

# Mechanisms of Thermal Decomposition of *trans*-Chloroneopentylbis(tricyclopentylphosphine)platinum(II)<sup>1</sup>

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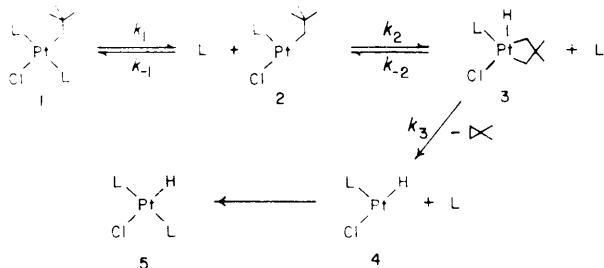
Received January 29, 1986

The most probable mechanism for the thermal decomposition of *trans*-chloroneopentylbis(tricyclopentylphosphine)platinum(II) ( $L_2PtNpCl$ , 1) to *trans*-chlorohydridobis(tricyclopentylphosphine)platinum(II) ( $L_2PtHCl$ , 5) and 1,1-dimethylcyclopropane (DMC) in cyclohexane solution involves initial equilibrium dissociation of tricyclopentylphosphine (L) from 1, reversible intramolecular oxidative addition of a  $\gamma$ -C-H bond of the neopentyl moiety to platinum and formation of an intermediate platinacyclobutane, 3, and rate-limiting reductive elimination of 1,1-dimethylcyclopropane (Scheme I). Reassociation of L yields 5. In the absence of added L, the reaction is half-order in 1; with added L (0.068–0.54 M), the reaction is first-order in 1 and inverse first-order in L. Arrhenius activation parameters  $A_1$  and  $E_{a,1}$  for the first-order decomposition of 1 to 5 and dimethylcyclopropane were determined in cyclohexane containing L ( $[L]_0 = 0.39$  M):  $E_{a,1} = 49 \pm 1$  kcal/mol;  $\log A_1 = 21 \pm 2$ ;  $\Delta H^* (156^\circ\text{C}) = 48 \pm 1$  kcal/mol;  $\Delta S^* (156^\circ\text{C}) = 34 \pm 1$  eu. Substitution of deuterium for hydrogen in the neopentyl group of 1 results in a deuterium kinetic isotope effect of  $k_H/k_D = 2.9$ . The dependence of the rate of reaction on the concentration of 1 allows estimation of the dissociation constant  $K_{eq}$  of L from 1;  $K_{eq} (156^\circ\text{C}) = 0.017 \pm 0.002$  M. From the Arrhenius parameters in the presence and absence of L, the temperature dependence of  $K_{eq}$  can be determined:  $\Delta S_{eq} = 30 \pm 5$  eu and  $\Delta H_{eq} = 16 \pm 3$  kcal/mol. A side reaction (3–20%) in the decomposition of 1 produces neopentane and appears to proceed through free neopentyl radicals. *trans*-Chloro(1-norbornylmethyl)-bis(tricyclopentylphosphine)platinum(II) ( $L_2Pt(CH_2Nb)Cl$ , 6) decomposes thermally at 156 °C and gives 1-methylnorbornane,  $L_2PtHCl$  (5), and a product, 7, derived from cyclometalation of the phosphine L.

## Introduction

This paper describes the mechanism of thermal decomposition of *trans*-chloroneopentylbis(tricyclopentylphosphine)platinum(II) (1,  $L_2PtNpCl$ ) to *trans*-chlorohydridobis(tricyclopentylphosphine)platinum(II) (5,  $L_2PtHCl$ ) and 1,1-dimethylcyclopropane (DMC) (Scheme I). This reaction is interesting for three reasons. First, in general, it provides further information about the details of elementary reactions which break and form C-H and C-C bonds by reaction with a platinum atom. Reforming,<sup>2,3</sup> hydrogenation,<sup>4</sup> intermolecular C-H activation,<sup>5–8</sup> intramolecular C-H activation,<sup>7–12</sup>  $\beta$ -hydride elimination–insertion,<sup>13–15</sup> and reductive elimination of C-H and

Scheme I. Postulated Mechanism for Conversion of 1 to 5 and 1,1-Dimethylcyclopropane  
(L = Tricyclopentylphosphine)



(1) Supported by the National Science Foundation (Grants CHE 82-05143 and CHE 85-08702).

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C-C bonds<sup>11,12,16–19</sup> all involve these types of elementary reactions. Second, comparison of this reaction with analogous studies of the mechanism of thermal decomposition of  $(Et_3P)_2PtNp_2$  to  $(Et_3P)_2PtCH_2C(CH_3)_2CH_2$ <sup>11</sup> and of  $(Cy_3P)_2PtCH_2C(CH_3)_2CH_2$  to  $(Cy_3P)_2Pt^0$  and 1,1-dimethylcyclopropane<sup>19</sup> permits us to draw mechanistically useful inferences concerning the structural factors determining the rates of these reactions. Third, the kinetic order of the reaction in 1 changes from half-order to first-order on addition of tricyclopentylphosphine (L). This kinetic feature permits us, for the first time in our studies of organoplatinum compounds, to analyze separately the thermodynamics of the preequilibrium dissociation of L from the platinum center.

We chose to use tricyclopentylphosphine (L) rather than, e.g., triethylphosphine or tricyclohexylphosphine in this

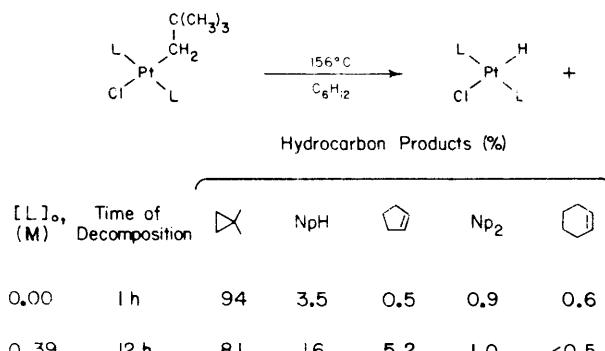
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**Scheme II. Products of Thermal Decomposition of 1<sup>a</sup>**

<sup>a</sup> Yields of products are given as percentages of one equiv/equiv of 1.

study for two reasons. First,  $(Et_3P)_2PtHCl$  reacts with  $Et_3P$  yielding  $(Et_3P)_3PtH^+Cl^-$ <sup>13</sup> and thus complicates the kinetics in the presence of phosphine; the analogous reaction does not occur with tricyclopentylphosphine. Second, platinum complexes made with tricyclopentylphosphine tend to be more soluble in cyclohexane than analogous complexes made with tricyclohexylphosphine.

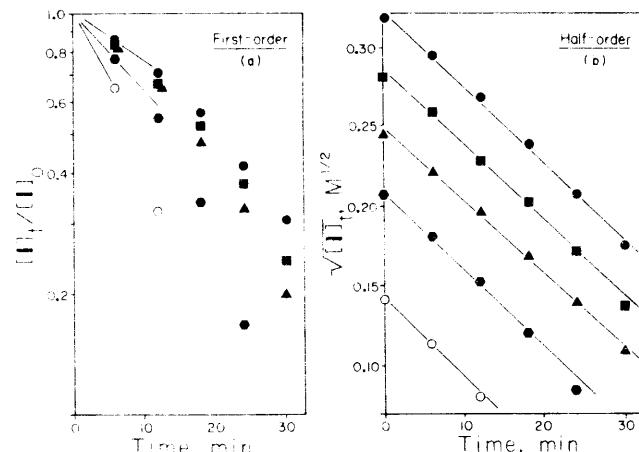
This study also examines a minor side reaction (3–20%) in the decomposition of 1 which yields 5 and neopentane. Deuterium-labeling studies indicate that protons originally present in the C–H bonds of cyclohexane (solvent), tricyclopentylphosphine, and the neopentyl group of 1 all take part in this reaction and are incorporated into neopentane. The major pathway yielding neopentane appears to involve neopentyl radicals, although pathways requiring cyclometallation of L may also be significant.

The thermal decomposition of a structurally analogous organoplatinum complex, *trans*-chloro(1-norbornylmethyl)bis(tricyclopentylphosphine)platinum(II) (**6**), yields 1-methylnorbornane, **5**, and a product of cyclometalation (**7**). This reaction parallels one of the side reactions in the decomposition of 1 which yields neopentane and **5**.

