The Mechanism of Thermal Decomposition of trans-Chloroethylbis(triethylphosphine)platinum(II)\(^{1}\)

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The thermal decomposition of trans-chloroethylbis(triethylphosphine)platinum(II) (L\(_2\)PtEtCl\(_2\), 1) in cyclohexane solution at 158 °C yields trans-chlorohydridobis(triethylphosphine)platinum(II) (3) and ethylene. The most probable rate-limiting step for this reaction is dissociation of ethylene from a five-coordinate 18-electron platinum(II) intermediate, L\(_2\)PtHCl(C\(_2\)H\(_5\)) (2). Three pathways might be involved in the formation of 2 from 1 (Scheme I): \(\beta\)-hydride elimination proceeding directly from 1 without prior dissociation of phosphine or chloride; phosphine dissociation, reversible \(\beta\)-hydride elimination, and phosphine reassociation; or chloride dissociation, reversible \(\beta\)-hydride elimination, and chloride reassociation. Presently available evidence does not distinguish between these three pathways. The conversion of 1 to 3 and ethylene has Arrhenius activation parameters \(E_a = 34 \text{ kcal/mol and } \log A = 13\). The reaction is effectively irreversible at low to moderate conversions, when ethylene concentrations in solution are low. At high conversions, the reverse reaction (3 + ethylene \(\rightarrow\) 1) is significant. The equilibrium constant for 1 \(\rightarrow\) 3 + ethylene was measured as a function of temperature giving \(K_{eq}(158 ^\circ \text{C}) = 0.69 \text{ M, } \Delta G^\circ(158 ^\circ \text{C}) = 0.32 \text{ kcal/mol, } \Delta H^\circ = 12 \text{ kcal/mol, and } \Delta S^\circ = 27 \text{ eu.}\) The deuterium equilibrium isotope effect for the reaction L\(_2\)PtCl(C\(_2\)H\(_5\))(D\(_2\)) \(\rightarrow\) L\(_2\)PtH(D) + C\(_2\)H\(_5\)(D\(_2\)) is \(K_{eq}(D)/K_{eq}(H) = 1.9 \pm 0.4;\) the deuterium kinetic isotope effect on the overall rate of decomposition of L\(_2\)PtCl(C\(_2\)H\(_5\))(D\(_2\)) under conditions in which the reverse reaction is slow is \(k_H/k_D = 2.5 \pm 0.2.\) The rate of reaction increases slightly with increasing concentration of phosphine and chloride ion (as benzylidimethyltetradecylammonium chloride) and with solvent polarity. Intermolecular exchange of phosphine ligands between platinum centers occurs within 30 min at room temperature in cyclohexane solution (measured by observing the NMR spectrum of mixtures of L\(_2\)PtEtCl and (L-d\(_{1}\))\(_2\)PtEtCl); halide ion exchange between L\(_2\)Pt(C\(_2\)H\(_5\))Cl and L\(_2\)Pt(C\(_2\)D\(_3\))Br is also observed within 30 min under these conditions.

Introduction

The transformation of metal alkyls to metal hydrides and olefins by \(\beta\)-hydride elimination is an important process in organometallic chemistry,\(^{3,4}\) but because the \(\beta\)-hydride elimination step is itself rarely rate limiting, this process remains incompletely understood mechanistically.

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Fifteen years ago, in one of the first studies of a mechanism involving β-hydride elimination, Thompson and co-workers studied the thermal decomposition of liquid (melted) trans-(Et₂P)₂Pt(C₂H₅)Br to L₂PtH(Br) and isotopically scrambled ethylene at 160-180 °C and proposed a mechanism in which reversible β-hydride elimination was followed by rate-limiting olefin loss.¹⁰ We have investigated the mechanism of thermal decomposition of the complex trans-(Et₂P)₂PtEtCl (I) (chosen instead of the analogous bromide because it is easier to prepare and purify) in cyclohexane solution. This reaction is mechanistically interesting for several reasons:

1. cis-Dialkylbis(trialkylphosphine)platinum(II) complexes decompose in hydrocarbon solutions containing no added phosphine by mechanisms in which phosphine dissociates from platinum before β-hydride elimination or γ-hydride activation occurs.¹¹⁻¹⁴ We anticipated that L₂PtEtCl would also dissociate phosphine before it underwent β-hydride elimination and wished to examine the influence of the effective electrophilicity of the platinum center on the rate of reaction.

2. Thorn and Hoffmann's molecular orbital investigations of olefin insertion into metal hydrides¹⁵ suggested that trans-(Et₂P)₂PtEtBr should have a high barrier to direct decomposition to a five-coordinate complex by β-hydride elimination and predicted a mechanism in which a ligand (phosphine or halide) would dissociate prior to β-hydride elimination. We wished to verify this prediction.

3. If the mechanism proposed by Thompson were followed in the decomposition of I, β-hydride elimination might be made to be rate limiting by proper choice of phosphine or halogen. The activation parameters of a reaction in which rate-limiting β-hydride elimination occurred directly, without prior phosphine dissociation, would be valuable in understanding this important elementary reaction.

This paper describes the thermal decomposition of trans-chloroethylbis(triethylphosphine)platinum(II) in cyclohexane solution. The available evidence is consistent with a rate-limiting transition state having elemental composition [L₂PtHCl(C₂H₄)]. A plausible rate-limiting step for the decomposition of I is loss of ethylene from a five-coordinate intermediate of structure 2 or similar processes in which ethylene is displaced from fourcoordinate species 4 or 5 (Scheme I). Three plausible and presently indistinguishable classes of mechanisms exist for conversion of 1 to 2: those involving direct reversible β-hydride elimination from four-coordinate 1 yielding five-coordinate 2; those involving phosphine dissociation from 1, reversible β-hydride elimination, and phosphine reassociation yielding 2; and those involving chloride ion dissociation from 1, reversible β-hydride elimination, and chloride ion reassociation. Throughout this paper, the platinum complexes will be named by reference to trans-chloroethylbis(triethylphosphine)platinum(II) (1, L₂PtEtCl). Thus, for example, trans-chloro(ethyl-d₅)bis(triethylphosphine)platinum(II) will be called L₂Pt(C₂D₅)Cl or L-d₅. Many of the studies of kinetics of decomposition were carried out in solutions containing added triethylphosphine, L. We use the term [L] to refer to the concentration of L in solution due to this added triethylphosphine.

