The Mechanism of Hydrogenolysis of Dideceny1bis(triethylphosphine)platinum(II)

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Abstract: Dideceny1bis(triethylphosphine)platinum(II) reacts with H₂ (34 psi) at 32 °C in hydrocarbon solvents and yields neopentane and trans-dihydridobis(triethylphosphine)platinum(II). The addition of triethylphosphine (L) changes the rate-limiting step of the reaction. When [L] = 0 M, the overall rate-limiting step is the dissociation of triethylphosphine from L₂PtR₂; no isotope effect is observed on substitution of D₂ for H₂, and the rate is independent of the pressure of H₂. When [L] > 0.1 M, phosphine loss is reversible, and a later step, either addition of H₂ to platinum or (more probably) elimination of neopentane from platinum, is rate limiting: the rate of reaction depends on the first order of the H₂ pressure, and an isotope effect of Δk₂/H₂ = 1.9 is observed on substitution of H₂ by D₂. Activation parameters obtained at 0.0, 0.1, and 0.5 M triethylphosphine are presented. These data are useful in understanding the differences in rates of inter- and intramolecular oxidative additions to platinum(II). The rate of reaction of H₂ with several structurally related bis(phosphine)dialkylplatinum(II) compounds was surveyed under similar reaction conditions. In general, bulky substituents on platinum accelerate the reaction. This observation suggests that phosphine dissociation is a general feature of reaction of bis(phosphine)dialkylplatinum(II) compounds with dihydrogen.

The formation and cleavage of bonds between carbon, hydrogen, and transition metals is important in many catalytic processes. This paper describes a study of the mechanism of the homogeneous hydrogenolysis of dideceny1bis(triethylphosphine)platinum(II) (I). The reaction proceeds under mild conditions (32 °C, 34 psi of H₂) and yields neopentane and trans-dihydridobis(triethylphosphine)platinum(II) (5) quantitatively (Scheme I). In Scheme I and throughout this paper R refers to triethylphosphine, R to CH₂C(CH₃)₂, and L₁ to PDCODCO₂). We use [L] to refer to the concentration of L resulting from added triethylphosphine (that is, triethylphosphine added to the solution rather than that present as a result of dissociation from L₂PtR₂). Thus, [L] = 0.0 M implies only that no phosphine has been added to the solution. We know from qualitative 31P NMR studies that the equilibrium constant for phosphine loss from I is low, but we have not measured it quantitatively.

Mechanistic studies of thermal reactions of biphosphinediallylplatinum(II) compounds involving intramolecular addition of β₈, 10, 14γ, 11 β, 11 and e 11 C-H bonds to platinum(II) have established the high reactivity of coordinatively unsaturated intermediates of structure L₂PtR₂ in such reactions. This study indicates that this same intermediate is also the reactive species in the intermolecular addition of H₂ to platinum(II) under the conditions studied, and it suggests broad mechanistic parallel between C-H and H-H addition to platinum(II).

In the absence of added triethylphosphine, the overall rate-limiting step in the hydrogenolysis of I was dissociation of phosphine. When L was present at concentrations greater than ~0.1 M, loss of phosphine was reversible and another step—either reductive elimination of a C-H bond from platinum or oxidative addition of an H-H bond to platinum—was rate limiting. We cannot presently distinguish between these alternatives.

Results

Products. In the absence of added L, the reaction of H₂ with I in cyclohexane yielded 15² and 2,2-dimethylpropane (neopentane) quantitatively. No 2,2,5,5-tetramethylhexane (dineopentyl) was formed. The solution became slightly yellow as the reaction proceeded, but only 5 was observed by 31P NMR spectroscopy 13. When deuterium (D₂) gas was substituted for H₂, neopentane-d₁ was the sole product derived from the neopentyl moieties. 14 When the hydrogenolysis was run in the presence of added L (≥0.1 M), the products were neopentane and dihydridotris(triethylphosphine)platinum(II) (6) (Scheme I). 15 Compound 6 was not observed by 31P NMR spectroscopy at room temperature because rapid phosphine exchange broadened the 31P resonances. At ~50 °C in toluene-d₈, compound 6 was visible by ¹H NMR spectroscopy, and the platinum hydride resonances (at ~3 ppm) 16 were split into a quartet (J₉ = 17 Hz). This observation suggests that 6 has a trigonal-bipyramidal structure containing three equivalent phosphines (Scheme I). No cis-5 was observed in this system. Panoneza and Trogler 17 have recently observed cis-5 in acetone.

