$_4$)]$^+$ (**9** or **10**) either directly or indirectly through its conversion into a "cis-like" [PtL$_2$(C$_2$H$_5$)]$^+$ (**8**) structure. At this stage, we are unable to establish whether both pathways in Scheme IV for β-hydride elimination are operative or to infer which is the favored one, but we are inclined to think that the pathway via 3-coordinate intermediates is very likely. The work on β-agostic interactions[19,28] would suggest that olefin extrusion from the T-shaped "cis-like" 3-coordinate **8** is a facile process leading to a cis geometry for [PtL$_2$(H)(C$_2$H$_4$)]$^+$ (**9**) but, as we have shown above, when L is a monodentate phosphine, the coordinatively unsaturated intermediate **8** very easily converts into its "trans-like" structure **7** before a complete β-extraction process can take

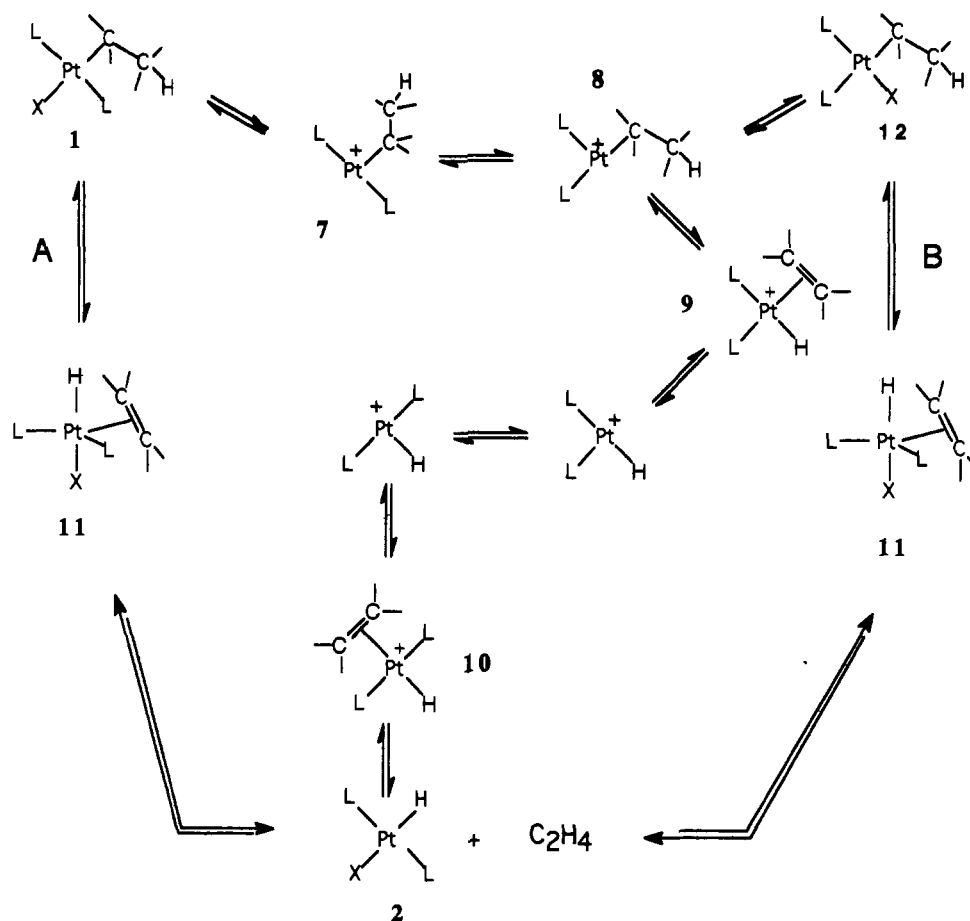(26) Romeo, R. *Comments Inorg. Chem.* **1990**, *11*, 21–57.
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Scheme IV