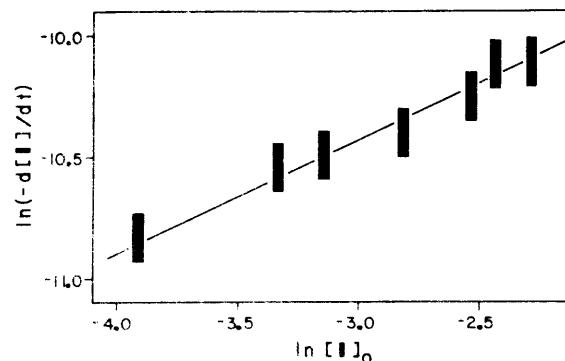
## Results

**Products.** A 0.06 M solution of 1 in cyclohexane yielded, on heating for 1 h at 156 °C, 1,1-dimethylcyclopropane, neopentane (NpH) and, as the only phosphorus-containing product detected by <sup>31</sup>P NMR spectroscopy, **5** (Scheme II). Small quantities of cyclohexene, dineopentyl (Np<sub>2</sub>)<sup>20</sup> and cyclopentene were also produced. A solution of 1 (0.06 M) and tricyclopentylphosphine (0.39 M) in cyclohexane yielded, on heating at 156 °C for 12 h, the same products, but the yields of neopentane and cyclopentene increased and that of dimethylcyclopropane decreased. The reaction mixtures at the conclusion of the thermal decomposition reactions were colorless and appeared homogeneous.

**Kinetic Behavior: No Added Phosphine.** We followed the kinetics of decomposition of 1 by <sup>31</sup>P NMR spectroscopy in sealed NMR tubes. Figure 1 shows first-order and half-order plots of kinetic data derived from several thermal decompositions of 1 in cyclohexane solution at 156 °C. The initial concentration of 1 ( $[1]_0$ ) was varied from 0.02 to 0.10 M. These data clearly give better half-order plots than first-order; half-order rate constants ( $k_{\text{half}}$ ) vary by a factor of 1.1 over this range of  $[1]_0$ ; first-order rate constants vary by a factor of 4.3, and the first-order plots show significant curvature.<sup>21</sup> An exam-



**Figure 1.** First-order (a) and half-order (b) kinetic plots of the decomposition of 1 in cyclohexane solution at 156 °C at several different initial concentrations of 1 ( $[1]_0$ ): ●, 0.10 M; ■, 0.08 M; ▲, 0.06 M; ○, 0.020 M.



**Figure 2.** The initial rate of decomposition of 1 ( $-d[1]/dt$ , in  $M \cdot s^{-1}$ , 156 °C, cyclohexane) increases with increasing initial concentrations of 1.

ination of the dependence of the initial rates on  $[1]_0$  (Figure 2) yield the empirical rate law (eq 1). Within experimental error, the order in 1 is one-half.<sup>22,23</sup>

$$-d[1]/dt = (1.1 \pm 0.2) \times 10^{-4} [1]^{0.45 \pm 0.1} \quad (1)$$

There is a slight downward curvature in the half-order rate plots (Figure 1b). We attribute this rate acceleration to the product **5**. The half-order rate constant for decomposition of 1 ( $[1]_0 = 0.06$  M) in cyclohexane containing **5** ( $[5]_0 = 0.028$  M) was 20% larger than the rate constant for decomposition in cyclohexane containing no added **5**. The rate of decomposition of 1 was independent of  $[5]_0$  from 0.028 to 0.113 M. We emphasize that the rate acceleration caused by **5** is small and cannot be responsible for the observed half-order kinetics.

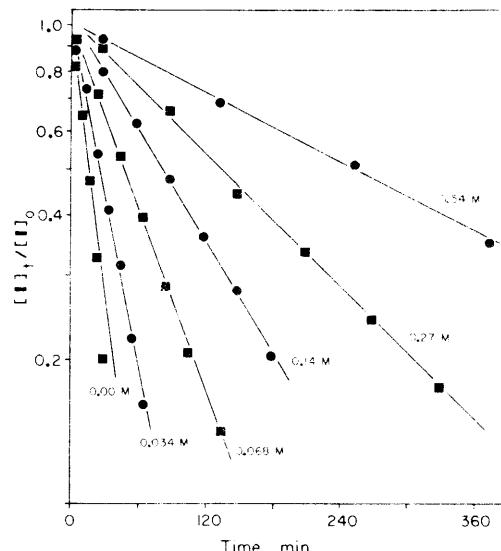
The rate of thermal decomposition depended slightly on solvent, but the distribution of products was independent of solvent. The rate of decomposition increased with increasing solvent polarity from *n*-hexane to cyclohexane to benzene to THF.

(22) The initial first-order rates were derived from the first two points of the kinetic plots (time = 0 and 6 min) and thus are only approximations of the true *initial* rates. This procedure overestimates the initial rates at low  $[1]_0$  and thus underestimates the value for the order in 1. If the two initial rates determined at  $[1]_0 = 0.020$  and 0.036 M are omitted, a least-squares analysis of the remaining data produces a higher value for the order in 1:  $-d[1]/dt = 1.3 \pm 0.1 [1]^{0.51 \pm 0.1}$ .

(23) Other examples of half-order kinetics are as follows: Chowdhury, D. M.; Poe, A.; Sharma, K. R. *J. Chem. Soc., Dalton Trans.* 1977, 1552–1555. Kohn, H.; Louw, W. J.; Palmer, D. A. *Inorg. Chem.* 1986, 19, 843–847.

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(21) The zero-order rate constants for this reaction vary by a factor of 1.1 over this range of  $[1]_0$ .



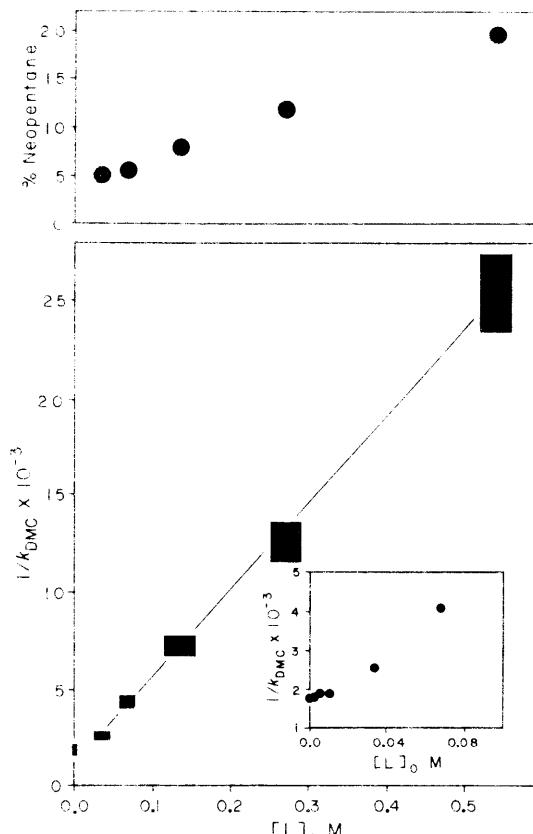
**Figure 3.** First-order kinetic plots for the decomposition of 1 in cyclohexane solutions in the presence of L:  $[L]_0 = 0.06$  M;  $T = 156$  °C.  $[L]_0$  is indicated on the figure for each curve.

Addition of the radical trap 2,2,6,6-tetramethyl-piperidinyloxy (TEMPO) (0.069 M) did not change the rate of decomposition of 1. The yield of neopentane in the decomposition of 1 decreased from 3–4% to ca. 1% in the presence of TEMPO. *N*-Neopentoxy-2,2,6,6-tetramethylpiperidine (TEMPO-Np) was detected in 1–2% yield in the decomposition of 1 carried out in the presence of TEMPO. The yields of neopentane and TEMPO-Np were independent of the concentration of TEMPO from 0.015 to 0.12 M.

The addition of mercury to NMR tubes containing solutions of  $L_2^D PtNp^D Cl^{24}$  in cyclohexane did not significantly change the rate or products of decomposition.<sup>25</sup> This observation and the observation that solutions are clear and colorless on completion of decomposition constitute evidence that this reaction is homogeneous.