Diagram:

Scheme I. Mechanism of Hydrogenolysis of I in Cyclohexane:

L = PE₃; R = CH₂C(CH₃)₃

1. L₂PtR₂ + R → L₂PtR₂ + L

2. L₂PtR₂ + H₂ → L₂PtR₂ + L + H₂

3. L₂PtR₂ + L → L₂PtR₂ + L

4. L₂PtR₂ + L → L₂PtR₂ + L

5. L₂PtR₂ + H₂ → L₂PtR₂ + H₂

6. L₂PtR₂ + L → L₂PtR₂ + L

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(13) The color is probably due to (E₂Pt)₂Pt from a reaction of 5 with trace amounts of O₂.

(14) The GC-MS of the alkane is indistinguishable from that of alkane obtained from a DCl quench of L₂Pt(CH₂C(CH₃)₃)₂.

(15) Compound 6 has been prepared by reaction of (E₂Pt)₂Pt(O) and H₂; Gerlach, D. H.; Kane, A. R.; Parshall, G. W.; Jesson, J. P.; Meutert, E. J. Am. Chem. Soc. 1971, 93, 2543-44. We have shown that compound 6 is also formed from (E₂Pt)₂PtH₂ and E₂Pt.
Figure 1. Hydrogenolysis of I in the presence of added triethylphosphine: [I]₀ = 0.026 M, H₂ pressure = 33.9 psi, T = 50 °C. [L] is indicated on the figure for each line.

and have noticed a decrease of the ratio of cis to trans isomers in less polar solvents. They report [cis-5]/[trans-5] = 0.03 in toluene. The absence of signals attributable to cis-5 in our spectra is consistent with their observations. In solution, compound 5 decomposes quickly when exposed to air. No decomposition of 5 in cyclohexane solution was observed after several months at room temperature when the compound was kept in an atmosphere of H₂ or argon.

Kinetics. The disappearance of I (followed by ³¹P NMR spectroscopy) was first order in I to greater than 3 half-lives. The observed pseudo-first-order rate constant (defined by eq 1) at 32 °C and 33.9 psi of H₂ in cyclohexane was k₇₀ = 3.0 ± 0.03 × 10⁻⁴ s⁻¹. The rate constant was independent of the initial concentration of I from 0.017 to 0.044 M.¹⁸

\[
\frac{d[I]}{dt} = -k_{70}[I] \tag{1}
\]

The observation of first-order kinetics indicates that a step involving two platinum centers is not important under the conditions studied. Bergman and Janowicz have concluded that the methane-producing autocatalytic hydrogenolysis of (σ⁵-cyclopentadienyl)(triphenylphosphine)dimethylcobalt(III) goes through a binuclear intermediate formed by the reaction of product Cp(P₃H₃)CoH₂ with starting material. We have observed an analogous reaction in the present system when and 5 are mixed in the absence of H₂ (eq 2). Although reaction 2 does occur,

\[
L₂PR₂ + L₂P₃H₅ \xrightarrow{-40, 25 °C, \text{cyclohexane}} L₃P₀ + 2RH + \text{Pt} \tag{2}
\]

it is apparently not fast enough under the conditions studied here to be important in hydrogenolysis of I. The ³¹P NMR spectra show that the concentration of 5 increases as the reaction proceeds. If the reaction of eq 2 were occurring, a deviation from first-order kinetics would be expected. We observe simple first-order kinetics, with no evidence of autocatalysis or of an induction period.

Dependence of Rate on Phosphine Concentration. Figure 1 shows first-order plots at various phosphine concentrations. All runs were conducted at 50 ± 0.3 °C and 33.9 ± 0.4 psi of H₂. Figure 2 plots pseudo-first-order rate constants at 50 and 56.5 °C (determined by eq 1) as a function of [L]⁻¹. The reactions were run at 56.5 °C so that reaction rates at higher phosphine concentrations could be measured in a convenient interval of time.