Results and Discussion

Products. A 0.08 M solution of L₂PtEtCl in cyclohexane, n-hexane, or THF decomposes on heating in a sealed NMR tube for 3.5 h at 158 °C and yields L₂PtHCl (identified by ¹H and ¹³C NMR spectroscopy) and free ethylene (by ¹H NMR). The solutions containing products of decomposition are colorless and homogeneous. Solutions obtained by decomposition of L₂PtEtCl in n-hexane containing added triethylphosphine (0.20 M ≤ [L] ≤ 2.0 M) are also colorless and homogeneous while at elevated temperature but when cooled to 0 °C form cloudy white precipitates. These precipitates redissolve spontaneously if the solutions are left at 0 °C for 15 min and remain in solution even at -42 °C. As the thermolysis reaction
Figure 2. Free energy ($\Delta G^\circ$) for the thermal decomposition of L$_2$PtEtCl to L$_2$PtHCl and C$_2$H$_4$ (soln) in cyclohexane plotted as a function of temperature: 1.5-3.8 equiv of ethylene added; [L$_2$PtEtCl]$_0$ = 0.08-0.13 M; solution volume = 1.0 mL; total NMR tube inner volume = 2.0 mL. The concentration of ethylene in solution (mole/liter) used to calculate $K_w$ and $\Delta G^\circ$ was 0.06-0.16 M at 158°C. Error bars represent 95% confidence limits for each value of $\Delta G^\circ$.

progresses, a signal attributable to L$_2$PtHCl does not appear in the $^{31}$P NMR spectrum for these samples; instead, the resonance of free phosphine broadens and moves to lower field while that of L diminishes in intensity. Low-temperature $^{31}$P and $^1$H NMR studies suggest that L$_2$Pt-HCl reacts with phosphine and gives 6 and/or 7 (eq 1). We suggest that the ionic complex 7 precipitates during the ice-water quench and then converts to the more soluble, covalent 4 at the lower temperature.

$$L + L_2PtHCl \rightarrow L_3PtCl \rightarrow L_3PtH_+Cl^- \quad (1)$$

Kinetics. The disappearance of L$_2$PtEtCl$^\dagger$ in cyclohexane solution (0.5 mL) in a sealed NMR tube (~2.0 mL total internal volume) is first order in L$_2$PtEtCl for 3.8 half-lives (Figure 1). We demonstrate below that the falloff in rate beyond this point reflects establishment of equilibrium between 1, 3, and ethylene. The rate expression for the first-order thermal decomposition of L$_2$PtEtCl by any of the mechanistic pathways listed in Scheme I is

$$-d[L_2PtEtCl]/dt = k^{\text{obs}}[L_2PtEtCl]$$

Equilibrium Studies. The equilibrium constants for the decomposition of 1 to 3 and ethylene were measured at four different temperatures. These experiments were run by using sufficiently concentrated solutions (0.08-0.13 M) that enough L$_2$PtEtCl was present at equilibrium to measure accurately by $^{31}$P NMR spectroscopy. (The initial concentration of 1 present in these experiments was 2-3 times greater than in kinetic experiments, the solution volume was doubled so that the ethylene concentration in solution would be higher than in kinetic experiments, and several equivalents of ethylene were added.) A plot of $\Delta G^\circ$ as a function of temperature (Figure 2) produced these thermodynamic parameters: $K_w(158^\circ C) = 0.69 \pm 0.09$ M; $\Delta G^\circ(158^\circ C) = 0.32 \pm 0.12$ kcal/mol; $\Delta H^\circ = 12 \pm 0.6$ kcal/mol; $\Delta S^\circ = 27 \pm 1.3$ eu.$^{15}$

The difference in the bond energies of the platinum-hydrogen bond of 3 and the platinum-carbon bond of 1 was estimated from the enthalpy of reaction and known bond energies: $D_{Pt-H} - D_{Pt-C} = 23 \pm 5$ kcal/mol.$^{19,21}$ The assumption in this estimation—that the bond energies of Pt-L and Pt-Cl bonds are constant in going from 1 to 3—is obviously an approximation.

Figure 3. Rate constant $k^{\text{obs}}$ for the thermal decomposition of L$_2$PtElCl plotted as a function of triethylphosphine concentration ([L$_2$PtElCl]$_0$ = 0.05 M; $T = 158^\circ C$): D, reaction conducted in cyclohexane, $^{31}$P NMR probe temperature = 13°C; , reaction conducted in n-hexane, $^{31}$P NMR probe temperature = -34°C.

Effects of Phosphine Concentration on Rate. L$_2$PtElCl (0.05 M) was allowed to decompose at 158°C in solutions of n-hexane and cyclohexane which contained 0.0-2.0 M added triethylphosphine. Figure 3 plots the first-order rate constants for these thermal decompositions. The rate constant increases slightly over the range of phosphine concentrations for both solvents. These results rule out a mechanism for thermal decomposition of 1 in which phosphine dissociates and remains dissociated during the rate-limiting step. We attribute the slight rate increase observed upon addition of phosphine to increasing polarity in the medium, but we have not excluded some other involvement.

