half-lives for $\beta,\gamma \rightarrow \alpha,\gamma$ or $\alpha,\gamma \rightarrow \alpha,\gamma \rightarrow \beta,\gamma$ conversions did not depend on initial platinum concentration, indicating that this isomerization is a first-order process. Addition of 0.1 M Cl^- did not change the half-lives significantly, nor were we able to detect any other new phosphato products. The estimated first-order rate constants at 25 °C for $\alpha,\gamma \rightarrow \beta,\gamma$ (pH 3.5) and for $\beta,\gamma \rightarrow \alpha,\gamma$ (pH 7.7) were estimated as 2×10^{-3} s^{-1} and 3×10^{-3} s^{-1}.

The rapid isomerization reaction is largely intramolecular. With $[Cl^-] \gg [P_3O_{10}^{n-}]$, it is expected that Cl^- would compete with the triphosphate if the reaction were to proceed largely through a solvent-assisted pathway. Absence of monodentate phosphato complexes precludes any major contribution by this pathway. A mechanism consistent with our data is shown in Scheme I. (Charges are omitted.)

An attack by the unbound α-phosphate group leads to a trigonal-bipyramid transition state. A cleavage of the Pt–O bond of the coordinated α-phosphate should result in the α,γ complex (V). The attack is facilitated by the presence of a deprotonated phosphate group at higher pH. Furthermore, the unbound phosphate is uniquely positioned to form a hydrogen bond with the amine hydrogens. Such bond formation should bring the phosphate oxygen in close proximity to the platinum atom and lower the energy barrier for the isomerization. We note that the formation of the β,γ isomer predominates below pH 4, while the α,γ form is preferred above pH 6. We were unable to determine the acidity constants for these complexes owing to a small change in the chemical shifts and the absence of one or the other isomer in the lower and higher pH values. However, the pH-dependent chemical shift data do support two acidity constants near 10^{-4} and 10^{-6} for the β,γ complex and an acidity constant for the α,γ complex of 10^{-6}. These estimated acidity constants and the distribution of isomers as a function of pH support our mechanism of isomerization (Scheme I).[35]

The rate for isomerization is at least 10 times greater than that for formation of triphosphate chelates. It is therefore most likely that the β,γ chelate is formed initially and then rapidly isomerizes to the α,γ chelate.

Cornelius and Reibenspies[36] proposed that the linkage isomerization of $Co(H_2P_3O_{10})(NH_3)_4$ proceeds through dissociative pathways. Isomerization rate constants for cobalt(III) complexes are about 3 orders of magnitude smaller than for the platinum(II) complexes investigated here.

Acknowledgment. Support of this research through grants from the National Institutes of Health (GM 40006-02) and Kent State University Research Council is gratefully acknowledged. We thank Johnson Matthey Co. for the loan of K_2PtCl_4 and Professors E. S. Gould and J. Reedijk for valuable suggestions.

(35) Two points by a reviewer deserve response. The first pertains to the change in chemical shift (above pH 6) of the α,γ-phosphorus atoms if the α,γ-complex is deprotonated near neutral pH. This complex may not be fully deprotonated near neutral pH. Three acidity constants are expected for this complex, corresponding to the loss of one proton each from the α-, β-, and γ-phosphate groups. Higher acidity constants are expected for the coordinated phosphate group, as compared to the similar constant for the uncoordinated β-phosphate group. A small secondary change in the chemical shift of α- and γ-phosphorus atoms perhaps reflects the deprotonation at the uncoordinated middle phosphate group. A second point concerns the possibility of a rapid equilibrium between the α,γ complex and a monodentate complex near neutral pH values. This can be ruled out, on the basis of the observation that aquation of platinum(II) phosphophato chelates is extremely slow ($t_{1/2} \approx 10$ h at pH 7) and is shown to be acid-catalyzed (see ref 7b).

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Kinetic Study of β-Hydride Elimination of Monoalkyl Complexes of Platinum(II): Effects of Varying the Alkyl Chain Length or the Cis Group in the Reaction of *cis*-Bis(triethylphosphine)(alkyl)(halo or pseudohalo)platinum(II) Complexes

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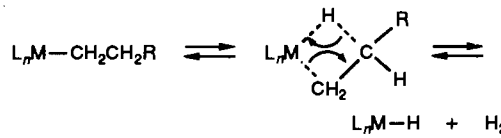
Received September 14, 1989