8

12

7

A

B

9

11

11

10

2

C_2H_4

place. In other words, although **8** offers favorable geometrical conditions for β-hydride elimination, its concentration in solution must be very low because of the low energy barrier required for its conversion into **7**. In view of the above, a direct conversion of **7** into **9** or **10** cannot be ruled out. However, we know from Thorn and Hoffmann's theoretical calculations[8] that the reverse process, insertion from **10** through a quasi-tetrahedral transition state, is characterized by a high energy barrier. In addition, the species *trans*-[Pt(PEt₃)₂(H)(C₂H₄)]BPh₄ is reported to be sufficiently stable as a solid to be stored indefinitely under nitrogen at 0 °C.[10] The saturation kinetics found by Clark and Jablonski[9a] for the dependence of the rate of ethylene insertion into **2** (for X = acetone) are consistent with formation of **10**, followed by facile loss of ethylene to yield "trans" [PtL₂(H)]⁺ which interconverts and takes up the olefin to form **9**. Migratory insertion into the latter leads to **8**, after which the reaction follows a pathway identical to that established for spontaneous isomerization of **12**. Therefore, it is likely that olefin deinsertion follows the reverse route. We have sufficient indications from theoretical calculations[8] and from studies of β-agostic interactions[19,28] that both processes, namely migratory insertion from **9** and β-hydride elimination form **8**, are characterized by very low energy barriers and therefore we expect a fast sequence of direct and reverse steps, which accounts for the pre-equilibrium discussed above, leading to alkyl isomerization. A possible rate-limiting step for decomposition can be loss of olefin from the 4-coordinate **9** or **10**.

When a strong nucleophile binds the platinum, thus blocking the fourth vacant coordination site, either β-hydride elimination or olefin insertion is forced to go through a higher energy pathway which involves the intermediacy of a 5-coordinate uncharged [PtL₂(H)(X)(C₂H₄)] (**11**) intermediate. This reaction pathway (route A) is followed by *trans*-[Pt(PEt₃)₂(ethyl)Cl] (**1**) when it is forced to decompose at high temperature in cyclohexane

solutions.[6] The activation parameters are $\Delta H^* = 138 \pm 6$ kJ mol⁻¹ and $\Delta S^* = -6 \pm 12$ J K⁻¹ mol⁻¹, and the rate constant calculated at 298.16 K is $k_{obsd} = 6 \times 10^{-12}$ s⁻¹, compared with $\Delta H^* = 115 \pm 3$ kJ mol⁻¹, $\Delta S^* = +63 \pm 6$ J K⁻¹ mol⁻¹, and $k_{obsd} = 0.824 \times 10^{-4}$ s⁻¹ found for *trans*-[Pt(PEt₃)₂(Et)(MeOH)]⁺ in this study. Thermal decomposition of alkyl complexes having cis geometry **12** takes place through the same 5-coordinate intermediate **11** (route B), the only difference with the trans isomer **1** being that the process is very much easier ($\Delta H^* = 101 \pm 2$ kJ mol⁻¹, $\Delta S^* = +5 \pm 4$ J K⁻¹ mol⁻¹, and $k_{obsd} = 0.23 \times 10^{-4}$ s⁻¹ for *cis*-[Pt(PEt₃)₂(ethyl)Br] at 298.16 K in acetone solution)[21] perhaps because of the different Pt–C(alkyl) bond energy in the starting 16-electron 4-coordinate complexes, as dictated by the different trans-activating ligands (Cl vs PEt₃). Thus, when dissociation is prevented by using nondissociating solvents or in the presence of strong nucleophiles that block the fourth vacant coordination site, the mechanism for the thermolysis of [Pt(PEt₃)₂-(alkyl)X] complexes involves a nondissociative pathway and the intermediacy of a 5-coordinate 18-electron [PtL₂(H)(olefin)X] intermediate.

Concluding Remarks

There are two main pathways by which thermolysis of alkylbis-(phosphine)platinum(II) complexes can take place: (i) that involving the 4-coordinate square planar 16-electron starting complex and (ii) that involving dissociation of a ligand and reversible β-hydride elimination from a coordinatively unsaturated intermediate. In the case of the reactions of the dialkyl [Pt-(L₂)(alkyl)₂] complexes, carried out at high temperature and in nonpolar solvents, dissociation of a phosphine ligand offers a low-energy pathway through the intermediacy of an uncharged 3-coordinate [Pt(L₂)(alkyl)] species. Irrespective of the mechanism, the process leads almost invariably to platinum(0) products

and to disproportionation liberating alkene and alkane in a 1:1 ratio. A kinetic study of the reverse process in unfeasible. The reactions of the corresponding monoalkyls fit all the characteristics required of a model system: (i) both the starting alkyls and the final hydride products are stable and can be isolated as discrete compounds, (ii) only alkenes are formed, (iii) it is possible to measure the sensitivity of the rates to slight structural changes imposed on the substrates. A low-energy pathway involves the removal of the halide from the coordination sphere of the metal and the intermediacy of a T-shaped 3-coordinate cationic [PtL₂-

(alkyl)]⁺ species. The ease with which a vacant coordination site is formed at the metal is essential for the occurrence of the process. Once the coordinatively unsaturated species is formed, its fate depends on the efficiency with which it can interconvert, undergo intramolecular β-hydride elimination, or be intercepted by the solvent, electron-donor molecules, or other chemical species.