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# Mechanisms of Thermal Decomposition of Diethylbis(triethylphosphine)platinum(II)[1]

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**Abstract:** The mechanism of thermal decomposition of diethylbis(triethylphosphine)platinum(II) ($L_2PtEt_2$) to ethylenebis(triethylphosphine)platinum(0) and ethane in cyclohexane depends on the concentration [L] of triethylphosphine added to the solution. When $[L] \simeq 0$ M, the overall rate-limiting step in the decomposition is dissociation of triethylphosphine from $L_2PtEt_2$; when $[L] \simeq 0.3$ M, the rate-limiting step is reductive elimination of ethane from an intermediate, ethylene(triethylphosphine)hydridoethylplatinum(II); when $[L] \geq 1.6$ M, the most probable mechanism involves rate-limiting reductive elimination of ethane from ethylhydridobis(triethylphosphine)(ethylene)platinum(II). The deuterium kinetic isotope effect for reductive elimination of ethane from L(ethylene)Pt(H,D)Et is $k_H/k_D \simeq 3.3$. Activation parameters for each reaction indicate that entropy terms (especially of dissociation and reductive elimination of ligands from platinum) play an important role in determining which process is most rapid.

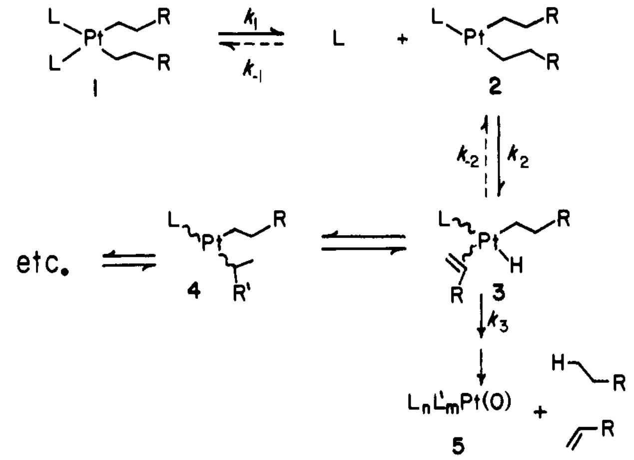
## Introduction

Metal alkyls are intermediates in many processes catalyzed by transition metals. Understanding the mechanisms by which these alkyls form and decompose is a prerequisite to understanding the mechanisms of catalysis. A previous study[4] of thermal decomposition of di(*n*-butyl)bis(triphenylphosphine)platinum(II) to butane, 1-butene, and a soluble platinum(0) complex (Scheme I, R = ethyl, L = triphenylphosphine, $CH_2Cl_2$ solution) identified three mechanistically significant features. First, when the concentration of free triphenylphosphine in solution was low, the overall rate-limiting step was generation of an additional vacant coordination site on platinum by dissociation of L (**1** → **2**). Second, at higher concentrations of free triphenylphosphine in solution, phosphine loss was reversible, and reductive elimination of alkane from an intermediate hydridoalkyl(triphenylphosphine)platinum(II) complex of undefined composition and stereochemistry (represented by **3**) was rate-limiting. Third, β-hydride elimination and its reverse ($\mathbf{3} \rightleftharpoons \mathbf{4} \rightleftharpoons ...$) rapidly scrambled the positions of isotopic labels present in the butyl groups attached to platinum. The intermediate butene(s) did not equilibrate with olefins present in solution. The structure of the platinum(0) complex **5** produced as a product was not established.

The present paper describes a more detailed study of the mechanism of thermal decomposition of diethylbis(triethylphosphine)platinum(II). This study confirms the basic mechanistic picture outlined in Scheme I (for L = triethylphosphine, R = H(D), cyclohexane solution), but establishes the importance of another competitive path (having *two* phosphines present in the overall rate-limiting transition state) and provides activation parameters and isotope effects useful in interpreting the details of the reaction coordinate(s) leading from starting materials to products. A closely analogous mechanism describes the conversion of dineopentylbis(triethylphosphine)platinum(II) to bis(triethylphosphine)-3,3-dimethylplatinacyclobutane and neopentane.[5]

Throughout, the platinum complexes will be named by reference to diethylbis(triethylphosphine)platinum(II), $L_2PtEt_2$. Thus for example, di(ethyl-$d_5$)bis(triethylphosphine-$d_{15}$)platinum(II) will be called $L^D{}_2Pt(C_2D_5)_2$. Many of the kinetic studies of the following reactions were carried out in solutions containing different amounts of added triethylphosphine, L. We use the term [L] to refer to the concentration of L due to this *added* triethylphosphine. We emphasize that [L] = 0.0 does *not* mean that there is no free L in solution; *it indicates only that no L was added to the solution.*

Scheme I



The equilibrium constant for dissociation of L from $L_2PtEt_2$ is clearly small, but we have not measured it quantitatively. This small concentration is kinetically important for low values of [L].

## Results

**Products.** Heating a 0.1 M solution of $L_2PtEt_2$ in cyclohexane produced cleanly 1 equiv each of ethane and ethylenebis(triethylphosphine)platinum(0). No butane was formed, and no *free* ethylene was visible in the $^1H$ NMR spectrum of the reaction mixture. The reaction was homogeneous throughout.

**$^{31}P$ NMR Spectroscopy of $L_2PtEt_2$.** Much of the mechanistic evidence which follows depends on the interpretation of the influence of triethylphosphine concentration on the rate of decomposition of $L_2PtEt_2$. Careful examination of the $^{31}P$ NMR spectrum of cyclohexane solutions of $L_2PtEt_2$, alone and in the presence of added triethylphosphine ([L] = 0 M to ~6.9 *M* (neat)), showed no evidence of either three-coordinate ($LPtEt_2$) or five-coordinate ($L_3PtEt_2$) species, or of fast (on the NMR time scale) exchange between coordinated and free phosphine. The conclusion that no significant association occurred between $L_2PtEt_2$ and L was confirmed by establishing that the solubility of this platinum complex was lower in cyclohexane containing 1 M triethylphosphine than in cyclohexane alone.[6]

The exchange of triethylphosphine-$d_{15}$ (1.64 M) with the platinum-coordinated triethylphosphine of $L_2PtEt_2$ (0.1 M in cyclohexane) was examined by $^{31}P$ NMR spectroscopy. Although the errors involved in this measurement prevented a precise determination of the rate constant for exchange, $k_{\text{exchange}}$, replacement

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(3) NCI Predoctoral Trainee, 1977-1979.

(4) Whitesides, G. M.; Gaasch, J. F.; Stedronsky, E. R. *J. Am. Chem. Soc.* **1972**, *94*, 5258-5270.

(5) Foley, P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1979**, *101*, 2732-2733. Foley, P.; DiCosimo, R.; Whitesides, G. M. *Ibid.* **1980**, *102*, 6713-6725.

(6) References 4 and 5 discuss the use of solubilities to distinguish associative and dissociative equilibria.

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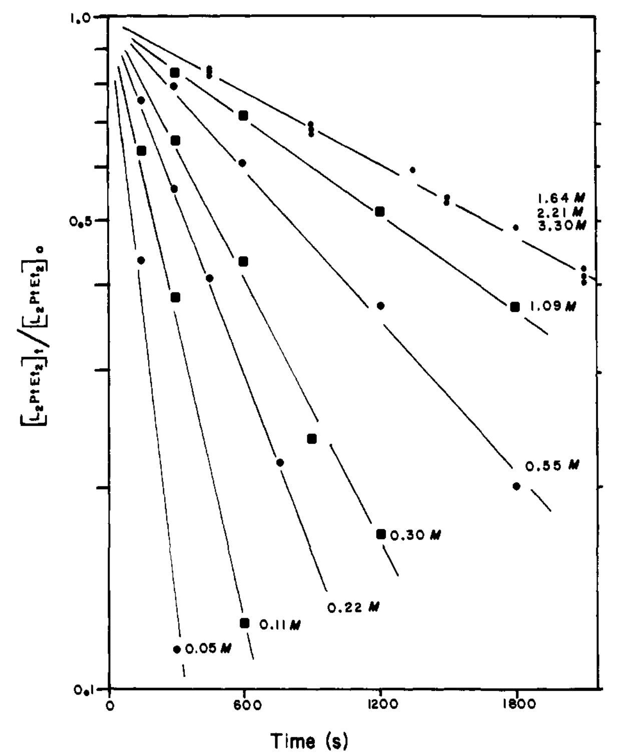

**Figure 1.** Thermal decomposition of $L_2PtEt_2$ in cyclohexane solution in the presence of added triethylphosphine: $[L_2PtEt_2]_0 = 0.1$ M, $T = 141$ °C. [L] is indicated on the figure for each curve.