**Kinetic Behavior: Added Tricyclopentylphosphine.** Figure 3 shows first-order kinetic plots for the thermal decomposition of 1 at 156 °C in cyclohexane solutions containing different concentrations of *added* tricyclopentylphosphine ( $[L]_0$ ). The kinetics were first-order in 1 when  $[L]_0 \geq 0.068$  M, and increasing  $[L]_0$  slowed the rate of thermal decomposition. Varying  $[L]_0$  from 0.041 to 0.101 M in the presence of  $[L]_0 = 0.39$  M did not change the rate of decomposition.

**Kinetic Analysis: Partitioning between DMC and NpH. Activation Parameters.** The change in rate law for decomposition of 1 to 5 from half-order to first-order in [1] on adding L is useful in mechanistic analysis (see below), and we have used kinetic information derived both



**Figure 4.** Upper: amount of neopentane increases with increasing  $[L]_0$ . Lower: reciprocal of the first-order rate constant  $k_{DMC}$  vs.  $[L]_0$ ;  $[1]_0 = 0.06$  M;  $T = 156$  °C. Error bars represent 95% confidence limits for  $1/k_{DMC}$  and error in  $[L]_0$ . The insert shows data with expanded axes and without error bars.

in the presence and absence of added L. For reference in what follows, we define several observed rate constants (eq 2–5); analysis of these empirical constants in terms of the

$$d[1]/dt = -k_{half}[1]^{1/2} \quad ([L]_0 = 0) \quad (2)$$

$$d[1]/dt = -k_{first}[1] \quad ([L]_0 \geq 0.068 \text{ M}) \quad (3)$$

$$k_{DMC} = k_{first}f_{DMC} \quad (4)$$

$$k_{Np} = k_{first}f_{Np} \quad (5)$$

elementary rate constants in Scheme I is deferred to the Discussion. We call the *observed* half-order rate constant (eq 2)  $k_{half}$  and the *observed* first-order rate constant  $k_{first}$ . The observed rate constants for formation of 1,1-dimethylcyclopropane ( $k_{DMC}$ ) or of neopentane ( $k_{Np}$ ) are given by eq 4 and 5, where, e.g.,  $f_{DMC}$  is the fraction of the decomposed 1 that appears as DMC.

Analysis of decomposition products by gas chromatography showed that the yield of neopentane increased with increasing  $[L]_0$  (Figure 4, upper). With  $[L]_0 = 0.39$  M, the relative yields of 1,1-dimethylcyclopropane and neopentane were independent of the extent of decomposition. We calculated the first-order rate constants for production of dimethylcyclopropane ( $k_{DMC}$ ) and neopentane ( $k_{Np}$ ) from the relative yields of these products at the end of the reaction. A plot of  $1/k_{DMC}$  vs.  $[L]_0$  (Figure 4) shows that the rate of formation of 1,1-dimethylcyclopropane is inversely proportional to  $[L]_0$  when  $[L]_0 \geq 0.034$  M and is less dependent upon  $[L]_0$  when  $[L]_0 < 0.034$  M. A plot of  $\ln k_{DMC}$  vs.  $\ln [L]_0$  ( $0.068 \leq [L]_0 \leq 0.54$  M) showed that

(24) Throughout this paper, platinum compounds will be named by reference to *trans*-chloroneopentylpotassium(tricyclopentylphosphine)platinum(II) (1,  $L_2PtNpCl$ ). Thus, for example, *trans*-chloro(neopentyld<sub>1,1</sub>bis(tricyclopentylphosphine)-<sub>2,2</sub>platinum(II)) will be named  $L_2^D PtNp^D Cl^{24}$ . Many of the kinetic studies of decomposition were carried out in solutions containing added tricyclopentylphosphine. We use the term  $[L]$ , to refer to the concentration of this *added* phosphine and use the term  $[L]$  to refer to the *total* concentration of phosphine in solution. The values of these two terms differ at low concentrations of added L because dissociation of L from  $L_2PtNpCl$  is significant.

(25) The suppression by mercury of unwanted heterogeneous platinum(0)-catalyzed reactions in a number of organoplatinum decompositions has been studied in detail. In particular, the thermal decomposition of  $L_2^D PtNp^D Cl^{24}$  in the presence of added mercury is discussed and thus will not be treated in detail here. Whitesides, G. M.; Hackett, M.; Brainard, R. L.; Lavallee, J. P. P. M.; Sowinsky, A. F.; Izumi, A. N.; Moore, S. S.; Brown, D. W.; Staudt, E. M. *Organometallics* 1985, 4,

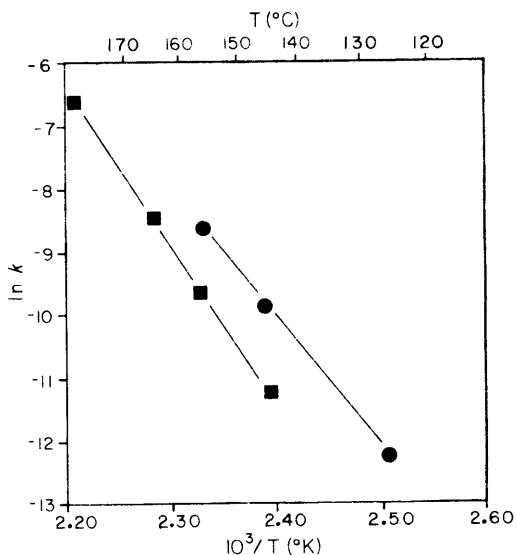


Figure 5. Arrhenius plot of  $\ln k_{\text{half}}$  ( $[L]_0 = 0.0 \text{ M}$ ) (●) and  $\ln k_{\text{DMC}}$  ( $[L]_0 = 0.39 \text{ M}$ ) (■) vs.  $1/T$ :  $[1]_0 = 0.06 \text{ M}$ .

Table I. Decomposition of Isotopically Labeled 1 in Cyclohexane at  $132 \text{ }^\circ\text{C}^a$

| compd  | <i>in</i> | $10^6 k_{\text{half}}^b$  |                           | NpD (or $\text{Np}^d D$ ) <sup>c</sup> , % |                           |
|--|-----------|---------------------------|---------------------------|--|---------------------------|
|  |           | $\text{C}_6\text{H}_{12}$ | $\text{C}_6\text{D}_{12}$ | $\text{C}_6\text{H}_{12}$                  | $\text{C}_6\text{D}_{12}$ |
| $\text{L}_2\text{PtNpCl}$                              |           | 9.4                       | 9.2                       | 0  | 17                        |
| $\text{L}_2^{\text{D}}\text{PtNpCl}$                   |           | 9.6                       | 9.1                       | 4  | 67                        |
| $\text{L}_2\text{PtNp}^{\text{D}}\text{Cl}$            |           | 3.4 <sup>d</sup>          | 3.4 <sup>d</sup>          | 3  | 37                        |
| $\text{L}_2^{\text{D}}\text{PtNp}^{\text{D}}\text{Cl}$ |           | 3.3 <sup>e</sup>          | 3.1 <sup>d</sup>          | 22   | 93                        |

<sup>a</sup>The initial concentration of 1 was 0.03–0.06 M. The yield of neopentane ( $d_0 + d_1$  or  $d_{11} + d_{12}$ ) in each experiment was  $5 \pm 3\%$  as determined by GC. <sup>b</sup>Half-order rate constants are in units of  $\text{M}^{1/2}\text{s}^{-1}$ . <sup>c</sup>The amount of neopentane- $d_1$  or neopentane- $d_{12}$  (as appropriate) relative to total amount of neopentane as determined by GC/MS. Details of these analyses are outlined in the Experimental Section. <sup>d</sup>Average of three experiments. <sup>e</sup>Average of two experiments.

is approximately independent of  $[L]_0$ : a plot of  $\ln k_{\text{Np}}$  vs.  $\ln [L]_0$  ( $0.068 \leq [L]_0 \leq 0.54 \text{ M}$ ) indicated an order of  $L$  of  $-0.2 \pm 0.1$ .