Exchange Broadening of the $^{31}$P NMR Spectrum of L$_2$PtEtCl. The $^{31}$P NMR signal of L$_2$PtEtCl in cyclohexane broadens on addition of triethylphosphine at 30°C. The line broadening increases with increasing concentration of phosphine and with increasing temperature. We interpret these effects as evidence that free L and L bonded to platinum are in rapid equilibrium. We suggest that the chloride ligand in L$_2$PtEtCl makes the platinum atom sufficiently electrophilic to add another phosphine (eq 3). In contrast the $^{31}$P signals of cis-(Et$_3$P)$_2$PtEl$_2$ and

$$\text{cis-}L_2PtElCl \rightarrow L_2PtElCl + L_3PtCl \rightarrow L_2PtElCl + L_3PtCl$$

(18) Error limits are reported at 95% confidence levels.

(19) The estimate of the difference in Pt-H and Pt-C bond energies was obtained by using this relation

$$D_{Pt-H} - D_{Pt-C} = D_{CH} - D_{HC} - \Delta H^\circ$$

(16) The rate of decomposition of L$_2$PtElCl was followed by $^{31}$P spectroscopy as described in the Experimental Section.

(17) We note that $K_w$ was calculated by using the observed concentration of ethylene in cyclohexane (mole/liter) and did not take into account ethylene in the vapor phase.

(19) The estimate of the difference in Pt-H and Pt-C bond energies was obtained by using this relation

$$D_{Pt-H} - D_{Pt-C} = D_{CH} - D_{HC} - \Delta H^\circ$$


(22) To emphasize how slightly the reaction rate is affected by the addition of phosphine, we note that the thermal decomposition of 1 is 1.7 times faster in cyclohexane than in n-hexane. We attribute this slight rate increase to the higher dielectric constant of cyclohexane ($\epsilon = 2.02$) than of n-hexane ($\epsilon = 1.89$). This same rate difference is observed as between n-hexane solutions which are 0.00 and ~1.2 M in B$_2$P.

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Dielectric constant. This holds true in cyclohexane as well, since this solvent has a lower boiling point. We assume that this holds true in cyclohexane as well, since this solvent has a lower dielectric constant.

These increases suggest that the rate-limiting transition state is not dependent on the concentration of unchanged starting material. The presence of added chloride ion in these solutions on adding the quaternary ammonium chloride is unclear, since this compound may be ion paired and aggregated. The conclusion is consistent with bromine quench experiments of ethyl and ethylene-d₃ in solution directly. Here we

The essentially statistical isotopic scrambling observed in the ethyl bromide (reflecting scrambling in recovered starting material) and the observation of significant quantities of ethylene-d₄ establish that β-hydride elimination in L₂PtCl is rapid and reversible. The absence of ethylene-d₄ and ethylene-d₃ demonstrates that reaction of free ethylene with L₂PtH(C₂H₅)Cl is not important under these conditions.

The deuterium equilibrium isotope effect for the thermal decomposition of L₂Pt(C₆H₅)Cl vs. L₂Pt(C₆H₅)Br was measured by allowing separate samples of each compound to react in sealed tubes having the same ratio of volumes of liquid and vapor phases and containing the same concentration of organoplatinum complex to reach equilibrium (eq 4 and 5). It is difficult to measure the concentration of ethylene in solution accurately rather than slow the rate of decomposition of 1. We attribute the small increase in rate observed on addition of chlorine ion, or on substitution of cyclohexane for THF, to an increase in solvent polarity. These increases suggest that the rate-limiting transition state for decomposition of 1 is more polar than the starting material.

### Table I. Effect of the Concentration of Chloride Ion on the Rate of Decomposition of 1

<table>
<thead>
<tr>
<th>solv</th>
<th>[Cl] M</th>
<th>10⁻⁶ s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₅CH₃</td>
<td>0.00</td>
<td>1.32 ± 0.02</td>
</tr>
<tr>
<td>THF/CH₂Cl₂ (1:1)</td>
<td>0.00</td>
<td>2.00 ± 0.04</td>
</tr>
<tr>
<td>THF</td>
<td>0.00</td>
<td>3.08 ± 0.10</td>
</tr>
<tr>
<td>THF/CH₂Cl₂</td>
<td>0.092</td>
<td>3.8 ± 0.2</td>
</tr>
<tr>
<td>THF</td>
<td>0.20</td>
<td>4.8 ± 0.2</td>
</tr>
<tr>
<td>THF</td>
<td>0.30</td>
<td>6.7 ± 0.2</td>
</tr>
<tr>
<td>THF</td>
<td>0.40</td>
<td>9.0 ± 0.2</td>
</tr>
</tbody>
</table>

α Decompositions were carried out starting with solutions containing 0.08 M 1 and 0.08 M (EtO)PO at 158.5 °C. Chloride was introduced as benzylidimethyltetradecylammonium chloride.

**Intermolecular Exchange of Halogen Ligands.** A solution of L₂PtCl (0.08 M) and L₂PtCl (0.07 M, L₁ = L₂PtCl) in cyclohexane underwent phosphine exchange and gave an equilibrium mixture of L₂PtCl, L₂PtCl, and L₂PtCl within ~30 min at room temperature. Because this intermolecular phosphine exchange is faster than thermal decomposition of 1, it is not possible to exclude a mechanism for the decomposition that requires reversible dissociation/reassociation of phosphine before the rate-limiting transition state.

**Effect of Chloride Ion Concentration on Rate.** One plausible mechanism for the decomposition of 1 involves chloride ion dissociation followed by a rate-limiting step in which chloride remains dissociated. To test this possibility, L₂PtEtCl was allowed to decompose in THF solutions containing several different concentrations of benzylidimethyltetradecylammonium chloride. Rates were cleanly first order to >97% disappearance of 1 and increased slightly with increasing chloride ion concentration (Table I). A comparison of rate constants for decompositions in cyclohexane, THF, and THF/cyclohexane (1:1), all containing no added chloride ion, showed a similar small increase. These experiments exclude mechanisms in which chloride ion dissociates from L₂PtEtCl and remains dissociated during the rate-limiting step,26 since for such mechanisms, the reaction rate would be expected to decrease with increasing chloride concentration. Instead, the rate increased, albeit only by a factor of 2.6, as the concentration of added chloride ion increased from 0.0 to 0.40 M. The extent of the increase in thermodynamic activity of chloride in these solutions on adding the quaternary ammonium chloride is unclear, since this compound may be ion paired and aggregated. The conclusion is, however, clear: the presence of added chloride ion in solution accelerates rather than slows the rate of decomposition of 1. We attribute the small increase in rate observed on addition of chloride ion, or on substitution of cyclohexane for THF, to an increase in solvent polarity. These increases suggest that the rate-limiting transition state for decomposition of 1 is more polar than the starting material.

