Protonolysis of Dialkyl- and Alkylarylplatinum(II) Complexes and Geometrical Isomerization of the Derived Monoorgano−Solvento Complexes: Clear-Cut Examples of Associative and Dissociative Pathways in Platinum(II) Chemistry

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Received April 28, 1997[⊗]

Protonolysis of the complexes *cis*-[$PtR_2(PEt_3)_2$] (R = Me, Et, Pr^n, Bu^n, $CH_2C(Me)_3$, $CH_2Si(Me)_3$) and *cis*-[Pt(R)(R′)$(PEt_3)_2$] (R = Ph, 2-MeC_6H_4, 2,4,6-$Me_3C_6H_2$; R′ = Me) in methanol selectively cleaves one alkyl group, yielding *cis*-[Pt(R)$(PEt_3)_2$(MeOH)]$^+$ and alkanes. The reactions occur as single-stage conversions from the substrate to the product. There is no evidence by UV and by low-temperature ^{1}H and ^{31}P NMR spectroscopy for the presence of significant amounts of Pt(II) or Pt(IV) intermediate species. Reactions are first order with respect to complex and proton concentrations and are strongly retarded by steric congestion at the Pt−C bond, varying from $k_2 = (2.65 \pm 0.08) \times 10^5$ M^{-1} s^{-1} for R = R′ = Et to $k_2 = 9.80 \pm 0.44$ $M^{-1}s^{-1}$ for R = R′= $CH_2Si(Me)_3$. Low enthalpies of activation and largely negative volumes of activation are associated with the process. The mechanism involves a rate-determining proton transfer either to the metal−carbon σ bond (S_E2 mechanism) or to the metal center (S_E(oxidative) mechanism), followed by fast extrusion of the alkane and simultaneous blocking of the vacant coordination site by the solvent to generate *cis*-[Pt(R)$(PEt_3)_2$(MeOH)]$^+$ species. The subsequent slower process, *cis* to *trans* isomerization of *cis*-[Pt(R)$(PEt_3)_2$(MeOH)]$^+$, is characterized by high values of enthalpies of activation, positive entropies of activation, and largely positive volumes of activation. The reaction is shown to proceed through the dissociative loss of the weakly bonded molecule of solvent and the interconversion of two geometrically distinct T-shaped 14-electron 3-coordinate intermediates. The presence of β-hydrogens on the residual alkyl chain produces a great acceleration of the rate (R = Me, $k_i = 0.0026$ s^{-1}; R = Et, $k_i = 44.9$ s^{-1}) as a consequence of the stabilization of the 3-coordinate [Pt(R)$(PEt_3)_2$]$^+$ transition state through an incipient agostic interaction. The results of this work, together with those of a previous paper, give a rationale of the "elusive" nature of these compounds. The following factors concur: (i) electron release by the phosphine ligands, (ii) steric repulsion and distortion of the square-planar configuration, and (iii) interaction of the metal with β-hydrogens.

Introduction

Platinum(II) monoorgano bis(phosphine) complexes of the type *cis*-[Pt(R)L_2X] (X = halo or pseudohalo group) show significant similarities or differences in their chemical behavior, depending upon the nature of the organic moiety bonded to the metal. When R is a phenyl or an aryl group, the compounds are fairly stable in nonpolar solvents, where their conversion into the corresponding trans isomers can be promoted by catalytic amounts of free ligand[1] or by photochemical activation.[2] In protic solvents the isomerization takes place spontaneously. The main features of the reaction mechanism involve dissociative loss of the coordinated halide group and the interconversion of two geometrically distinct T-shaped 14-electron cationic intermediates. This simple reaction scheme was substantiated by a number of studies of the relationship between structure and reactivity of these compounds.[3] Since the first recognition of 3-coordinate intermediates in the isomerization of *cis*-[Pt(*o*-tolyl)Cl$(PEt_3)_2$],[4] it has been found that coordinatively unsaturated species of this type are key intermediates in a number of other fundamental organometallic processes,[5] including thermal decomposition of mono- and dialkyl compounds,[6] olefin insertion into the Pt−H bond,[7] symmetrization reactions,[8] nucleophilic substitutions,[9] etc.

The pattern of behavior of monoalkyl bis(phosphine) complexes appears to be strictly similar to that of the corresponding

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⊗ Abstract published in *Advance ACS Abstracts,* October 15, 1997.

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S0020-1669(97)00490-4 CCC: $14.00

monoaryl compounds, except when the organic moiety contains β-hydrogens. The ethyl, *n*-propyl, and *n*-butyl derivatives isomerize at a much greater rate than the complexes containing alkyl groups with no β-hydrogens (CH_3 or $CH_2Si(CH_3)_3$),[10] and in addition to isomerization, they undergo β-hydride elimination through a concurrent pathway, yielding *trans*-$[Pt(H)X(PEt_3)_2]$ and olefins.[10,11]

Very little is known about the chemistry of the corresponding solvento complexes, a field in which we have a longstanding interest.[12] Some cationic solvento complexes of *trans* geometry have been known for many years, and their chemical relevance has been recognized in reactions of olefin insertion[13] or of thermal decomposition,[14] while cationic organoplatinum solvento complexes with monodentate tertiary phosphines that have a *cis* configuration are considered very labile species.[15] The usual preparative method of removing the chloride ligand from the *cis*-monoorganoplatinum chloride by silver salts leads exclusively to the formation of the *trans*-$[Pt(R)(PEt_3)_2(S)]^+$ complex. Such a difficulty can be overcome by reacting precursor dialkyl or mixed alkyl−aryl complexes of the type *cis*-$[Pt(R)(R')(PEt_3)_2]$ with the acid H^+A^- (A^- = unreactive counteranion).[16] Using this method, we were able to prepare and to characterize in methanol solution, at low temperature, a number of *cis*-$[Pt(Me)L_2(S)]^+$ complexes (L = an extended series of phosphines of widely different steric and electronic properties). The rates of isomerization were found to be strongly accelerated by the bulk and by the electron release of the phosphine ligands.[17]

This paper reports a thorough study of the proton, temperature, and pressure dependencies of the rates of protonolysis of the dialkyl complexes *cis*-$[PtR_2(PEt_3)_2]$ (R = Me, Et, Pr^n, Bu^n, $CH_2C(Me)_3$, $CH_2Si(Me)_3$) and of the mixed alkyl−aryl complexes *cis*-$[Pt(R)(R')(PEt_3)_2]$ (R = Ph, 2-MeC_6H_4, 2,4,6-$Me_3C_6H_2$; R′ = Me) in methanol and of the rates of *cis*−*trans* isomerization of the resultant transient solvento complexes. The aim of this work was to investigate the sensitivity of both processes to the nature of the bonded organic moiety (alkyl or aryl), its structure (linear or branched), and/or the availability of β-hydrogens. It was possible to measure independently the very fast rates associated with the complexes containing alkyl groups with β-hydrogens by use of rapid-scanning techniques. The measure of the volumes of activation in the two cases has been shown to be particularly diagnostic in assessing the mechanisms. The protonolysis involves a rate-determining bimolecular proton transfer to the substrate. Other specific features, such as the site of proton attack, remain speculative. The mechanistic picture of the isomerization process is completely clarified. The results of this study, together with those of a previous investigation,[17] shed light on the reasons why cationic organoplatinum(II) solvento complexes with monodentate tertiary phosphines having a *cis* configuration are very short-lived.