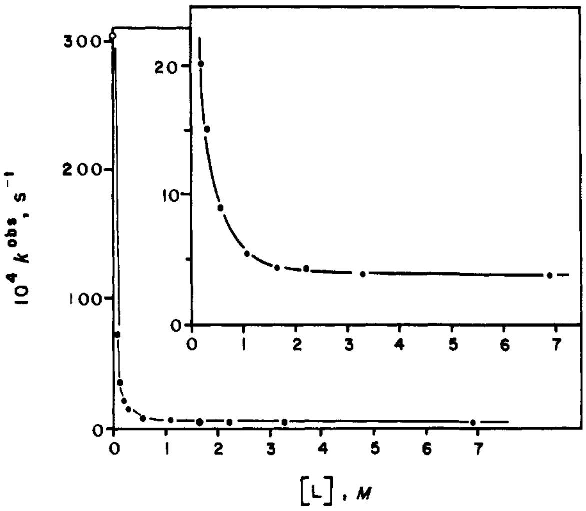

**Figure 2.** Observed first-order rate constant for decomposition of $L_2PtEt_2$ ($[L_2PtEt_2]_0 = 0.1$ M, cyclohexane, $T = 141$ °C) as a function of added triethylphosphine [L]. The insert shows the same data with an expanded vertical axis. The value at [L] = 0 was obtained by extrapolation of rates measured at lower temperatures.

of L by $L^D$ at 75 °C occurred without significant decomposition of the $L_2PtEt_2$.

**Kinetics.** The disappearance of $L_2PtEt_2$ in cyclohexane (followed by $\{^1H\}$ $^{31}P$ NMR spectroscopy was first-order in $L_2PtEt_2$ to greater than 3 half-lives. The decomposition was inhibited by added L. Figure 1 summarizes representative data; Figure 2 plots first-order rate constants (defined by eq 1) observed for several

$$-d[L_2PtEt_2]/dt = k_L^{obsd}[L_2PtEt_2] \quad (1)$$

concentrations of added phosphine, [L], as a function of [L]. The starting concentration of $L_2PtEt_2$ in these experiments (0.10 M) was small compared with the concentration of added phosphine for all points except that for [L] = 0.05 M, and [L] was assumed constant over the course of a kinetic run: this assumption is supported by the linearity of the plots in Figure 1. The decomposition at [L] = 0 was too fast to be followed at 141 °C; the rate reported at this temperature was obtained by extrapolation from lower temperatures.

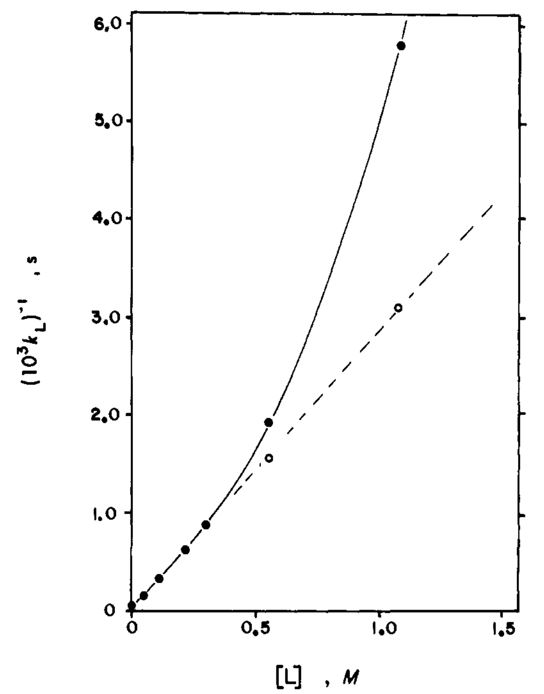

**Figure 3.** Rate constant $k_L$ (eq 2b) for decomposition of $L_2PtEt_2$ plotted according to eq 3 (cyclohexane, 0.1 M, 141 °C): —●, $k_4 = 4.4 \times 10^{-4}$ $s^{-1}$ (obtained from the value of $k_L^{obsd}$ at [L] = 1.64 M, Figure 2); --- O, $k_4 = 2.35 \times 10^{-4}$ $s^{-1}$ (chosen to maximize the linear regin of this plot).

The initial decrease in $k_L^{obsd}$ on increasing [L] is compatible with Scheme I and reflects a decrease in the concentration of the three-coordinate intermediate $LPtEt_2$ present in equilibrium before the rate-limiting step. At high concentrations of L, this scheme appears to break down, since $k_L^{obsd}$ is independent of [L]. We suggest that a new mechanism appears at high [L], in which both the ground state ($L_2PtEt_2$) and the rate-limiting transition state contain two triethylphosphines. This suggestion, coupled with an unexceptional steady-state treatment of Scheme I, leads to an expression for $k_L^{obsd}$ of the form of eq 2 for the decomposition over the entire range of L:[7]

$$k_L^{obsd} = \frac{k_1k_2k_3}{k_2k_3 + k_{-1}(k_{-2} + k_3)[L]} + k_4 \quad (2a)$$

$$k_1 = k_L^{obsd} - k_4 \quad (2b)$$

In these equations, $k_4$ represents the rate constant for decomposition of $L_2PtEt_2$ by the pathway which is independent of [L], that is, the pathway having two triethylphosphines coordinated to platinum in the transition state. The magnitude of $k_4$ can be estimated, in principle, to be the value of $k_L^{obsd}$ found at high concentrations of L (Figure 2). We have used $k_4 = 4.4 \times 10^{-4}$ $s^{-1}$, but we point out three factors which make this value uncertain. First, decomposition rates are intrinsically very slow at high [L], and difficult to measure accurately. Second, the presence of high concentrations of triethylphosphine changes the character of the medium, and it is not clear that the value of $k_4$ is the same in cyclohexane as in triethylphosphine . Third, it is not evident that the value of $k_L^{obsd}$ at [L] > 1.64 M represents only decomposition by the phosphine-independent pathway; a residual contribution from a pathway requiring phosphine dissociation may still be significant. The uncertainty in $k_4$ notwithstanding, subtraction of $k_4$ from $k_L^{obsd}$ yields a rate constant $k_L$ corrected for the phosphine-independent decomposition (eq 2b). Plotting the re-

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[7] The individual rate constants in eq 2 will themselves be composites of other rate constants, if other intermediates not shown in Scheme I lie along the reaction coordinate leading to the rate-limiting transition state.

Table I. Characteristics of the Decomposition of $L_2PtEt_2$ at Different Concentrations of Added L

| | [L], M | | |
|---|---|---|---|
| | 0.0 | 0.30 | 1.64 |
| kinetic order in L | ? | $[L]^1$ | $[L]^0$ |
| $k_H/k_D$ | 1.0 | 3.3 | 1.7 |
| ethyl bromide obtained from $L_2Pt(CH_2CD_3)_2$[a] | 95% $BrCH_2CD_3$ | $C_2H_2D_3$ scrambled | $C_2H_2D_3$ scrambled |
| ethylene from $L_2Pt(CH_2CD_3)_2$ | 43 $d_2$:57 $d_3$ | 42 $d_2$:58 $d_3$ | 47 $d_2$:53 $d_3$ |
| $L_2PtEt_2 + L^D{}_2PtEt_2 \rightleftharpoons 2LL^DPtEt_2$[b] | no | yes | yes |
| $E_a$, kcal/mol | 29 ± 2 | 46 ± 3 | 37 ± 3 |
| log $A$ | 14 ± 1 | 22 ± 2 | 16 ± 1 |
| $\Delta G^{\ddagger}$, kcal/mol | 27 ± 3 | 31 ± 4 | 31 ± 4 |
| $\Delta H^{\ddagger}$ (118 °C), kcal/mol | 28 ± 2 | 45 ± 3 | 36 ± 3 |
| $\Delta S^{\ddagger}$ (118 °C), eu | 3 ± 5 | 35 ± 5 | 12 ± 7 |

[a] $L_2Pt(Et\text{-}d_3)_2$ was treated with $Br_2$ in toluene solution at −78 °C; these conditions do not scramble the position of the deuterium. The entry "scrambled" in this table indicates that the deuterium was estimated by $^1H$ and $^2H$ NMR to be essentially statistically distributed between the two carbons of the ethyl group. [b] Under conditions of the thermal decomposition (118 °C, cyclohexane).

