Table V. Atomic Positional (× 10⁴) and Thermal (× 10³) Parameters[a]

atom	x	y	z	U_{eq}, Å²
Pt1	32027 (2)	2500	8604 (8)	422 (2)
Pt2	41770 (3)	2500	38994 (7)	434 (2)
I1	32216 (4)	2500	39114 (13)	561 (4)
I2	6880 (5)	2500	46750 (19)	648 (4)
Cl1	3885 (4)	7500	4427 (12)	138 (4)
Cl2	3014 (3)	7500	5878 (13)	176 (5)
P1	3259 (1)	4444 (3)	907 (4)	49.3 (9)
P2	4238 (1)	4056 (3)	2185 (4)	44.6 (9)
C1	3132 (7)	2500	−1498 (22)	56 (6)
C2	3343 (6)	5164 (13)	−876 (16)	69 (5)
C3	2768 (5)	5199 (14)	1705 (21)	86 (6)
C4	3720 (4)	4944 (12)	2093 (15)	50 (4)
C5	4399 (5)	3892 (13)	204 (13)	52 (4)
C6	4656 (5)	5084 (13)	2793 (18)	74 (5)
C7	4881 (7)	2500	4164 (21)	64 (6)
C8	4134 (5)	3707 (15)	5660 (14)	67 (5)
C9	3579 (14)	7500	6021 (30)	167 (17)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^1/_6\pi^2[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$. Positional parameters for Pt and I atoms (× 10⁵). Values without estimated standard deviations were fixed in the refinement. Thermal parameters for Pt and I atoms (× 10⁴).

weight, due to systematic error. The final cycles of refinement included 128 variables, a p value of 0.07, used 1646 unique observations with $I > 3\sigma$, and converged at agreement factors of R_1 = 0.035 and R_2 = 0.048. The largest parameter shift in the final cycle was 0.01σ. In a total difference Fourier synthesis the top 10 peaks (ranging from 1.2 (2) to 0.8 (2) e Å⁻³) were all within 1.2 Å of the Pt and I atoms. The error in an observation of unit weight is 1.04 e, and an analysis of R_2 in terms of the magnitude of F_o, $\lambda^{-1} \sin \theta$, and various combinations of Miller indices showed no unusual trends. Final positional and U(equiv) thermal parameters are given in Table V for all non-hydrogen atoms. Anisotropic thermal parameters, hydrogen atom parameters, root-mean-square amplitudes of vibration, supplementary bond distances and angles, weighted least-squares planes, torsion angles, and structure amplitudes have been deposited.[29]

Supplementary Material Available: Tables of anisotropic thermal parameters, thermal parameters, root-mean-square amplitudes of vibration, hydrogen atom parameters, supplementary dimensions, weighted least-squares planes, torsion angles, and structure amplitudes ($10F_o$ vs. $10F_c$ in electrons) (16 pages). Ordering information is given on any current masthead page.

(29) Supplementary material.

The Mechanism of Thermal Decomposition of *trans*-Chloroethylbis(triethylphosphine)platinum(II)[1]

Robert L. Brainard and George M. Whitesides*[2]

Departments of Chemistry, Harvard University and Massachusetts Institute of Technology, Cambridge, Massachusetts 02138

Received March 6, 1985

The thermal decomposition of *trans*-chloroethylbis(triethylphosphine)platinum(II) (L₂PtEtCl, 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, L₂PtHCl(C₂H₄) (2). Three pathways might be involved in the formation of 2 from 1 (Scheme I): β-hydride elimination proceeding directly from 1 *without* prior dissociation of phosphine or chloride; phosphine dissociation, reversible β-hydride elimination, and phosphine reassociation; or chloride dissociation, reversible β-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 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 → 1) is significant. The equilibrium constant for 1 ⇌ 3 + ethylene was measured as a function of temperature giving K_{eq}(158 °C) = 0.69 M, $\Delta G°$(158 °C) = 0.32 kcal/mol, $\Delta H°$ = 12 kcal/mol, and $\Delta S°$ = 27 eu. The deuterium *equilibrium* isotope effect for the reaction L₂PtClC₂H₅(D₅) → L₂PtClH(D) + C₂H₄(D₄) is K_{eq}^H/K_{eq}^D = 1.9 ± 0.4; the deuterium *kinetic* isotope effect on the overall rate of decomposition of L₂PtClC₂H₅(D₅) under conditions in which the reverse reaction is slow is k_H/k_D = 2.5 ± 0.2. The rate of reaction increases slightly with increasing concentration of phosphine and chloride ion (as benzyldimethyltetradecylammonium 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 L₂PtEtCl and (L-d_{15})₂PtEtCl); halide ion exchange between L₂Pt(C₂H₅)Cl and L₂Pt(C₂D₅)Br is also observed within 30 min under these conditions.

Introduction

The transformation of metal alkyls to metal hydrides and olefins by β-hydride elimination is an important process in organometallic chemistry,[3–9] but because the β-hydride elimination step is itself rarely rate limiting, this process remains incompletely understood mechanistically.

(1) Supported by the National Science Foundation, Grant CHE-82-05143.

(2) To whom correspondence should be addressed at Harvard University.

(3) Tsutsui, M.; Courtney, A. *Adv. Organomet. Chem.* **1977**, *16*, 241–282. James, B. R. *Ibid.* **1979**, *17*, 319–405.

Scheme I. Thermal Decomposition of
trans-Chloroethylbis(triethylphosphine)platinum(II)[a]
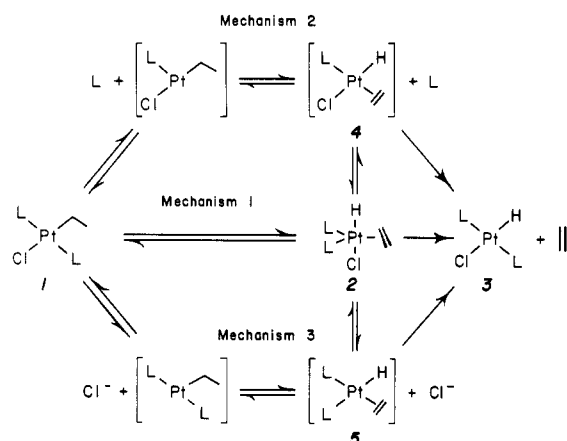
[a] There is no direct evidence for any species indicated
in brackets: they are given to indicate plausible
intermediates in mechanisms 2 and 3 (L = Et_3P).