### Table II. Isotopic Scrambling in Ethylene from Thermal Decomposition of L₂Pt(C₂H₅)Cl and of Ethyl-d₃ Bromide Derived from Recovered Starting Material

<table>
<thead>
<tr>
<th>no. of half-lives</th>
<th>ethylene-d₄/d₃</th>
<th>ethyl bromide H₃/H₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8/92</td>
<td>9/91</td>
</tr>
<tr>
<td>1</td>
<td>14/86</td>
<td>12/88</td>
</tr>
<tr>
<td>2</td>
<td>16/84</td>
<td>20/80</td>
</tr>
</tbody>
</table>

α L₂Pt(C₂H₅)Cl was thermalized at 158.5 °C in cyclohexane. Since isotope effects caused the kinetics of these reactions to deviate from first-order, the number of half-lives are approximate. All values are averages of at least two experiments. A statistical distribution would be 40:60. ([L], M).

**Intermolecular Exchange of Halogen Ligands.** A mixture of L₂PtCl (0.054 M) and L₂Pt(C₆H₅)Br (0.055 M) in cyclohexane exchanged halogen atoms and yielded an equilibrium mixture of L₂PtCl, L₂PtCl, and L₂PtBr, and L₂Pt(C₆H₅)Br in less than ~20 min at room temperature. A less concentrated solution of L₂PtCl (0.028 M) and L₂Pt(C₆H₅)Br (0.027 M) took ~40 min to achieve equilibrium at room temperature. The course of the reaction was followed by 3¹P NMR spectroscopy. These experiments only demonstrate that mechanism 3 in Scheme I cannot be ruled out, since halogen exchange may occur by dissociation of chloride or bromide. We consider it more likely, however, that exchange of halogen atoms occurs by a bimolecular pathway since the rate of exchange increases with increasing concentration of reactants.
Table III. Deuterium Isotope Effects and Equilibrium Data for Conversion of 1 to 3 and Ethylene

| $k_{1-d_5}^{obsd}/k_{1-d_5}^{obsd}$ ([L] = 0 M) | $2.5 \pm 0.2^a$ |
| $k_{1-d_5}^{obsd}/k_{1-d_5}^{obsd}$ ([L] = 0.60 M) | $2.5 \pm 0.8$ |
| $K_{eq}^{H}$ | 1.9 $\pm$ 0.4 |
| $K_{eq}^{D}$ | $0.69 \pm 0.09$ |
| $\Delta G^o(158^oC)$ | $0.32 \pm 0.12$ kcal/mol |

*All values were determined at 158 °C and are reported to 95% confidence levels. This value is an average of four independent experiments, including only one value in which 1-ds and 1-d5 were in the same NMR tube. trans-(Et3P)2Pt(C2H5)Cl vs. trans-(Et3P)2Pt(C2D5)Cl.*

Assume that the concentrations of ethylene and ethylene-d4 were proportional, with the same proportionality constant, r, to the concentrations of 3 and 3-d1 (eq 6). The concentration:

$$\frac{[C_2H_4]}{[3]} = r = \frac{[C_2D_4]}{[3-d_1]}$$

(6)

centrations of 1, 1-ds, 3, and 3-d1 at equilibrium can be calculated from the initial concentrations of 1 or 1-ds and by comparing their initial and equilibrium 31P NMR peak heights with those of (EtO)2PO (an internal standard for integration). Assuming the correctness of eq 6, the equilibrium deuterium isotope effect for decomposition of 1 (1-ds) at 158.5 °C is given by eq 7. This value is probably not highly accurate, but the principal conclusion from it—that there is a substantial deuterium equilibrium isotope effect favoring decomposition of the entirely protonated species—is undoubtedly correct.

This equilibrium isotope effect is probably determined by two opposing effects. In going from 1 (r-c-H 2951-2857 cm$^{-1}$) to 3 (r-c-H 2198 cm$^{-1}$) and ethylene (r-c-H 3080, 2972 cm$^{-1}$) one stretching vibration is created having substantially lower frequency and four with slightly higher frequencies. The bending vibrations probably shift in similar directions. The magnitude of the isotope effect suggests that the change in frequency from an aliphatic C-H bond to a Pt-H bond dominates the isotope effect. A crude calculation of this isotope effect, based only on stretching vibrations, gives a value in qualitative agreement with the observed value. The deuterium isotope effects and equilibrium data for conversion of 1 to 3 and ethylene are summarized in Table III.

The conversion of (C5Me5)Rh(PMe3)(C6H4)D to (C5Me5)Rh(PMe3)(C2D4)D also gives a substantial equilibrium isotope effect: $K_{eq}^{H}/K_{eq}^{D} = 2.7$. Here again, the change in frequency from a C-H bond to a M-H bond probably determines the isotope effect. In this case, however, the C-H bond has a slightly higher frequency (r-c-H 3030 cm$^{-1}$) and the effect is not diminished by the formation of four ethylene C-H bonds. These differences are probably important in determining the greater magnitude of this equilibrium isotope effect.