The straight lines observed in Figure 2 establish an inverse first-order dependence of rate on [L] for [L] < 1.0 M. This behavior is consistent with the mechanism outlined in Scheme I with either 2 → 3 or 3 → 4 as the rate-limiting step: both involve dissociation of L before the rate-limiting step, and are indistinguishable by this criterion. In principle, this kinetic dependence

![Figure 2](attachment:image2.png)

Figure 2. Observed first-order rate constants ([I]₀ = 0.026 M, H₂ pressure = 33.9 psi) as a function of [L]⁻¹: (a) T = 50 °C; (b) T = 56.5 °C. The lines indicate a first-order dependence of k₇₀ on [L]⁻¹.

![Figure 3](attachment:image3.png)

Figure 3. Observed rate constants as a function of H₂ pressure at three different phosphine concentrations: (a) [L] = 0.0 M, T = 32 °C; (b) [L] = 0.1 M, T = 50 °C; (c) [L] = 0.5 M, T = 56.5 °C. For a the line indicates a zero-order dependence on H₂. For b and c the line indicates a first-order dependence. [I]₀ = 0.026 M.

![Table 1](attachment:table1.png)

Table 1. Characteristics of the Hydrogenolysis of I at Different Concentrations of L

<table>
<thead>
<tr>
<th>[L], M</th>
<th>0.0</th>
<th>0.1</th>
<th>0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>kinetic order in L</td>
<td>[L]⁻¹</td>
<td>[L]⁻¹</td>
<td>[L]⁻¹</td>
</tr>
<tr>
<td>kinetic order in H₂</td>
<td>[H₂]₀</td>
<td>[H₂]₁</td>
<td>[H₂]₁</td>
</tr>
<tr>
<td>k₇₀/k₇₀</td>
<td>1.0 ± 0.2</td>
<td>1.9 ± 0.2</td>
<td>1.9 ± 0.2</td>
</tr>
<tr>
<td>Eₚ, kcal/mol</td>
<td>29 ± 2</td>
<td>30 ± 2</td>
<td>29 ± 3</td>
</tr>
<tr>
<td>log A</td>
<td>18 ± 1</td>
<td>18 ± 2</td>
<td>17 ± 2</td>
</tr>
<tr>
<td>ΔHₚ(50 °C), kcal/mol</td>
<td>21 ± 4</td>
<td>22 ± 5</td>
<td>23 ± 6</td>
</tr>
<tr>
<td>ΔSₚ(50 °C), kcal/mol</td>
<td>28 ± 2</td>
<td>29 ± 2</td>
<td>28 ± 3</td>
</tr>
<tr>
<td>Δₐₚ(50 °C), eu</td>
<td>22 ± 5</td>
<td>22 ± 9</td>
<td>17 ± 9</td>
</tr>
</tbody>
</table>

* Kinetic parameters were determined from k₇₀ on [L] = 0.0 M, and from kₐ on [L] = 0.0 M, T = 32 °C.

On [L]⁻¹ might also be rationalized by association of L with L₂PR₂ before the rate-limiting step, but the absence of L₃PR₂ species detectable in the ³¹P NMR spectra in the presence of added L and the observation that the solubility of I is not increased in solutions containing added L indicate that association of L with I is not important.²⁰

When [L] > 1.0 M the rate constants in Figure 2 deviate from linearity (Figure 2b). The deviations are not large and more probably due to solvent effects (at 2.0 M, the solution is 30% w/w triethylphosphine).

Dependence of Rate on the Pressure of H₂. Figure 3 plots the dependence of the pseudo-first-order rate constants on H₂ pressure at [L] = 0.0, 0.1, and 0.5 M. When [L] = 0.0 M, the reaction

(18) The limit of solubility of I in cyclohexane at 32 °C is approximately 0.0045 M.
(20) These tests for association are described fully in ref 10.
Figure 4. Hydrogenolysis of I with H$_2$ (a) and D$_2$ (c) at four values of [L]. Temperatures are indicated above plots. H$_2$ pressure = 33.9 psi, [H$_2$]$_0$ = 0.026 M.

is approximately zero order in H$_2$ pressure over the range of 15.7 to 33.9 psi (Figure 3a). When [L] = 0.1 or 0.5 M, the dependence on H$_2$ pressure is first order.