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-$(Et_3P)_2Pt(CD_2CH_3)Br$ to $L_2PtH(D)Br$ and isotopi-
cally scrambled ethylene at 160–190 °C and proposed a
mechanism in which reversible β-hydride elimination was
followed by rate-limiting olefin loss.[10] We have investi-
gated the mechanism of thermal decomposition of the
complex *trans*-$(Et_3P)_2PtEtCl$ (1) (chosen instead of the
analogous bromide because it is easier to prepare and
purify) in cyclohexane solution. This reaction is mecha-
nistically interesting for several reasons:

(1) *cis*-Dialkylbis(trialkylphosphine)platinum(II) com-
plexes 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
$L_2PtEtCl$ would also dissociate phosphine before it un-
derwent 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 investiga-
tion of olefin insertion into metal hydrides[15] suggested that
trans-$(Et_3P)_2PtEtBr$ 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
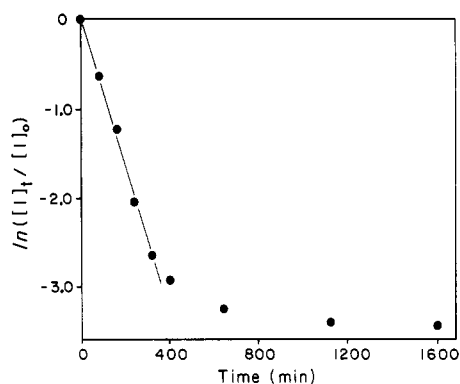(phosphine or halide) would dissociate prior to β-hydride

(4) Deeming, A. J.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton* **1973**, 1848–1852.

(5) Werner, H.; Feser, R. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 157–158.

(6) Kazlauskas, R. J.; Wrighton, M. S. *Organometallics* **1982**, *1*, 602–611.

(7) Ozawa, F.; Ito, T.; Yamamoto, A. *J. Am. Chem. Soc.* **1980**, *102*, 6457–6463.

(8) Ikariya, T.; Yamamoto, A. *J. Organomet. Chem.* **1976**, *120*, 257–284.

(9) Evans, J.; Schwartz, J.; Urquhart, P. W. *J. Organomet. Chem.* **1974**, *81*, C37–C39.

(10) Chatt, J.; Coffey, R. S.; Gough, A.; Thompson, D. T. *J. Chem. Soc. A* **1968**, 190–194.
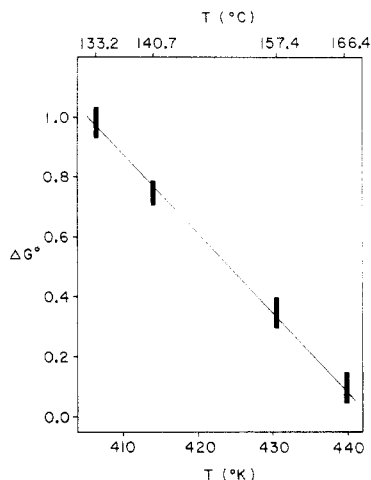
(11) McCarthy, T. J.; Nuzzo, R. G.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 3396–3403.

(12) Nuzzo, R. G.; McCarthy, T. J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 3404–3410.

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

(14) Foley, P.; DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 6713–6725.

(15) Thorn, D. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079–2090.

Figure 1. Thermal decomposition and approach to equilibrium
of $L_2PtEtCl$ to give L_2PtHCl and ethylene as a solution in cy-
clohexane ($V = 0.50$ mL) in a 5-mm NMR tube (V = ca. 2.0 mL):
$[L_2PtEtCl]_0 = 0.09$ M; $T = 158$ °C.

elimination. We wished to verify this prediction.

(3) If the mechanism proposed by Thompson were fol-
lowed in the decomposition of 1, 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 oc-
curred directly, without prior phosphine dissociation,
would be valuable in understanding this important ele-
mentary 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 $[L_2PtHCl(C_2H_4)]$. A plausible rate-limiting
step for the decomposition of 1 is loss of ethylene from a
five-coordinate intermediate of structure 2 or similar
processes in which ethylene is displaced from four-coor-
dinate 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,
$L_2PtEtCl$). Thus, for example, *trans*-chloro(ethyl-d_5)bis-
(triethylphosphine)platinum(II) will be called $L_2Pt(C_2-D_5)Cl$ or 1-d_5. Many of the studies of kinetics of decom-
position 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 tri-
ethylphosphine.

Results and Discussion

Products. A 0.08 M solution of $L_2PtEtCl$ in cyclo-
hexane, *n*-hexane, or THF decomposes on heating in a
sealed NMR tube for 3.5 h at 158 °C and yields L_2PtHCl
(identified by ^{31}P and ^{1}H NMR spectroscopy) and free
ethylene (by ^{1}H NMR). The solutions containing products
of decomposition are colorless and homogeneous. Solutions
obtained by decomposition of $L_2PtEtCl$ in *n*-hexane con-
taining added triethylphosphine (0.20 M $\leq$ [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 (ΔG°) for the thermal decomposition of $L_2PtEtCl$ to L_2PtHCl and $C_2H_4(soln)$ in cyclohexane plotted as a function of temperature: 1.5–3.8 equiv of ethylene added; $[L_2PtEtCl]_0 = 0.08$–0.13 M; solution volume = 1.0 mL; total NMR tube inner volume = 2.0 mL. The concentration of ethylene in solution (moles/liter) used to calculate K_{eq} and ΔG° was 0.06–0.16 M at 158 °C. Error bars represent 95% confidence limits for each value of ΔG°.

progresses, a signal attributable to L_2PtHCl 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 1 diminishes in intensity. Low-temperature ^{31}P and ^{1}H NMR studies suggest that L_2Pt-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.

$$L + L_2PtHCl \rightleftharpoons L_3PtHCl \rightleftharpoons L_3PtH^+Cl^- \qquad (1)$$
$$\; 3 \; 6 \; 7$$
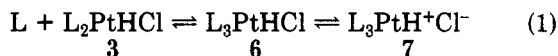
Kinetics. The disappearance of $L_2PtEtCl$[16] in cyclohexane solution (0.5 mL) in a sealed NMR tube ($\sim$2.0-mL total internal volume) is first order in $L_2PtEtCl$ for 3.8 half-lives (Figure 1). We demonstrate below that the falloff in rate beyond this point reflects establishment of equilibrium between 1, 3, and ethylene. The rate expression for the first-order thermal decomposition of $L_2PtEtCl$ by any of the mechanistic pathways listed in Scheme I is

$$-d[L_2PtEtCl]/dt = k^{obsd}[L_2PtEtCl] \qquad (2)$$

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 $L_2PtEtCl$ 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 ΔG° as a function of temperature (Figure 2) produced these thermodynamic parameters: $K_{eq}(158\ °C) = 0.69 \pm 0.09$ M;[17] $\Delta G^\circ(158\ °C) = 0.32 \pm 0.12$ kcal/mol; $\Delta H^\circ = 12 \pm 0.6$ kcal/mol; $\Delta S^\circ = 27 \pm 1.3$ eu.[18]

(16) The rate of decomposition of $L_2PtEtCl$ was followed by ^{31}P spectroscopy as described in the Experimental Section.