Experimental Section

Preparation of Complexes. All reactions were carried out under a dry, oxygen-free nitrogen atmosphere using standard Schlenk-tube techniques. Solvents were throughly dried over the appropriate reagents and freshly distilled prior to use. The dialkyl substrates *cis*-$[Pt(PEt_3)_2(R)_2]$ (R = methyl,[18] ethyl,[1] *n*-propyl,[6c] *n*-butyl,[10] neopentyl,[6f] (trimethylsilyl)methyl[10]) and the mixed alkyl−aryl complexes *cis*-$[Pt(R)(Me)(PEt_3)_2]$ (R = mesityl,[16] phenyl[16]) were prepared by literature methods. The purity and identity of the complexes were checked by elemental analysis and by ^1H and ^{31}P NMR spectroscopy. Elemental analyses were consistent with the theoretical formulas. Microanalyses were performed by Redox Analytical Laboratories, Milan, Italy.

***cis*-[Pt(2-MeC$_6$H$_4$)(Me)(PEt$_3$)$_2$].** Methyllithium in diethyl ether (6.0 cm^3, 0.5 M solution) was added dropwise to a suspension of *cis*-$[Pt(2\text{-}MeC_6H_4)Cl(PEt_3)_2]$ (0.2 g) in diethyl ether (40 cm^3) under an atmosphere of N_2. After 2 h of stirring at room temperature, the mixture was hydrolyzed with ice and water. The crude product isolated from the dried organic layer was crystallized from petroleum ether (at −15 °C) as a white compound, mp 80.0 °C. ^1H NMR ($CDCl_3$): δ 7.27 (m, $^3J_{HH}$ = 7.0 Hz, $^3J_{PtH}$ = 58.0 Hz, 1H, H_6), 6.95 (d, $^3J_{HH}$ = 7.7 Hz, 1H, H_3), 6.87 (dd, $^3J_{av}$ = 7.7 Hz, 1H, H_5), 6.79 (dd, $^3J_{av}$ = 7.7 Hz, 1H, H_4), 2.33 (s, 3H, 2-CH_3C), 1.80 (m, $^3J_{PtH}$ = 14.9 Hz, 6H, PCH_2CH$_3$), 1.49 (m, 6H, PCH_2CH$_3$), 1.13 (m, 9H, PCH$_2$CH_3), 1.00 (m, 9H, PCH$_2$CH_3), 0.23 (dd, $^2J_{PtH}$ = 67.0 Hz, 3H, CH_3Pt). ^{31}P NMR: δ 7.5 ($^2J_{PP}$ = 13 Hz, $^1J_{PtP}$ = 1718 Hz), 5.4 ($^2J_{PP}$ = 13 Hz, $^1J_{PtP}$ = 1900 Hz). Anal. Calcd for $C_{20}H_{40}P_2Pt$: H, 7.50; C, 44.69. Found: H, 7.43; C, 44.80.

Materials. Methanol for use in kinetic runs was obtained by purification of spectrophotometric grade methanol (Aldrich). Deuterated solvents for NMR measurements were used as received from Aldrich Chemical Co. All other chemical products were reagent grade materials and were used without further purification.

Instrumentation. ^1H and ^{31}P NMR spectra were obtained on a Bruker AMX R-300 spectrometer equipped with a broad-band probe operating at 300.13 and 121.49 MHz, respectively. ^1H chemical shifts were measured relative to the residual solvent peak and are reported in δ units downfield from Me_4Si. ^{31}P chemical shifts, in parts per million, are given relative to external phosphoric acid. The temperature within the probe was checked using the methanol or ethylene glycol method.[19] Slow reactions were carried out in a silica cell in the thermostated cell compartment of a Cary 219 or a Perkin-Elmer Lambda 5 spectrophotometer, with a temperature accuracy of ±0.02 °C. Fast reactions required the use of an Applied Photophysics Bio Sequential SX-17 MX stopped-flow ASVD spectrofluorometer. Rate constants were evaluated by the Applied Photophysics software package[20] and are reported as average values from five to seven independent runs. The kinetics at high pressure were followed by use of an HPSF-56 Hi-Tech high-pressure stopped-flow spectrophotometer equipped with a digital pressure indicator.[21] Kinetic runs were evaluated by use of the OLIS Model 4000 Data System Stopped-Flow, version 9.04, software.[22]

Kinetics. Since the dialkyl complexes appear to decompose slowly in methanol at room temperature, even in the absence of acid, fresh solutions of complex were used for all kinetic runs. Protonolysis reactions were followed under pseudo-first-order conditions with acid in excess. The drive syringes of the stopped-flow instrument were filled with solutions of the platinum complex and acid, respectively. In most of the kinetic runs the concentration of acid was regulated to produce

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Table 1. Selected ^{1}H NMR Data for Alkyl and Aryl Groups and ^{31}P NMR Resonances of the Triethylphosphine Ligand in *cis*-[Pt(R)(R′)(PEt$_3$)$_2$][a]

compd no.	R	R′	δ(^{1}H)[b]	δ(^{31}P)[c]
1	2,4,6-Me$_3$C$_6$H$_2$	CH$_3$	6.65, s, $H_{3,5}$; 2.34, s, *2,6*-CH_3C; 2.20, s, *4*-CH_3C; 0.20 (67.0), dd, CH_3Pt	8.2 (1751); 4.4 (1919)
2	2-MeC$_6$H$_4$	CH$_3$	7.27 (58.0), m, H_6; 2.33, s, *2*-CH_3C; 0.23 (67.0), dd, CH_3Pt	7.5 (1718); 5.4 (1900)
3	C$_6$H$_5$	CH$_3$	7.33 (55.0), m, $H_{2,6}$; 0.29 (68.0), m, CH_3Pt	7.1 (1741); 7.1 (1867)
4	CH$_3$	CH$_3$	0.40 (66.0), m, CH_3Pt	9.5 (1842)
5	C$_2$H$_5$	C$_2$H$_5$	1.23, q, CH$_3$CH_2Pt; 1.11, t, CH_3CH$_2$Pt	8.4 (1685)
6	*n*-C$_3$H$_7$	*n*-C$_3$H$_7$	1.41, m, CH$_3$CH$_2$CH_2Pt; 1.15, m, CH$_3$CH_2CH$_2$Pt; 0.96, t, CH_3CH$_2$CH$_2$Pt	8.7 (1699)
7	*n*-C$_4$H$_9$	*n*-C$_4$H$_9$	1.32, m, CH$_3$CH$_2$CH$_2$CH_2Pt + CH$_3$CH$_2$CH_2CH$_2$Pt; 1.16, m, CH$_3$CH_2CH$_2$CH$_2$; 0.89, t, CH_3CH$_2$CH$_2$CH$_2$Pt	8.6 (1705)
8	CH$_2$C(CH$_3$)$_3$	CH$_2$C(CH$_3$)$_3$	1.61, s, br, (CH$_3$)$_3$CCH_2Pt; 1.02, s, (CH_3)$_3$CCH$_2$Pt	−0.8 (1634)
9	CH$_2$Si(CH$_3$)$_3$	CH$_2$Si(CH$_3$)$_3$	0.37 (76.0), m, (CH$_3$)$_3$SiCH_2Pt; 0.01, s, (CH_3)$_3$SiCH$_2$Pt	5.4 (1996)