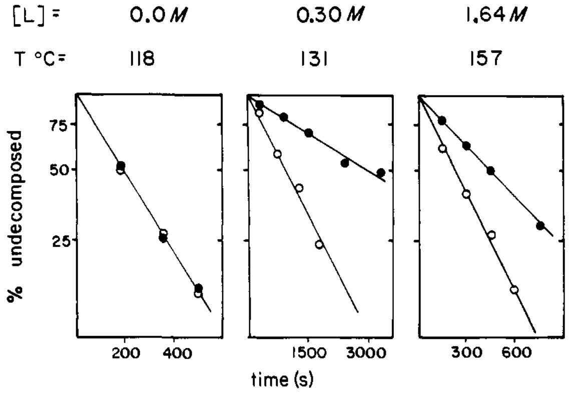

Figure 4. Decomposition of $L_2Pt(C_2H_5)_2$ (○) and $L_2Pt(C_2D_5)_2$ (●) in cyclohexane at three values of [L] ($[Pt]_0$ = 0.1 M, cyclohexane solution).

sulting expression in the form $(k_L)^{-1}$ vs. [L] (Figure 3) yields the straight line expected on the basis of eq 3 ($k'[L] > k_2k_3$) at

$$\frac{1}{k_L} = \frac{k_2k_3 + k_{-1}(k_{-2} + k_3)[L]}{k_1k_2k_3} \simeq \frac{k_{-1}(k_{-2} + k_3)[L]}{k_1k_2k_3} = k'[L] \tag{3}$$

concentrations of L up to ca. 0.3 M. The deviation from linearity at higher values of [L] may reflect any of the factors contributing to the uncertainty in $k_4$. By choosing a different value of $k_4 = 2.35 \times 10^{-4}$ s$^{-1}$ the plot of Figure 3 becomes linear over a broader range. The important conclusion from these manipulations is not a numerical estimate of $k_4$, but rather that a reasonable choice of $k_4$ allows the calculation of a set of rate constants $k_L$, corrected for the hypothesized phosphine-independent path for decomposition of $L_2PtEt_2$, which are compatible (Figure 3, eq 3) with a mechanism requiring dissociation of 1 equiv of phosphine before the rate-limiting transition state.

These data concerning the kinetic order of the decomposition of $L_2PtEt_2$ in added L combine with evidence in the following sections and indicate the existence of three paths for this decomposition, with the dominant path determined by the concentration of free triethylphosphine in solution. Table I summarizes the important evidence from each section, and facilitates comparisons of these paths: the particular choice of concentrations of added phosphine used as the points for comparisons was made on the basis of Figure 2; [L] = 0.0 M was the lowest possible value; [L] = 1.64 M seemed within the region showing little or no dependence on phosphine concentration; and [L] = 0.3 M was in the kinetic regime intermediate between these two extremes.

**Deuterium kinetic isotope effects** were obtained by comparing the rates of decomposition of $L_2Pt(CH_2CH_3)_2$ and $L_2Pt(CD_2CD_3)_2$ (Table II). Figure 4 shows the rate data from which these isotope effects were derived. For convenience, and to avoid long reaction times, rates for solutions containing added triethylphosphine were measured at higher temperatures than those without. The isotope effect at intermediate concentrations of $Et_3P$ was calculated using values for the corrected rate constants $k_L$ (eq 2b, $k_4 = 4.4 \times 10^{-4}$ s$^{-1}$). We assume that the values of $k_H/k_D$ can be compared directly without correction for these temperature differences. The observation that there is no observable isotope effect at [L] = 0.0 M is compatible with the hypothesis that phosphine dissociation is rate limiting (Scheme I). The value of $k_H/k_D$ = 3.3 calculated for [L] = 0.3 M indicates C–H(D) bond making or breaking in the transition state, and is compatible with rate-limiting reductive elimination of alkane from the Pt(H,D)Et group. Halpern et al. have reported a similar value of $k_H/k_D$ = 3.3 for elimination of methane(D) from $(Ph_3P)_2Pt(H,D)CH_3$.[8] The decrease in the value of $k_H/k_D$ from 3.3 to 1.7 as [L] increases from 0.3 to 1.64 M is well outside the limits of experimental error; we suggest that this increase reflects a change in mechanism. Figure 5 demon-

Table II. Deuterium Kinetic Isotope Effects[a]

| | $10^3k_L^{obsd}$, s$^{-1}$ | | | |
|---|---|---|---|---|
| [L] | H | D | $T$, °C | $k_H/k_D$[b] |
| 0.0 | 3.6[c] | 3.5[d] | 118 | 1.0 ± 0.3 |
| 0.30 | 0.67[d] | 0.25[d] | 131 | 3.3 ± 0.5[e] |
| 1.64 | 2.7 | 1.6[d] | 157 | 1.7 ± 0.3 |

[a] The starting concentration of $L_2Pt(C_2D_5)_2$ was 0.1 M in cyclohexane. [L] is the concentration of added triethylphosphine. [b] The errors in $k_H/k_D$ were estimated by determining the standard deviations of the least-squares slopes used to calculate $k_L$, and propagating these errors using standard procedures. See ref 12 for details. [c] Average of three experiments. [d] Average of two experiments. [e] This value has been adjusted to eliminate the effect of $k_4$; the values of $k_4$ that were subtracted from $k_L^{obsd}$ are: $k_4(H) = 1.6 \times 10^{-4}$ s$^{-1}$, $k_4(D) = 8.4 \times 10^{-5}$ s$^{-1}$. Error in this number due to uncertainties in $k_4$ (see text and Figure 3) and measured rate constants are within the indicated error limits.

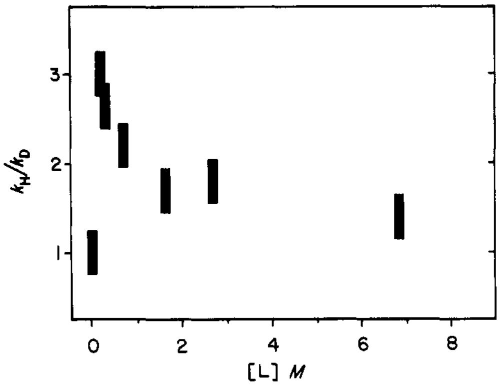

Figure 5. Observed deuterium kinetic isotope effects ($k_L^{obsd}(H)/k_L^{obsd}(D)$) as a function of [L] ($[L_2Pt(C_2H_5)_2]_0 = [L_2Pt(C_2D_5)_2]_0$ = 0.10–0.05 M, cyclohexane).

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(8) Abis, L.; Sen, A.; Halpern, J. J. Am. Chem. Soc. 1978, 100, 2915–2916.

strates clearly the trend of observed deuterium kinetic isotope effects as a function of [L]: in the range of 1.64–6.9 M triethylphosphine little or no change occurs in the observed kinetic isotope effect. We interpret this observation as evidence that experimental results obtained at [L] = 1.64 M accurately reflect an independent, distinct decomposition pathway.

**Isotope Scrambling in Products and Starting Materials.** The extent of isotopic scrambling in recovered starting material and products was assayed separately. For the former ca. 50% of a sample of $L_2Pt(CH_2CD_3)_2$ was allowed to decompose at 118 °C in cyclohexane, the undecomposed starting material was recovered, the ethylplatinum moieties were converted to ethyl bromide by reaction with bromine in toluene at −78 °C,[9] and the position of the deuterium and hydrogen in the ethyl bromide was assayed by $^1H$ and $^2H$ NMR spectroscopy. For the latter, a sample of $L_2Pt(CH_2CD_3)_2$ was allowed to decompose to completion under the same circumstances, and the isotopic composition of the resulting ethylene assayed by GC/MS. The results of these experiments are summarized in Table I.