The monoalkyl complexes *cis*-$[Pt(PEt_3)_2(R)Br]$ (R = C_2H_5, C_2D_5, *n*-C_3H_7, *n*-C_4H_9) and *cis*-$[Pt(PEt_3)_2(n\text{-}C_4H_9)X]$ (X = Cl, Br, I, NO_2, N_3, SCN, SeCN) undergo a facile β-hydride elimination in acetone, yielding *trans*-$[Pt(PEt_3)_2HX]$ and olefins. No alkanes are produced in these reactions that go to completion and are unaffected by the presence of an excess of halide ion in solution that serves to prevent a possible concurrent geometrical isomerization. The corresponding trans-monoalkyl species are stable under the same experimental conditions. The systems were characterized by ^1H and ^{31}P NMR. The rates of thermal decomposition were obtained by GLC, measuring the relative amounts of volatile products at various times. The ethyl complex decomposes at a rate ten times slower than that of the *n*-propyl and *n*-butyl analogues. For the complexes *cis*-$[Pt(PEt_3)_2(R)Br]$, the activation parameters are as follows: R = C_2H_5, $\Delta H^\ddagger = 101 \pm 2$ kJ mol^{-1}, $\Delta S^\ddagger = +5 \pm 4$ J K^{-1} mol^{-1}; R = *n*-C_3H_7, $\Delta H^\ddagger = 91 \pm 4$ kJ mol^{-1}, $\Delta S^\ddagger = -7 \pm 10$ J K^{-1} mol^{-1}; R = *n*-C_4H_9, $\Delta H^\ddagger = 90 \pm 2$ kJ mol^{-1}, $\Delta S^\ddagger = -4 \pm 4$ J K^{-1} mol^{-1}; R = C_2D_5, $\Delta H^\ddagger = 99 \pm 2$ kJ mol^{-1}, $\Delta S^\ddagger = -10 \pm 5$ J K^{-1} mol^{-1}. At 298.16 K, the kinetic isotope effect ($k_d(C_2H_5)/k_d(C_2D_5)$) is 3.1. The rates of decomposition of the complexes *cis*-$[Pt(PEt_3)_2(n\text{-}C_4H_9)X]$ are strongly dependent on the nature of the X group, the overall difference of reactivity being at least 4 orders of magnitude between the first and the last members of the series. The reactivity sequence X = N_3 < NO_2 < Cl < NCS < Br < NCSe < I correlates well with some NMR parameters ($\delta(^1H)$, $\delta(^{195}Pt)$, and $^1J(PtP)$) of the *trans*-$[Pt(PEt_3)_2HX]$ hydride products. The distribution of the olefin products, 1-butene, *cis*-2-butene, and *trans*-2-butene is also dependent on the nature of X. The most probable mechanism for the thermolysis involves fast and reversible β-hydride elimination and olefin insertion in a pre-rate-determining step, followed by slow olefin loss from a 5-coordinate $[PtL_2(H)(olefin)X]$ intermediate.

Introduction

The ease with which a hydrogen atom transfers from the β-carbon atom of an alkyl chain to the metal to produce a metal hydride as in the reaction



$$L_nM{-}H + H_2C{=}C(R)H \quad (1)$$

is of fundamental importance for the stability of organotransition-metal compounds.[1] Indeed, β-elimination is the best documented low-energy route leading to transition-metal–carbon

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bond scission.[2] With the reverse reaction, olefin insertion into a metal–hydrogen bond, being a key step in many catalytic cycles (e.g. hydroformylation, hydrogenation, and olefin isomerization), the importance of the process is unquestionable. The general interest in the details of elementary steps that break and form C–H and C–C bonds by reaction with a metal atom has led to extensive studies of both sides of reacton 1 for platinum(II) and palladium(II) complexes. Clark et al.[3] have investigated the conditions that facilitate the olefin insertion into a platinum–hydrogen bond, while Whitesides and Yamamoto et al.[4] have studied in great detail the mechanistic aspects of the thermal decomposition of several platinum(II) and palladium(II) alkyl complexes including, among others, monoalkyl *trans*-$[PtL_2RX]$ (L = phosphine),[5-7] symmetrical[8] and unsymmetrical dialkyls,[9] and related metallacyclic compounds.[10] The thermolysis takes place most easily when dissociation of the phosphine ligand produces a coordinatively unsaturated T-shaped intermediate having a vacant coordination site for β-hydride elimination, but there is evidence against dissociation being a prerequisite for the occurrence of the process.[11] More recent studies refer to β-hydride elimination and C–H activation.[12]

Despite the considerable research effort in this field, it appears that factors influencing thermolysis pathways of square-planar metal alkyls are not fully understood. The pattern of behavior of strictly similar substrates can be extremely different. For example, the thermolysis of *trans*-$[PdEt_2(PR_3)_2]$ proceeds cleanly by a β-hydrogen transfer process liberating ethane and ethene and it is not inhibited by addition of tertiary phosphines.[11] The corresponding *cis*-$[PdEt_2(PR_3)_2]$ complex undergoes reductive elimination of the ethyl groups to give butane through a dissociative pathway (mass law retardation by phosphine)[13] while the thermolysis reaction of *cis*-$[PtEt_2(PR_3)_2]$ follows a dissociative β-hydride elimination route.[8] This variety of thermolysis behavior makes it difficult to predict the stability and reactivity of such compounds. If we refer only to β-hydride elimination, then theoretical, crystallographic, and NMR studies have been used to investigate the molecular motions involved in reaching the transition state,[14] but as yet the factors that govern the rates of these processes remain unclear.

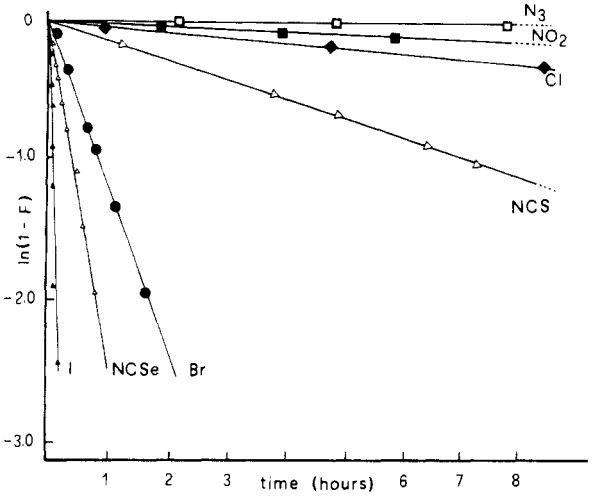

Figure 1. First-order kinetic plots for the decomposition of *cis*-$[Pt(PEt_3)_2(n\text{-Bu})X]$ complexes in acetone at 298.16 K.