Arrhenius activation parameters were determined for the decomposition of 1 in cyclohexane and in cyclohexane containing  $[L]_0 = 0.39 \text{ M}$ . In the half-order kinetic regime ( $[L]_0 = 0.0 \text{ M}$ ), plotting  $\log k_{\text{half}}$  vs.  $1/T$  gave  $E_{\text{a},1/2} = 41 \pm 1 \text{ kcal/mol}$  and  $\log A_{1/2} = 17 \pm 2$  ( $A_{1/2}$  is in units of  $\text{M}^{1/2}\text{s}^{-1}$ ) (Figure 5). In the first-order regime ( $[L]_0 = 0.39 \text{ M}$ ), plotting  $\log k_{\text{DMC}}$  vs.  $1/T$  gave  $E_{\text{a},1} = 49 \pm 1 \text{ kcal/mol}$  and  $\log A_1 = 21 \pm 2$  ( $A_1$  is in units of  $\text{s}^{-1}$ ).

We recorded the  $^{31}\text{P}$  NMR spectrum of a mixture of 1 and 5 in decalin- $d_{18}$  at  $125 \text{ }^\circ\text{C}$ . The signals due to 5 were sharp, but only a single very broad signal was observed for 1. We infer that interchange of L on 1 is fast on the NMR time scale, while that of 5 is slow.

**Deuterium-Labeling Experiments.** The compounds  $\text{L}_2\text{PtNpCl}$ ,  $\text{L}_2\text{PtNp}^{\text{D}}\text{Cl}$ ,  $\text{L}_2^{\text{D}}\text{PtNpCl}$ , and  $\text{L}_2^{\text{D}}\text{PtNp}^{\text{D}}\text{Cl}$  were decomposed at  $132 \text{ }^\circ\text{C}$  in cyclohexane- $d_0$  or cyclohexane- $d_{12}$  ( $\text{Np}^{\text{D}} = \text{CD}_2\text{C}(\text{CD}_3)_3$ ;  $\text{L}^{\text{D}} = \text{P}(\text{C}_5\text{D}_{11})_3$ ). The rate of decomposition for each combination of compound and solvent in separate NMR tubes (Figure 6) was determined by  $^{31}\text{P}$  NMR spectroscopy. The half-order rate constants (Table I) were an average of at least two experiments. Table II presents the deuterium kinetic isotope effects

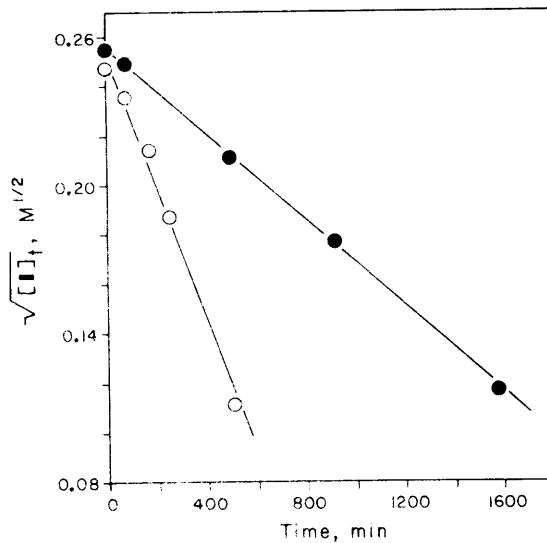


Figure 6. Half-order kinetic plots for the decomposition of  $\text{L}_2^{\text{D}}\text{PtNp}^{\text{D}}\text{Cl}$  (●) and  $\text{L}_2^{\text{D}}\text{PtNpCl}$  (○) in cyclohexane- $d_{12}$  at  $132 \text{ }^\circ\text{C}$ .

Table II. Deuterium Kinetic Isotope Effects for the Thermal Decomposition of  $\text{L}_2\text{PtNpCl}$

| compd <sup>H</sup>   | compd <sup>D</sup> | $(k^{\text{H}}_{\text{half}}/k^{\text{D}}_{\text{half}})^a$ |
|--|--------------------|---|
| $\text{L}_2\text{PtNpCl}/\text{L}_2^{\text{D}}\text{PtNp}^{\text{D}}\text{Cl}^b$ |                    | $2.9 \pm 0.3$   |
| $\text{L}_2\text{PtNpCl}/\text{L}_2^{\text{D}}\text{PtNp}^{\text{D}}\text{Cl}^b$ |                    | $2.8 \pm 0.4$   |
| $\text{L}_2\text{PtNp}^{\text{D}}\text{Cl}/\text{L}_2^{\text{D}}\text{PtNpCl}^b$ |                    | $1.0 \pm 0.1$   |
| $\text{C}_6\text{H}_{12}/\text{C}_6\text{D}_{12}^b$                              |                    | $1.0 \pm 0.1$   |

<sup>a</sup>The half-order rate constants (units of  $\text{M}^{1/2}\text{s}^{-1}$ ) are listed in Table I. Deuterium kinetic isotope effect (KIE) error limits are set to 95% confidence levels. Methods used to propagate errors are discussed in the Experimental Section. <sup>b</sup>KIE experiments were performed in both  $\text{C}_6\text{H}_{12}$  and  $\text{C}_6\text{D}_{12}$ , but rate comparisons were made only between experiments conducted in the same solvent. The  $k^{\text{H}}_{\text{half}}/k^{\text{D}}_{\text{half}}$  values obtained in  $\text{C}_6\text{H}_{12}$  and  $\text{C}_6\text{D}_{12}$  were averaged to give the indicated KIE values. <sup>c</sup>Rate comparisons between  $\text{L}_2\text{PtNpCl}$  and  $\text{L}_2^{\text{D}}\text{PtNpCl}$  and between  $\text{L}_2\text{PtNp}^{\text{D}}\text{Cl}$  and  $\text{L}_2^{\text{D}}\text{PtNpCl}$  were averaged to give the final value. <sup>d</sup>Rate comparisons were made between experiments conducted in  $\text{C}_6\text{H}_{12}$  and  $\text{C}_6\text{D}_{12}$  for the thermal decompositions of  $\text{L}_2\text{PtNpCl}$ ,  $\text{L}_2^{\text{D}}\text{PtNpCl}$ ,  $\text{L}_2\text{PtNp}^{\text{D}}\text{Cl}$ , and  $\text{L}_2^{\text{D}}\text{PtNp}^{\text{D}}\text{Cl}$ . Only one isotope component (e.g.,  $\text{C}_6\text{H}_{12}$  and  $\text{C}_6\text{D}_{12}$ ) was changed at a time for any pair of experiments; the combination of all these comparisons provided the averaged value.

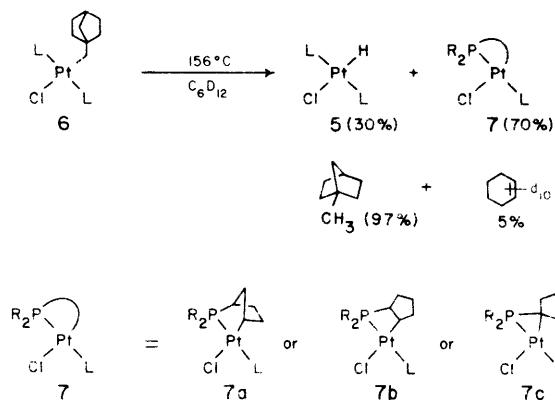
obtained by comparing the half-order rate constants of pairs of experiments that differ in the isotopic labeling of one ligand (or solvent). For example, the kinetic isotope effect obtained by comparison of  $\text{L}_2^{\text{D}}\text{PtNp}^{\text{D}}\text{Cl}$  and  $\text{L}_2^{\text{D}}\text{PtNpCl}$  in cyclohexane was 2.9 and the kinetic isotope effect of the same compounds in cyclohexane- $d_{12}$  was 2.9. We averaged these two values to get the isotope effect presented in Table II.

We thermally decomposed  $\text{L}_2\text{Pt}(\text{CD}_2\text{C}(\text{CH}_3)_3)\text{Cl}$  ( $1-d_2$ ) in cyclohexane at  $145 \text{ }^\circ\text{C}$  and in cyclohexane containing 0.40 M L at  $165 \text{ }^\circ\text{C}$ . Deuterium NMR spectroscopy of the products of complete decomposition of  $1-d_2$  showed  $\text{CHD}_2\text{C}(\text{CH}_3)_3$ ,  $\text{CH}_2\text{CD}_2\text{C}(\text{CH}_3)_2$ , and  $\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_3$  were formed in the ratio of 1:34:1 in the absence of L and in the ratio of 3:13:1 with L.