The observation of little scrambling in recovered ethyl-$d_3$ moieties at [L] = 0 M is consistent with rate-limiting phosphine dissociation (Scheme I). The extensive scrambling observed for [L] ≥ 0.3 M indicates that the initial $\beta$-hydride elimination is reversible at this concentration of L.[10] The ethylene produced at all concentrations of L must be derived from scrambled ethyl-$d_3$ moieties, since it contains at least 50% $d_3$ material. The fact that the observed proportions of $d_2$- to $d_3$-ethylene are similar at all three concentrations of L, and that *hydrogen* is lost preferentially (a statistical loss of $^1H$ or $^2H$ would yield 60% $d_2$ and 40% $d_3$), is compatible with an isotope effect $k_H/k_D > 1$ in a slow reductive elimination of alkane from an intermediate, reversibly formed, ethylene(hydrido)alkylplatinum(II).

**Tests for Bimolecular Processes.** The kinetic behavior observed at all phosphine concentrations is first order in platinum. Two further experiments were conducted to test for kinetically masked bimolecular processes. First, decomposition of a 1:1 mixture of $L_2Pt(CD_2CD_3)_2$ and $L_2Pt(CH_2CH_3)_2$ was carried out, and the ethane and ethylene produced as products were examined by GC/MS. Isotopic compositions were determined by mass spectroscopy using normalized selected ion monitoring (Scan Mode) at 70, 40, 20, and 15 eV ionization potentials. These studies revealed no exchange of labels between the protio and deuterio complexes. In particular, a product mixture of ethane containing predominately $d_0$ and $d_6$ species was obtained (eq 4). The small

$$\begin{matrix} HCD_2CD_3 \\ DCH_2CH_3 \end{matrix} \quad \overset{157\,°C}{\not\longleftarrow} \quad \left\{\begin{matrix} L_2Pt(CD_2CD_3)_2 \\ L_2Pt(CH_2CH_3)_2 \end{matrix}\right\} \quad \xrightarrow{157\,°C} \quad \begin{matrix} CD_3CD_3 \\ CH_3CH_3 \end{matrix} \tag{4}$$

$$\begin{matrix} L_2PtEt_2 \\ L^D_2PtEt_2 \end{matrix} \quad \underset{\text{decomposition}}{\overset{89\,°C}{\not\longrightarrow}}{}_{50\%} \quad LL^DPtEt_2 \tag{5}$$

amount of ethane-$d_5$ present was shown to be at the level of the isotopic purity of the deuterated platinum complex.

Decomposition of a 1:1 molar ratio mixture of $(Et_3P)_2PtEt_2$ and $(Et_3P\text{-}d_{15})_2PtEt_2$ to 50% conversion followed by analysis by $^{31}P$ NMR revealed no detectable (<10%) exchange of ligands in the remaining starting material.[11] This result is consistent with the assumption that loss of phosphine is rate determining in the absence of added phosphine, and establishes in addition that there are no kinetically significant processes which exchange ligands under the decomposition conditions used.

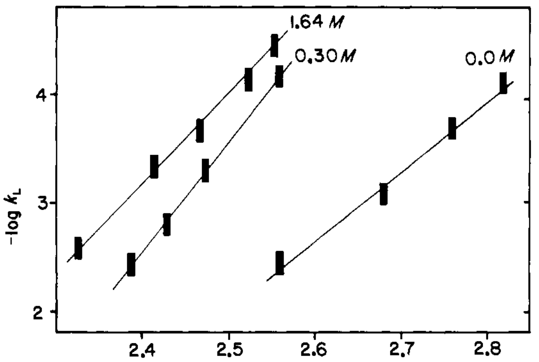

Figure 6. Arrhenius plots for thermal decomposition of $L_2PtEt_2$ in cyclohexane at [L] = 1.64, 0.30, and 0.0 M.

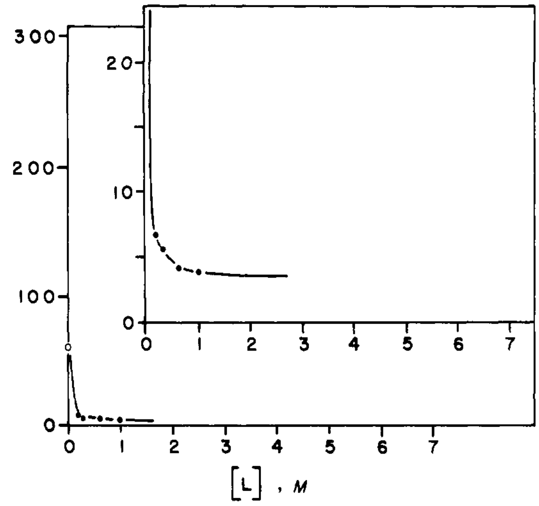

Figure 7. Observed first-order rate constants for thermal decomposition of $L_2Pt(CH_2CH_2CH_3)_2$ in cyclohexane solution at $T$ = 118 °C ($[L_2PtPr_2]_0$ = 0.1 M).

**Activation Parameters.** Arrhenius activation parameters were determined at [L] = 0.0, 0.30, and 1.64 M. Table I lists these values (and, for convenience, activation enthalpies and entropies). Figure 6 shows the Arrhenius plots from which they were derived.[12] Comparison of activation energies calculated from $k_L^{obsd}$ and from $k_L$ at [L] = 0.30 M indicated that these activation parameters are relatively insensitive to small contributions to the observed rate from competing processes. The values reported are calculated using $k_L$.

**Thermal Decomposition of Di-*n*-propylbis(triethylphosphine)platinum(II) ($L_2PtPr_2$).** We have compared this thermal decomposition with that of $L_2PtEt_2$ in order to determine the sensitivity of the mechanism to small changes in structure. We also hoped that the differences between ethylene and propylene as ligands for platinum(0) or platinum(II) might result in kinetic differences which would be useful in interpreting the structure(s) of the transition state(s). Heating a 0.1 M solution of $L_2PtPr_2$ in cyclohexane ($T$ = 78 to 118 °C) yielded 1 equiv each of propane

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(9) When bromination of $L_2Pt(CH_2CD_3)_2$ was carried out in $CD_2Cl_2$ at 0 °C or −78 °C, the ethyl-$d_3$ bromide was extensively scrambled.

(10) Analysis by $^1H$ NMR spectroscopy indicates that the distribution of protons between the methylene and methyl positions is approximately 45:55 (a statistical distribution is 40:60).

(11) The $^{31}P$ chemical shifts of equivalent $(Et_3P\text{-}d_{15})Pt$ and $Et_3PPt$ groups differ by 56 Hz as a result of a deuterium isotope effect. The $(Et_3P\text{-}d_{15})(Et_3P)Pt$ group is distinguishable in the $\{^1H\}$ $^{31}P$ NMR spectrum on the basis of the observable coupling $J_{PP}$ = 12 Hz.[5] This analysis has only modest sensitivity, and <10% exchange would have gone undetected.

(12) Two methods of error analysis were used and found to be comparable. Standard deviations from least-squares analyses were adjusted to 95% confidence levels ($t$ value for $N$ - 2 degrees of freedom). To check this method, one rate constant was measured four times and the absolute error was approximated from the standard deviation (t value for 3 degrees of freedom), and assumed to approximate the error in all rate constants. Errors in rate constants were totally propagated by differential regression in determining errors in thermodynamic data, activation parameters, and isotope effects. For a discussion of such treatments, see: Davis, W. H.; Pryor, W. A. *J. Chem. Educ.* **1976**, *53*, 285–287.