Thus, there is a strong need for very simple systems suitable for kinetic studies in which it is possible to measure the sensitivity of the rates of β-hydride elimination to slight structural changes of the substrate. A system which fits these requirements is given in eq 2, which has been shown in a previous study[15] to proceed

$$cis\text{-}[Pt(PEt_3)_2(alkyl)X] \rightarrow trans\text{-}[Pt(PEt_3)_2(H)X] + \text{olefins} \quad (2)$$

readily to completion in 2-propanol. It is worth remembering here that the thermal decomposition of the corresponding trans complexes requires more drastic conditions (melt or temperatures higher than 150 °C in solution) and leads to an equilibrium.[5-7]

In this study, we were interested in searching for a correlation between the lability of the substrates and the nature of the X group in the position cis to the alkyl and for any effect(s) associated with the length of the alkyl chain. Thus, we prepared as solids or "in situ" a series of complexes of the type *cis*-$[Pt(PEt_3)_2(R)X]$ (R = n-C_4H_9, X = Cl, Br, I, N_3, NO_2, NCS, NCSe; R = C_2H_5, C_2D_5, n-C_3H_7, n-C_4H_9, X = Br) and have carried out a kinetic study of reaction 2 in acetone.

The results are discussed in the framework of a nondissociative mechanism and provide a means of ascertaining the importance of the electronic properties of the alkyls and of the cis groups in governing the lability of the substrates.

Experimental Section

Preparation of Complexes. The synthesis of the complexes *cis*-$[Pt(PEt_3)_2(R)Cl]$ (R = ethyl, mp 71–73 °C; R = ethyl-d_5, mp 70–72 °C; R = n-propyl, mp 73–75 °C; R = n-butyl, mp 68–69 °C) has been reported elsewhere.[15]

***cis*-$[Pt(PEt_3)_2(n\text{-Bu})Br]$** was prepared by metathetical exchange from the corresponding chloro compound. *cis*-$[Pt(PEt_3)_2(n\text{-Bu})Cl]$ (0.25 g, 0.48 mmol) was combined with LiBr (0.41 g, 4.8 mmol) in acetone at −10 °C and left to react for 15 min. After evaporation of the solvent, the residue was washed with cold water, dried over P_4O_{10} under vacuum, and then crystallized as white needles from a diethyl ether–petroleum ether mixture. Mp = 59–60 °C.

***cis*-$[Pt(PEt_3)_2(n\text{-Bu})NO_2]$** was prepared in a similar way from *cis*-$[Pt(PEt_3)_2(n\text{-Bu})Cl]$ (0.25 g, 0.48 mmol) and $NaNO_2$ (0.33 g, 4.8 mmol) in acetone containing 10% water. The oil obtained after evaporation of the solvent, which was washed with water and dried under vacuum,

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Table I. Spectroscopic Properties of the Starting *cis*-[Pt(PEt$_3$)$_2$(*n*-Bu)X] Complexes and of the Decomposition Products *trans*-[Pt(PEt$_3$)$_2$(H)X][a]

	cis alkyls $^{31}P\{^1H\}$			trans hydrides $^{31}P\{^1H\}$		^1H	
X	δ/ppm	^1J(PtP)/Hz	^2J(PP)/Hz	δ/ppm	^1J(PtP)/Hz	δ/ppm	^1J(PtH)/Hz
Cl	8.83	4345	13.1	23.2	2723	−17.50	1287
	15.04	1582					
Br	9.42	4392	12.8	21.6	2685	−16.14	1353
	11.97	1600					
I	8.82	4270	13.9	19.4	2612	−13.24	1395
	7.78	1640					
NO_2	−0.66	3411	12.0	21.4	2766	−19.89	1013
	10.94	1740					
N_3	6.97[b]	4026[b]	12.8[b]	22.9	2766	−18.57	1169
	16.86	1615					
NCS	4.74	4160	15.5	22.5	2668	−17.94	1117
	14.60	1547					
NCSe	4.63	4164	15.5	19.4	2625	−12.7	1258
	14.80	1556					

[a] In [$^2H_6$]acetone. [b] In [$^2H_6$]benzene.

crystallized in a few hours after addition of petroleum ether at −20 °C. Mp = 65–66 °C. Anal. Calcd for $C_{16}H_{39}P_2NO_2Pt$: C, 35.9; H, 7.3. Found: C, 35.5; H, 7.4.

***cis*-[Pt(PEt$_3$)$_2$(*n*-Bu)N$_3$].** *cis*-[Pt(PEt$_3$)$_2$(*n*-Bu)Cl] (0.25 g, 0.48 mmol) was combined with NaN_3 (0.31 g, 4.8 mmol) in a acetone–water (10%) mixture at −20 °C. After 15 min, the solvent was evaporated under vacuum, and the residue was extracted with diethyl ether and crystallized from a diethyl ether–petroleum ether mixture. Mp = 70–71 °C. Anal. Calcd for $C_{16}H_{39}P_2N_3Pt$: C, 36.2; H, 7.4; N, 7.9. Found: C, 36.0; H, 7.2; N, 7.9.