[a] Recorded in $CDCl_3$ as solvent at 298.2 K. [b] Chemical shifts (δ) in ppm relative to TMS. $^3J_{PtH}$, coupling constants, in Hz are given in parentheses. [c] Chemical shifts (δ) in ppm relative to H_3PO_4. $^1J_{PtP}$, coupling constants, in Hz are given in parentheses.

a large difference of rate between the two processes. Under these circumstances, using the same batch of reagents and regulating properly the scanning time of the instrument, it was possible to collect independently the spectral changes associated with protonolysis and the subsequent isomerization reaction. A fitting of the rate data to the equation for consecutive first-order reactions proved that the procedure followed was correct. Second-order rate constants for the protonolysis (k_H) at 298.2 K were obtained by least-squares regression analysis of the linear plots of the pseudo-first-order rate constants *vs* the concentration of acid. At other temperatures, the values of k_H were obtained from the ratio of the measured pseudo-first-order rate constants k_{obsd} to [H$^+$].

The slowest isomerization reactions of the solvento *cis*-[Pt(PEt$_3$)$_2$(R)(MeOH)]$^+$ complexes (R = *o*-tolyl, neopentyl, (trimethylsilyl)methyl) were followed spectrophotometrically by repetitive scanning of the spectrum at suitable times in the range 320−220 nm or at a fixed wavelength, where the absorbance change was largest. The complexes were generated *in situ* in a silica cell by adding with a syringe a prethermostated solution of *cis*-[Pt(PEt$_3$)$_2$(R)(Me)] to a methanolic thermostated solution of H$^+$BF$_4^-$. In all cases the concentration of acid was calculated to produce a very fast cleavage of the Pt−Me bond. All reactions obeyed a first-order rate law until well over 90% conversion. Rate constants k_i (s^{-1}) were obtained from a nonlinear least-squares fit of the experimental data to $A_t = A_\infty + (A_0 - A_\infty)\exp(-k_i t)$ with A_0, A_∞, and k_i as the parameters to be optimized (A_0 = absorbance after mixing of reagents, A_∞ = absorbance at completion of reaction). The rates of isomerization were independent of the amount of acid in solution.

Enthalpies and entropies of activation for protonolysis were derived from a linear least-squares analysis of $\ln(k_H/T)$ *vs* T^{-1} data. Likewise, enthalpies and entropies of activation for isomerization were derived from the temperature dependence of the first-order rate constants k_i (s^{-1}).

Kinetic runs at high pressure were followed using the procedure described. The drive syringes of the high-pressure stopped-flow instrument were filled with solutions of platinum complex and acid, respectively, the bomb was kept at 24.8 °C for approximately 30 min, and the kinetics were followed as a function of pressure between 0.1 and 200 MPa. Volumes of activation were obtained by a fit of the variable-pressure data to eq 1, where k_0 denotes the rate constant at zero pressure and 24.8 °C.

$$\ln k = \ln k_0 - \Delta V^{\ddagger} P/RT \qquad (1)$$

Results

The complexes *cis*-[Pt(R)(R′)(PEt$_3$)$_2$] were synthesized by literature methods and characterized by ^{1}H and ^{31}P NMR. A selection of the most relevant NMR peaks is reported in Table 1, and a complete assignment of the resonances is reported in Table S1 (Supporting Information). Satisfactory indications of the stereochemistry of both dialkyl and alkyl−aryl compounds came from their ^{31}P NMR spectra. The dialkyls **4**−**9** showed only one phosphorus resonance and the alkyl aryls **1**−**3** two resonances, with low values of $^1J_{PtP}$ coupling constants, typical of phosphorus atoms *trans* to carbon in platinum(II) complexes.

Cleavage of the Pt−C(alkyl) Bond. The selective cleavage of the Pt−C(alkyl) σ bond takes place according to the reaction

$$cis\text{-}[Pt(R)(R')(PEt_3)_2] \xrightarrow[MeOH]{H^+A^-} cis\text{-}[Pt(R)(PEt_3)_2(MeOH)]^+A^- + R'H \qquad (2)$$

The final *cis* product can be recognized by ^{31}P NMR, at low temperature (253 K), only when R is an aryl group or an alkyl group with no β-hydrogens (compounds **1**−**4, 8,** and **9**). Upon addition of a sufficient amount of an ethereal solution of HBF_4 to a solution of the platinum complex in a CD_2Cl_2/CD_3OD mixture (3:1 v/v) there is an immediate and sharp change of the spectrum. As a typical example, in the case of *cis*-[Pt(Me)(PEt$_3$)$_2$(MeOH)]$^+$, the two inequivalent phosphine ligands give two ^{31}P resonances, $\delta(P_A) = 25.5$ ($^1J_{PtP} = 1827$ Hz) and $\delta(P_B) = 8.9$ ($^1J_{PtP} = 4427$ Hz). Essentially the same pattern is observed when a moderate excess of acid is used and, therefore, the *cis* configuration is retained at 253 K, as a result of the Pt−C(alkyl) bond breaking. Attempts to detect the presence of possible alkylhydridoplatinum(IV) intermediates of the type [Pt(R)(Me)(H)X(PEt$_3$)$_2$], similar to those described recently in the literature for platinum compounds containing dinitrogen ligands,[23−25] were unsuccessful, even at lower temperatures. Thus, **4** was dissolved in CD_2Cl_2 and cooled to −78 °C before adding CD_3OD (CD_3OD:CD_2Cl_2 = 4:1). Subsequent addition of HBF_4 or HCl leads exclusively to the formation of *cis*-[Pt(Me)(PEt$_3$)$_2$(MeOH)]$^+$ or *cis*-[Pt(Me)Cl(PEt$_3$)$_2$], respectively. The same pattern of behavior is shown by the complexes **1** and **2**, the only difference being that protonolysis takes place at a lower rate than for **4**, with no evidence for buildup of any intermediate species.[26]

Spontaneous Isomerization of *cis*-[Pt(R)(PEt$_3$)$_2$(MeOH)]$^+$. When the temperature of the reaction mixture of **4** and HBF_4 is increased, the isomerization can be monitored through the decrease in the ^{31}P signals associated with *cis*-[Pt(Me)(PEt$_3$)$_2$(MeOH)]$^+$ and the parallel and matching increase in the ^{31}P signal of the corresponding *trans* complex, which appears at δ 25.9 with ^{195}Pt satellites ($^1J_{PtP} = 2817$ Hz). Therefore, the isomerization process is described by the reaction