We found that the neopentane produced in the decomposition of 1 (Table I) contained deuterium (hydrogen) atoms which had originated in the phosphine ligands of 1, in the neopentyl group of 1, and in the cyclohexane solvent. A comparison of the amount of neopentane- $d_1$  produced upon thermolysis of  $\text{L}_2\text{PtNpCl}$  in cyclohexane with the amount produced in cyclohexane- $d_{12}$  suggested that 17% of the neopentane was formed by reaction with  $\text{L}_2^{\text{D}}\text{PtNp}^{\text{D}}\text{Cl}$  in

(26) We suggest that the order in  $L_0$  ( $-0.9 \pm 0.15$ ) is not  $-1.0$  because the addition of tricyclohexylphosphine increases the polarity of the reaction medium and thus increases the rate. This effect slightly counter-

Scheme III. Products of Thermal Decomposition of 6



hexane and cyclohexane- $d_{12}$ , however, suggested that 71% of the neopentane was formed by reaction with cyclohexane. This variation is compatible with the observed isotope effect: deuteration of L slows hydrogen (deuterium) transfer from it and renders reaction with solvent (by whatever mechanism) more important. Similar variations were observed in the amount of deuterium (hydrogen) transferred from L (4–50%) and from the neopentane group of the starting material (3–20%).

**Thermal Decomposition of *trans*-Chloro(1-norbornylmethyl)bis(tricyclopentylphosphine)platinum(II) ( $L_2Pt(CH_2Nb)Cl$ , 6).** In an effort to understand the side reaction(s) which produced neopentane in the thermal decomposition of 1, we studied the thermal decomposition of 6 (Scheme III). We reasoned that intramolecular activation of the C–H bonds of the 1-norbornylmethyl group of this compound would be slower than that of the neopentyl group of 1 because attack of platinum on the  $\gamma$  or  $\delta$  C–H bonds would produce (apparently) strained tricyclic ring systems. Thus, with these reaction pathways unavailable, we expected that the predominant reaction pathway(s) for the decomposition of 6 would parallel those which produced neopentane from 1 and, in this case, would produce methylnorbornane.

Decomposition of 6 (0.04 M) in cyclohexane- $d_{12}$  at 156 °C for 49 h yielded a clear colorless solution containing methylnorbornane (95%), cyclohexene (5%),<sup>18</sup> 5 (30%), and a platinum-containing compound with inequivalent phosphines (7, 70%) (Scheme III). We believe that 7 is a product resulting from cyclometalation of a C–H bond of L. Due to the complexity of the  $^1H$  NMR spectrum, however, we cannot distinguish between structures 7a, 7b, and 7c.<sup>27</sup> In support of this structural assignment are the observations that 7 contains no norbornylmethyl group (by  $^1H$  NMR spectroscopy), 7 is a product of the thermal decomposition of *trans*- $L_2PtMeCl$  in cyclohexane,<sup>28</sup> and deuterium-labeling experiments indicate that protons (H or D) originating on L are transferred to the methylnorbornyl group, yielding methylnorbornane (vide infra). Decomposition of 7 in cyclohexane at 195 °C slowly yielded 5.<sup>28</sup>

(27) Although we are unable to distinguish between structures 7a, 7b, and 7c based on our experiments, other workers have demonstrated that H/D exchange of C–H bonds in trialkylphosphines occurs with this selectivity:  $C_3 > C_4 > C_2 \gg C_1$ . On this basis we prefer structure 7a. Zeiher, E. H. K.; DeWit, D. G.; Caulton, K. G. *J. Am. Chem. Soc.* 1984, 106, 7006–7011. Kiffen, A. A.; Masters, C.; Raynard, L. *J. Chem. Soc., Dalton Trans.* 1975, 853–857. An empirical correlation has been shown to exist between the ring size of organometallic complexes containing chelated phosphines and the chemical shift of the  $^{31}P$  nucleus: Garrou, P. E. *Chem. Rev.* 1981, 81, 229–266. The observation of a downfield shift on metalation also supports structure 7a.

(28) Brainard, R. L. Ph.D. Dissertation, Massachusetts Institute of Technology, Cambridge, MA 1985.

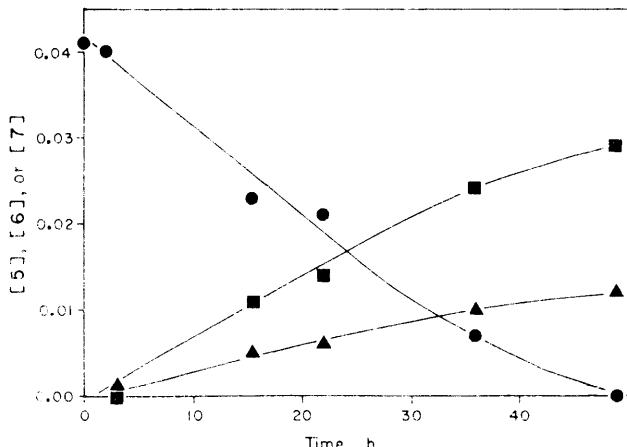


Figure 7. Decomposition of 6 in cyclohexane- $d_{12}$  at 156 °C ( $[6]_0 = 0.06$  M): ●: [6], ■: [7], ▲: [5], △:  $[CH_3]$ .

Table III. Methylnorbornane Derived from the Decomposition of  $L_2Pt(CH_2Nb)Cl$  and  $L^D_2Pt(CH_2Nb)Cl$

| compd               | NbCH <sub>2</sub> D <sup>b</sup> % |                                |
|---------------------|------------------------------------|--------------------------------|
|                     | in C <sub>6</sub> H <sub>12</sub>  | C <sub>6</sub> D <sub>12</sub> |
| $L_2Pt(CH_2Nb)Cl$   | 0                                  | 2                              |
| $L^D_2Pt(CH_2Nb)Cl$ | 85                                 | 93                             |

<sup>a</sup>The initial concentration of  $L_2Pt(CH_2Nb)Cl$  ( $L^D_2Pt(CH_2Nb)Cl$ ) was 0.03–0.04 M. Decompositions were carried out at 156 °C. <sup>b</sup> 1-Methylnorbornane- $d_1$ , relative to the total 1-methylnorbornane ( $d_1$  and  $d_0$ ), produced as determined by GC/MS.

Figure 7 shows the relative concentrations of 5, 6, and 7 as a function of time. The kinetics of the decomposition were neither cleanly first-order nor half-order in 6 and were not examined in detail. The rate of decomposition of 6 at 156 °C was ca. 10<sup>2</sup> times slower than the rate at which 1 forms 1,1-dimethylcyclopropane and ca. 3 times slower than the rate at which 1 forms neopentane. Table III shows the percentage of 1-methylnorbornane that is deuterated in the decomposition of  $L_2Pt(CH_2Nb)Cl$  and  $L^D_2Pt(CH_2Nb)Cl$  in cyclohexane and in cyclohexane- $d_{12}$ .

## Discussion

The reaction of major interest in this work is the conversion of 1 to dimethylcyclopropane (DMC, 80–95% yield); the second observed hydrocarbon product neopentane (3–20%) appears to be formed by several competing pathways, including one involving free neopentyl radicals. The major pieces of evidence relevant to the mechanism of formation of DMC are as follows:

(i) Formation of DMC proceeds by a reaction that is kinetically half-order in 1 when no added tricyclopentylphosphine is present in solution; when  $[L]_0 \geq 0.07$  M, the reaction becomes first-order in 1 and inverse first-order in L.

(ii) In the first-order regime,  $\log A = 21 \pm 2$ . This value is compatible with conversion of 1 to three particles in the rate-limiting transition state.

(iii) The deuterium kinetic isotope effect observed on substitution of deuterium for hydrogen in the neopentyl group is  $k_H/k_D \approx 2.9$ .

(iv) A minor process is interchange of methyl and methylene groups in 1 (as inferred from formation of  $CH_2CH_2C(CH_2D)(CH_3)$  from  $L_2Pt[CD_2C(CH_3)_3]Cl$  in yields approximately 3–10% of those of  $CH_2CD_2C(CH_3)_2$ .