***cis*-[Pt(PEt$_3$)$_2$(*n*-Bu)NCS].** *cis*-[Pt(PEt$_3$)$_2$(*n*-Bu)Cl] (0.25 g, 0.48 mmol) was reacted with (Ph_4As)SCN (2.1 g, 4.8 mmol) in acetone at −20 °C. The residue obtained after evaporation of the solvent was crystallized from a diethyl ether–petroleum ether mixture.

Infrared spectra were recorded as Nujol mulls or in acetone on a Perkin-Elmer 783 spectrophotometer equipped with a 3600 IR data station; ^1H NMR and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker WP 80 SY spectrometer with [$^2H_6$]benzene and [$^2H_6$]acetone as the solvents. ^{31}P chemical shifts, in parts per million, are relative to external phosphoric acid.

Anhydrous acetone was obtained by standard methods. Diethyl ether was distilled under nitrogen from disodium benzophenone dianion. All the other chemical products were reagent grade commercial materials and were used without further purification.

Kinetics. The thermal decomposition reactions were followed by GLC measurements of the volatile products obtained after hydrochloric acid quenching of individual reaction mixtures at various time intervals. The starting materials were authentic *cis*-[Pt(PEt$_3$)$_2$(R)X] complexes or were prepared "in situ" from the corresponding chloride by metathetical exchange with LiX (X = Br, I), NaX (X = NCS, NCSe), and (Ph_4As)X (X = N_3, NO_2). Thus, weighed amounts of *cis*-[Pt(PEt$_3$)$_2$(R)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 acetone (2 mL) containing MX (0.01–01 M) was added by means of a syringe, and the solid was rapidly dissolved by shaking. Quenching was carried out 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. 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 the alkanes produced on quenching from the undecomposed starting material. The rate constants k_{obsd}, s^{-1}, were obtained from linear plots of ln (1 − F) vs *t*, where *F* is the decomposition fraction (see Figure 1). 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 and C_2 separation. Activation parameters were derived from a linear least-square analysis of ln (k/T) vs T^{-1} data, as illustrated in Figure 2.

Results

The synthesis and characterization of the complexes *cis*-[Pt(PEt$_3$)$_2$(R)Cl] (R = Et, [$^2H_5$]Et, *n*-Pr) has been already reported.[15] These compounds served as starting materials for the "in situ" formation of the corresponding bromide complexes by metathetical exchange with excess of LiBr.

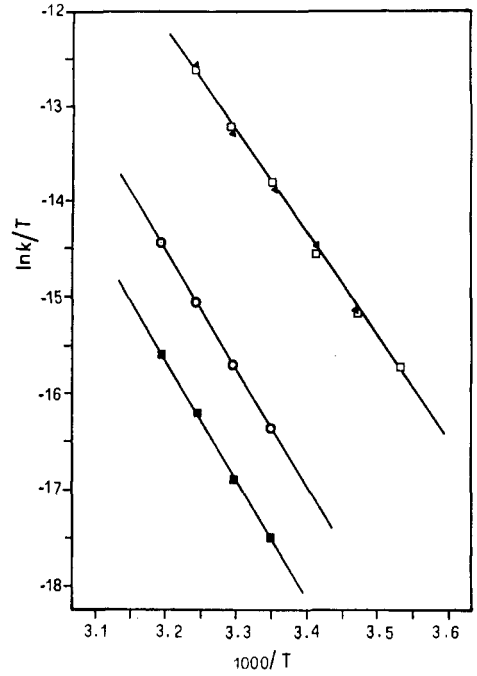

Figure 2. Eyring plot for thermal decomposition of *cis*-[Pt(PEt$_3$)$_2$(R)Br] complexes in acetone solution: (▲) R = *n*-butyl; (□) R = *n*-propyl; (○) R = ethyl; (■) R = ethyl-d_5.

The synthesis of the complexes *cis*-[Pt(PEt$_3$)$_2$(*n*-Bu)X] (X = Br, I, NO_2, N_3, SCN, SeCN) by metathetical exchange in acetone from the corresponding chloride complex requires some care since either the starting material or the final compounds can undergo two unwanted processes, namely geometrical isomerization to the trans derivatives or thermal decomposition.

We were able to get solid compounds for all the groups as described above, except for SeCN. However, *cis*-[Pt(PEt$_3$)$_2$(*n*-Bu)I], soon after separation as a solid, starts to change color rapidly from white to pale yellow, yielding *trans*-[Pt(PEt$_3$)$_2$(H)I], as revealed by the increase with time of the Pt–H absorption at 2185 cm^{-1} in the IR spectrum. The same conversion of *cis*-[Pt(PEt$_3$)$_2$(*n*-Bu)Br] to the trans hydride is very much slower.