(17) We note that K_{eq} was calculated by using the observed concentration of ethylene in cyclohexane (mole/liter) and did not take into account ethylene in the vapor phase.
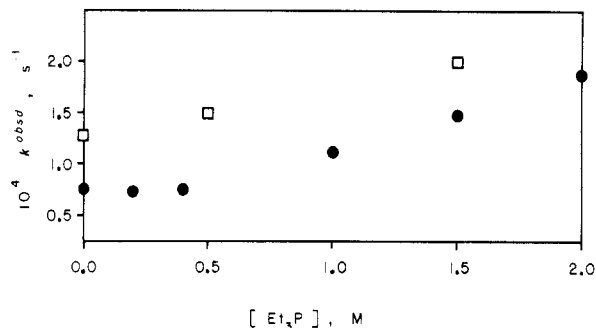
Figure 3. Rate constant k^{obsd} for the thermal decomposition of $L_2PtEtCl$ plotted as a function of triethylphosphine concentration ($[L_2PtEtCl]_0 = 0.05$ M; $T = 158\ °C$): $\square$, reaction conducted in cyclohexane, ^{31}P NMR probe temperature = 13 °C; $\bullet$, reaction conducted in n-hexane, ^{31}P NMR probe temperature = −34 °C.

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.

Effects of Phosphine Concentration on Rate. $L_2PtEtCl$ (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,[22] but we have not excluded some other involvement.

Exchange Broadening of the ^{31}P NMR Spectrum of $L_2PtEtCl$. The ^{31}P NMR signal of $L_2PtEtCl$ 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 $L_2PtEtCl$ makes the platinum atom sufficiently electrophilic to add another phosphine (eq 3). In contrast the ^{31}P signals of cis-$(Et_3P)_2PtEt_2$ and

(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

$$D_{PtH} - D_{PtC} = D_{CH} - D_{\pi CC} - \Delta H^\circ$$
$$= 98 - 63 - 12\ \text{kcal/mol}$$
$$= 23 \pm 5\ \text{kcal/mol}$$

The bond dissociation energies used here for C–H bonds and C–C π-bonds are typical values for organic compounds.[20] Since we consider these values to be accurate to about 2 kcal/mol, we set the error limits for this calculation at $\pm$5 kcal/mol.

(20) Streitwieser, A., Jr.; Heathcock, C. H. "Introduction to Organic Chemistry"; Macmillan: New York, 1976.

(21) This difference in bond energies is consistent with other studies which show that M–H bonds are stronger than M–C bonds for the third-row transition metals. In contrast, M–H bonds are weaker than M–C bonds among the first-row transition metals. Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6501–6502. Po, P. L.; Radus, T. P.; Porter, R. F. *J. Phys. Chem.* **1978**, *82*, 520–526.

(22) To emphasize how slightly the reaction rate is affected by the addition of phosphine, we note that the thermal decomposition of 1 is $\sim$1.7 times faster in cyclohexane than in n-hexane. We attribute this slight rate increase to the higher dielectric constant of cyclohexane ($\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 $\sim$1.2 M in Et_3P.

Table I. Effect of the Concentration of Chloride Ion on Rate of Decomposition of 1[a]

solv	$[Cl^-]$,[b] M	$10^4 k^{obsd}$, s^{-1}
C_6H_{12}	0.00	1.32 ± 0.02
THF/C_6H_{12} (1:1)	0.00	2.00 ± 0.04
THF	0.00	3.08 ± 0.10
	0.092	3.8 ± 0.2
	0.20	4.8 ± 0.2
	0.30	6.7 ± 0.2
	0.40	8.0 ± 0.2

[a] Decompositions were carried out starting with solutions containing 0.08 M 1 and 0.08 M $(EtO)_3PO$ at 158.5 °C. [b] Chloride was introduced as benzyldimethyltetradecylammonium chloride.

cis-$(Et_3P)_2Pt(CH_2C(CH_3)_3)_2$ remain sharp in high concentrations of Et_3P.[11,14,23]

$$L_2PtEtCl + L \rightleftharpoons L_3PtEtCl \qquad (3)$$

Intermolecular Exchange of Phosphine Ligands. A solution of $L_2PtEtCl$ (0.06 M) and $L^D_2PtEtCl$ (0.07 M, L^D = L-d_{15}) in cyclohexane underwent phosphine exchange and gave an equilibrium mixture of $L_2PtEtCl$, $LL^DPtEtCl$, and $L^D_2PtEtCl$ 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.[24]

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, $L_2PtEtCl$ was allowed to decompose in THF solutions containing several different concentrations of benzyldimethyltetradecylammonium chloride.[25] Rates were cleanly first order to >90% 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 $L_2PtEtCl$ 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 $L_2Pt(CD_2CH_3)Cl$ and of Ethyl-d_2 Bromide Derived from Recovered Starting Material[a]

no. of half-lives thermalized	ethylene-d_1/d_2		ethyl bromide H_α/H_β[b]	
	0.00[c]	0.60[c]	0.00[c]	0.60[c]
0			8/92	9/91
1	14/86	12/88	36/64	36/64
2	16/84	20/80	41/59	38/62

[a] $L_2Pt(CD_2CH_3)Cl$ 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. [b] A statistical distribution would be 40/60. [c] [L], M.

Intermolecular Exchange of Halogen Ligands. A mixture of $L_2PtEtCl$ (0.054 M) and $L_2Pt(C_2D_5)Br$ (0.055 M) in cyclohexane exchanged halogen atoms and yielded an equilibrium mixture of $L_2PtEtCl$, $L_2Pt(C_2D_5)Cl$, $L_2PtEtBr$, and $L_2Pt(C_2D_5)Br$ in less than ~20 min at room temperature.[27] A less concentrated solution of $L_2PtEtCl$ (0.026 M) and $L_2Pt(C_2D_5)Br$ (0.027 M) took ~40 min to reach equilibrium at room temperature. The course of the reaction was followed by ^{31}P 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.