Deuterium kinetic isotope effects were determined by measuring the change in the rate of reaction on substitution of D$_2$ for H$_2$. The isotope effects (k$_{D}$/k$_{H}$) are listed in Table I. Figure 4 shows representative rate data. The slowing of the rate with increasing phosphate concentration made it necessary to measure the isotope effects at different temperatures for different values of [L]. We assume that the effect of temperature on the isotope effect is negligible. When [L] = 0.0, no isotope effect was observed (k$_{D}$/k$_{H}$ = 1.0). This observation and the independence of the reaction rate on H$_2$ pressure are consistent with dissociation of phosphate (1 → 2) as rate determining.

In the presence of added phosphate ([L] ≥ 0.1 M) we observed both an isotope effect (k$_{D}$/k$_{H}$ = 1.9) and a first-order dependence of rate on H$_2$ pressure. These data are consistent with either 2 → 3 or 3 → 4 as rate determining. The expression for the observed rate constant (k$_{obs}$) that is predicted by the mechanism of Scheme I is given in eq 3. If k$_3$ is the rate-determining step, the expression simplifies to eq 4. If k$_2$ is rate determining, the expression is given by eq 5.

$$k_{obs} = \frac{k_1k_2k_3[H_2]}{k_2k_3[H_2] + k_{-1}(k_2 + k_3)[L]}$$ (3)

$$k_{obs} = \frac{k_1k_2k_3[L]}{[L]}$$ (4)

$$k_{obs} = \frac{k_1k_3}{[L]}$$ (5)

$$k' = \frac{k_{obs}[L]}{[H_2]}$$ (6)

The observed isotope effect of k$_{D}$/k$_{H}$ = 1.9 is similar to that (k$_{D}$/k$_{H}$ = 1.7 ± 0.3) observed for what is believed to be reductive elimination of a C–H bond from a 5-coordinate platinum species similar to 3 (LPrR)$^+$ (H rather than LPrR$_2$)$_2$. The third step of Scheme I (3 → 4) is also reductive elimination from a 5-coordinate platinum species. An isotope effect of k$_{D}$/k$_{H}$ = 1.22 (30 °C) has been measured by Chock and Halpern and that of k$_{D}$/k$_{H}$ = 1.026 (30 °C) by Vitale and San Filippo for H$_2$ (D$_2$) addition to Vaska's complex (IrCl(CO)(Ph$_3$P)$_2$). These values do not permit us to distinguish between competitive elimination (step 3) and H$_2$ (D$_2$) addition (step 2) as the rate-limiting step for conversion of 1 to 5. Both these isotope effects for oxidative addition of H$_2$ to a metal center and the isotope effects for H$_2$ and D$_2$ addition to a metal center are sufficiently similar that criteria other than simple hydrogen kinetic isotope effects will be required to distinguish H–H bond breaking and C–H bond formation.

We note that the reverse of step 3 (4 → 5) is the activation of a C–H bond of neopentane by addition to platinum(II). We conclude from previous experience that intermolecular C–H bond activation does not occur under the mild conditions used in this work. We therefore assume that 3 → 4 is irreversible, and we conclude that transformations between 4 and 5 (or 6) do not influence the kinetics.

Arrhenius Parameters. Figure 5 shows Arrhenius plots (log k$_{obs}$ vs. 1/T) for [L] = 0.0, 0.1, and 0.5 M. Table I lists Arrhenius and Eyring parameters calculated from k$_{obs}$ for [L] = 0.0 M and k' (eq 6) for [L] = 0.1 and 0.5 M. Both k$_{obs}$ and k' have units of s$^{-1}$. When [L] = 0.0 M, E$_a$ = 29 ± 2 kcal/mol. This value for the activation energy is consistent with rate-limiting loss of phosphate: an E$_a$ of 29 ± 2 kcal/mol was obtained previously for rate-limiting dissociation of phosphate in the thermal decomposition of (PEt$_3$)$_2$Pr(CH$_2$CH$_2$)$_2$. The observed value of log A is consistent with a reaction in which one particle goes to two in the transition state.