For the ambidentate ligands there is the additional problem of determining which donor atom binds to platinum. The compound obtained as a solid from the reaction with (Ph_4As)SCN, before decomposing, showed a C–S stretch (as Nujol mull) at 830 cm^{-1} indicative of the isothiocyanato linkage.[16] The same peak in acetone appears at 831 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum, recorded soon after the metathetical exchange with an excess of

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Table II. Temperature Dependence of the Rate Constants for Thermal Decomposition of *cis*-[Pt(PEt$_3$)$_2$(R)Br] Complexes in Acetone[a]

	$10^4k_d/s^{-1}$			
t/K	R = Et	R = [$^2H_5$]Et	R = *n*-Pr	R = *n*-Bu
283.66				0.440
288.16			0.780	0.750
293.16			1.60	1.42
298.16	0.227	0.0733	2.66	3.00
303.16	0.458	0.139	4.98	5.52
308.16	0.887	0.275	10.60	10.1
313.16	1.70	0.520		
	$\Delta H^\ddagger = 101 \pm 2$	$\Delta H^\ddagger = 99 \pm 2$	$\Delta H^\ddagger = 91 \pm 4$	$\Delta H^\ddagger = 90 \pm 2$
	$\Delta S^\ddagger = +5 \pm 4$	$\Delta S^\ddagger = -10 \pm 5$	$\Delta S^\ddagger = -7 \pm 10$	$\Delta S^\ddagger = -4 \pm 4$

[a] $\Delta H^\ddagger$ in kJ mol^{-1}; $\Delta S^\ddagger$ in J mol^{-1} K^{-1}.

salt in [$^2H_6$]acetone at 0 °C, showed a sharp peak at 14.6 ppm (^1J(PtP) = 1547 Hz) (see Table I) for the phosphorus trans to carbon and a broad resonance at 4.74 ppm (^1J(PtP) = 4160 Hz) assigned to the phosphorus trans to the N-bound ligand. The broadening can be attributed to quadrupole relaxation of the ^{14}N nucleus[17] and confirms that the isothiocyanato linkage is maintained in solution. The alkyl *cis*-[Pt(PEt$_3$)$_2$(*n*-Bu)(NCS)] slowly decomposes to *trans*-[Pt(PEt$_3$)$_2$(H)(NCS)] and *trans*-[Pt(PEt$_3$)$_2$(H)(SCN)], as shown by the decrease of the signals due to the starting cis complex and a parallel matching increase of the signals of two trans hydride compounds (δ 22.5, ^1J(PtP) = 2668 Hz, for the isothiocyanato and δ 20.2, ^1J(PtP) = 2642 Hz, for the thiocyanato, respectively).[18] The final ratio of the two linkage isomers is 3:2. The simultaneous formation of the nitrogen-bonded and the sulfur-bonded isomers can be followed also by ^1H NMR (a broad signal at δ −17.94, ^1J(PtH) = 1117 Hz, is assigned to the isothiocyanato complex, and a sharp 1:2:1 triplet at δ −13.2, ^1J(PtH) = 1238 Hz, is assigned to the thiocyanato complex).[19]

The infrared spectrum of *cis*-[Pt(PEt$_3$)$_2$(*n*-Bu)NO$_2$] (as a Nujol mull) shows a very strong band at 1325 cm^{-1} and a sharp peak at 810 cm^{-1} as would be expected for a nitro (N-bonded) complex and no bands attributable to a nitrito complex (O-bonded).[16-20] The $^{31}P\{^1H\}$ NMR spectrum in [$^2H_6$]acetone showed two sharp peaks (at −0.66 ppm, $^1J(PtP_A)$ = 3411 Hz, and at 10.94 ppm, $^1J(PtP_B)$ = 1740 Hz) consistent with a cis geometry and with the contemporaneous presence of a poor and a good trans-activating group trans to P_A and P_B, respectively. Also in this case the thermal decomposition can be followed by $^{31}P\{^1H\}$ NMR through the increase of a resonance at 21.4 ppm (^1J(PtP) = 2766 Hz) due to *trans*-[Pt(PEt$_3$)$_2$(H)NO$_2$]. The sharpness of the 1:2:1 triplet in the ^1H NMR spectrum (at −19.89 ppm, ^1J(PtH) = 1013 Hz) suggests that the final hydride compound is mainly present in the nitrito form.[21]

On the basis of the $^{31}P\{^1H\}$ NMR spectrum the *cis*-[Pt(PEt$_3$)$_2$(*n*-Bu)SeCN] compound formed "in situ" (a broad resonance at 4.63 ppm, ^1J(PtP) = 4164 Hz, and a sharp one at 14.80 ppm, ^1J(PtP) = 1556 Hz) can be formulated as a isoselenocyanate complex. The product of the thermal decomposition is a hydride selenocyanate species *trans*-[Pt(PEt$_3$)$_2$(H)SeCN] (a sharp ^{31}P resonance at 19.4 ppm, ^1J(PtP) = 2625 Hz, and a sharp 1:2:1 triplet for the ^1H resonance at −12.7 ppm, ^1J(PtH) = 1258 Hz). When the reaction is carried out in [$^2H_8$]-2-propanol the formation of two isomers is observed in the ratio 1:1 (selenocyanate, ^1H NMR δ −12.7 (^1J(PtH) = 1258 Hz, ^2J(PH) = 13.7 Hz); isoselenocyanate, ^1H NMR δ −17.5 (^1J(PtH) = 1286 Hz, ^2J(PH) = 14.3 Hz)). Linkage isomerization is only observed for the hydride products and, although it is dependent on the solvent, was not found to exert any influence on the thermal decomposition. The $^{31}P\{^1H\}$ NMR spectra of the most labile compounds were taken at low temperature, in order to avoid thermal decomposition taking place. In no case was there evidence for the buildup in solution of any other intermediate species except the starting cis alkyl and the final hydride compound.