Isotopic Scrambling in Starting Material and Products. Solutions of $L_2Pt(CD_2CH_3)Cl$ in cyclohexane ([L] = 0.00 or 0.60 M) were heated at 158.5 °C for 1 or 2 half-lives. The isotopic composition of the ethylene generated by decomposition of the platinum complex was determined by GC/MS. The solvent was removed, and the residual solid mixture of platinum compounds was dissolved in toluene-d_8 and allowed to react with bromine at −78 °C. The distribution of protons between the α- and β-position of the resulting ethyl bromide was determined by ^{1}H NMR spectroscopy.[28] The results of these experiments are summarized in Table II.

The essentially statistical isotopic scrambling observed in the ethyl bromide (reflecting scrambling in recovered starting material) and the observation of significant quantities of ethylene-d_1 establish that β-hydride elimination in $L_2PtEtCl$ is rapid and reversible. The absence of ethylene-d_0 and -d_3 demonstrates that reaction of free ethylene (d_n) with $L_2PtH(D)Cl$ is not important under these conditions.

The deuterium equilibrium isotope effect for the thermal decomposition of $L_2Pt(C_2H_5)Cl$ vs. $L_2Pt(C_2D_5)Cl$ was measured by allowing separate samples of each compound 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

$$1 \rightleftharpoons 3 + C_2H_4 \qquad (4)$$

$$1\text{-}d_5 \rightleftharpoons 3\text{-}d_1 + C_2D_4 \qquad (5)$$

of ethylene and ethylene-d_4 in solution directly. Here we

(23) McCarthy, T. J.; DiCosimo, R., personal communication.

(24) The phosphine exchange broadening experiments described in this paper indicate that phosphine ligands could exchange by associative mechanisms. Thus, a small amount of triethylphosphine impurity could cause phosphine scrambling.

(25) THF was used in these experiments because benzyldimethyltetradecylammonium chloride is insoluble in cyclohexane at room temperature.

(26) This mechanistic evidence suggests that in THF, chloride is bonded to platinum during the rate-limiting transition state. We assume that this holds true in cyclohexane as well, since this solvent has a lower dielectric constant.

(27) We judged that the reaction had reached completion when changes in the relative concentrations of $L_2PtEtCl$ and $L_2PtEtBr$ were less than the error limits for their measurement.

(28) The ratio of α/β protons in the ethyl bromide resulting from the bromine quench of unthermalized $L_2Pt(CD_2CH_3)Cl$ was reproducibly 8/92. We suspect that $L_2Pt(CD_2CH_3)Cl$ was initially scrambled to this extent and the bromine quench occurs with no scrambling. This observation is consistent with bromine quenches of $(Et_3P)_2Pt(CH_2CD_3)_2$.[11]

Table III. Deuterium Isotope Effects and Equilibrium Data for Conversion of 1 to 3 and Ethylene[a]

k_H^{obsd}/k_D^{obsd} [b] ([L] = 0 M)	2.5 ± 0.2 [b]
k_H^{obsd}/k_D^{obsd} ([L] = 0.60 M)	2.5 ± 0.8
K_{eq}^H/K_{eq}^D [c]	1.9 ± 0.4
K_{eq}(158 °C)	$0.69 \pm .09$
$\Delta G°$(158 °C)	0.32 ± 0.12 kcal/mol

[a] All values were determined at 158 °C and are reported to 95% confidence levels. [b] This value is an average of four independent experiments, including one value in which 1-d_0 and 1-d_5 were in the same NMR tube. [c] *trans*-(Et$_3$P)$_2$Pt(C$_2$H$_5$)Cl vs. *trans*-(Et$_3$P)$_2$Pt(C$_2$D$_5$)Cl.

assume that the concentrations of ethylene and ethylene-d_4 were proportional, *with the same proportionality constant*, r, to the concentrations of 3 and 3-d_1 (eq 6). The con-

$$\frac{[C_2H_4]}{[3]} = r = \frac{[C_2D_4]}{[3-d_1]} \quad (6)$$

centrations of 1, 1-d_5, 3, and 3-d_1 at equilibrium can be calculated from the initial concentrations of 1 or 1-d_5 and by comparing their initial and equilibrium ^{31}P NMR peak heights with those of (EtO)$_3$PO (an internal standard for integration). Assuming the correctness of eq 6, the equilibrium deuterium isotope effect for decomposition of 1 (1-d_5) at 158.5 °C is given by eq 7. This value is probably

$$\frac{K_{eq}^H}{K_{eq}^D} = \frac{[3]^2[1-d_5]}{[3-d_1]^2[1]} = 1.9 \pm 0.4 \quad (7)$$

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 (ν_{C-H} 2951–2857 cm^{-1}) to 3 (ν_{Pt-H} 2198 cm^{-1}) and ethylene (ν_{C-H} 3080, 2972 cm^{-1})[29] 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.[30] The deuterium isotope effects and equilibrium data for conversion of 1 to 3 and ethylene are summarized in Table III.

The conversion of (C$_5$Me$_5$)Rh(PMe$_3$)(C$_6$D$_4$H)D to (C$_5$Me$_5$)Rh(PMe$_3$)(C$_6$D$_5$)H also gives a substantial equilibrium isotope effect: $K_{eq}^H/K_{eq}^D = 2.7$.[31] 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 ($\nu_{C-H} \simeq 3030$ cm^{-1})[20] and the effect is not diminished by the formation of four ethylene C–H bonds. These differences are probably important in determining the greater
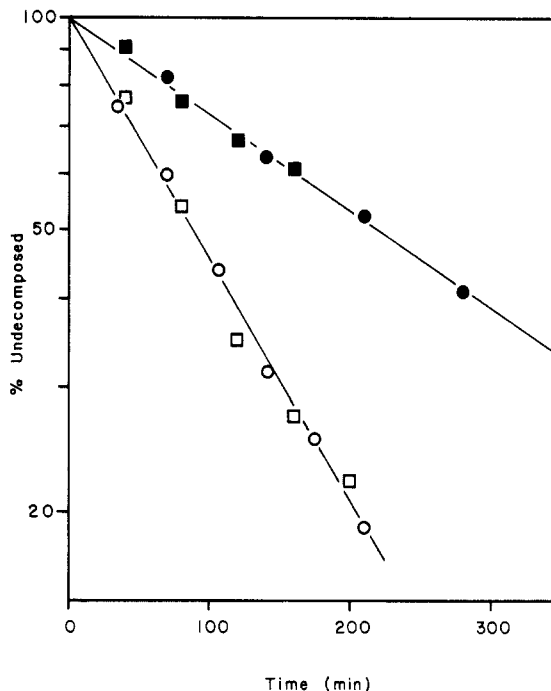
(29) Comeford, J. J.; Gould, J. H. *J. Mol. Spectrosc.* **1960**, *5*, 474–481.