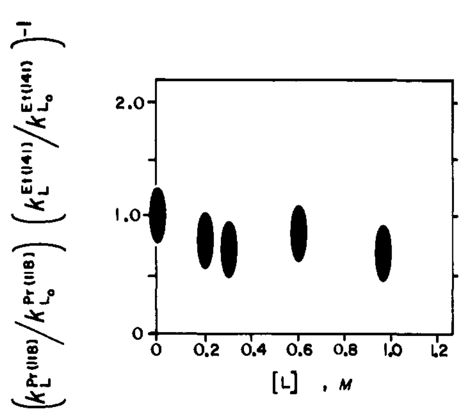


**Figure 8.** Changes in the concentration of [L] have similar influence on the magnitude of $k_L$ for $L_2PtEt_2$ and $L_2PtPr_2$. Rates for each compound are referenced to the rate at [L] = 0.0.

and propylene (by GC). Free propylene was not visible in the $^1H$ NMR spectra of samples decomposed below 85 °C; $\{^1H\}$ $^{31}P$ NMR of these samples showed a single set of resonances attributable to $L_2Pt$(propylene). At higher temperatures dark solutions exhibiting complex spectra containing $L_3Pt^0$ were observed. The disappearance of $L_2PtPr_2$ (followed by $\{^1H\}$ $^{31}P$ NMR) followed first-order kinetics to greater than 3 half-lives. The decomposition was inhibited by added triethylphosphine (Figure 7); the form of this dependence is qualitatively similar to that observed for $L_2PtEt_2$ (Figure 7).

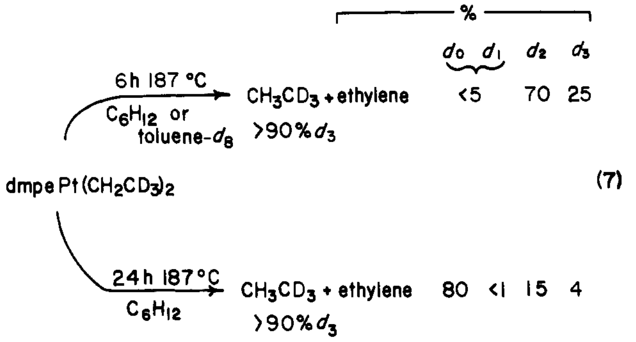
Figure 8 compares the relative rates of thermal decomposition of $L_2PtPr_2$ and $L_2PtEt_2$ described by the rate constant $k_l$ (eq 2) over a range of concentrations of added L. The vertical axis of this plot is the *ratio* of the rates of decomposition of the two complexes, *each normalized to the rate at* [*L*] = *0.0.* A separate measurement established that the relative rates of decomposition of the two complexes at [L] = 0 were close to one ($k^{Pr}{}_{L=0}/k^{Et}{}_{L=0}$ = 1.3 at 118 °C). Thus the vertical axis is approximately $k^{Pr}{}_L/k^{Et}{}_L$. For convenience, measurements for the more rapidly decomposing $L_2PtPr_2$ complexes were made at 118 °C, while those for $L_2PtEt_2$ were made at 141 °C. Any corrections to the plot resulting from this procedure should be small.

The observation that $L_2PtPr_2$ decomposes 30% more rapidly than $L_2PtEt_2$ at [L] = 0.0 probably reflects a small steric effect on the rate-limiting phosphine dissociation, with this rate being higher for the larger propyl group. Addition of triethylphosphine results in comparable decreases in $k_L$ (eq 2) for each complex (Figure 8). Thus, in intermediate regimes of [L] where phosphine dissociation and β-hydride elimination are preequilibrium steps, rates of thermal decomposition are similar; apparently, the abilities of ethylene and propylene to stabilize the platinum atom in the transition state are similar.[13] At high concentrations of added triethylphosphine (where the rates are independent of [L]), the rate of decomposition of $L_2PtPr_2$ is approximately 12 times faster than that of $L_2PtEt_2$. Since the changes in $k_L$ are comparable, the differences in thermal stability of the ethyl and propyl complexes as a function of [L] reflect principally the relative magnitudes of $k_4$ (eq 2). We believe (see below) that the transition state at high [L] is more sterically hindered than at low [L], and suggest that this steric hinderance may be responsible for the (relatively) rapid decomposition of $L_2PtPr_2$ at high [L].

**Thermal Decomposition of Diethyl(1,2-dimethylphosphinoethane)platinum(II) (dmpePtEt₂).** To explore the consequences of further inhibition of dissociation of phosphines from the $PtEt_2$ moiety, we examined the thermal decomposition of $dmpePtEt_2$. In the presence of 1 equiv of added dmpe, this decomposition yielded the products shown in eq 6; in the absence of added dmpe, platinum metal precipitated and other hydrocarbon products were formed, although ethylene and ethane dominated.

$$\text{dmpePtEt}_2 \xrightarrow[\substack{C_6H_{12} \\ 182\ ^\circ\text{C}}]{\text{1 dmpe}} (\text{dmpe})_2\text{Pt}(0) + CH_2{=}CH_2 + CH_3CH_3 \quad (6)$$

This decomposition follows a quite different course than that of $L_2PtEt_2$ in several respects. First, $dmpePtEt_2$ is much more stable than $L_2PtEt_2$. Decomposition of a 0.05 M solution of $dmpePtEt_2$ proceeds with a first-order rate constant $k^{obsd} = 1.2 \times 10^{-4}\ s^{-1}$ at 182 °C. Extrapolation of the rate constant for $L_2PtEt_2$ ([L] = 1.64 M) to this temperature indicates that $k^{L_2PtEt_2}/k^{dmpePtEt_2} \simeq 10^4$. Second, the rate constant for decomposition of $dmpePtEt_2$ is independent of [dmpe] from concentrations of 0.0 to 0.1 M. Third, the decomposition of $dmpePtEt_2$ (perhaps because of the high temperatures required) often showed pronounced autocatalysis, and could be followed reproducibly only over approximately the first 30–40% of the reaction. Finally the results of isotopic labeling experiments suggested a complex course for these reactions (eq 7). In the decomposition of $dmpePt(CH_2CD_3)_2$, very little transfer of deuterium from one ethyl-$d_3$ group to the other occurred (the ethane produced is >90% $CH_3CD_3$ by mass spectroscopy,[14] even in the early stages of the reaction). Thus the hydrogen consumed on generating ethane probably originates in the dmpe ligand (or, less probably, in the solvent). Further, the deuterium content of the ethylene is time dependent; at long reaction times (>15 h), either deuterium is lost from the (predominantly) ethylene-$d_2$ generated originally or (more probably) nondeuterated ethylene is generated from dmpe or solvent. Since these thermal decompositions are partially heterogeneous, we have not examined their mechanism in any detail. We have, however, compared the initial rates of decomposition of $dmpePt(C_2H_5)_2$ and $dmpePt(C_2D_5)_2$, and observed an isotope effect of $k_H/k_D$ = 1.6 ± 0.3. This isotope effect is (perhaps coincidentally) similar to that observed for $L_2PtEt_2$ for [L] = 1.64 M ($k_H/k_D$ = 1.7).



(7)

Although the thermal decomposition of $dmpePtEt_2$ cannot be compared in detail with that of $L_2PtEt_2$ since the reactions appear to have different mechanisms, there is nonetheless one useful qualitative observation to be extracted from the former; viz., $dmpePtEt_2$ is much more thermally stable than $L_2PtEt_2$, *even in the regime* ([*L*] ~ *1.6 M*) *in which the rate-limiting transition state for decomposition of* $L_2PtEt_2$ *contains two* $Et_3P$ *moieties.*

## Discussion

The thermal decomposition of $L_2PtEt_2$ in cyclohexane can occur by three distinct mechanisms (or variations of the rate-limiting step within a common mechanism), depending on the concentration of added L present in the solution. Each is discussed in turn.

**[L] = 0 M.** The scrambling of deuterium labels in the ethylene product, the absence of scrambling in recovered $PtC_2H_2D_3$ groups, the absence of intermolecular phosphine exchange, and the isotope effect of $k_H/k_D$ = 1 are all observations consistent with rate-limiting triethylphosphine dissociation (Figure 9). The value of $E_a$ observed for this reaction is compatible with this mechanism,[15]

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[13] Association constants of transition metals with olefins (especially ethylene and propylene) have been extensively reviewed; see: Hartley, F. R. *Chem. Rev.* **1973**, *73*, 163–190, and references cited therein.

[14] The ethane generated by thermolysis was identified as largely $CH_3CD_3$ by comparison of its mass spectrum with that of reference spectra ("Index of Mass Spectral Data"; Stehagen, E.; Abrahamsson, S.; McLafferty, F. W., Eds.; Wiley: New York, 1974; Vol. 1) and with that of ethane obtained by reaction of $L_2Pt(CH_2CD_3)_2$ with HCl.