The first task in analyzing the mechanism of reaction is to rationalize the change in kinetic order in [1] from one-half to one on changing from  $[L]_0 = 0$  M to  $[L]_0 \geq 0.07$  M. This change is the most interesting and informative

kinetic feature of the reaction. We propose that it is a straightforward consequence of phosphine dissociation prior to the rate-limiting step. In principle, this type of kinetic behavior should be observed for many decompositions of complexes of the structure  $L_2PtRR'$ ; phosphine dissociation seems to be a common feature in these decompositions. The difference between half-order and first-order kinetic behavior is, however, difficult to detect experimentally, and the decomposition of **1** is the first system we have examined in which the quality of the data was high enough to permit this distinction.

We relate the rate of appearance of product ( $d[5]/dt$ , eq 6) to the rate constants contained in Scheme I and the

$$d[5]/dt = \frac{k_1 k_2 k_3 [1]}{k_{-1} (k_{-2} + k_3) [L]} \quad (6)$$

concentration of **1** by application of the steady-state approximation to **3** ( $d[3]/dt = 0$ ) and application of the equilibrium approximation to **2** ( $K_{eq} = [2][L]/[1] = k_1/k_{-1}$ ).<sup>29</sup> The concentrations of **1** and **5** were measured at room temperature. Equation 6 is applicable at elevated temperatures at which the decompositions were carried out. At room temperature the only species present in significant concentrations are **1** and **5**, and we assume that all of **2** and **3** revert to **1** during the thermal quench before concentrations are measured. This assumption allows  $d[5]/dt$  and  $-d[1]/dt$  to be equated. Setting  $K_{eq} = k_1/k_{-1}$  and  $k_2' = k_2 k_3 / (k_{-2} + k_3)$ , eq 6 can be rewritten (eq 7). We assume that in the absence of added L dissociation of **1** into **2** and L determines the concentration of L (that is, that the concentration of L is essentially independent of the concentrations of **3**, **4**, and **5**) and that  $k_{-2} > k_2$ , and thus  $[L] = [2]$ . With these assumptions, the concentration of [L] is given by eq 8 and 9. Substitution of this value

$$d[1]/dt = -k_2' K_{eq} [1]/[L] \quad (7)$$

$$K_{eq} = [2][L]/[1] \approx [L]^2/[1] \quad (8)$$

$$[L] = K_{eq}^{1/2} [1]^{1/2} \quad (9)$$

$$d[1]/dt = -k_2' K_{eq}^{1/2} [1]^{1/2} = -k_{half} [1]^{1/2} \quad (10)$$

$$[1]^{1/2} = [1]_0^{1/2} - (\frac{1}{2}) k_2' K_{eq}^{1/2} t \quad (11)$$

of [L] into eq 7 yields eq 10; integration yields eq 11. We observe experimentally that in the absence of added L, the kinetics of decomposition of **1** in cyclohexane solution follow a half-order rate law over the concentration range  $0.02 \leq [1]_0 \leq 0.1$  M (Figure 1b). The slopes of the lines in this figure are thus equal to  $-(\frac{1}{2}) k_2' K_{eq}^{1/2}$ . Half-order kinetics were also observed in *n*-hexane, benzene, and THF, indicating that a trace contaminant in cyclohexane is not causing unusual kinetic behavior. We have not identified the origin of the small increase in rate observed with increasing solvent polarity.

When decompositions of **1** were carried out in the presence of  $[L]_0 \geq 0.07$  M, first-order kinetics were observed for the disappearance of **1**. Under these conditions, the concentration of L in solution is negligibly affected by dissociation of L from **1**. Substitution of  $[L]_0$  for [L] in eq 7 and integration yields eq 12. Experimentally, the rate

$$\ln ([1]/[1]_0) = k_2' K_{eq} [1] [L]_0^{-1} t \quad (12)$$

of decomposition was inversely proportional to  $[L]_0$  for  $[L]_0 \geq 0.034$  M and first-order in  $[1]$  for  $0.04 \text{ M} \leq [1]_0 \leq 0.10$  M and  $[L]_0 \geq 0.07$  M.

The data in Table II show that substitution of deuterium for hydrogen in the cyclohexane used as solvent or in L does not produce a kinetic isotope effect which differs significantly from  $k_H/k_D = 1$ . The value of  $k_H/k_D = 2.9 \pm 0.3$  obtained on substitution of deuterium for hydrogen in the neopentyl group of **1** indicates that a carbon–hydrogen bond is being broken or formed before or during the rate-limiting step in the absence of added L. (We did not measure a KIE in the presence of added L.) Observation of  $\text{CH}_2\text{CH}_2\text{C}(\text{CD}_2\text{H})\text{CH}_3$  in the decomposition of **1-d**<sub>2</sub> suggests that the process which produces dimethylcyclopropane also slowly exchanges the methylene and methyl positions of the neopentyl group of **1** and is compatible with the proposal that conversion of **3** to **2** is at least competitive with conversion of **3** to **4**. The yield of this isotopically substituted cyclopropane is, however, low (approximately 3–10% that of  $\text{CH}_2\text{CD}_2\text{C}(\text{CH}_3)_2$  in the same experiment) and thus not sufficient to distinguish between conversion of **2** to **3** (C–H bond breaking) and **3** to **4** (C–C bond forming) as rate limiting. Analysis of the Arrhenius parameters for the reaction argue for the latter (see below). Thus, the observed isotope effect is interpreted as an equilibrium isotope effect reflecting conversion of a C–H(D) bond in **1** to a Pt–H(D) bond in the transition state. We and others have observed equilibrium kinetic isotope effects of this magnitude previously.<sup>6,13</sup>

We have found preexponential factors derived from first-order kinetics to be very useful for determining the number of translationally independent particles created from the starting material in the rate-limiting transition state in studies of other organoplatinum compounds in weakly interacting solvents.<sup>11,14,19,30</sup> The observed value ( $\log A_1 = 21$ ) obtained with  $[L]_0 = 0.39$  M suggests that three particles are formed from one before or during the rate-limiting transition state. A similar value ( $\log A = 21$ ) was observed previously for thermal decomposition of  $(\text{Cy}_3\text{P})_2\text{PtCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2$ , a mechanistically related reaction we believe to involve dissociation of phosphine and rate-limiting reductive elimination of 1,1-dimethylcyclopropane.<sup>19</sup>

The Arrhenius parameters for the decomposition of **1** in the first-order and half-order kinetic regimes differ substantially. We have no experience in interpreting the value of A observed in the half-order regime. Because, as derived here from the temperature dependence of  $k_{half}$ ,  $A_{1/2}$  has units containing concentration, it cannot be compared directly with values obtained from first-order reactions. Nonetheless, we do not expect decreasing the concentration of L present in solution—the result of working at  $[L]_0 = 0$ —to change the mechanism.

We propose the mechanism presented in Scheme I for the decomposition of **1** to dimethylcyclopropane and **5**. Reversible dissociation of L is supported by precedence in other organoplatinum studies,<sup>11,12,14,19,31</sup> the half-order dependence on **1** in the absence of L, the inverse order in  $[L]_0$ , the broadening of the signals due to **1** in the <sup>31</sup>P NMR spectrum of **1** at high temperature, and the value of  $\log A_1 = 21$  obtained in the first-order kinetic regime. This value of  $\log A$  suggests that reductive elimination of dimethylcyclopropane is overall rate-limiting. This suggestion is supported by the observation of small quantities of  $\text{CH}_2\text{CH}_2\text{C}(\text{CHD}_2)\text{CH}_3$  on decomposition of  $\text{L}_2\text{Pt}[\text{CD}_2\text{C}(\text{CH}_3)_3]\text{Cl}$ . The fact that larger quantities of this deu-

(30) 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.

terium-scrambled cyclopropane are not observed cannot, however, be used as an argument that conversion of **3** to **4** is faster than return of **3** to **2**: there is no reason to believe that the Pt–H bond of **3** is symmetrically disposed with respect to the two Pt–C bonds of this intermediate.