(30) The equilibrium isotope effect for the decomposition of L$_2$PtCl-C$_2$H$_5$(D$_5$) to give L$_2$PtClH(D) and C$_2$H$_4$(D$_4$) was calculated by using a simplified version of the method of Wolfsberg and Stern in which only the stretching vibrations for each type of hydrogen (deuterium) bond were used. The calculated value of $K_{eq}^H/K_{eq}^D = 1.7$ supports the experimental value $K_{eq}^H/K_{eq}^D = 1.9 \pm 0.4$. Wolfsberg, M.; Stern, M. J. *Pure Appl. Chem.* **1964**, *8*, 225–242.

(31) In the original work by Jones and Feher, this reaction was run in the direction opposite to that described here; hence, the equilibrium isotope effect was reported to be 0.37 rather than its reciprocal 2.7. We use the latter value so that a direct comparison can be made between these two systems.

Figure 4. Decomposition of L$_2$Pt(C$_2$H$_5$)Cl (open symbols) and L$_2$Pt(C$_2$D$_5$)Cl (filled symbols) in cyclohexane at 158 °C. The thermolyses of 1-d_0 (O) and 1-d_5 (●) were each conducted in separate NMR tubes ([Pt]$_0$ = 0.08 M in either tube). The competitive thermolyses of 1-d_0 (□) and 1-d_5 (■) were conducted in the same NMR tube ([1-d_0]$_0$ = 0.05 M; [1-d_5]$_0$ = 0.05 M).

magnitude of this equilibrium isotope effect.

The deuterium kinetic isotope effect was determined by comparing the rates of thermal decomposition of L$_2$-Pt(C$_2$H$_5$)Cl and L$_2$Pt(C$_2$D$_5$)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 β-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 L$_2$PtHCl(C$_2$H$_4$). Since both the Pt–H(D) and C$_2$H$_4$(C$_2$D$_4$) 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 $A = 13 \pm 1$[32] (Figure 5).

(32) Forward kinetic parameters: $\Delta G^{\ddagger}$ (158 °C) = 33 ± 1.5 kcal/mol; $\Delta H^{\ddagger}$ = 33 ± 1.5 kcal/mol; $\Delta S^{\ddagger}$ = -1.4 ± 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 = 22 ± 2 kcal/mol; log A = 7 ± 1; $\Delta G^{\ddagger}$ = 33 ± 2 kcal/mol; $\Delta H^{\ddagger}$ = 21 ± 2 kcal/mol; $\Delta S^{\ddagger}$(158 °C) = -28 ± 4 eu.
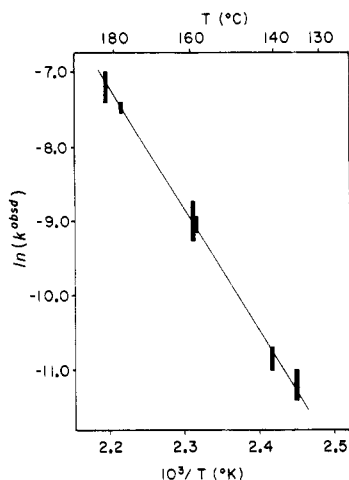
Figure 5. Arrhenius plot for the thermal decomposition of $L_2PtEtCl$ in cyclohexane ($[L_2PtEtCl]_0$ = 0.08 M). Error bars represent 95% confidence limits for each value of ln (k^{obsd}).

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.[11,12,14,33] Unimolecular isomerizations (one particle remaining as one particle in the transition state) have log $A \simeq$ 9–13.[34–36] Reactions in which two particles are generated from one have log $A \simeq$ 13–16[11,12,33] and those in which three particles are created from one have log $A \simeq$ 20–22.[11,14]

The observed value of log A = 13 for the decomposition of 1 is consistent with rate-limiting ethylene dissociation from $(Et_3P)_2PtHCl(C_2H_4)$ (2). For comparison, log A = 14 for rate-limiting dissociation of Et_3P from *cis*-$(Et_3P)_2PtEt_2$.[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 ΔS° = 27 eu; that for the dissociation of Et_3P from $(Et_3P)_4Pt$ in *n*-octane is ΔS° = 49 ± 4 eu.[37] We believe that the difference in values of ΔS° for these two reactions provides a satisfactory rationalization for the differences in $\Delta S^\ddagger$ (and log A) for the ligand dissociation reactions of 1 and L_2PtEt_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 $PtCH_2CH_3$ group present in the starting material is converted to a $Pt(H)(C_2H_4)$ moiety in the transition state.

(33) Reamey, R. H.; Whitesides, G. M. *J. Am. Chem. Soc.* **1984**, *106*, 81–85. Whitesides, G. M.; Reamey, R. H.; Brainard, R. L.; Izumi, A. N.; McCarthy, T. J. *Ann. N.Y. Acad. Sci.* **1983**, *415*, 56–66.

(34) The unimolecular isomerization of $HNiL_3^+$ has log A = 11.3. Meakin, P.; Schunn, R. A.; Jesson, J. P. *J. Am. Chem. Soc.* **1976**, *98*, 422–436.

(35) The kinetics of cis–trans isomerization for a series of 17 CpMo(CO)$_2$LX complexes has been investigated. The log A values for these reactions all range from 11 to 13. Faller, J. W.; Anderson, A. S. *J. Am. Chem. Soc.* **1970**, *92*, 5852–5860.

(36) The unimolecular isomerization of CpM(CO)$_2$Et to *cis*-CpM(CO)$_2$H(C$_2$H$_4$) followed by rate-limiting cis–trans isomerization to *trans*-CpM(CO)$_2$H(C$_2$H$_4$) has log A values of 9 ± 2 and 11 ± 3 for M = Mo and W, respectively. Kazlauskas, R. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 6005–6015.

(37) Mann, B. E.; Musco, A. *J. Chem. Soc., Dalton Trans.* **1980**, 776–785.

(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 $PtCD_2CH_3$ 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 $L_2Pt(C_2H_5)Cl$ (vs. $L_2Pt(C_2D_5)Cl$) are similar.