Table III. Effect of the Nature of the Cis Group X on the Rate of Thermal Decomposition of *cis*-[Pt(PEt$_3$)$_2$(*n*-Bu)X] Complexes and on the Distribution of the Olefin Products[a]

			% product			
X	$10^4k_d/s^{-1}$	k_X/k_{N_3}	1-butene	*cis*-2-butene	*trans*-2-butene	$\delta(^{195}Pt)$/ppm[b]
N_3	0.00478	1	69.4	26.2	4.4	
NO_2	0.065	14	69.1	27.6	3.3	60.3
Cl	0.125	26	70.2	25.8	4.0	137.4
NCS	0.377	79	81.0	15.8	4.0	
Br	3.00	696	80.0	16.5	3.5	249.3
NCSe	7.30	1527	90.6	5.4	4.0	
I	41.8	8750	91.8	5.9	3.1	442.9

[a] In acetone at 298.16 K. [X] = 0.01 M. [b] ^{195}Pt chemical shift of *trans*-[Pt(PEt$_3$)$_2$(H)X] complexes in [$^2H_6$] acetone.[27]

Although the reactions, as we have seen above, can be effectively monitored by means of $^{31}P\{^1H\}$ NMR, all the kinetics of β-hydride eliminations were followed by GLC, conventional spectrophotometry being prevented by the strong absorption of the solvent in the region (280–220 nm) where the spectral changes take place. 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 1-butene, *cis*-2-butene, and *trans*-2-butene. 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 the amount of salt added to the solution. No alkanes were detected in these reactions. The kinetics obey a first-order rate law until well over 90% of the reaction, are independent of the concentration of the complex, and are unaffected by [X^-] in solution up to 0.01 M. The specific rate constants k_d, s^{-1}, at various temperatures for the β-hydride elimination of the *cis*-[Pt(PEt$_3$)$_2$(R)Br] (R = Et, [$^2H_5$]Et, *n*-Pr, *n*-Bu) complexes are listed in Table II together with the associated activation parameters. The rate constants at 298.16 K for the β-hydride elimination of the *cis*-[Pt(PEt$_3$)$_2$(*n*-Bu)X] (X = Cl, Br, I, NO_2, N_3, SCN, SeCN) complexes are reported in Table III together with the changes in the distribution of the olefin products.

Discussion

We reported before that *cis*-[Pt(PEt$_3$)$_2$(alkyl)Cl] complexes, in which the alkyl group contains β-hydrogens, undergo competitive uncatalyzed geometrical isomerization and β-hydride elimination in protic solvents.[15] In methanol, the only observed process was isomerization, while in 2-propanol the relative rates of the two competing processes were controlled by adding free chloride ion, which does not affect β-hydride elimination but greatly decreases the rate of isomerization. Under these circumstances, it was possible to obtain the rates of thermal decomposition for the *n*-propyl and the *n*-butyl derivatives, but in the case of the ethyl complex, the β-hydride elimination was hidden by its high rate of cis–trans isomerization. In acetone, cis–trans isomerization

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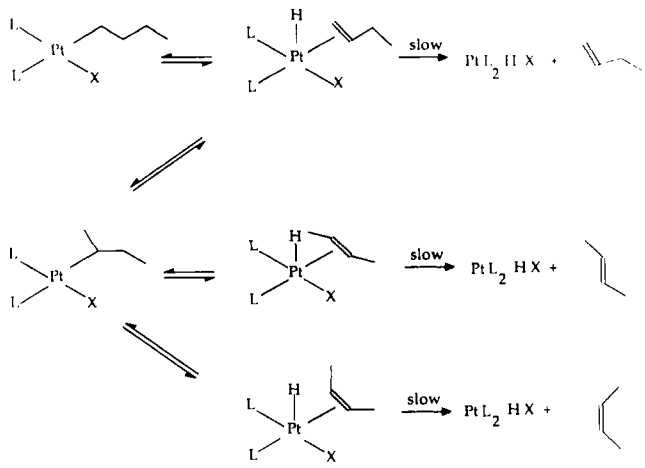
Scheme I



is completely blocked and the principal effect of the addition of X^- in solution is to generate the starting complex "in situ".

The mechanism that has been suggested for β-hydride elimination, shown in Scheme I, involves fast and reversible addition of a C–H bond to platinum in the square-planar 16-electron complex, yielding a 5-coordinate $[PtL_2(H)(olefin)X]$ intermediate. Rate-determining loss of olefin follows to yield *trans*-$[PtL_2(H)X]$.

A pathway involving halide loss and reversible β-hydride elimination through a cationic $[PtL_2(alkyl)]^+$ intermediate has been excluded since this is a low-energy route to isomerization, at least in solvents that can promote Pt–X bond breaking.[22] The platinum cation changes into a geometrically distinct "trans-like" structure before a β-extraction process can take place and the two processes, β-elimination and isomerization, do not have a common intermediate. An uncharged T-shaped 14-electron [PtL(alkyl)Cl] intermediate, formed by phosphine dissociation, is also expected to lead to isomerization, in agreement with the low-energy barrier found for the fluxionality of coordinatively unsaturated reaction intermediates such as $H(PH_3)_2Pt$,[23] Me_3Au,[24] or $Et_2(PEt_3)Pt$.[25] However, if phosphine is liberated from the *cis*-$[Pt(PEt_3)_2(alkyl)X]$ complexes, it is expected to produce a fast autocatalytic cis to trans isomerization through a sequence of consecutive displacements or through a "pseudo-rotation" of a 5-coordinate intermediate.[26] Indeed, a proper study of the phosphine effect on the rate of β-elimination is prevented by its role as isomerization catalyst. Summing up, dissociation of ligands from the square-planar complex would lead to isomerization, through different possible routes, rather than to β-hydride elimination.