Phosphine Exchange. Reaction of a 1:1 mixture of L$_2$Pr$_2$ and L$_2$D$_2$Pr$_2$ with H$_2$ to 50% completion followed by $^{31}$P NMR analysis of the reaction mixture showed no detectable exchange of L$^0$ for L$^0$. The absence of exchange under these conditions ([L] = 0.0 M) is a necessary consequence of rate-limiting dissociation of L.

Hydrogenolysis of Related Organoplatinum Compounds. The reactions of several compounds having the structure L$_2$Pr$_2$ with H$_2$ are summarized in Table II. When L was Me$_2$P or Ph$_3$P, hydrogenolysis did not yield a stable platinum(II) dihydride. The solution darkened and a black precipitate (apparently platinum metal) formed. The $^{31}$P NMR spectra taken during and after the reaction showed (Me$_2$P)$_2$Pr$^+$ and (Ph$_3$P)$_2$Pr$^+$ respectively as

(22) [H$_2$] was calculated from solubility data for H$_2$ in heptane and octave.
(25) Halpern, J. J. Am. Chem. Soc. 1982, 105, 332–8 for reductive elimination of CH$_3$(H,D) from (Ph$_3$P)$_2$Pr(He)$_2$CH$_2$. k$_{D}$/k$_{H}$ = 3.3 ± 0.3.
(27) Due to the sensitivity of the instrument under the conditions of the experiment, <10% exchange could have gone undetected.
Table II. Reactions of cis-L₂PtR₂ with H₂

<table>
<thead>
<tr>
<th>L</th>
<th>R solvent</th>
<th>conditions for complete reaction</th>
<th>products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₂P</td>
<td>-CH₂C(CH₃)₂</td>
<td>C₂H₆</td>
<td>&lt;5 h, 25 °C</td>
</tr>
<tr>
<td>Et₂P</td>
<td>-CH₂C(CH₃)₂</td>
<td>C₂H₆, C₆H₁₂</td>
<td>&lt;5 h, 25 °C</td>
</tr>
<tr>
<td>Ph₂P</td>
<td>-CH₂C(CH₃)₂</td>
<td>C₂H₆</td>
<td>&lt;2.5 h, 25 °C</td>
</tr>
<tr>
<td>dmpe</td>
<td>-CH₂C(CH₃)₂</td>
<td>no reaction, 48 h, 140 °C</td>
<td>no reaction, 48 h, 140 °C</td>
</tr>
<tr>
<td>i-Pr₂P</td>
<td>-CH₃</td>
<td>C₂H₆, C₂H₁₂</td>
<td>&lt;2.5 h, 25 °C</td>
</tr>
<tr>
<td>PH₂P</td>
<td>-CH₂C(CH₃)₂</td>
<td>C₂H₆</td>
<td>&lt;2.5 h, 25 °C</td>
</tr>
<tr>
<td>Et₂P</td>
<td>-CH₂C(CH₃)₂</td>
<td>no reaction, 3 days, 25 °C</td>
<td>no reaction, 3 days, 25 °C</td>
</tr>
<tr>
<td>(7)</td>
<td>-CH₂C(CH₃)₂</td>
<td>&lt;44 h, 100 °C</td>
<td>trans-L₂PtH₂ + C₆H₁₂</td>
</tr>
</tbody>
</table>

a Reactions were carried out in cyclohexane or benzene solutions with [L₂PtR₂]₀ = 0.03 M, H₂ pressure = 2-4 atm. b dmpe = 1,2-bis(dimethylphosphino)ethane. c 3,3-Bis(dimethylplatinum)cyclobutane.

Discussion

Our evidence indicates that reaction of 1 with H₂ proceeds by the mechanism outlined in Scheme I. This mechanism parallels that observed previously for intramolecular C–H additions to platinum(II) in similar coordination environments. The identity of the rate-limiting step in this mechanism depends on [L]. We discuss the mechanism at [L] = 0 M and in the presence of added L separately.

[L] = 0. The independence of rate on H₂ pressure, the absence of a deuterium kinetic isotope effect, and the lack of phosphine exchange in starting material recovered after partial reaction indicate that phosphine dissociation is overall rate limiting. The Eₛ of 29 kcal/mol is compatible with this assertion, and the log A is that expected for one particle going to two in the transition state.