(iv) The Arrhenius 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 $L_2PtHCl(C_2H_4)$ (eq 8).

$$L_2PtCl(C_2H_5) \rightarrow [L_2PtHCl(C_2H_4)]^\ddagger \rightarrow$$
$$L_2PtHCl + C_2H_4 \quad (8)$$
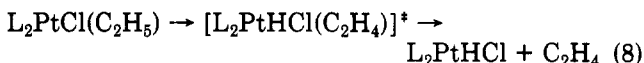
The mechanism of conversion of 1 to this transition state and the details of the structure of the transition state remain ill-defined by our evidence. In particular, we cannot distinguish between a process in which β-hydride elimination occurs reversibly without dissociation of phosphine (or chloride) 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 β-hydride elimination (eq 9). We also cannot
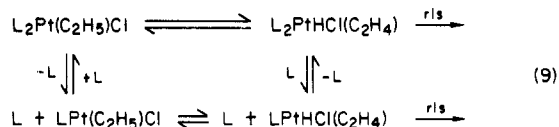
distinguish between rate-limiting steps involving loss of ethylene from $L_2PtHCl(C_2H_4)$ and displacement of ethylene from $LPtHCl(C_2H_4)$ by L (or similar mechanisms involving chloride). These mechanistic ambiguities reflect the usual difficulties in establishing whether a reversible dissociation/association equilibrium occurring before the rate-limiting transition state is required mechanistically or is simply parasitic.

The kinetic isotope effect for decomposition of $L_2Pt(C_2D_5)Cl$ is relatively large ($k_H/k_D \simeq 2.5$). Values of this magnitude have been interpreted in other instances as evidence for C–H bond breaking (i.e., β-hydride elimination) in the rate-limiting step.[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 ($PtCD_2CD_3$) moiety to a ($Pt(D)(C_2D_4)$) 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 $(Et_3P)_2PtEt_2$ in solution in cyclohexane containing high concentrations of added triethylphosphine.[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 $L_2Pt(H)(C_2H_5)(C_2H_4)$. The same ambiguities concerning the importance of possible preequilibrium 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*-$(Et_2PCH_2CH_2PEt_2)PtEtCl$ is not useful in this regard, since its mechanism of thermal decomposition seems to differ considerably from that of $L_2PtEtCl$.[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 P_2O_5 and distilled from disodium benzophenone dianion/tetraglyme[39] under argon. Tetrahydrofuran (THF) and diethyl ether were distilled from disodium benzophenone dianion prior to use. Other commercial reagents were used without purification. Melting points were obtained in sealed tubes and are corrected. Proton-decoupled ^{31}P 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 250-MHz spectrometer. Mass spectra were obtained by using a Hewlett-Packard 5990A GC/MS, with 70-eV ionization voltage.

trans-**Chloroethylbis(triethylphosphine)platinum(II) (1)** was prepared by the methods of Parshall and Weil[40] from *cis*-dichlorobis(triethylphosphine)platinum(II) with a crude yield of 73%. Flash chromatography (ether/petroleum ether, 1:3) followed by three recrystallizations from methanol gave 1 in 67% yield: mp 53.5–54.5 °C (lit.[40] mp 53.5–55 °C); ^{31}P NMR (C_6D_6) δ 15.08 (J_{P-Pt} = 2979 Hz), (C_6H_{12}) δ 15.5 (J_{P-Pt} = 3013 Hz); ^1H NMR (C_6D_6) δ 1.75 (m, 12 H), 1.32 (m, 5 H), 0.97 (m, 18 H). Anal. Calcd for $C_{14}H_{35}ClP_2Pt$: C, 33.91; H, 7.01; Cl, 7.15; P, 12.49. Found: C, 33.76; H, 7.09; Cl, 7.04; P, 12.55.

(1,5-Cyclooctadiene)di(ethyl-*1,1*-d_2)platinum(II). To a stirred suspension of 922 mg of $CODPtCl_2$ (2.46 mmol) in 25 mL of ether at -78 °C was added 13 mL of CH_3CD_2MgI in ether[41] (0.54 M, 7.02 mmol, 2.85 equiv) in one portion. The reaction mixture was allowed to warm to 0 °C over 5 h, cooled to -78 °C, quenched with 0.85 mL of 1 M aqueous NH_4Cl solution, allowed to warm slowly to 0 °C, and dried by stirring with ca. 3 mL of $MgSO_4$. The ethereal suspension was filtered through Celite. The reaction vessel and Celite plug were then washed liberally with ether. The collected ethereal solutions totaled ca. 200 mL in volume. This solution of $CODPt(CD_2CH_3)_2$ was reduced in volume by rotary evaporation (<30 °C), dissolved in pentane and passed through 10 mL of silica gel[42] to give 787 mg of $CODPt(CD_2CH_3)_2$ (88%) as a white solid: mp 29–29.5 °C.

Chloro(1,5-cyclooctadiene)(ethyl-*1,1*-d_2)platinum(II). To a stirred solution of 645 mg of $CODPt(CD_2CH_3)_2$ (1.77 mmol) in 30 mL of ether/methanol (1:1) at 0 °C was added 135 μL of acetyl chloride (1.89 mmol, 1.07 equiv) dropwise over 1 min. The reaction mixture was allowed to warm to room temperature over 4 h.

(38) Thermolysis of *cis*-$(Et_2PCH_2CH_2PEt_2)PtEtCl$ in benzene-d_6 for 4 h at 131 °C produces *cis*-$(Et_2PCH_2CH_2PEt_2)Pt(C_6D_5)Cl$, $C_2H_{6-n}D_n$, and $C_2H_{4-m}D_m$ (n = 0–6 and m = 0–4; relative yields of ethane/ethylene are 2:1). The mechanism(s) of formation of these products is (are) not understood and is (are) currently under investigation. These preliminary experiments were performed in this laboratory by Marifaith Hackett and RLB.

(39) Tetraglyme is added to promote the reduction of benzophenone by sodium.

(40) Parshall, G. M. *Inorg. Synth.* **1970**, *12*, 26–33. Weil, T. A. *Ibid.* **1977**, *17*, 132–134.

(41) CH_3CD_2MgI was made from CH_3CD_2I by the usual procedures. The CH_3CD_2I was shown to have an α/β proton distribution of 3/97 by ^1H NMR.