Thus, we suggest that reaction Scheme I is operative in the thermal decomposition of these *cis*-$[Pt(PEt_3)_2(alkyl)X]$ complexes. The simultaneous formation of three olefin isomers, 1-butene, *cis*-2-butene and *trans*-2-butene, is a straightforward indication that the release of organic products must be preceded by a preequilibrium in which fast and reversible β-hydride elimination and olefin insertion lead to a facile skeletal isomerization of linear to branched alkyl groups. Brainard and Whitesides[5] have provided elegant labeling studies which show that a similar mechanism is operating for *trans*-$[Pt(PEt_3)_2(Et)Cl]$, even though the thermolysis occurs at 150 °C in cyclohexane solution and leads to an equilibrium. In contrast, an essential feature of β-hydrogen elimination from *cis*-$[Pt(PEt_3)_2(Et)_2]$, as for most of the *cis*-dialkyls studied previously, is dissociation of the phosphine ligand and the formation of a coordinatively unsaturated T-shaped intermediate having a vacant coordination site for a facile β-hydride elimination. These results suggest that the ancillary ligands have more than a spectator role and play an important part in determining the reactivity of the substrates. If a strong σ-donor alkyl group is substituted for a weak σ-donor as the halide ion, there is a changeover of reaction mechanism, and perhaps because of the increased electrophilicity of the central atom, a low-energy β-elimination from the 16-electron starting complex becomes competitive with the dissociative route.

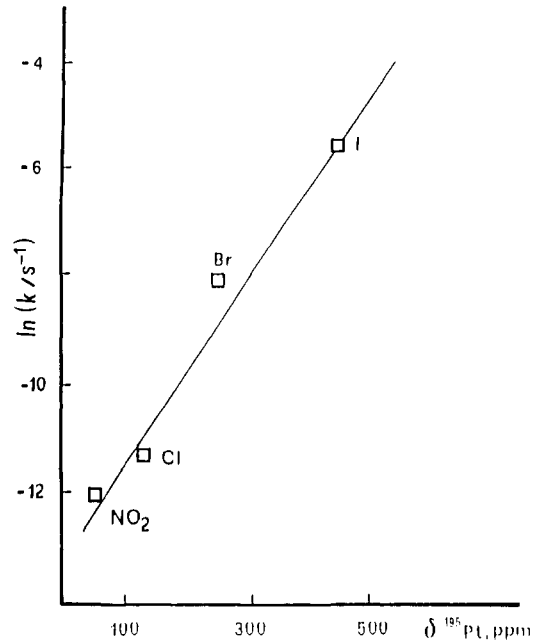


Figure 3. Correlation between the rates of β-hydride elimination of *cis*-$[Pt(PEt_3)_2(n\text{-}Bu)X]$ complexes and the chemical shifts of the platinum nucleus of the corresponding *trans*-$[Pt(PEt_3)_2(H)X]$ products.

Effect of the Alkyl Chain Length. The kinetic data in Table II give the following sequence of lability for the thermal decomposition of *cis*-$[Pt(PEt_3)_2(alkyl)Br]$ complexes: Et ≪ *n*-Pr ~ *n*-Bu (at 303.16 K, 10^4k = 0.458, 4.98 and 5.52 s^{-1} respectively). The smaller rate of β-hydride elimination for the ethyl complex compared to that of the *n*-propyl and *n*-butyl analogues seems entirely due to an increase of about 10 kJ mol^{-1} in the enthalpy of activation, which outweighs a small increase in the entropy of activation. Two competing factors are responsible for the rates in these systems. The first is the relative stability of the 5-coordinate $[PtL_2(olefin)(H)Br]$ intermediates and the second is the rate at which these intermediates lose the olefin to yield the metal hydride. If the first factor does not vary very much on changing the complexity of the alkyl chain, then the reactivity sequence ethene ≪ propene ~ butene will reflect the ease of olefin liberation from the intermediate. These results would suggest that metal-to-olefin back-bonding is important in the transient 5-coordinate species, since electron-donating substituents raise the energy of the olefin π* orbital and contribute to bond lengthening by decreasing back-donation.

The kinetic isotope effect for decomposition of *cis*-$[PtL_2(C_2D_5)Br]$ is relatively large (k_H/k_D = 3.1 at 298.16 K). Values of this magnitude could be interpreted as evidence of a direct involvement of the C–H bond breaking in the rate-determining step. Brainard and Whitesides[5] found a deuterium equilibrium isotope effect K_H/K_D = 1.9 ± 0.4 for the reaction *trans*-$[PtL_2C_2H_5(D_5)Cl] \rightarrow$ *trans*-$[PtL_2ClH(D)] + C_2H_4(D_4)$ and a deuterium kinetic isotope effect for the same reaction k_H/k_D = 2.5 ± 0.2. Their interpretation was that the isotope effect essentially derives from the preequilibrium step, which favors the decomposition of the completely protonated species, and it is dominated by the change in IR stretching frequency on going from an aliphatic C–H bond to a Pt–H bond. The most plausible rate-determining step remains that in which ethene leaves from

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the 5-coordinate $[PtL_2Cl(H)C_2H_4]$ intermediate. The same explanation applies here.