The inference that decomposition of **1** to **5** proceeds by the same mechanism but with different rate laws at different values of  $[L]_0$  permits a determination of  $k'_2$  and  $K_{eq}$ . We have used methods of analysis based on two sets of experimental data; the agreement between them is good.

The first method proceeds from data summarized in Figures 1b and 4. The average of the slopes of the lines in Figure 1b yields  $(1/2)k'_2 K_{eq}^{1/2} = (8.43 \pm 0.62) \times 10^{-5} M^{1/2} \cdot s^{-1}$  (eq 11). The reciprocal of the slope of  $1/k_{DCM}$  vs.  $[L]_0$  (Figure 4) gives  $k'_2 K_{eq} = (2.22 \pm 0.23) \times 10^{-5} M \cdot s^{-1}$  (eq 7). Comparison of these two numerical values of distinct combinations of  $k'_2$  and  $K_{eq}$  allows these parameters to be evaluated:  $K_{eq}$  (156 °C) =  $0.017 \pm 0.002 M$ ,  $k'_2$  (156 °C) =  $(1.31 \pm 0.18) \times 10^{-3} s^{-1}$ . The value of  $\Delta G_{eq}$  (156 °C) =  $-RT \ln K_{eq} = 3.5 \pm 0.2$  kcal/mol is compatible with dissociation constants of bulky phosphines from analogous metal centers.<sup>31</sup>

The second method is based on the different Arrhenius parameters obtained in the half-order and first-order kinetic regimes. Equations 13 and 14 give the Arrhenius expressions describing the temperature dependence of  $k_{half}$  and  $k_{DCM}$ . Combination of these equations and rearrangement yields expressions for  $k'_2$  and  $K_{eq}$  (eq 15 and 16). Insertion of the values of  $A_{1/2}$ ,  $A_1$ ,  $E_{a,1/2}$ , and  $E_{a,1}$

$$\ln k_{half} = \ln (k'_2 K_{eq}^{1/2}) = \ln A_{1/2} - E_{a,1/2}/RT \quad (13)$$

$$\ln k_{DCM} = \ln (k'_2 K_{eq}/[L]_0) = \ln A_1 - E_{a,1}/RT \quad (14)$$

$$\ln k'_2 = \ln (A_{1/2}^2/A_1 [L]_0) + (E_{a,1} - 2E_{a,1/2})/RT \quad (15)$$

$$\ln K_{eq} = 2[\ln (A_1 [L]_0/A_{1/2}) + (E_{a,1/2} - E_{a,1})/RT] \quad (16)$$

derived from the plots in Figure 5 into these equations yields  $K_{eq}$  (156 °C) =  $0.016 M$  and  $k'_2$  (156 °C) =  $1.47 \times 10^{-3} s^{-1}$ . These numbers are within the experimental errors of those obtained by the first method. Equation 16 also yields directly values of  $\Delta H_{eq}$  and  $\Delta S_{eq}$  (eq 17–19). The

$$\ln K_{eq} = -\Delta G_{eq}/RT = \Delta S_{eq}/R - \Delta H_{eq}/RT \quad (17)$$

$$\Delta S_{eq} = 2R \ln (A_1 [L]_0/A_{1/2}) = 30 \pm 5 \text{ eu} \quad (18)$$

$$\Delta H_{eq} = 2(E_{a,1} - E_{a,1/2}) = 16 \pm 3 \text{ kcal/mol} \quad (19)$$

value of  $\Delta H_{eq}$  is of interest as the bond dissociation enthalpy of **L** from **1**. Evaluation of the terms in eq 15 yields the activation parameters for decomposition of intermediate **2**:  $E_a(2 \rightarrow 5) = 33 \pm 1$  kcal/mol;  $\log A(2 \rightarrow 5) = 14 \pm 2$ . The latter number is consistent with the conversion of one particle to two postulated in Scheme I.

The production of the byproduct neopentane in the decomposition of **1** appears to proceed by a pathway unrelated to that for formation of dimethylcyclopropane: in particular, neopentane is generated by a path which is kinetically independent of  $[L]_0$ , and neopentyl moieties are trapped to a significant extent by the radical scavenger TEMPO.<sup>32</sup> The rate of decomposition of **1** in the presence of 0.069 M TEMPO was unchanged from that in the absence of TEMPO, indicating that TEMPO does not react rapidly with **1**. We attribute the decrease in the yield of neopentane in the decomposition of **1** with TEMPO and

the observation of TEMPO-Np to trapping of neopentyl radicals which otherwise abstract hydrogen or deuterium atoms from solvent, **L** or **1**. The data in Table I indicate that more deuteriums are transferred from a specific proton source (ligands or cyclohexane) to form neopentane when the other proton sources are deuterated, an observation which is consistent with formation of neopentyl radicals. It nonetheless appears that although most (ca.  $2/3$ ) of the neopentane is produced via a radical process, another nonradical process may also be operative, since even in the presence of a large excess of TEMPO (0.12 M) some neopentane (ca. 1%) is still observed. The observation of small amounts of dineopentyl and cyclohexene in the decomposition of **1** is also consistent with production of neopentyl radicals. We propose that the major pathway yielding neopentane in the decomposition of **1** involves direct homolytic cleavage of the Pt–C bond. Other conceivable pathways, for which we have no experimental evidence, may include cyclometalation of **L** or intermolecular activation of a C–H bond of cyclohexane by **2**.

The decomposition of **6** to methylnorbornane and the decomposition of **1** to neopentane are mechanistically dissimilar. A major pathway for decomposition of **1** to neopentane appears to involve neopentyl radicals. The large amount of 1-methylnorbornane-*d*<sub>1</sub> formed during the decomposition of L<sup>D</sup><sub>2</sub>Pt(CH<sub>2</sub>Nb)Cl and the production of substantial amounts of **7** resulting from cyclometalation of **L** suggest that the major pathway for decomposition of **6** involves cyclometalation of **L**. At present, we cannot rationalize these differences in behavior.

## Experimental Section

**General Information.** All reactions and transfers involving organometallic compounds were carried out under nitrogen or argon. Cyclohexane and cyclohexane-*d*<sub>12</sub> (Merck) were stirred over sulfuric acid/nitric acid (ca. 2:1) for 8 days, washed sequentially with sulfuric acid and water, and stirred over aqueous sat. sodium bicarbonate for 1 day. They were then washed with water, passed through a column of silica gel, and distilled from Na/K alloy into Schlenk flasks containing lithium aluminum hydride. Diethyl ether and THF were distilled from disodium benzophenone dianion, and benzene was distilled from Na/K alloy prior to use. Other commercial reagents were used without purification. Melting points were obtained in sealed tubes under argon and were not corrected. <sup>31</sup>P NMR spectra were recorded on a Bruker WM 300 spectrometer and were proton decoupled; chemical shifts are relative to 85% phosphoric acid (upfield shifts positive).

**Tricyclopentylphosphine-*d*<sub>27</sub>.** A solution of (cyclopentyl-*d*<sub>9</sub>)magnesium bromide<sup>33</sup> in diethyl ether (150 mL, 0.46 M, 4.14 equiv) in a 300-mL round-bottomed flask equipped with a septum and a magnetic stirring bar was cooled to -78 °C. Phosphorus trichloride (1.45 mL, 2.28 g, 16.6 mmol) was added in one portion. The reaction solution was allowed to warm to 0 °C over 6 h, stirred at room temperature for 18 h, quickly heated to reflux (ca. 10 min), cooled to 0 °C, and quenched with 80 mL of saturated ammonium chloride/water (1:1). The ethereal layer was separated via cannula, and the aqueous layer was washed with three 30-mL portions of ether. Ethereal fractions were combined, dried over sodium sulfate, and filtered through magnesium sulfate/cotton. The filtrate was reduced in volume under a steady stream of nitrogen (*T* = 25–60 °C), 2 mL of a 2.2 M solution of *n*-butyllithium in *n*-hexane<sup>34</sup> was added, and the resulting solution was distilled yielding 2.92 g (66%) of tricyclopentylphosphine-*d*<sub>27</sub>, bp 113–116 °C (0.01 torr). <sup>31</sup>P NMR (C<sub>6</sub>H<sub>12</sub>): δ 3.37. This substance was contaminated by 33% of the corresponding phosphine oxide. <sup>31</sup>P NMR (C<sub>6</sub>H<sub>12</sub>): δ 42.5.