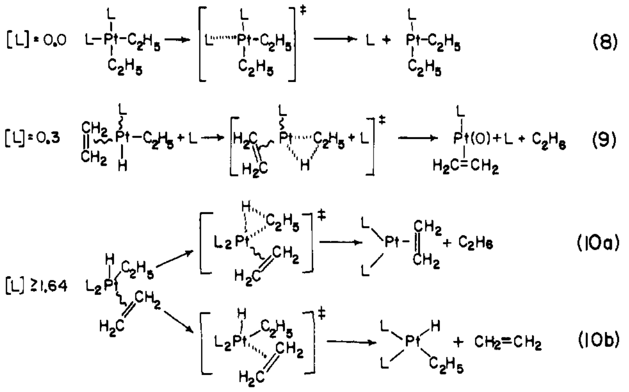

**Figure 9.** Proposed rate-limiting steps and transition state structures for decomposition of $L_2PtEt_2$ at different values of [L].

and the $A$ value is appropriate for a process in which two particles are created from one in the transition state.[16] The absence of a kinetic isotope effect indicates that $\beta$-hydride elimination is *not* concerted with triethylphosphine loss and occurs as a separate step from an intermediate, three-coordinate species, $LPtEt_2$.

**[L] = 0.3 M.** The inverse first-order dependence of rate on [L] and the observed scrambling of deuterium in the ethyl groups of recovered starting material establish that phosphine dissociation and $\beta$-hydride elimination/readdition are fully or partially reversible. The kinetic isotope effect is similar to that observed by Halpern et al. for reductive elimination of methane and bis(triphenylphosphine)methylhydridoplatinum(II).[8] We conclude that the overall rate-limiting step in this kinetic regime is reductive elimination of ethane from an intermediate (triethylphosphine)(ethylene)ethylhydridoplatinum(II) (Figure 9). In this figure, we include the previously dissociated triethylphosphine moiety in the transition-state representation simply for bookkeeping; its inclusion is not intended to imply any interaction, but is helpful in considering the magnitude of the activation parameters, especially the entropy of activation.[16]

Several features of the evidence in Table I concerning this process warrant elaboration. First, we place the ethylene in the transition state using indirect arguments. Kinetic evidence indicates that only one platinum and one phosphine are present in the transition state. The observed product, $(Et_3P)_2Pt$(ethylene), contains coordinated ethylene. Ethylene is a good ligand for both platinum(II) and platinum(0).[17] If the ethylene were *not* coordinated to platinum, it would seem that the decomposition of LPt(H)Et must generate LPt(0), unsolvated by other species (other than possibly cyclohexane). Monocoordinated platinum(0) is an unstable, high-energy species, and we include ethylene in the transition state to avoid its formation. Second, $LPt{\cdot}CH_2{=}CH_2$ is also a relatively high-energy species (although more stable than LPt(0)), and a reaction generating it is expected to have (and has) a high activation energy ($E_a$ = 46 kcal/mol). This reaction proceeds only because of a compensating high value for the preexponential term (log $A$ = 22), reflecting the conversion of one particle ($L_2PtEt_2$) to three ($LPtCH_2{=}CH_2$, L, and $CH_3CH_3$) in the transition state. This process emphasizes the potential importance of entropic terms in organometallic reactions involving relatively readily dissociated ligands and raises question concerning the generality of proposals that enthalpic terms dominate the course of organometallic reactions.[18] Third, the isotopic composition of the ethyl-$d_3$ bromide and ethylene-$d_n$ derived from $L_2Pt(CH_2CD_3)_2$ suggests that the label scrambling is not complete in either. Qualitatively, this observation indicates that olefin insertion into the platinum hydride bond (3 → 2, 3 → 4, Scheme I) is only slightly faster than reductive elimination of ethane.

**[L] = 1.64 M.** The independence of the rate to changes in [L] in this regime indicates that two phosphines are present in the transition state. Extensive $^2H$ scrambling in the $PtC_2H_2D_3$ group derived from $PtCH_2CD_3$ moieties establishes that $\beta$-hydride elimination and readdition are rapid and reversible. The rate at 157 °C was not affected by making the solution ~0.1 M in ethylene: thus, reversible ethylene loss before the rate-limiting transition state is apparently not important. The magnitude of the preexponential factor (log $A$ = 16 ± 1.5) is consistent with the generation of two particles from one at the transition state.

Two plausible candidates for the structure of the transition state seem compatible with these data. One, involving reductive elimination of ethane as the rate-limiting step, is analogous to that proposed at [L] = 0.3 M, with the addition of a second equivalent of triethylphosphine (eq 10a). The second (eq 10b) would invoke ethylene loss as the overall rate-limiting step, followed by a fast post-rate-determining reductive elimination of ethane. In the first of these mechanisms, the low value of $k_H/k_D$ = 1.4–1.7 (relative to the value of $k_H/k_D \simeq 3$ observed for [L] = 0.3 M) would be rationalized on the basis of an early transition state; in the second, it would be rationalized as a combination of secondary isotope effects reflecting changes in force constants for Pt(H) and $C_2H_4(D_4)$ bonds on dissociation of ethylene and small preequilibrium isotope effects.

Although the available data do not clearly distinguish between the processes shown in eq 10a and 10b, we favor the former because it is analogous to the mechanism already established as occurring at intermediate concentrations of phosphine ([L] = 0.3 M), and is therefore the simpler alternative.[19]

In summary, these thermal decomposition reactions display three mechanistically interesting features.

(1) The same organic products are generated from the alkylplatinum moieties by three distinct reactions. These processes have very similar values of $\Delta G^{\ddagger}$. Which process dominates is determined by [L]: that is, by $\Delta S^{\ddagger}$.

(2) Although the products generated from the alkylplatinum moieties reflect $\beta$-hydride elimination, in none of the three reactions is $\beta$-hydride elimination itself rate limiting.

(3) These $\beta$-hydride elimination processes are very closely related to intramolecular $\gamma$-, $\delta$-, and $\epsilon$-C–H bond activation reactions of other $L_2PtR_2$ complexes.[5,20] In all of these processes, the slow step is dissociation of phosphine or reductive elimination of a C–H bond. Cleavage of C–H bonds by oxidative addition

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[15] Johnston, R. D.; Basolo, F.; Pearson, R. G. *Inorg. Chem.*, **1971**, *10*, 247–251.

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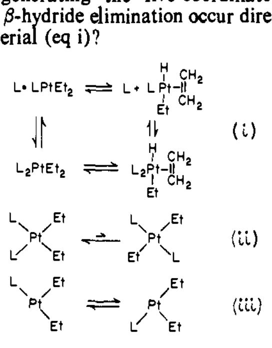
[19] Another unresolved mechanistic ambiguity concerning the reaction at [L] = 1.64 N concerns the coordination number at platinum during the $\beta$-hydride elimination step: are triethylphosphine dissociation and recombination involved in generating the five-coordinate intermediate $L_2Pt(H)(C_2H_4)R$, or does $\beta$-hydride elimination occur directly from the four-coordinate starting material (eq i)?



In addition, in all of the mechanistic regimes, we have no experimental evidence concerning possible equilibration of *cis*- and *trans*-$L_2PtEt_2$. Evidence described elsewhere indicates that at [L] = 0 the two ethyl groups of $LPtEt_2$ are equivalent: that is, *both* are converted to ethane. This observation suggests either that equilibration of "T"-shaped isomers of $LPtEt_2$ is fast (eq ii), that the structure of this material is "Y"-shaped, or that some other process renders the ethyl groups equivalent. Cf., McCarthy, T. J.; Nuzzo, R. G.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 1676–1678.

[20] DiCosimo, R.; Moore, S. S.; Sowinski, A. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 948–949. Sowinski, A. F. PhD. Thesis, Massacusetts Institute of Technology, Cambridge, Mass., 1979.

at a vacant coordination site of platinum(II) is fast compared with creation of that vacant coordination site.