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$$cis\text{-}[Pt(R)(PEt_3)_2(MeOH)]^+ \rightarrow trans\text{-}[Pt(R)(PEt_3)_2(MeOH)]^+ \quad (3)$$

The rate of *cis* to *trans* conversion was too fast to be followed by this method for the complexes containing alkyl groups with β-hydrogens (**5**−**7**) and, therefore, soon after the addition of acid, even at the lowest temperatures used, only the ^{31}P signals due to the *trans* isomers were observed. These latter compounds undergo a subsequent slow thermal decomposition leading to *trans*-$[Pt(H)(PEt_3)_2(MeOH)]^+$ and olefins.[14]

Spectrophotometric Studies. Typical spectral changes are shown in Figure 1 for the protonolysis of *cis*-$[Pt(Et)_2(PEt_3)_2]$ (upper plot) and the isomerization of the intermediate solvento complex *cis*-$[Pt(Et)(PEt_3)_2(MeOH)]^+$ (lower plot), obtained by rapid scanning spectrophotometry.

The pseudo-first-order rate constants k_{obsd} for reaction 2 are reported in Table S2 (Supporting Information) for a range of H^+ concentrations at 298.2 K. The addition of Cl^-, in some of the kinetic runs of complexes **2**, **8**, and **9**, had no influence on the rates but led to the formation of *cis*-$[Pt(R)Cl(PEt_3)_2]$ as the final product. Figure 2 (upper plot, compounds **4**−**7**; lower plot, compounds **2**, **8**, and **9**) shows that the k_{obsd} values are linearly dependent on proton concentration; *i.e.*, $k_{obsd} = k_H[H^+]$. The values of k_H at 298.2 K are given in Table 2. The values of k_H at different temperatures are set forth in Table S3 (Supporting Information), and the associated activation parameters are listed in Table 2. The pseudo-first-order rate constants k_i for reaction 3 at various temperatures are reported in Table S4 (Supporting Information). The values of k_i at 298.2 K, together with the associated activation parameters, are listed in Table 3. Figure 3 illustrates the pressure dependence of the protonolysis (upper plot, compounds **1**−**4** and **9**) and isomerization reactions (lower plot, compounds **1**, **5**, **6**, and **7**). The primary kinetic data are listed in Tables S5 and S6 (Supporting Information), and the derived volumes of activation are given in Tables 2 and 3, respectively.

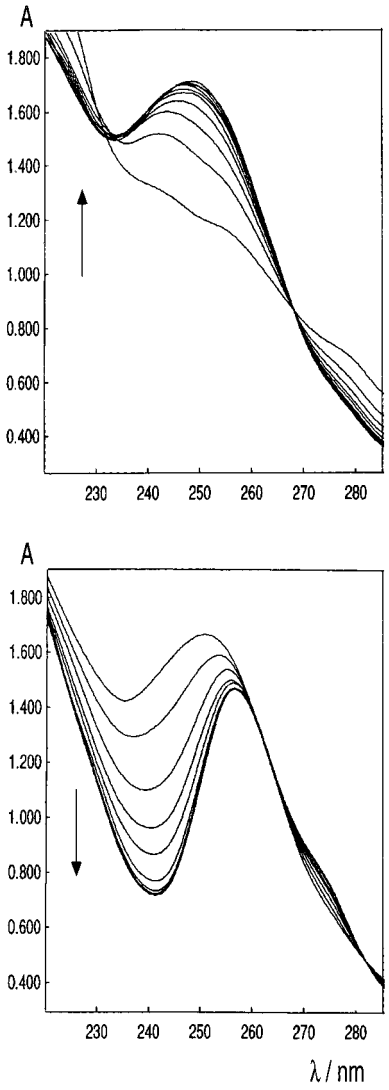


Figure 1. Upper plot: Spectral changes for protonolysis of *cis*-$[Pt(Et)_2(PEt_3)_2]$ in methanol ($T = 298.2$ K; $[H^+] = 1.0$ mM; time between consecutive spectra 0.001 25 s). Lower plot: spectral changes for isomerization of *cis*-$[Pt(Et)(PEt_3)_2(MeOH)]^+$ ($T = 298.2$ K; time between consecutive spectra 0.006 25 s).

Discussion

The aim in preparing the *cis*-$[Pt(R)(R')(PEt_3)_2]$ complexes listed in Table 1 was to study the effect of the R group (phenyl and aryls; linear and branched alkyls) on the rates of selective cleavage of the residual Pt−C (R′) bond by the proton and on the rates of isomerization of the intermediate *cis*-$[Pt(PEt_3)(R)(MeOH)]^+$ solvento complexes. We knew from previous studies[16] that for the dialkyl complexes the rate of proton attack was fast, at the limit of the conventional spectrophotometric techniques, and that the isomerization of the complexes with R = ethyl, *n*-propyl, and *n*-butyl was too fast to be followed by conventional spectrophotometry or NMR. We were also interested in measuring the complete set of activation parameters, including the volumes of activation. To the best of our knowledge, this is the first study of the pressure dependence of protonolysis of organometallic compounds and previous pressure data on the spontaneous isomerization of neutral *cis*-$[Pt(PEt_3)_2(R)X]$ complexes were interpreted in favor of an associative mechanism.[27]

Protonolysis. Attack of the proton at the metal-carbon bond results in the cleavage of this bond by the classical S_E2 mechanism, but the same product can be formed by attack at the metal leading to a labile Pt(IV) alkyl hydrido species via oxidative addition, followed by reductive elimination (S_E(oxidative) mechanism).[28] The nature of the highest occupied molecular orbital (HOMO), whether it is the M−C σ-bond or a nonbonding d orbital, can play a major role in determining

(26) Data from low-temperature NMR experiments are as follows: *cis*-$[Pt(PEt_3)_2(2\text{-}MeC_6H_4)(MeOH)](BF_4)$: ^1H NMR (CD_2Cl_2−CD_3OD at 195 K) δ 7.25 (m, 1H, H_6), 6.86 (m, 2H, H_3, H_5), 6.61 (m, 1H, H_4), 2.46 (s, 3H, 2-CH_3C), 1.69 (m, 6H, PCH_2CH_3), 1.52 (m, 6H, PCH_2CH_3), 1.10−0.96 (m, 18H, PCH_2CH_3); ^{31}P NMR δ 22.8 ($^2J_{PP}$ = 13 Hz, $^1J_{PtP}$ = 1657 Hz), 5.5 ($^2J_{PP}$ = 13 Hz, $^1J_{PtP}$ = 4420 Hz). *cis*-$[Pt(PEt_3)_2(2\text{-}MeC_6H_4)(Cl)]$: ^1H NMR (CD_2Cl_2−CD_3OD at 195 K) δ 7.17 (m, 1H), 6.81−6.72 (m, 3H), 2.31 (s, 3H, 2-CH_3C), 1.84 (m, 6H, PCH_2CH_3), 1.48 (m, 6H, PCH_2CH_3), 0.98 (m, 18H, PCH_2CH_3); ^{31}P NMR δ 13.9 ($^2J_{PP}$ = 17 Hz, $^1J_{PtP}$ = 1605 Hz), 6.0 ($^2J_{PP}$ = 17 Hz, $^1J_{PtP}$ = 4210 Hz). *cis*-$[Pt(PEt_3)_2(2,4,6\text{-}Me_3C_6H_2)(Cl)]$: ^1H NMR (CD_2Cl_2−CD_3OD at 195 K) δ 7.06 (m, 2H), 2.36 (s, 6H, 2-CH_3C), 2.08 (s, 3H, 4-CH_3C), 1.87 (m, 6H, PCH_2CH_3), 1.53 (m, 6H, PCH_2CH_3), 0.97 (m, 18H, PCH_2CH_3); ^{31}P NMR δ 14.7 ($^2J_{PP}$ = 17 Hz, $^1J_{PtP}$ = 1524 Hz), 3.2 ($^2J_{PP}$ = 17 Hz, $^1J_{PtP}$ = 4310 Hz).