The deuterium kinetic isotope effect was determined by comparing the rates of thermal decomposition of L2-Pt(C2H5)Cl and L2Pt(C2D5)Cl in separate experiments and, as a check, by competitive decompositions of these two compounds in the same tube (Figure 4). The value obtained, $k_{H}^{obsd}/k_{D}^{obsd} = 2.5 \pm 0.2$, is apparently slightly larger than the equilibrium isotope effect, but the uncertainties in the two numbers are such that the difference between them may not be statistically significant. The deuterium kinetic isotope effect measured in solutions containing added phosphine ([L] = 0.60 M) does not differ significantly from the value obtained in the absence of added phosphine, although the uncertainty is large: $k_{H}^{obsd}/k_{D}^{obsd} = 2.5 \pm 0.8$. We rationalize this kinetic isotope effect in much the same way as we rationalized the equilibrium isotope effect. The isotopic scrambling experiments indicate that $\beta$-hydride elimination occurs before the rate-limiting step and is reversible; the absence of a rate depression upon addition of chloride ion or phosphine to reaction mixtures indicates that the chloride and both phosphines are bound to platinum during the rate-limiting transition state. Thus, the most plausible rate-limiting transition state is that in which ethylene leaves from a five-coordinate complex of the structure L2PtHCl(C2H5). Since both the Pt–H(D) and C2H4(C2D4) moieties have been formed in the transition state, the kinetic and equilibrium isotope effects should be similar.

The Arrhenius activation parameters for the thermal decomposition of 1 in cyclohexane solution are $E_a = 34 \pm 1.5$ kcal/mol and log A = $13 \pm 3^2$ (Figure 5).

(32) Forward kinetic parameters: $\Delta G^o(158^oC) = 33 \pm 1.5$ kcal/mol; $\Delta H^o = 33 \pm 1.5$ kcal/mol; $\Delta S^o = -1.4 \pm 3$ eu. The kinetic parameters for reverse reaction (reaction of 3 with ethylene to give 1) were calculated by a combination of forward kinetic parameters and thermodynamic values: $E_a = 29 \pm 2$ kcal/mol; log A = $7 \pm 1$; $\Delta G^o = 33 \pm 2$ kcal/mol; $\Delta H^o = 21 \pm 2$ kcal/mol; $\Delta S^o(158^oC) = -28 \pm 4$ eu.
Preexponential factors have proved very useful in studies of thermal decomposition of other organoplatinum compounds in weakly interacting solvents in estimating the number of translationally independent particles being created from the starting material in the rate-limiting transition state.\textsuperscript{11,12,14,33} Unimolecular isomerizations (one particle remaining as one particle in the transition state) have log $A \approx 9 - 13.34 - 36$ Reactions in which two particles are generated from one have log $A \approx 13 - 16$.\textsuperscript{11,12,33} and those in which three particles are created from one have log $A \approx 20 - 22$.\textsuperscript{11,14}

The observed value of log $A = 13$ for the decomposition of 1 is consistent with rate-limiting ethylene dissociation from (Et$_3$P)$_2$PtHCICl(C$_2$H$_4$) (2). For comparison, log $A = 14$ for rate-limiting dissociation of Et$_3$P from cis-(Et$_3$P)$_2$PtEt.\textsuperscript{11} We rationalize the small difference in these values of log $A$ using an argument based on entropies. The change in entropy on conversion of 1 to 3 and ethylene is $\Delta S^ \circ = 27 \text{ eu}$; that for the dissociation of Et$_3$P from (Et$_3$P)$_2$PtEt in n-octane is $\Delta S^ \circ = 49 \pm 4 \text{ eu.}$\textsuperscript{37} We believe that the difference in values of $\Delta S^ \circ$ for these two reactions provides a satisfactory rationalization for the differences in $\Delta S^ \circ$ (and log $A$) for the ligand dissociation reactions of 1 and L$_2$PtEt$_2$.

**Conclusion**

Several types of evidence indicate that the rate-limiting transition state for the thermal decomposition of compound 1 has the same elemental composition as this substance but that the PtC$_2$H$_4$Cl$_2$ group present in the starting material is converted to a Pt($\text{C}_2$H$_4$) moiety in the transition state.

(i) The rate of reaction is not significantly changed by addition of phosphine or chloride ion to the reaction mixture.

(ii) Deuterium originally present in PtCD$_2$CH$_4$ moiety is extensively scrambled both in product ethylene and in recovered starting material.

(iii) The significant kinetic and equilibrium isotope effects observed in the decomposition of L$_2$Pt(C$_2$H$_4$)Cl (vs. L$_2$Pt(C$_2$D$_4$)Cl) are similar.

(iv) The Arhenius preexponential factor (log $A = 13$) is consistent with a process in which no overall dissociation has taken place prior to the rate-limiting step.

We propose on the basis of these data that the rate-limiting step is decomposition to product of a species having the elemental composition L$_2$PtHCl(C$_2$H$_4$) (eq 8).

$$\text{L}_2\text{PtCl(C}_2\text{H}_4\text{)} \rightarrow [\text{L}_2\text{PtHCl(C}_2\text{H}_4\text{)]}^+ \rightarrow \text{L}_2\text{PtHCl + C}_2\text{H}_4 \quad (8)$$

The mechanism of conversion of 1 to this transition state and the details of the structure of the transition state remain ill-defined by our evidence. In particular, we cannot distinguish between a process in which $\beta$-hydride elimination occurs reversibly without dissociation of phosphine (or chloride) and one in which reversible dissociation of phosphine (or chloride) and creation of a vacant coordination site on platinum is required as a prerequisite for $\beta$-hydride elimination (eq 9).

$$\text{L}_2\text{PtCl(C}_2\text{H}_4\text{)} \rightarrow [\text{L}_2\text{PtHCl(C}_2\text{H}_4\text{)]}^+ \rightarrow \text{L}_2\text{PtHCl + C}_2\text{H}_4 \quad (9)$$

The kinetic isotope effect observed for decomposition of L$_2$Pt(C$_2$D$_4$)Cl is relatively large ($k_{1}/k_{2} \sim 2.5$). Values of this magnitude have been interpreted in other instances as evidence for C–H bond breaking (i.e., $\beta$-hydride elimination) in the rate-limiting step.\textsuperscript{7,9} We note that this interpretation is not required and suggest that the observed similarity between the kinetic and equilibrium isotope effects observed in our system suggests that the combination of isotope effects characterizing the conversion of a (Pt(CD$_2$CD$_4$)) moiety to a (Pt(D)(CD$_3$)) moiety is sufficient to explain this magnitude of isotope effect, without invoking C–H(D) bond breaking in the transition state.