In the Presence of Added [L]. The inverse first-order dependence of rate on [L] establishes a reversible loss of phosphine before the rate-limiting step. It is not surprising that the creation of a vacant coordination site would increase the reactivity of platinum toward an H–H bond, since it strongly increases reactivity toward C–H bonds. The first-order dependence of the rate on H₂ pressure and the isotope effect of K_H/K_D ~ 1.9 confirm that the loss of phosphine is no longer rate limiting in the presence of added L.

We cannot clearly distinguish between 2 → 3 and 3 → 4 as the rate-limiting step for [L] > 0.1 M. The transition states 8 and 9 for these steps are similar. We favor 9, but only on the weak grounds that reductive elimination of C–H bonds seems to be slow in related systems. A transition state such as 10, in which cleavage of the H–H bond is concerted with cleavage of the Pt–C bond and formation of the C–H bond, also cannot be rigorously excluded by using the available data.

The interest in this study lies in its demonstration that intermolecular reactions involving the intermediate L₃PtC₂ can be facile. Previous studies had indicated that intramolecular reactions involving PtCl₂-H₂ may be unstable under the reaction conditions: the compound (Ph₃P)₂PtCl₂ is unknown; (Me₂P)₂PdCl₂ has only recently been characterized.

![Figure 6](image-url) Comparison of kinetic parameters and an estimate of the rate of intermolecular carbon–hydrogen bond activation. In this estimate [L] = 0.1 M; [H₂] and [C–H] are set to 110 M (the concentration of C–H bonds in cyclohexane) to facilitate comparison. The value of log A used here, marked with a superscript a, is higher than that given in Table I due to the high molarity of H₂ assumed in this analysis ([H₂] is 10⁻⁴ greater).

The reaction of n-propylcyclobutane with L₃PtC₂ was found to be facile but had provided neither an example of an intramolecular reaction involving a C–H bond (i.e., hydrocarbon solvent activation) nor a clear rationale for the fact that intermolecular reactions do not seem to compete effectively with intramolecular ones. This work establishes that the intermolecular reaction of L₃PtC₂ with H₂ is facile and suggests that there is no inherent entropic barrier to intermolecular reactions with the C–H bonds of solvent. If we make the crude assumption that the Eₛ for solvent activation would be the same as that observed for intramolecular γ-C–H activation and that the log A would be the same as that for intermolecular H₂ activation, we estimate (clearly erroneously) that the relative rate of intermolecular C–H activation for cyclohexane should be 10 times greater than that of the intramolecular reaction (Figure 6).

The fact that this analysis predicts such a high rate for the intermolecular reaction indicates that the entropic disadvantage to intermolecular reactions attributable to the combination of two particles into one in the transition state is not so far responsible for the unobservably slow rate of solvent C–H activation. The reason why intermolecular C–H activation is slower than predicted by this crude analysis may be that the analysis neglects nonbonded steric interactions. The added strain should tend to increase Eₛ and to slow these reactions. Restrictions to vibrations in a sterically crowded transition state may also slow the intermolecular addition of molecules larger than H₂.

Why do hydrocarbon solvents not react with L₃PtC₂? The facts that intramolecular C–H addition and intermolecular H–H addition both occur establish that there are not large intrinsic barriers to such reactions. The recent successful additions of alkanes to iridium and rhenium also establish that intermolecular C–H activation is not an intrinsically difficult reaction.

(32) Additional evidence which supports phosphine loss as a prerequisite for hydrogenolysis is that compound cis-7 hydrolyzes slowly at 100 °C. Under these conditions cis-7 is known to isomerize to trans-7 (presumably via phosphine dissociation). Nuovo, R. G.; McCarthy, T. J.; Whitesides, G. M. J. Am. Chem. Soc. 1981, 103, 3404-3410.
Figure 7. Reactors used for $^3$P NMR kinetics.