(27) (a) van Eldik, R.; Palmer, D. A.; Kelm, H. *Inorg. Chem.* **1979**, *18*, 572. (b) Kelm, H.; Louw, W. J.; Palmer, D. A. *Inorg. Chem.* **1980**, *19*, 843. (c) Louw, W. J.; van Eldik, R.; Kelm, H. *Inorg. Chem.* **1980**, *19*, 2878. (d) van Eldik, R.; Palmer, D. A.; Kelm, H.; Louw, W. J. *Inorg. Chem.* **1980**, *19*, 3551.

(28) (a) Johnson, M. D. *Acc. Chem. Res.* **1978**, *11*, 57. (b) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978; pp 292−340. (c) Abraham, M. H. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier, Amsterdam, 1973; Vol. 12. (d) Eaborn, C. *J. Organomet. Chem.* **1975**, *100*, 43.

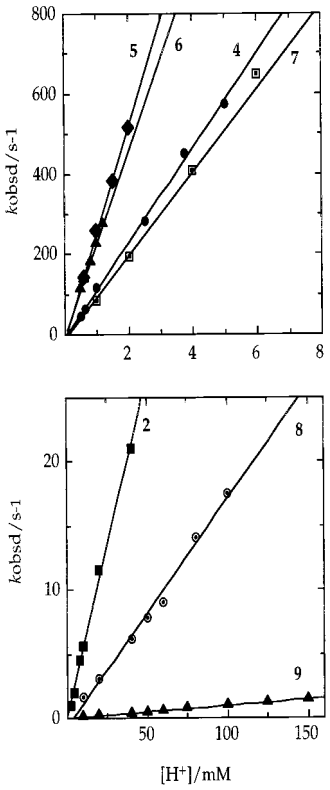


Figure 2. Dependence of the pseudo-first-order rate constants (k_{obsd}) on the proton concentration for the cleavage of the Pt−R′(alkyl) bond in *cis*-[Pt(R)(R′)(PEt_3)$_2$] complexes (in methanol, at 298.2 K). Numbers refer to the compounds as listed in Table 1.

the reaction pathway.[29] Previous investigations on the protonolysis of alkyl- and arylplatinum(II) compounds were based on the analysis of rate laws, isotope effects, competition experiments, and observed dependencies of the rates upon the structural properties of these organometallic compounds.[30] It is difficult to decide from kinetic evidence alone whether the attack of the proton commences at one or the other center, and it becomes impossible if the mechanism entails a rate-determining proton transfer. On the other hand, the detection of an alkylhydridoplatinum(IV) intermediate gives the most definitive evidence for the oxidative-addition mechanism.[23] The two alternate mechanisms that are thought to rationalize the diverse kinetic results reported so far for the protonolysis of Pt−C σ bonds within a unified picture are shown in Schemes S1 and S2 (Supporting Information), respectively. In Scheme S1 the proposed mechanism[30f] involves a fast preequilibrium (K) between the starting uncharged substrate and a halide ion, usually chloride, to form a platinum(II) anionic intermediate, combined with slow protonation and breakage of the metal−carbon σ bond of both the substrate (k_H) and the intermediate (k_{Cl}).

(29) (a) Yang, D. S.; Bancroft, G. M.; Bozek, J. D.; Puddephatt, R. J. *Inorg. Chem.* **1989**, *28*, 1. (b) Behan, J.; Johnstone, R. A. W.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun*. **1978**, 444. (c) Dong, D.; Slack, D. A.; Baird, M. C. *Inorg. Chem.* **1979**, *18*, 188. (d) Slack, D. A.; Baird, M. C. *J. Am. Chem. Soc.* **1976**, *98*, 5539.

(30) (a) Belluco, U.; Giustiniani, M.; Graziani, M. *J. Am. Chem. Soc.* **1967**, *89*, 6494. (b) Belluco, U.; Croatto, U.; Uguagliati, P.; Pietropaolo, R. *Inorg. Chem.* **1967**, *6*, 718. (c) Romeo, R.; Minniti, D.; Lanza, S. *J. Organomet. Chem.* **1979**, *165*, C36−C38. (d) Uguagliati, P.; Michelin, R. A.; Belluco, U.; Ros, R. *J. Organomet. Chem.* **1979**, *169*, 115. (e) Romeo, R.; Minniti, D.; Lanza, S.; Uguagliati, P.; Belluco, U. *Inorg. Chem.* **1978**, *17*, 2813. (f) Alibrandi, G.; Minniti, D.; Romeo, R.; Uguagliati, P.; Calligaro, L.; Belluco, U.; Crociani, B. *Inorg. Chim. Acta* **1985**, *100*, 107. (g) Alibrandi, G.; Minniti, D.; Romeo, R.; Uguagliati, P.; Calligaro, L.; Belluco, U. *Inorg. Chim. Acta* **1986**, *112*, L15. (h) Belluco, U.; Michelin, R. A.; Uguagliati, P.; Crociani, B. *J. Organomet. Chem.* **1983**, *250*, 565.