The mechanism of thermal decomposition of 1 deserves brief comparison with those observed for other organoplatinum compounds. The mechanism of decomposition of 1 differs from that of most of the organoplatinum compounds studied previously in the fact that no ligand (phosphine or chloride) appears to be dissociated (or dissociating) in the rate-limiting transition state. The creation of a vacant coordination site on platinum has previously appeared to be a prerequisite for most thermal decomposition reactions, with the dissociation of phosphine occurring either before or as the rate-limiting step. One of the few examples to the contrary is provided by the thermal decomposition of (Et$_3$P)$_2$PtEt$_2$ in solution in cyclohexane containing high concentrations of added triethylphosphine.\textsuperscript{11} We inferred for this reaction a mechanism very similar to that suggested here for 1—that is, a...
mechanism involving rate-limiting loss of ethane or ethylene from a five-coordinate species of composition L2PtH(C2H5)(C2H6). The same ambiguities concerning the importance of possible pre-equilibrium dissociation of phosphine were unsettled at the conclusion of that study as remain at the conclusion of this one.

One approach that might be used to distinguish between a mechanism in which phosphine dissociation does not occur and a mechanism in which phosphine dissociation/reassociation occurs before the rate-limiting step is to study the reaction mechanism of a structurally related compound which contains a chelating diphosphine. Unfortunately, cis-(Et2PCH2CH2PEt2)PIEtCl is not useful in this regard, since its mechanism of thermal decomposition seems to differ considerably from that of L2PtCl.38

Experimental Section

General Data. All reactions and transfers involving organometallic compounds were carried out under argon. Cyclohexane and n-hexane were stirred over sulfuric acid for three days, washed with dilute sodium bicarbonate, water, dried over P2O5 and distilled from disodium benzenophenone di-anion/tetracyclone39 under argon. Tetrahydrofuran (THF) and diisopropyl ether were distilled from disodium benzenophenone di-anion prior to use. Other commercial reagents were used without purification. Melting points were obtained in sealed tubes and are corrected.

Proton-decoupled 31P NMR spectra were taken on a JEOL FX-90Q or a Bruker WM 300 spectrometer; chemical shifts are relative to 85% phosphoric acid. 1H NMR spectra were taken on a JEOL FX-90Q or a Bruker WM 500-MHz spectrometer. Mass spectra were obtained by using a JEOL WM 250-MHz spectrometer. Mass spectra were obtained by using a JEOL WM 300 spectrometer. IR spectra were obtained by using a Beckman IR 2000 spectrophotometer. Chemical shifts of 1-d6 and 1-d5 (15.54 and 15.61 ppm, respectively) were used as internal standards.

31P NMR spectra were taken on a JEOL FX-90Q or a Bruker WM 300-MHz spectrometer; chemical shifts are relative to 85% phosphoric acid. 1H NMR spectra were taken on a JEOL FX-90Q or a Bruker WM 500-MHz spectrometer; chemical shifts are relative to 85% phosphoric acid.

Chloro(cyclooctadiene)(ethyl-di-d)bis(triethylphosphine)platinum(II). To a stirred solution of 750 mg of CODPT(CD2CH2)Cl (1.70 mmol) in 25 mL of ether at -78 °C was added 135 mL of acetyl chloride (1.02 equiv) dropwise over 5 min. The reaction mixture was allowed to warm to room temperature over 45 min, concentrated by rotary evaporation, and filtered through 1 mL of silica gel with ether. The crude L2Pt(CD2CH2)Cl was washed with ether and then filtered through a column of silica gel with ether washing. Rotary evaporation followed by two recrystallizations from methanol and one from pentane gave 523 mg of white crystals of L2Pt(CD2CH2)Cl28 with a 73% yield; mp 53.5-54.5 °C (lit.39 mp 53.5-55 °C); 31P NMR (CDCl3) d 15.08 (Jp-pτ = 2979 Hz), (CaHr2) 6 15.5 (Jp-pτ = 3013 Hz); 1H NMR (CCl4) δ 2.43 (m, 2 H), 2.32-2.24 (m, 4 H), 1.88 (s, 2 H), 1.75-1.67 (m, 2 H), 1.50-1.33 (m, 5 H), 0.95 (m, 18 H). Anal. Calcd for C20H36Cl2P2: C, 56.1; H, 8.8; P, 13.2. Found: C, 56.2; H, 8.5; P, 13.1. 16. 1H NMR tubes according to previously described procedures.31,34 The thermal decompositions were performed in constant temperature oil baths. Temperatures were determined with a calibrated thermometer and were found to be constant to ±0.4 °C (95% confidence). NMR tubes were removed from the oil baths at regular intervals and cooled rapidly by immersion in ice water. The extent of thermal decomposition was determined by comparing proton-decoupled 31P NMR peak heights of starting material against an internal standard (0.08 M triethylphosphate).

The deuterium kinetic isotope effect was determined by comparing the relative rates of reaction of L2Pt(CD2CH2)Cl and L2Pt(CD2CH2)Cl in the same NMR tube (fT/ fD = 2.42) as a check of the normal procedure which used separate tubes. The 31P NMR chemical shifts of 1-d6 and 1-d5 (15.54 and 15.61 ppm, respectively) were used as internal standards.