## Experimental Section

**General.** All reactions and transfers involving organometallic compounds were carried out under argon or nitrogen. Diethyl ether was distilled from disodium benzophenone dianion under argon. Methanol was distilled from Mg activated with $I_2$ under argon. Cyclohexane was stirred over sulfuric acid for 48 h, washed with dilute sodium bicarbonate, then water, dried with phosphorus pentoxide, and distilled under argon. Diglyme and triethyl phosphate were distilled at reduced pressure and dried with 5A molecular sieves. Iodomethane and ethyl bromide were passed thorough a 10-cm column of Woelm activity I alumina and degassed prior to use. Other commerical reagents were used without purification. Yields of Grignard reagents and organolithium reagents were determined by titration against 2-propanol in xylenes, using, 2,2′-biquinoline as indicator.[21] Melting points were determined in sealed capillaries using a Thomas-Hoover apparatus and are corrected. Grignard and lithium reagents were prepared in diethyl ether. Proton-decoupled $^{31}P$ and $^{2}H$ NMR spectra were recorded at 36.4 and 13.8 MHz, respectively, on Bruker HFX-90 and Jeol FX-90Q spectrometers; $^{31}P$ chemical shifts, in parts per million, are relative to 85% phosphoric acid (downfield shifts positive). Mass spectra were recorded on a Varian Mat 44, and GC/MS data obtained with either a Perkin-Elmer 990 chromatograph interfaced with a Hitachi-Perkin-Elmer RMU-6E mass spectrometer or a Hewlett-Packard 5990 GC/MS spectrometer. Satisfactory elemental analyses were obtained for all nondeuterated platinum(II) complexes reported here. Isotopic purity of deuterated complexes was assayed by GC/MS of the hydrocarbon products from HCl quenches.

**Deuterated Reagents.** Perdeuterioethyl bromide and ethyl-*2,2,2-d*$_3$ bromide were prepared (87% yield) from commerical perdeuterioethanol and ethanol-*2,2,2-d*$_3$ by a literature method.[22] Ethanol-*2,2,2-d*$_3$ was prepared in 70% yield by reduction of acetic-$d_3$ acid-*d* with $LiAlH_4$.[23]

**Triethylphosphine-$d_{15}$.** All manipulations were carried out under argon. Triphenyl phosphite (9.3 g, 30 mmol), 75 mL of ether, and a stirring bar were placed in a 500-mL flask and cooled to −55 °C. A 0.63 M solution (145 mL, 91 mmol) of perdeuterioethylmagnesium bromide was added via cannula to the stirred solution over a period of 30 min. The mixture was stirred at this temperature for 4 h and then allowed to warm to 0 °C at which temperature it was stirred for 2 h. The flask was cooled to −30 °C and ca. 20 mL of degassed 15% aqueous sodium hydroxide solution was added; the fine white precipitate became granular. The liquid was transferred through a cannula to another flask and the residual precipitate washed with two 50-mL portions of ether. The ether layers were combined and distilled through a 35-cm Holzmann column under argon. Triethylphosphine-$d_{15}$ (2.1 g, 59%) boiled at 124–129 °C.

**Diethylbis(triethylphosphine)platinum(II) (from Ethylmagnesium Bromide).** Ethylmagnesium bromide (6.25 mL, 0.4 M, 2.5 mmol) was added by syringe to a stirred suspension of 0.374 g of dichloro(1,5-cyclooctadiene)platinum(II) (1.0 mmol) in 10 mL of ether at −78 °C. The dry ice/acetone bath was allowed to warm to −20 °C over 4 h, then was returned to −78 °C, at which temperature the excess Grignard reagent was quenched with a degassed solution of 0.1 mL of distilled water in 1 mL of methanol. The mixture was slowly warmed to 0 °C, dried with magnesium sulfate, filtered under argon, and concentrated at reduced pressure to ca. 2 mL. Degassed methanol (5 mL) was added and the solution was cooled to −78 °C at which temperature 0.3 mL (0.243 g, 2.06 mmol) of triethylphosphine was added dropwise. After 30 min, the resulting white product was separated by filtration and dried at reduced pressure at low temperature. The material had mp 31–33 °C (yield 0.41 g, 82%). The product was recrystallized from ether/methanol twice to yield needles with mp 35.5–36 °C (lit.[24] 35–36 °C).

**Diethylbis(triethylphosphine)platinum(II) (from Ethyllithium).** The lithium reagent was prepared in ether from ethyl bromide. Ethyllithium (10.0 mL, 0.25 M, 2.5 mmol) was added to a stirred suspension of 0.50 g (1.0 mmol) of *cis*-dichlorobis(triethylphosphine)platinum(II) in 10 mL of ether at −78 °C. The mixture was allowed to warm to 0 °C, and to stir for 15 min before it was treated as described above. The yield of a sample, mp 29–30 °C, was 0.43 g (86%). This material was recrystallized to mp 35.5–36 °C.

**Diethyl-*2,2,2-d*$_3$-bis(triethylphosphine)platinum(II) and diethyl-$d_6$-bis(triethylphosphine)platinum(II)** were prepared from either organolithium or organomagnesium reagents. The latter were preferred, because the yields of organomagnesium compounds (80–90%) were higher than those of organolithium reagents (63–70%).

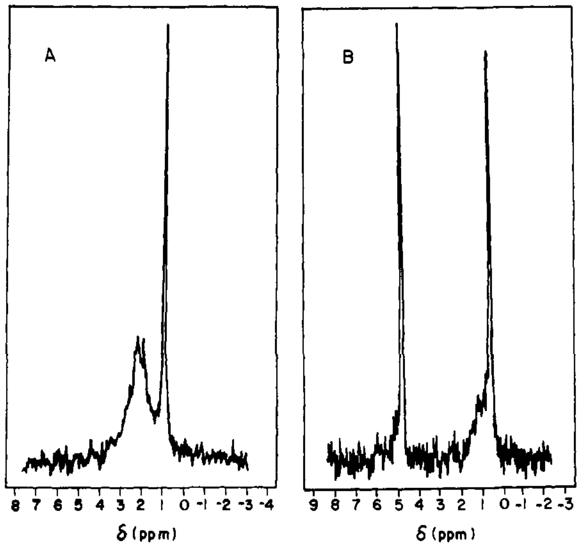


**Figure 10.** $^{2}H$ NMR spectra: (A) the solution produced from the thermal decomposition of $L_2Pt(CD_2CD_3)_2$ (containing $CD_3CD_3$ and $L_2Pt(CD_2{=}CD_2)$); (B) after treatment with excess L.

**Di-*n*-propylbis(triethylphosphine)platinum(II)** was prepared from *n*-propylmagnesium bromide by a procedure analogous to that described for $L_2PtEt_2$. Recrystallization from ether/methanol at low temperature gave a glassy compound melting below 0 °C; $^{31}P$ NMR $\delta$ 10.7, $J_{Pt-P}$ = 1701 Hz.

**Diethyl(bis(1,2-dimethylphosphino)ethane)platinum(II), Diethyl-*2,2,2-d*$_3$-(bis(1,2-dimethylphosphino)ethane)platinum(II), Diethyl-$d_5$-(bis(1,2-dimethylphosphino)ethane)platinum(II).** Procedures analogous to that described for the triethylphosphine compounds were used (Grignard method). White crystalline compounds were obtained, mp (protio) 133–134 °C; mp (trideuterio) 133–134 °C; mp (perdeuterio) 133–134 °C; $^{31}P$ NMR $\delta$ 19.0, $J_{Pt-P}$ = 1558 Hz.

**Decomposition Products of $L_2PtEt_2$.** A 0.1 M solution of $L_2PtEt_2$ in cyclohexane was heated for 4 h at 89 °C. The solution changed from colorless to dark orange and remained homogeneous. GC analysis of an aliquot of the reaction mixture showed the presence of equal quantities of ethane and ethylene (100% yield based on $PtEt_2$ groups). Free ethylene ($\delta$ 5.3) was not visible in the $^{1}H$ NMR spectrum; $Pt{\cdot}CH_2CH_2$ resonances ($\delta$ 2.2, $J_{Pt-H}$ = 54 Hz) were partially obscured by the triethylphosphine absorption and $^{2}H$ NMR identified $(Et_3P)_2Pt(CD_2CD_2)$ (Figure 10). The $^{31}P$ NMR spectrum showed only one signal ($\delta$ 20.6 $J$ = 3551 Hz) characteristic of a platinum(0) complex. When 1 equiv. of triethylphosphine was added to the solution, it turned bright yellow and free ethylene appeared in the $^{1}H$ NMR spectrum; the $^{31}P$ NMR spectrum exhibited a very broad absorbance which we attribute to rapidly equilibrating free and platinum-coordinated phosphine.