The bivariate rate law

$$k_{obsd} = \frac{k_H + k_{Cl}K[Cl^-]}{1 + K[Cl^-]}[H^+] \qquad (4)$$

can accommodate all the observed kinetic results (in particular the diverse halide ion dependence). The ease with which the halide adduct is formed and its reactivity dictate the particular form of the rate expression. Rate law 4 is consistent with a positive curvilinear dependence on [Cl$^-$],[30f] but reduced forms of eq 4 can explain a variety of other cases observed, including the linear dependence of the rate on [Cl$^-$],[30a,d] no influence of [Cl$^-$] on the rate, as in this work and in refs 16 and 30b,c,e, and eventually a [Cl$^-$] retardation on the rate.[30g]

Unmistakable evidence for the operation of a S_E2(oxidative) mechanism has been obtained recently by Stahl, Labinger, and Bercaw[23] for the protonolysis of [Pt(CH_2Ph)Cl(tmeda)], [$PtMe_2$(tmeda)] (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine), and *trans*-[PtMeCl(PEt_3)$_2$] through the detection of alkylhydridoplatinum(IV) intermediates by low-temperature ^{1}H NMR spectroscopy and hydrogen/deuterium exchange experiments. The various steps of the reaction pathway are shown in Scheme S2. Other complexes of the type [$PtMe_2$(N-N)] (N-N = 2,2′-bipyridine, 4,4′-di-*tert*-butyl-2,2′-bipyridine, 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline), at low temperature, undergo oxidative addition by HX to generate alkylhydridoplatinum(IV) species that, at higher temperatures, reductively eliminate methane to yield [PMeX(N-N)] complexes.[24,25]

From the body of evidence gathered so far, it appears that several factors, in particular the electron-donating ability of the ancillary ligands and the nature of the *trans*-activating group, can dictate the reaction pathway. We are inclined to think that the variety of effects observed in the kinetics for carbon−platinum bond cleavage via electrophilic attack, depending on very small structural changes imposed to the substrates, barely can be fitted within an unified mechanism (S_E2 or S_E(oxidative)). Rather, it would be better to try to distinguish two main categories of reactions: (i) those involving a rate-determining proton transfer either to the Pt−C σ-bond or to the metal and (ii) reactions where the important target of detecting an intermediate with an intact Pt−C bond can be achieved.

For the protonolysis of *cis*-[Pt(R)(R′)(PEt_3)$_2$] complexes we obtain no evidence for the presence of intermediates in the reaction and the kinetic analysis strongly indicates a rate-determining proton transfer. From the data in Table 2 it is possible to see that the rates of proton attack on the less sterically hindered dialkyl complexes (R = methyl, ethyl, *n*-propyl and *n*-butyl) are high and of comparable magnitude. The length of the alkyl chain, for both the *cis* and the leaving group, does not influence the rates. Therefore, in all these compounds (**4**−**7**) the Pt−C(alkyl) bond appears to be very labile and sensitive to easy attack by electrophiles. Increasing the steric bulk at the protonation site as for the compounds **8** and **9** provokes a very large decrease of the rate of protonolysis (on going from the di-*n*-propyl species **4** to the bis(trimethylsilyl)methyl compound **9**, a decrease in rate of 5 orders of magnitude is observed). A significant steric congestion at the transition state is indicated by the increase in the value of the enthalpy of activation ($\Delta H^{\ddagger}$ = 43 ± 3 and 66 ± 3 kJ mol^{-1} for **4** and **9**, respectively).

The proton attack at the mixed alkyl−aryl compounds cleaves the Pt−C(alkyl) bond selectively. The selective cleavage of a methyl group from *cis*-[PtMe(4-MeC_6H_4)(PMe_2Ph_2)$_2$] and *cis*-[PtMePh(PMe_2Ph_2)$_2$] has been taken as evidence for the S_E-

Table 2. Rate Constants and Activation Parameters for Protonolysis of the Pt-R′ (alkyl) Bond in *cis*-[Pt(R)(R′)(PEt_3)$_2$][a]

compd no.	R	R′	k_H[b]	$\Delta H^{\ddagger}$[c]	$\Delta S^{\ddagger}$[d]	$\Delta V^{\ddagger}$[e]
1	2,4,6-$Me_3C_6H_2$	CH_3	9.1 ± 0.8	64.9 ± 2	−9 ± 5	−10.3 ± 0.8
2	2-MeC_6H_5	CH_3	530 ± 26	33.3 ± 0.3	−81 ± 1	−9 ± 0.6
3	C_6H_5	CH_3	2380 ± 80	37 ± 1	−55 ± 3	−8.3 ± 0.3
4	CH_3	CH_3	118 000 ± 5000	43 ± 3	−5 ± 5	−13.1 ± 0.4
5	C_2H_5	C_2H_5	265 000 ± 10000	42 ± 1	−2 ± 5	
6	*n*-C_3H_7	*n*-C_3H_7	229 000 ± 2200	47 ± 2	+14 ± 4	
7	*n*-C_4H_9	*n*-C_4H_9	104 000 ± 9000	56.2 ± 0.5	+39 ± 2	
8	$CH_2C(Me)_3$	$CH_2C(Me)_3$	178 ± 14	62 ± 1	+6 ± 3	
9	$CH_2Si(Me)_3$	$CH_2Si(Me)_3$	9.8 ± 0.5	66 ± 3	−3 ± 8	−16.0 ± 0.4

[a] In methanol [complex] = 0.05−0.1 mM. [b] In M^{-1} s^{-1} at 298.2 K. [c] In kJ mol^{-1}. [d] In J K^{-1} mol^{-1}. [e] In cm^3 mol^{-1}.

Table 3. Rate Constants and Activation Parameters for the Geometrical Isomerization of *cis*-[Pt(R)(PEt_3)$_2$(MeOH)]$^+$ [a]

compd no.	R	k_{is}[b]	$\Delta H^{\ddagger}$[c]	$\Delta S^{\ddagger}$[d]	$\Delta V^{\ddagger}$[e]
1	2,4,6-$Me_3C_6H_2$	0.0153[f]	106 ± 3[f]	+75 ± 8[f]	+15.6 ± 0.8
2	2-MeC_6H_5	0.00527[f]	118 ± 1[f]	+106 ± 2	
3	C_6H_5	0.00474[f]	112 ± 3[f]	+84 ± 8[f]	
4	CH_3	0.00266[f]	106 ± 4[f]	+63 ± 12[f]	
5	C_2H_5	44.9	96.8 ± 0.2	+112 ± 1	+20.1 ± 1
6	*n*-C_3H_7	41.2	93.7 ± 3	+100 ± 15	+16.5 ± 0.5
7	*n*-C_4H_9	49.2	99.4 ± 3	+120 ± 15	+19.8 ± 2
8	$CH_2C(Me)_3$	0.0113	107 ± 5	+78 ± 15	
9	$CH_2Si(Me)_3$	0.0056	100 ± 2	+48 ± 6	

[a] In methanol [complex] = 0.05−0.1 mM. [b] In s^{-1}, at 298.2 K. [c] In kJ mol^{-1}. [d] In J K^{-1} mol^{-1}. [e] In cm^3 mol^{-1}. [f] From ref 15.

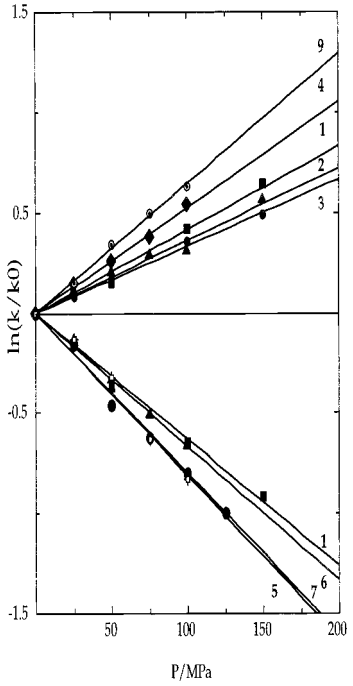


Figure 3. Upper plot: pressure dependence of the second-order rate constants k_H for the cleavage of the Pt−R′(alkyl) bond in *cis*-[Pt((R)-(R′)PEt_3)$_2$] complexes. Lower plot: pressure dependence of the pseudo-first-order rate constants (k_i) for isomerization of *cis*-[Pt(R)(PEt_3)$_2$-(MeOH)]$^+$ complexes. Numbers refer to the compounds as listed in Table 1.