Phosphine rate dependence experiments were performed in n-hexane and cyclohexane. The extent of thermal decomposition was determined by comparing the 31P NMR peak heights of L2PtEtCl and (Et2)PO (an internal standard) at a probe temperature of approximately 34 °C and 55 °C, respectively, for these two solvents. This solvent was necessary to prevent excessive exchange broadening and concomitantly to improve the signal-to-noise ratio for the L2PtEtCl peak at high phosphine concentrations.46 Most of these experiments were conducted in n-hexane.

<table>
<thead>
<tr>
<th>Table IV. IR Data for Some Organoplatinum Complexes</th>
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<tr>
<td>Compound</td>
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<tr>
<td>trans-L2Pt(CD2CH2)Cl</td>
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<tr>
<td>trans-L2Pt(C2H5)Cl</td>
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<td>trans-L2Pt(CD2CH2)Cl</td>
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<td>trans-L2Pt(CD2CH2)Cl</td>
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<tr>
<td>trans-L2Pt(PhCl)</td>
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<td>trans-L2Pt(PhCl)</td>
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28 | L = Et3P; I = (CD2CH2)3P | Rotatory evaporation gave CODPT(CD2CH2)Cl (568 mg, 95%) as white crystals: mp 121-124 °C; 1H NMR (CDCl3) δ 5.41 (br t, JCD3 = 28 Hz, 2 H), 3.69 (br t, JCD3 = 75 Hz, 2 H), 1.66-1.50 (m, 11 H). H NMR of this spectrum with the 1H NMR of CODPtEtCl showed that the deuterium atoms in CODPt(CD2CH2)Cl were not scrambled: Pt-CH2-CH2 of CODPtCl δ 1.94 (t, JCD2CH3 = 74, JCD2CH3 = 7.5 Hz, 2 H).43

Chloro(ethyl-1-1-d)bis(triethylphosphine)platinum(II). To a stirred solution of 1.034 g of L2Pt(CD2CH2)Cl11 (2.07 mmol) in 36 mL of methanol/ether (1:1) at -78 °C was added 150 mL of acetyl chloride (1.02 equiv) dropwise over 5 min. The reaction mixture was allowed to warm to room temperature over 45 min, concentrated by rotary evaporation, and filtered through 1 mL of silica gel with ether. The crude L2Pt(CD2CH2)Cl was flash chromatographed on 30 mL of silica gel (ether/petroleum ether, 1:3) to give 585 mg of L2Pt(CD2CH2)Cl (92% yield; mp 52.5-53.5 °C; infrared data are summarized in Table IV.

Chloro(ethyl-1-1-d)bis(triethylphosphine)platinum(II). To a stirred solution of 1.034 g of L2Pt(CD2CH2)Cl11 (2.07 mmol) in 36 mL of methanol/ether (1:1) at -78 °C was added 150 mL of acetyl chloride (1.02 equiv) dropwise over 5 min. The reaction mixture was allowed to warm to room temperature over 45 min, concentrated by rotary evaporation, and filtered through 1 mL of silica gel with ether. The crude L2Pt(CD2CH2)Cl was flash chromatographed on 30 mL of silica gel (ether/petroleum ether, 1:3) to give 585 mg of L2Pt(CD2CH2)Cl (92% yield). Two recrystallizations from methanol gave white crystals: mp 54-55 °C; IR, Table IV.

Kinetics of Thermal Decomposition. Cyclohexane or tetrahydrofuran solutions of L2PtECl (0.08 M) were prepared in NMR tubes according to previously described procedures.31,34 The thermal decompositions were performed in constant temperature oil baths. Temperatures were determined with a calibrated thermometer and were found to be constant to ±0.4 °C (95% confidence). NMR tubes were removed from the oil baths at regular intervals and cooled rapidly by immersion in ice water. The extent of thermal decomposition was determined by comparing proton-decoupled 31P NMR peak heights of starting material against an internal standard (0.08 M triethylphosphate). The deuterium kinetic isotope effect was determined by comparing the relative rates of reaction of L2Pt(CD2CH2)Cl and L2Pt(CD2CH2)Cl in the same NMR tube (fT/ fD = 2.42) as a check of the normal procedure which used separate tubes. The 31P NMR chemical shifts of 1-d6 and 1-d5 (15.54 and 15.61 ppm, respectively) are sufficiently resolved to give linear kinetic plots on a Bruker WM 300 spectrometer.

Phosphine rate dependence experiments were performed in n-hexane and cyclohexane. The extent of thermal decomposition was determined by comparing the 31P NMR peak heights of L2PtEtCl and (Et2)PO (an internal standard) at a probe temperature of approximately 34 °C and 55 °C, respectively, for these two solvents. This solvent was necessary to prevent excessive exchange broadening and concomitantly to improve the signal-to-noise ratio for the L2PtEtCl peak at high phosphine concentrations.46 Most of these experiments were conducted in n-hexane.

(44) When this reaction was performed at 0 °C with a 27% excess of EtP, the resulting L2Pt(CD2CH2)Cl was isotopically scrambled. We suspect that the formation of LSPI(CD2CH3)Cl may be a source of scrambling.

so that lower probe temperatures could be used.

The decomposition of \( \text{L}_{\text{Pt}}\text{EtCl}(\text{II}) \) (0.05 M) in the presence of added phosphine is first order in \( \text{L}_{\text{Pt}}\text{EtCl} \) up to about 60% completion. The reaction rate then begins to increase, and curvature is observed in the first-order plot. The rate constants derived were from the linear portion of the plot.