(42) Silica gel was 230–400 mesh, suitable for flash chromatography.[45]

Table IV. IR Data for Some Organoplatinum Complexes

compound[a]	solv	absorbance, cm^{-1}	assignmt
trans-$L_2Pt(CD_2CH_3)Cl$	CHCl$_3$	2218, 2199, 2171, 2159, 2118	C–D
trans-$L_2Pt(C_2D_5)Cl$	CHCl$_3$	2216, 2198, 2141, 2123, 2113, 2068, 2059	C–D
trans-$L^D_2Pt(C_2H_5)Cl$	CHCl$_3$	2951, 2901, 2897, 2857	C–H
trans-L_2PtHCl	C$_6$H$_{12}$	2198	Pt–H
trans-L_2PtDCl	C$_6$H$_{12}$	1578	Pt–D

^{a} L = Et$_3$P; L^D = $(C_2D_5)_3P$.

Rotary evaporation gave $CODPt(CD_2CH_3)Cl$ (568 mg, 95%) as white crystals: mp 121–124 °C; ^1H NMR (C_6D_6) δ 5.41 (br t, J_{HPt} = 28 Hz, 2 H),[43] 3.69 (br t, J_{HPt} = 75 Hz, 2 H), 1.66–1.50 (m, 11 H). Comparison of this spectrum with the ^1H NMR of CODPtEtCl showed that the deuterium atoms in $CODPt(CD_2CH_3)Cl$ were not scrambled: Pt–CH_2CH_3 of CODPtEtCl δ 1.94 (t of t, J_{HPt} = 74, J_{HH} = 7.5 Hz, 2 H).[43]

Chloro(ethyl-*1,1*-d_2)bis(triethylphosphine)platinum(II). To a stirred suspension of 570 mg of $CODPt(CD_2CH_3)Cl$ (1.70 mmol) in 25 mL of ether at -78 °C was added 540 μL of triethylphosphine (3.70 mmol, 2.18 equiv) in one portion.[44] The reaction solution was allowed to stir at -78 °C for 1 h, warmed to 0 °C over 1.5 h, and then filtered through 3 mL of silica gel with ethereal washing. Rotary evaporation followed by three recrystallizations from methanol and one from pentane gave 523 mg of white crystals of $L_2Pt(CD_2CH_3)Cl$:[28] yield 62%; mp 52.5–53.5 °C; infrared data are summarized in Table IV.

Chloro(ethyl-d_5)bis(triethylphosphine)platinum(II). To a stirred solution of 1.034 g of $L_2Pt(C_2D_5)_2$[11] (2.07 mmol) in 36 mL of methanol/ether (1:1) at -78 °C was added 150 μL 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 $L_2Pt(C_2D_5)Cl$ was flash chromatographed[45] on 30 mL of silica gel (ether/petroleum ether, 1:3) to give 958 mg of $L_2Pt(C_2D_5)Cl$ (92%). Two recrystallizations from methanol gave white crystals: mp 54–55 °C; IR, Table IV.

Kinetics of Thermal Decomposition. Cyclohexane or tetrahydrofuran solutions of $L_2PtEtCl$ (0.08 M) were prepared in NMR tubes according to previously described procedures.[11,14] The thermal decompositions were performed in constant temperature oil baths. Temperatures were determined with a calibrated thermometer and were found to be constant to ±0.40 °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 ^{31}P 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 $L_2Pt(C_2H_5)Cl$ and $L_2Pt(C_2D_5)Cl$ in the same NMR tube (k_H/k_D = 2.42) as a check of the normal procedure which used separate tubes. The ^{31}P NMR chemical shifts of 1-d_0 and 1-d_5 (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 ^{31}P NMR peak heights of $L_2PtEtCl$ and $(EtO)_3PO$ (an internal standard) at a probe temperature of -34 ± 0.5 and 13 ± 0.5 °C, respectively, for these two solvents. This temperature was necessary to prevent excessive exchange broadening and concomitantly to improve the signal-to-noise ratio for the $L_2PtEtCl$ peak at high phosphine concentrations.[46] Most of these experiments were conducted in *n*-hexane

(43) Platinum is composed of one-third ^{195}Pt (spin 1/2) and two-thirds other isotopes (spin 0). A characteristic coupling pattern is the 1:4:1 platinum "triplet".

(44) When this reaction was performed at 0 °C with a 2% excess of Et_3P, the resulting $L_2Pt(C_2D_2H_3)Cl$ was isotopically scrambled. We suspect that the formation of $LSPt(CD_2CH_3)Cl$ (S = diethyl ether) may cause the scrambling.

(45) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.

so that lower probe temperatures could be used.

The decomposition of $L_2PtEtCl$ ($[1]_0$ = 0.05 M) in the presence of added phosphine is first order in $L_2PtEtCl$ up to about 60% completion. The reaction rate then begins to increase, and curvature is observed in the first-order plot.[47] The rate constants were derived from the linear portion of the plot.

Phosphine Exchange Experiments. Into a 5-mm NMR tube were weighed 21.1 mg of $L_2PtEtCl$ and 17.3 mg of $L^D_2PtEtCl$ (L^D = Et_3P-d_{15}).[48] A solution of 0.05 M $(EtO)_3PO$ in cyclohexane (0.50 mL) was added,[49] 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}P NMR spectrum of this sample taken as rapidly as possible (<15 min) showed that the phosphines were completely scrambled. Thermolysis of this mixture at 158 °C for 2 h showed no further change in the relative integrated areas corresponding to $L_2PtEtCl$, $LL^DPtEtCl$, and $L^D_2PtEtCl$. ^{31}P NMR (C_6H_{12}) spectra: $L_2PtEtCl$, δ 15.5 (J = 3014 Hz); $LL^DPtEtCl$, δ 15.0 (J = 3012 Hz, L^H), 14.7 (J = 3013 Hz, L^D); $L^D_2PtEtCl$, δ 14.1 (J = 3011 Hz).

Halogen Exchange Experiments. Into a 5-mm NMR tube were weighed 13.7 mg of $L_2PtEtCl$ and 14.8 mg of $L_2Pt(C_2D_5)Br$. 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 ^{31}P NMR signals for $L_2PtEtCl$ and $L_2PtEtBr$. The ^{31}P NMR spectra of all four compounds present at equilibrium corresponded to ^{31}P NMR spectra of these compounds when prepared independently. ^{31}P NMR (C_6H_{12}): $L_2PtEtCl$, δ 15.54 (J = 3013 Hz); $L_2Pt(C_2D_5)Cl$, 15.61 (J = 3015 Hz); $L_2PtEtBr$, δ 13.43 (J = 2993 Hz); $L_2Pt(C_2D_5)Br$, δ 13.51 (J = 2991 Hz).