(oxidative) mechanism.[31] In contrast, the fairly large value of the kinetic isotope effect for protonolysis of the methyl−platinum bond in *trans*-[PtMeAr(PEt_3)$_2$] ($k(H^+)/k(D^+) = 7$) has been interpreted as showing rate-determining proton transfer to the Pt−C σ bond with release of CH_4 in a three-center transition state.[30c] In the series of complexes **1**−**4** the rate of protonolysis decreases in the order Me ≫ Ph > *o*-tolyl > mesityl

(31) Jawad, J. K.; Puddephatt, R. S.; Stalteri, M. A. *Inorg. Chem.* **1982**, *21*, 332.

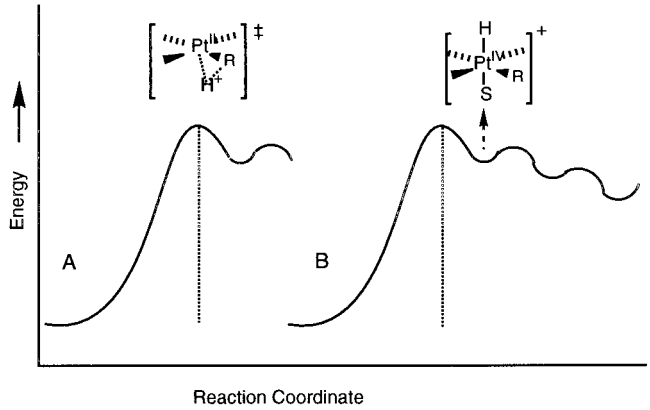
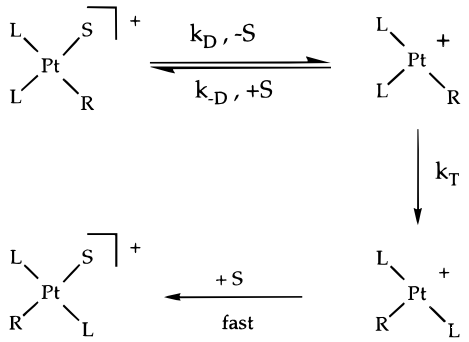


Figure 4. Alternative reaction profiles for the one-step proton transfer to the substrate in the protonolysis of *cis*-[Pt(R)(R′)(PEt_3)$_2$] complexes: (A) rate-determining attack at the Pt−C σ bond with release of alkane in a three-center transition state (S_E2 mechanism); (B) rate-determining formation of a solvent alkylhydridoplatinum(IV) intermediate, before dissociation of alkane.

and, therefore, shows the same pattern of behavior as observed for the dialkyls. The activation parameters along this series exhibit some irregularity. While complex **1** is characterized by values of enthalpy and entropy of activation comparable to those of compounds **8** and **9**, as expected on the basis of the encumbrance of the coordinated ligands (mesityl *vs* neopentyl and (trimethylsilyl)methyl), compound **2** seems to owe all its decrease in reactivity to a sharp decrease of the entropy of activation. We do not have a definite explanation for this particular deviation, but it is safe to conclude that steric effects both from *cis* and leaving groups hinder these reactions.

First-order dependence on the proton concentration and steric retardation are in keeping with both S_E2 and S_E(oxidative) mechanisms, and no distinction can be made on the basis of the rate law or the structural effects observed. However, the values of the activation volumes give an insight into the characteristics of the transition state. For all the compounds examined in this work (**1**−**4** and **9**) the natural logarithm of the rate of acidolysis was found to increase linearly with pressure (see Figure 3) and the values of the volumes of activation are negative, in agreement with the formation of a compact transition state. Negative volumes of activation (data in Table 2), together with the large isotope effect mentioned before, provide unmistakable evidence that the driving force of protonolysis is the rate-determining transfer of the proton to the substrate. At this stage, any discussion on the site of proton attack risks becoming semantic in nature. If the synchronous attack takes place at the Pt−C σ-bond (S_E2 mechanism), the energy profile has the form illustrated in Figure 4A, where the point of highest energy is a three-center transition state in which there is a considerable stretch of the Pt−C bond. This can still be the most likely pathway if the Pt−C σ bond is the highest occupied molecular orbital.[31] In the alternative energy profile

Scheme 1



(Figure 4B), for an S_E2(oxidative) mechanism, the rate-determining protonation of the metal leads to an alkylhydrido-platinum(IV) solvento intermediate of high energy, and the other points of minima along the profile are for the intermediates (5-coordinate species and σ complex) that are thought[23] to be involved in the following *fast* reductive elimination.

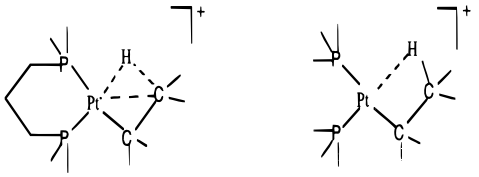
In conclusion, with dialkyl, *cis*- and *trans*-diaryl, and mixed aryl−alkyl phosphine complexes of platinum(II), the primary kinetic step in the reaction pathway is a one-step proton transfer to the substrate. In all these cases, the rate law is $k_{obs} = k_H[H^+]$ and halide ions have no influence on the rate. Whatever the site of proton attack is, the Pt−C σ bond or the metal, no reaction intermediates can be detected. When the phosphines are substituted with dinitrogen ancillary ligands, fast protonation of the metal is strongly favored and Pt(IV) intermediates are detected.[23−25]

Isomerization. A prerequisite for detecting transient species of the type *cis*-$[Pt(R)L_2(S)]^+$ (L = phosphine; R = alkyl or aryl; S = solvent) in solution is a fast breakage of the Pt−C bond of the precursor compounds. In order to fit this condition, the Pt−C bond must be that of an alkyl group, as for the *cis*-dialkyl or mixed alkyl−aryl compounds studied in this work. Acidolysis of diaryl compounds, as for *cis*-$[Pt(R)_2(PEt_3)_2]$,[30e] led ineluctably to the formation of *trans*-$[Pt(R)(S)(PEt_3)_2]^+$, since the rate of isomerization is faster than that of acidolysis, even when proton attack is carried out using large amounts of acid. The spontaneous conversion of *cis*-$[Pt(R)(PEt_3)_2(S)]^+$ can be conveniently followed by conventional or rapid-scanning spectrophotometry, once the preceding protonolysis process is over. The spectral changes in the UV region (Figure 1, lower plot) show well-defined isosbestic points, confirming that the two isomers are the only absorbing species in solution. The conversion is complete, the *trans* isomer is the only species at the end of the reaction, and the process follows a first-order rate law. For the compounds **5**−**7** thermal decomposition of the *trans* solvento complex follows at a much lower rate.[14]

An important feature of the isomerization is that the rates of the compounds with R = Me, neopentyl, (trimethylsilyl)methyl, Ph, *o*-tolyl, and mesityl are similar and appear to be almost insensitive to the nature (alkyl *vs* aryl) and to the steric bulk of the *cis* group. This is not a new finding, as far the sequence of Me, Ph, and mesityl complexes is concerned.[16] The trend of the steric effects is significantly different from that observed for bimolecular nucleophilic substitutions or even for the preceding bimolecular electrophilic attack by H^+, where the steric bulk of the *cis* group produces a decrease of 4−5 orders of magnitude in the rate.