Best present rationalization for the apparent low reactivity of \( \text{LPR}_2 \) toward unactivated \( \text{C-H} \) bonds in intermolecular reactions seems to be that other intramolecular reactions (cyclometalations involving \( \text{C-H} \) bonds to neopentyl and triethylphosphine moieties, reductive elimination of \( \text{R} \) from \( \text{PR}_2 \) moieties, migration of alkyl groups from phosphorus to platinum) occur more rapidly.

**Experimental Section**

**General.** \(^3\)P and \(^1\)H NMR spectra were taken on a JEOL FX 90Q spectrometer. Mass spectra were obtained on a Hewlett-Packard 5390-A GC-MS with 70-eV ionization voltage. Olefins were removed from cyclohexane and dodecane by stirring over \( \text{H}_2\text{SO}_4 \) for 3 days. The hydrocarbons were washed with sodium bicarbonate solution and water, dried with phosphorus pentoxide, and distilled under argon. Benzenes were purified by distillation from calcium hydride under argon. Dineopentylbis(triethylphosphine)platinum(II) \(^{10}\) and triethylphosphine-\( \text{d}_2 \) \(^{11}\) were prepared as described previously. \( \text{H}_2 \) (Airco Inc) and \( \text{D}_2 \) (Matheson) were used without further purification.

Kinetic studies by NMR were performed in septum-capped tubes with 5-mm NMR tubes attached (Figure 7). The reactors allowed the rate of the reaction to be measured without disturbing the pressure by transfer of the solution or removal of aliquots. The reactors also allowed the solution to be stirred under constant \( \text{H}_2 \) pressure between spectra. Stirring of the solution was necessary so that the rate of hydrolysis would not be limited by the rate of \( \text{H}_2 \) mass transport. The vessel need not spin in the spectrometer probe because the line width for \(^3\)P in these samples is large enough that effects due to field inhomogeneity are negligible. \( T_2 \approx T_2^* \). On an average spectrum the line width at half height was \( n_{1/2} = 0.8 \) Hz. The JEOL FX-90Q NMR spectrometer used in this work had an open-top electromagnet. This feature is necessary for the use of these reactors, as their size precludes their being lowered into a superconducting or closed-top electromagnet.

Cyclohexane was used as a solvent when the reaction temperature was low (<50 °C). Dodecane was used at higher temperature to avoid solvent loss (through the septum) over the course of the kinetic run. This solvent change had no effect on the rate at 50 °C. In a typical run, 15 mg of \( \text{I} \) and 1.0 mL of cyclohexane or dodecane (containing 0.05 M triethylphosphate as internal standard) were added to reactors under argon. The reactors were flushed with \( \text{H}_2 \) at 0 °C and then put into a temperature-controlled (±0.3 °C) water bath. The reactors were kept under an atmosphere of \( \text{H}_2 \) at the desired pressure (404 psi). The reactors were removed at intervals and cooled to 0 °C. Spectra were taken (within 10 min) on external lock with the NMR probe at 12 ± 0.2 °C (the reaction rate was considered to be zero at this temperature). The loss of starting material was followed by measuring peak heights relative to an internal standard.

**Phosphine Exchange Experiment.** \( \text{L}_2\text{PR}_2 \) (13 mg) and \( \text{L}^2\text{PR}_2 \) (13 mg) (\( \text{R} = \text{CH}_3\text{C(CH}_3)_2 \)) and 0.75 mL of cyclohexane-\( \text{d}_2 \) (a deuterated solvent used as internal lock for the spectrometer) were added to a reactor and hydrogenolysis (31 psi of \( \text{H}_2 \), 32 °C, 40 min) to ~50% completion. The solution was transferred by cannula into an NMR tube. The \(^3\)P NMR spectrum showed only \( \text{L}_2\text{PR}_2 \) and \( \text{L}^2\text{PR}_2 \). No \( \text{LP}_2\text{PR}_2 \) could be detected.\(^{10}\) \( \text{LP}_2\text{PR}_2 \) can be observed by equilibration of \( \text{L}_2\text{PR}_2 \) and \( \text{L}^2\text{PR}_2 \) as a doublet (\( \delta = -1.1, J_{\text{PP}} = 8 \) Hz).