***trans*-Bromo(ethyl-d_5)bis(triethylphosphine)platinum-(II).** $L_2PtC_2D_5Br$ was prepared by the method of Chatt and Shaw[50] from 595 mg of $L_2Pt(C_2D_5)Cl$. The resulting $L_2Pt(C_2D_5)Br$ 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; yield 56%; ^1H NMR (C_6D_6) δ 1.86 (m, 12 H), 0.96 (m, 18 H); ^{31}P NMR (C_6H_{12}) δ 13.51 (J = 2991 Hz). $L_2PtEtBr$ was prepared by using a procedure analogous to that used to synthesize $L_2Pt(C_2D_5)Br$: mp 63–64 °C.

Reliability of Kinetics, Independent of Phosphine Exchange Broadening. The ^{31}P NMR signal of $L_2PtEtCl$ exhibits phosphine exchange broadening which increases with increasing temperature. This experiment was designed to show that this broadening has no effect on the measurement of kinetics other than to introduce problems with signal-to-noise. Several solutions of $L_2PtEtCl$ in 0.40 M Et_3P and 0.10 M Et_3PO_4 in *n*-hexane were

sealed into NMR tubes. The concentration of $L_2PtEtCl$ varied from tube to tube between 0.021 and 0.123 M. The relative ^{31}P NMR peak heights of $L_2PtEtCl$ and $(EtO)_3PO$ were measured at probe temperatures of 35, 0, –34, and –42 °C. The ^{31}P NMR peak heights of $L_2PtEtCl$ against $(EtO)_3PO$ were found to be proportional to the concentration of $L_2PtEtCl$ at each temperature.

$[(Et_3P)_3PtH]^+Cl^-$. A solution of 24.1 mg of L_2PtHCl (0.051 mmol) and of 7.3 μL of Et_3P (0.05 mmol) in 0.5 mL of toluene-d_8 was sealed into an NMR tube. At 30 °C, nothing was visible in the ^{31}P NMR or in the hydride region (–1 to –20 ppm) of the ^1H NMR. At –61 °C, the proton-decoupled ^{31}P NMR showed an AB_2M pattern: δ 11.6 (t of t, $J_{L_aL_b}$ = 19.5, J_{L_aPt} = 1997 Hz, 1 L),[43] 16.8 (d of t, $J_{L_bL_a}$ = 19.5, J_{L_bPt} = 2451 Hz, 2 L). The platinum hydride was also observed at –61 °C in the ^1H NMR: δ –5.9 m (d of t of t, J_{HL_a} = 158, J_{HL_b} = 16, J_{HP_t} = 810 Hz).[43] These spectra are nearly identical with the ^{31}P and ^1H NMR spectra reported for $[(Et_3P)_3PtH]^+BPh_4^-$.[34]

Isotopic Scrambling Experiments. In a typical experiment, 1.0 mL of a cyclohexane solution which was 0.08 M in $L_2Pt(C-D_2CH_3)Cl$ and 0.08 M in $(EtO)_3PO$ was decomposed thermally at 158 °C for 1 half-life (or 2 half-lives) and the gas above the solution was analyzed by GC/MS. The $L_2Pt(C_2D_2H_3)Cl$ remaining in solution was then quenched with bromine as previously described.[11] The isotopic compositions of ethylene products (d_1/d_2) were determined by comparison with literature[51] values for M, M – 1, and M + 1 peaks of ethylene-d_2.

Equilibrium Studies. To four freeze–thaw–degassed solutions of $L_2PtEtCl$ (0.08–0.13 M), 0.06 M $(EtO)_3PO$, and 0.036 M biphenyl in cyclohexane-d_{12} (1.0 mL) in NMR tubes was added ca. 8 mL of ethylene (1 atm). The ethylene was condensed with liquid nitrogen, and the tubes were sealed. A fifth tube was prepared starting with L_2PtHCl instead of $L_2PtEtCl$. These tubes were heated at 157.4 °C until equilibrium was reached (30 h, ~22 half-lives). The relative concentrations of 1 and 3 were determined by ^{31}P NMR at room temperature.[52] The concentration of ethylene in solution was determined by comparing its ^1H NMR resonance against that of biphenyl in a spectrometer probe heated to 157.4 °C.[53] This procedure was repeated three times at 166.4, 140.7, and 133.2 °C. The tube which initially contained L_2PtHCl gave the same results as the tubes which initially contained $L_2PtEtCl$.

(46) In solutions of high phosphine concentration, signal to noise is a significant problem because low gain settings must be used to prevent the phosphine ^{31}P NMR signal from saturating the receiver.

(47) We suggest that the reason for the increased reaction rate is the formation of $[L_3PtH]^+Cl^-$ (7), because the linearity of the first-order plot is lost very quickly when the initial concentration of $L_2PtEtCl$ is large (e.g., 0.12 M) and not as quickly when the initial concentration of $L_2PtEtCl$ is small (e.g., 0.048 M). For this reason, the initial concentration of $L_2PtEtCl$ used in these experiments was only 0.05 M instead of 0.08 M—the concentration of 1 in kinetic experiments with no added phosphine. The ionic $[L_3PtH]^+Cl^-$ could, like $(C_6H_5CH_2)(CH_3)_2$-$(C_{14}H_{29})N^+Cl^-$, increase the reaction rate by increasing the solvent polarity.

(48) Et_3P-d_{15} was prepared by Thomas J. McCarthy as previously described.[11] $L^D_2PtEtCl$ was prepared by using procedures analogous to those used for $L_2PtEtCl$: mp 51.5–52.5 °C; ^1H NMR (C_6D_6) δ 1.31 (m); ^{31}P NMR (C_6D_6) δ 13.7 (J = 2974 Hz); infrared data are summarized in Table IV.

(49) Essentially the same results were obtained in solutions not containing $(EtO)_3PO$.

(50) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1959**, 705–716.

(51) Stenhagen, E.; Abrahamsson, S.; McLafferty, F. W. "Atlas of Mass Spectral Data"; Interscience: New York, 1969; Vol. I, pp 4–6.

(52) The equilibrium concentrations of $L_2PtEtCl$ and L_2PtHCl were determined from the initial concentration of 1, by comparing the relative ^{31}P NMR peak heights of 1 and $(EtO)_3PO$ before thermolysis and at equilibrium and by comparing the ^{31}P NMR integrals of 1 and 3 using long pulse delays (>5t_1). Both methods gave comparable results.

(53) An NMR tube containing dodecane and a calibrated thermocouple wire was lowered into the NMR probe to measure its temperature with the decoupler turned off. The temperature measured in this way was probably accurate to ±1 °C.