The mechanism for isomerization in Scheme 1 assumes as the rate-determining step the dissociation of the solvent (S) from the *cis* solvento species (via k_D), followed by conversion of the T-shaped 3-coordinate 14-electron intermediate (via k_T) and fast re-entry of the solvent on the "*trans*-like" 3-coordinate intermediate. A rate law of the form $k_i = k_D/\{1 + (k_{-D}/k_T)[S]\}$ can be derived, in which the term $(k_{-D}/k_T)[S]$ measures the retardation due to the capture of the first intermediate by the bulk solvent. The mechanism is consistent with (i) mass-law retardation by [MeOH] in diethyl ether−methanol mixtures and (ii) high values of $\Delta H^{\ddagger}$ and largely positive values of $\Delta S^{\ddagger}$.[16] From the data in Table 3 it is possible to see that the complexes in which R = Et, Pr^n, and Bu^n isomerize at a much higher rate with respect to that of complexes containing alkyl groups with no β-hydrogens. For instance, the reactivity ratio k_i(Et)/k_i(Me) $= 1.7 \times 10^4$. The rate enhancement is much greater than that found in the isomerization of monoalkyl halo complexes of the type *cis*-$[Pt(PEt_3)_2(R)(Cl)]$, where the reactivity ratio k_i(Et)/k_i(Me) $= 7.5 \times 10^2$ was measured in 2-propanol.[10]

Chart 1



The chelating phosphine allows for retention of geometrical configuration.

Transient species :β -hydrogen interaction favours fluxionality

Inductive or steric effects cannot account for the large β-hydrogen kinetic effect. A specific interaction of these hydrogens with the metal must be responsible for the large enhancement of the rate of isomerization. The simplest way of envisaging this interaction comes from the structural characterization of a very interesting example of β-agostic interaction reported by Spencer, Orpen, *et al*.[32] In structure **A** the chelating ligand prevents isomerization (P-P = $(Bu^t)_2P(CH_2)_3P(Bu^t)_2$) and the platinum−hydrogen interaction is so extended as to favor the formation of a well-defined three-center−two-electron Pt−H−C bond. The structures of the 3-coordinate transition state and of the first transient cationic intermediate containing modentate phosphines, depicted as **B** in Chart 1, are expected to be similar to **A**, the only difference being related to the extent of Pt−H interaction, which is less than in **A**. However, this interaction satisfies partly the coordinative unsaturation of **B**, decreases its energy, and favors its fluxionality. A very low-energy barrier for the fluxionality of coordinatively unsaturated 3-coordinated species of this type was indicated by theoretical calculations.[7,33] The isomerization process is characterized by high values of enthalpy of activation and largely positive entropies and volumes of activation (Table 3). All these values are in contrast to and go in the opposite direction with respect to those of the one-step bimolecular electrophilic attack observed in the protonolysis (Table 2) and are perfectly in keeping with a dissociative mechanism, predicting an increase in disorder and in volume for the transition state with respect to the ground state.

Volumes of activation are composed of one intrinsic contribution, due to bond making or breaking in the activation process,

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and one solvational term: $\Delta V^{\ddagger} = \Delta V_{intr}^{\ddagger} + \Delta V_{sol}^{\ddagger}$.[34] In the present system the observed volumes of activation reflect primarily intrisic changes, since there is no net change in ionic charge in the activation process. All these values are positive, corresponding to an overall expansion, as expected for a process dominated by bond breaking. The differences among the values of $\Delta V^{\ddagger}$ in Table 3 do not seem particularly notable (for instance the differences of $\Delta V^{\ddagger}$ for R = mesityl and R = Pr^n are within experimental errors), and therefore it must be concluded that the nature of the *cis* group does not play a significant role in controlling the volumes of activation, even though electronic effects from the *cis* group, such as the β-hydrogen effect, can be of crucial importance in controlling the rates.

We can implement the knowledge of these systems by referring to the results of a recent kinetic study of the *cis* to *trans* isomerization of the cationic solvento species $[PtL_2(Me)(MeOH)]^+$ (L = an extended series of phosphines of widely different steric and electronic properties),[17] where we were interested in searching for a correlation between the lability of bis(phosphine) monoalkyl solvento complexes of *cis* geometry and the nature of the coordinated phosphines. The values of the rate constants for isomerization were found to increase with increasing basicity and size of the "spectator" phosphine ligands. These rates were resolved quantitatively into steric and electronic contributions of the phosphine ligands, by means of correlations with parameters which reflect their σ-donor ability and size. Inductive effects stabilize the flexible 3-coordinate T-shaped 14-electron transition state, and steric effects destabilize the rigid 4-coordinate square-planar ground state.

Conclusions

Steric effects and negative volumes of activation for the protonolysis reactions strongly support a rate-determining proton transfer to the substrate. Two alternative mechanisms can be envisaged, according to the rate law: (i) a synchronous attack by the electrophile H^+ at the Pt−C σ bond with formation of a three-center transition state or (ii) a multistep mechanism involving slow oxidative addition by H^+A^- on the metal, followed by *fast* reductive elimination. These features are not compatible with the detection of reaction intermediates. Complexes of the type *cis*-$[Pt(R)(L)_2(S)]^+$ are "elusive" species that can be intercepted only upon fast selective proton attack on the Pt−C(alkyl) bond of dialkyl or mixed alkyl−aryl precursor compounds. The instability of the cationic monoorgano solvento complexes stems from their spontaneous conversion into the corresponding *trans* isomers. The mechanism is *dissociative*, as supported by positive entropies and volumes of activation. The velocity of the geometrical isomerization depends dramatically upon the nature of the ancillary ligands. The following factors concur: (i) electron release by the phosphine ligands,[17] (ii) steric repulsions and distortion of the square-planar configuration,[17] and (iii) interaction of the metal with β-hydrogens.

Acknowledgment. Financial support from the Ministero Università Ricerca Scientifica Tecnologica, the Consiglio Nazionale Ricerche, the Swedish Natural Science Research Council, and the K. and A. Wallenberg Foundation is gratefully acknowledged.

Supporting Information Available: Tables listing ^1H and ^{31}P NMR resonances of compounds **1**−**9** and observed first-order rate constants for protonolysis of **1**−**9** as a function of $[H^+]$, temperature, and pressure, and for isomerization as a function of temperature and pressure and alternate reaction schemes for protonolysis (9 pages). Ordering information is given on any current masthead page.

IC9704905

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