**Phosphine Exchange Experiments.** Into a 5-mm NMR tube were weighed 11.3 mg of \( \text{L}_{\text{Pt}}\text{EtCl} \) and 17.2 mg of \( \text{L}_{\text{Pt}}\text{EtBr} \). A solution of 0.05 M (EtO) \(_3\)PO in cyclohexane (0.50 mL) was added, and the sample was freeze-thaw-degassed three times, and the NMR tube was sealed under vacuum. Except during the freeze-thaw-degas cycles, the sample was kept at -196 °C until it was placed into the probe of the NMR spectrometer. The room-temperature \(^{31}\text{P} \) NMR spectrum of this sample taken as rapidly as possible (<15 min) showed that the phosphines were completely scrambled. Thermoanalysis of this mixture at 158 °C for 2 h showed no further change in the relative integrated areas corresponding to \( \text{L}_{\text{Pt}}\text{EtCl}, \text{L}_{\text{Pt}}\text{EtBr}, \text{and L}_{\text{Pt}}\text{EtCl} \). 31P NMR (C\(_6\)H\(_6\)) spectra: \( \text{L}_{\text{Pt}}\text{EtCl}, \delta 15.54 \) (J = 3013 Hz); \( \text{L}_{\text{Pt}}\text{EtBr}, \delta 15.00 \) (J = 3012 Hz, \( J \)) and 14.7 (J = 3013 Hz, \( J \)), \( \text{L}_{\text{Pt}}\text{EtCl} \) and \( \text{L}_{\text{Pt}}\text{EtBr} \) at 311 Hz. (J = 3011 Hz). 31P NMR (C\(_6\)H\(_6\)) spectra: \( \text{L}_{\text{Pt}}\text{EtCl} \), \( \delta 15.54 \) (J = 3013 Hz); \( \text{L}_{\text{Pt}}\text{EtBr} \), \( \delta 15.00 \) (J = 3012 Hz, \( J \)) and 14.7 (J = 3013 Hz, \( J \)), \( \text{L}_{\text{Pt}}\text{EtCl} \) and \( \text{L}_{\text{Pt}}\text{EtBr} \) at 311 Hz.

**Halogen Exchange Experiments.** Into a 5-mm NMR tube were weighed 13.7 mg of \( \text{L}_{\text{Pt}}\text{EtCl} \) and 14.8 mg of \( \text{L}_{\text{Pt}}\text{EtBr} \). The tube was capped with a septum and deoxygenated under argon with several vacuum-argon cycles. Within 5 min, 0.50 mL of cyclohexane was added to the NMR tube by syringe, the compounds were dissolved at room temperature, and the NMR tube was placed in the spectrometer probe. The progress of this equilibration study was followed by comparing the electronic integrations of the 31P NMR signals for \( \text{L}_{\text{Pt}}\text{EtCl} \) and \( \text{L}_{\text{Pt}}\text{EtBr} \). The 31P NMR spectra of all four compounds present at equilibrium corresponded to 31P NMR spectra of these compounds when prepared independently. 31P NMR (C\(_6\)H\(_6\)) spectra: \( \text{L}_{\text{Pt}}\text{EtCl} \), \( \delta 15.54 \) (J = 3013 Hz); \( \text{L}_{\text{Pt}}\text{EtBr} \), \( \delta 15.16 \) (J = 3015 Hz); \( \text{L}_{\text{Pt}}\text{EtBr} \), \( \delta 13.43 \) (J = 2993 Hz); \( \text{L}_{\text{Pt}}\text{EtBr} \), \( \delta 13.51 \) (J = 2991 Hz).

**trans-Bromo(ethyl-ds) bis(triethylphosphine)platinum(II) \( (\text{I}) \).** \( \text{L}_{\text{Pt}}\text{C}_{\text{D}}\text{Br} \) was prepared by the method of Chatt and Shaw.\(^{46} \) From 556 mg of \( \text{L}_{\text{Pt}}\text{C}_{\text{D}}\text{Br} \). The resulting \( \text{L}_{\text{Pt}}\text{C}_{\text{D}}\text{Br} \) was purified by passing an ethereal solution of it through ca. 8 mL of silica gel, followed by two recrystallizations from degassed methanol, and gave 363 mg of white needles: mp 62.5-63.5 °C; \( \text{I} \) \( \delta 1.86 \) (m, 12 H), \( 0.96 \) (m, 18 H); \( \text{II} \) \( \delta 13.51 \) \( (J = 2991 \text{Hz}) \). \( \text{L}_{\text{Pt}}\text{C}_{\text{D}}\text{Br} \) was prepared independently. 31P NMR (C\(_6\)H\(_6\)): \( \text{L}_{\text{Pt}}\text{EtCl} \), \( \delta 15.54 \) (J = 3013 Hz); \( \text{L}_{\text{Pt}}\text{EtBr} \), 13.43 (J = 2991 Hz); \( \text{L}_{\text{Pt}}\text{C}_{\text{D}}\text{Br} \), 13.51 (J = 2991 Hz).}

**Equilibrium Studies.** To four freeze-thaw-degassed solutions of \( \text{L}_{\text{Pt}}\text{PtCl}(0.08-0.13 \text{ M}) \), 0.06 M (EtO) \(_3\)PO, and 0.036 M bis-(Et\(_3\)P)\(_3\)PtCl remained in solution was then quenched with bromine as previously described.\(^{47} \) The isotopic compositions of ethylene products at each temperature were determined by comparison with literature \(^{51} \) values for M, M+1, and M+2 peaks of ethylene-d\(_2\).

**Acknowledgment.** We thank Mariathia Hackett for help with the initial investigation of \( \text{Et}_{\text{C}}\text{H}_{\text{C}}\text{H}_{\text{C}}\text{H}_{\text{C}}\text{Et}_{\text{C}}\text{Et}_{\text{C}}\text{Cl} \) and thank Thomas J. McCarthy, Cynthia Friend, Robert DiCosimo, and Robert Reamey for many helpful discussions. We thank Jim Simmons for help with the 31P NMR kinetics and Shaw G. Huang for help with the high-temperature 1H NMR experiments. The NMR spectrometer used at Harvard was purchased in part through NSF CHE 8008891.