**Stability of 2 in Solution.** To each of two reactors (similar to those in Figure 6, but having high vacuum Teflon stopcocks rather than septa) were added 15 mg of \( \text{I} \) and 1.0 mL of cyclohexane (with 0.05 M triethylphosphate as internal standard). Each was hydrogenolyzed to completion. One was purged with, and left under, 25 psi of argon. The other was left under 25 psi of \( \text{H}_2 \). Both were heated for 24 h at 42 °C and then left for over 2 months at room temperature. \(^3\)P NMR spectra taken throughout this time showed that little or no decomposition had taken place in either reactor.

**Preparation of \( \text{L}_2\text{PR}_2 \).** The compound \( \text{Pic}_{2}\text{Pr(CH}_3)_2\text{C(CH}_3)_2 \) was prepared by thermolysis of 1 in cyclohexane.\(^{10}\) All other compounds in Table II were prepared by the reaction of dichloro(1,5-cyclooctadiene)-platinum(II) with the corresponding Grignard reagent (\( \text{RMgX; X = Br, Cl} \)) followed by displacement of the 1,5-cyclooctadiene with the desired phosphine to give \( \text{cis-L}_2\text{PR}_2 \). This procedure is described in detail elsewhere.\(^{10,13}\) The \( \text{L}_2\text{PR}_2 \) compounds were recrystallized from ether/methanol at ~78 °C. Their \(^3\)P NMR spectra are summarized in Table III.

**Reaction of \( \text{H}_2 \) with \( \text{L}_2\text{PR}_2 \).** Reactions were run in pressure tubes with crown cap and septa (Lab Glass Inc.) or in the reactors shown in Figure 7. A magnetic stirring bar and the platinum compound were added to the tube, which was sealed, evacuated, and reflipped with argon (three times); 1–2 mL of cyclohexane or benzene was transferred into the tube by cannula under argon ([\( \text{L}_2\text{PR}_2 \) = 0.03 M]). The tube was flushed with \( \text{H}_2 \) and pressurized to 2–4 atm. The reactions were followed by \(^3\)P NMR spectroscopy and gas chromatography.

**Registry No.** 1, 75110-84-8; 7, 77965-24-3; \( \text{cis-} \text{(Me}_2\text{P})_2\text{Pt(CH}_2\text{C(CH}_3)_2\text{)}_2 \), 86761-52-5; \( \text{cis-} \text{(Ph}_2\text{P})_2\text{Pt(CH}_2\text{C(CH}_3)_2\text{)}_2 \), 86761-53-6; \( \text{cis-} \text{(dmpe)}_2\text{Pt(CH}_2\text{C(CH}_3)_2\text{)}_2 \), 86761-54-7; \( \text{cis-} \text{(i-Pr}_2\text{P})_2\text{Pt(CH}_2\text{)}_2 \), 86761-55-8; \( \text{cis-} \text{(Ph}_2\text{P})_2\text{Pt(CH}_2\text{)}_2 \), 17567-35-0; \( \text{cis-} \text{(Et}_2\text{P})_2\text{Pt(CH}_2\text{)}_2 \), 75847-39-1; \( \text{cis-} \text{(Et}_2\text{P})_2\text{Pt(CH}_2\text{Ph)}_2 \), 42167-76-0; \( \text{cis-} \text{(Et}_2\text{P})_2\text{Pt(} \text{(CH}_2\text{)}_2\text{C(CH}_3)_2\text{)}_2 \), 70620-74-5.

**Table III. **\(^3\)P NMR Spectra of \( \text{cis-L}_2\text{PR}_2 \)

<table>
<thead>
<tr>
<th>L</th>
<th>R</th>
<th>( \delta^a )</th>
<th>( J_{\text{Hz}} )</th>
<th>solvent</th>
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<td>Me(_2\text{P} )</td>
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<td>( \text{C}_8\text{H}_8 )</td>
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<td>( \text{C}_8\text{H}_12 )</td>
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<td>dmpe</td>
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<tr>
<td>( \text{d}_2\text{(Pr}_2\text{P} )</td>
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<td>1833</td>
<td>( \text{C}_8\text{H}_12 )</td>
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<td>( -\text{CH}_2\text{C(} \text{CH}_3\text{)}_2 )</td>
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\( ^a \) Relative to 85% phosphoric acid (downfield shifts positive).