Effect of Varying the X Group in *cis*-$[Pt(PEt_3)_2$ (*n*-Bu)X]. The data in Table III show that the rates of decomposition of the complexes *cis*-$[Pt(PEt_3)_2(n\text{-Bu})X]$ are strongly dependent on the nature of the ion X, increasing in the order $N_3 < NO_2 < Cl < NCS < Br < NCSe < I$, the overall difference of reactivity being at least 4 orders of magnitude between the first and the last members of the series.

Figure 3 shows that these rate data are correlated by a linear free energy relationship of the type $\ln k = m\delta(^{195}Pt)$, where $\delta(^{195}Pt)$ is the chemical shift of the platinum nucleus of the corresponding *trans*-$[PtL_2HX]$ complex[27] and m represents the sensitivity of β-hydride elimination to the changes of these chemical shifts ($m = 0.017$, $R = 0.986$, by linear regression analysis). Similar LFER correlations including all data points can be obtained with the hydride chemical shift $\delta(^1H)$ ($m = 0.99$, $R = 0.867$, seven data points) and with the platinum–phosphorus coupling constants $^1J(PtP)$ ($m = -0.04$, $R = 0.926$, seven data points).

All these three NMR parameters can be regarded as good indicators of the covalency of the Pt–X bond and are a measure of the involvement of the d orbitals of platinum in π bonds.[28] In other words, the ligand that is capable of the strongest covalent bond or that forms the strongest π bonds with the metal will produce the highest rate of β-hydride elimination. These results emphasize once again the role of π back-bonding to the empty π^* of the olefinic moiety in determining the kinetic stability of the 18-electron $[PtL_2(H)olefinX]$ intermediate. Increased π donation from the platinum center to the X group decreases back-bonding from this center to the olefin, thereby decreasing the strength of platinum–olefin interactions. The same explanation can be applied to the very important observation made by Brindza[29] that the activation barrier for β-hydride elimination from [(COD)Pt(Et)I] (COD = cycloocta-1,5-diene) is much lower than that of the strictly related $[(COD)PtEt_2]$, even though the trans labilizing power of I is far lower than that of Et. Thermal decomposition of these substrates proceeds also by initial preequilibrium β-hydride migration to the metal followed by rate-limiting release of organic products.

Steric factors do not appear to play an important role in these reactions. During the past few years several 5-coordinate platinum–olefin complexes have been isolated. Nearly all the compounds described so far belong to the species (i) $[PtMe(\eta^2\text{-olefin})((pz)_3BH)]$,[30] where $(Pz)_3BH$ is the tridentate anionic ligand hydrotris(1-pyrazolyl)borate, and (ii) $[PtCl_2(\eta^2\text{-olefin})(N\text{-}N)]$,[31] where N–N is a neutral bidentate nitrogen ligand such as a diamine, a bis(hydrazone), or a diimine, or (iii) $[PtMeCl(\eta^2\text{-olefin})(N\text{-}N)]$.[32] Generally these compounds have a trigonal-bipyramidal array with the N–N ligand and the olefin occupying the equatorial plane. The systematic rationalization of the factors affecting the stability of these 5-coordinate species is difficult, but some relevant remarks have been made. For example, increasing steric hindrance on both sides of a planar N–N′ ligand increases the kinetic stability of 5-coordinate species while the corresponding 4-coordinate species is comparatively much more destabilized by repulsive interactions of the substituents on N and N′ with the ligands in cis position. While a moderate bulk at the nitrogen atoms must be present in order to obtain stable complexes, the stability is increased by σ donation from the N–N ligand or from a methyl group. In contrast, the stability was found to be decreased when the π-acceptor ability of the olefin decreases,[33] and this is fully in keeping with our kinetic results.

Finally, it is also worth mentioning here that the relative amounts of the three butenes produced on β-hydride elimination from *cis*-$[Pt(PEt_3)_2(n\text{-Bu})X]$ complexes is dependent of the nature of the X group (see Table III). While the amount of *trans*-2-butene produced is relatively low, being in all cases lower than 5%, and does not change appreciably with X, the amount of 1-butene increases at the expense of *cis*-2-butene on going from $X = N_3$ to X = I, following roughly the same trend as the rate of β-hydride elimination. Here again, for a given X group, the relative abundance of the three olefins will depend upon the relative abundance of the alkyl metal isomers, the $[Pt(PEt_3)_2(H)(olefin)X]$ intermediates and their rate constants for dissociation to form the metal hydride.

There is only limited information in the literature on the factors that determine the equilibrium between different alkyl metal isomers and the preference of transition metals for different types of carbon atoms. In most cases the direction of the skeletal isomerization of the alkyl chain is from branched to straight chain.[34] Reger and Culbertson have reported that the *sec*-butyl group in the $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(s\text{-Bu})$ complex isomerizes to a *n*-butyl group when heated in xylene.[35] The preference for a primary carbon atom seems also to be a characteristic of some $[Pt(L\text{–}L)(PR_3)(alkyl)]$ (L–L = bischelate monoanionic ligand) complexes.[36] In our reactions it is clear that the nature of X exerts a profound influence on the distribution of the olefins, with a terminal olefin being more prefered as X changes from N_3 to I, but at this stage a deeper analysis is premature.

Acknowledgment. We wish to thank the Italian Ministry of Education for financial support and Prof. M. L. Tobe for stimulating discussions.

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