In a separate experiment, a 31-mg (0.063-mmol) sample of $L_2PtEt_2$ was decomposed in cyclohexane (0.5 mL) for 1 h at 118 °C (10 half-lives). The tube was opened in a glove box and treated with 0.1 mL of degassed methyl iodide. The orange color disappeared and the solution became nearly colorless. The contents of the tube was poured onto a watchglass; evaporation yielded 36.3 mg (100%) of off-white *trans*-iodomethylbis(triethylphosphine)platinum(II) identified by its mp of 68–71 °C (lit.[24] 71–71.5 °C), mass spectrum (573 $M^+$), and $^{31}P$ NMR spectrum: $\delta$ 10.6 m, $J_{P-Pt}$ = 2778 (lit.[25] $\delta$ 9.4, $J_{P-Pt}$ = 2754 Hz).

**Kinetics of Thermal Decomposition.** Cyclohexane solutions of platinum complexes (0.1 M) were prepared in Wilmad-507PP NMR tubes according to previously described procedures.[5] The thermal decompositions were performed in constant-temperature oil baths thermostatically controlled (±0.25 °C) with a calibrated thermometer; temperatures are believed to be accurate to ±0.25 °C. Samples were removed from the baths at intervals and cooled to room temperature. These samples were stored no longer than 15 min at room temperature prior to analysis by $^{31}P$ NMR.[26] The extent of decomposition was determined by comparing proton-decoupled peak heights of the starting material and an internal

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(26) A sample stored overnight gave a spectrum identical with one taken the previous day.

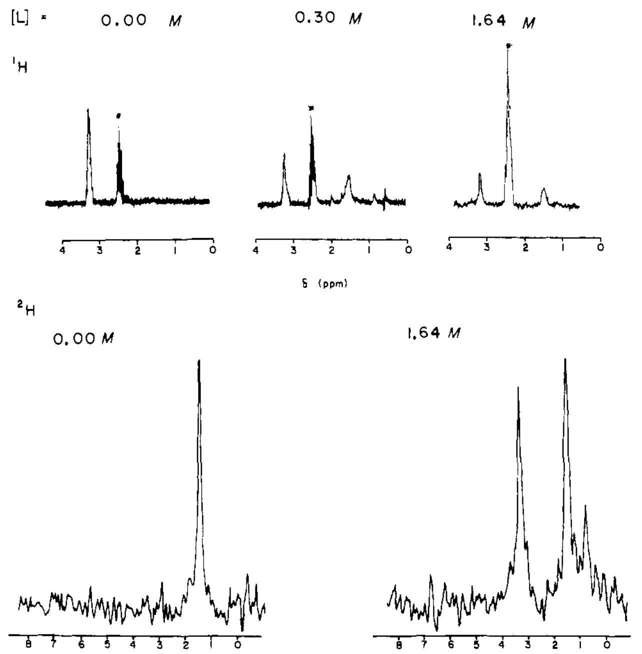

**Figure 11.** (Upper) $^1H$ NMR spectra ($C_7H_8$) of samples of ethyl-$d_3$ bromide derived from bromine quenches of $L_2Pt(C_2H_2D_3)_2$ recovered after 50% decomposition of $L_2Pt(CH_2CD_3)_2$ in solutions having different values of [L]. The multiplet marked with an asterisk is $^1H$ impurities in the solvent. The peak at $\delta$ 3.3 is due to BrCH resonances, and that at $\delta$ 1.6 to BrCCH resonances. Both samples at [L] = 0.3 and 1.64 M show scrambling of $^1H$ into the methyl group; that at [L] = 0.0 does not. (Lower) $^2H$ NMR spectra ($C_6H_{12}$) of similar samples at [L] = 0.0 (left) and 1.64 M (right). The former shows $^2H$ only in the methyl group; the latter shows $^2H$ both in the methyl and methylene positions.

standard (0.237 M triethyl phosphate). Independent experiments established that the triethyl phosphate had no influence on the course of the reactions.

**Test of Intramolecularity.** $L_2PtEt_2$ (15 mg) and $L_2Pt(C_2D_5)_2$ (15 mg) were sealed in a tube containing 0.30 M triethylphosphine in cyclohexane. The tube was heated at 157 °C for 30 min (several half-lives). The tube was cooled to -200 °C, broken open, and subjected to GC/MS analysis. The mass chromatograms at 70, 40, 20, and 15 eV all indicated 94% $d_6$ ethane and 6% $d_5$ ethane. As the ethane from a DCl quench of $L_2Pt(Et\text{-}d_5)_2$ gave an identical isotopic distribution, we conclude that the reaction is intramolecular.

**Bromine Quenches of $L_2Pt(C_2H_2D_3)_2$.** Three tubes were sealed and decomposed to 1 half-life. Each contained 35 mg of $L_2Pt(CH_2CD_3)_2$ and 0.5 mL of solvent: cyclohexane (decomposed for 1 h at 89 °C), 0.30 M $Et_3P$ in cyclohexane (17 min at 131 °C), and 1.64 M $Et_3P$ in cyclohexane (25 min at 141 °C). The tubes were opened and transferred to flasks and the volatiles removed at 0.01 Torr. Toluene-$d_8$ (0.25 mL) was added and the solution cooled to -78 °C. Two drops of bromine in 0.25 mL of toluene-$d_8$ was added. Trap-to-trap transfers of the volatiles were performed; $^1H$ and $^2H$ spectra of the ethyl bromide in the resulting samples were recorded. The sample decomposed with phosphine absent was not scrambled; the ones with phosphine present were nearly statistically scrambled (Figure 11).

**GC/MS Analysis of Ethylene from Decomposition of $L_2Pt(CH_2CD_3)$.** Three samples, identical with those described above, were decomposed to 4 half-lives. Isotopic compositions of the ethylene produced (from integration of mass chromatograms corrected for the contribution of fragment ions) are [L] (M), $m/e$ = 30 (%), $m/e$ = 31 (%); 0.0, 43, 57; 0.30, 42, 58; 1.64, 47, 53.

**Decomposition of Mixtures of $L^D{}_2PtEt_2$ and $L_2PtEt_2$.** $L^D{}_2PtEt_2$ (15 mg) and ($L_2PtEt_2$) (15 mg) were sealed in a tube in 0.5 mL of cyclohexane and decomposed for 1 h at 89 °C (1 half-life). The $^{31}P$ spectrum showed only two sharp signals corresponding to $L_2PtEt_2$ and $L^D{}_2PtEt_2$ in the same ratio as before decomposition. The formation of $LL^DPtEt_2$ would have been reflected in spectral changes of the type observed previously.[5,11]

**Decomposition Products of $L_2PtPr_2$.** A 0.1 M solution of $L_2PtPr_2$ in cyclohexane was heated for ~4 h at 84 °C. The solution changed from colorless to dark orange and remained homogeneous. GC analysis of an aliquot of the reaction mixture showed the presence of equal quantities of propane and propene. The $^{31}P$ NMR spectrum showed a complex pattern consisting of a non-first-order doublet of doublets each with a distinct coupling to platinum. Spectral data are summarized below. $L_2Pt(C_3H_6)$: $^{31}P$ NMR, $\delta_1$ 23.1, $\delta_2$ 20.5; $J_{Pt-P_1}$ = 3642 Hz, $J_{Pt-P_2}$ = 3310 Hz, $J_{P_1-P_2}$ = 66 Hz. Thermolysis at 118 °C gave very dark solutions containing a new species having $^{31}P$ NMR $\delta$ 43, $J_{Pt-P}$ = 4224 Hz (lit.[27] ($L_3Pt(0)$) $\delta$ 42, $J_{Pt-P}$ = 4220 Hz). Decompositions in the presence of excess phosphine gave yellow solutions whose $^{31}P$ NMR spectra were analogous to those obtained for $L_2PtEt_2$ under similar conditions.

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