(33) Cyclopentyl-*d*<sub>9</sub>-magnesium bromide was prepared from cyclopentyl-*d*<sub>9</sub> bromide (Merck, Sharp and Dohme) in 76% yield using unexceptional procedures.

(34) Tricyclopentylphosphine-*d*<sub>27</sub> was distilled from *n*-butyllithium to remove (C<sub>5</sub>D<sub>9</sub>)<sub>2</sub>PH and (C<sub>5</sub>D<sub>9</sub>)<sub>3</sub>PO.

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

(32) Nigam, S.; Asmus, K.-D.; Willson, R. L. J. Chem. Soc., Faraday Trans. 1 1976, 72, 2324–2340.

Tricyclopentylphosphine-*d*<sub>0</sub> was synthesized from PCl<sub>3</sub> (15.1 g, 0.110 mol) and cyclopentylmagnesium bromide (700 mL, 0.725 M, 4.6 equiv) with use of a similar procedure; crude yield 61%; bp 125–130 °C (0.05 torr). A second distillation from *n*-butyllithium yielded pure tricyclopentylphosphine (>99% by <sup>31</sup>P NMR). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 1.7–3.0 (m, 9 H), 1.2–1.7 (m, 18 H). <sup>31</sup>P NMR (C<sub>6</sub>H<sub>12</sub>): δ 4.88.

**Pivalic-*d*<sub>9</sub> Acid [(CD<sub>3</sub>)<sub>3</sub>CCO<sub>2</sub>H]** was prepared in 59% yield from 18 g of *tert*-butyl-*d*<sub>9</sub> chloride (Aldrich) by using the procedure of Puntambeker and Zoellner;<sup>35</sup> bp 163–165 °C (lit.<sup>11</sup> bp 162–164 °C). (CD<sub>3</sub>)<sub>3</sub>CCD<sub>2</sub>OH was prepared in 88% yield by reaction of 11.68 g of pivalic-*d*<sub>9</sub> acid with 15 g of LiAlD<sub>4</sub> in diethyl ether,<sup>35</sup> bp 113–114 °C. IR (neat): 3390, 2215, 2100, 2080, 2060 cm<sup>-1</sup>. **Neopentyl-*d*<sub>11</sub> tosylate** was prepared in 72% yield from (C<sub>2</sub>D<sub>3</sub>)<sub>3</sub>CD<sub>2</sub>OH; mp 42–44 °C (lit.<sup>36</sup> (*d*<sub>0</sub>) mp 43.4–44.5 °C). **Neopentyl-*d*<sub>11</sub> bromide** was prepared on a 17-g scale from neopentyl-*d*<sub>11</sub> tosylate with use of the procedure of Mosher et al.<sup>37</sup> and was used to make a 0.09 M ethereal solution of (neopentyl-*d*<sub>11</sub>)magnesium bromide (160 mL) in 22% yield overall.

**(1,5-Cyclooctadiene)dineopentylplatinum(II).** A suspension of dichloro(1,5-cyclooctadiene)platinum(II) (3.1 g, 8.3 mmol)<sup>38</sup> in diethyl ether (150 mL) in a flame-dried 300-mL flask equipped with a septum and a magnetic stirring bar was cooled to –78 °C. An ethereal solution of neopentylmagnesium bromide (50 mL, 0.41 M, 20.5 mmol) was added over 10 min. This reaction was allowed to warm to –10 °C over 3 h and kept between –10 and –5 °C for 2 h during which time it turned dark yellow. The reaction mixture was then cooled to –70 °C, quenched with an aqueous solution of NH<sub>4</sub>Cl (2.0 mL, 2.5 M), quickly warmed to room temperature, and filtered through Celite with liberal washing with ether. The filtrate (ca. 400 mL) was reduced in volume to 40 mL by rotary evaporation, dissolved in ether/petroleum ether (1:1), and quickly passed through 60 g of silica gel,<sup>39</sup> yielding a yellow oil. Flash chromatography (80 g of silica gel, petroleum ether)<sup>40</sup> yielded CODPtNp<sub>2</sub> (3.21 g, 87%) as a yellow crystalline solid, mp 106–108 °C (lit.<sup>11</sup> mp 109 °C). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 4.71 (br t, J<sub>H-Pt</sub> = 38 Hz, 4 H),<sup>41</sup> 2.17 (t, J<sub>H-Pt</sub> = 92 Hz, 4 H), 1.6–1.9 (m, 8 H), 1.32 (t, J<sub>H-Pt</sub> = 4 Hz, 18 H).

CODPtNp<sup>D</sup><sub>2</sub> was synthesized from CODPtCl<sub>2</sub> in 89% yield with use of a similar procedure; mp 106–107.5 °C. <sup>1</sup>H NMR spectrum was consistent with the assigned structure.

**Chloro(1,5-cyclooctadiene)neopentylplatinum(II).** To a solution of CODPtNp<sub>2</sub> (960 mg, 2.15 mmol) in 25 mL of petroleum ether at room temperature in a 50-mL round-bottomed flask equipped with a magnetic stirring bar was added 1.0 mL of concentrated hydrochloric acid. The reaction was allowed to stir at room temperature for 2.25 h at which point it was judged to be complete by TLC (ether/petroleum ether, 1:1). The reaction solution was passed through ca. 100 g of silica gel with liberal ethereal washing. Solvent was removed by rotary evaporation, yielding 1.05 g of a white solid (64% crude yield). Flash chromatography (30 g silica gel; diethyl ether/petroleum ether, 1:2) of this solid yielded CODPtNp<sup>Cl</sup> (794 mg, 90%) as white crystals, mp 127–128 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 5.42 (br t, J<sub>H-Pt</sub> = 34 Hz, 2 H), 3.95 (br t, J<sub>H-Pt</sub> = 73 Hz, 2 H), 1.96 (t, J<sub>H-Pt</sub> = 81 Hz, 2 H), 1.9–1.3 (m, 8 H), 1.36 (s, 9 H). Anal. Calcd for C<sub>13</sub>H<sub>22</sub>ClPt: C, 38.10; H, 5.66; Cl, 8.65. Found: C, 38.02; H, 5.36; Cl, 8.69. CODPtNp<sup>D</sup>Cl was synthesized from CODPtNp<sup>D</sup><sub>2</sub> in 94% yield with use of a similar procedure; mp 124.5–125.5 °C. <sup>1</sup>H NMR spectrum was consistent with the assigned structure.

#### trans-Chloroneopentylbis(tricyclopentylphosphine)-

(35) Puntambeker, S. U.; Zoellner, E. A. *Org. Synth.*, 1928, 8, 104–106.

(36) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; Wiley: New York, 1967; Vol. I, pp 581–584, 1179–1181.

(37) Stephenson, B.; Solladie, G.; Mosher, H. S. *J. Am. Chem. Soc.*, 1972, 94, 4184–4188.

(38) Best results are obtained when (COD)PtCl<sub>2</sub> is in the form of a deliquescent white powder as is obtained from a previously described recrystallization procedure. Drew, D.; Doyle, J. R. *Inorg. Synth.* 1972, 13, 47–43.

(39) Silica gel was 230–400 mesh, suitable for flash chromatography; Still, C. S.; Kahn, M.; Mitra, A. *J. Org. Chem.*, 1978, 43, 2923–2925.

(40) Flash chromatography is a useful method of separating CODPtNp<sub>2</sub> (large R<sub>f</sub>) from the major side product CODPtNp(C<sub>6</sub>H<sub>12</sub>)PtNp<sub>2</sub> (small R<sub>f</sub>).

(41) Platinum is composed of one third <sup>195</sup>Pt (spin 1/2) and two-thirds other isotopes (spin 0). A characteristic coupling pattern is 1:4:1 "triplet".

**platinum(II) (1).** A suspension of CODPtNpCl (429 mg, 1.05 mmol) in 12 mL of diethyl ether in a 50-mL round-bottom flask equipped with a septum and a magnetic stirring bar was cooled to –78 °C. Tricyclopentylphosphine (0.59 mL, 2.43 mmol, 2.31 equiv, d = 0.98 g/mL) was added in one portion. The reaction mixture was stirred at –78 °C for 6 h, then warmed to room temperature, and filtered through 1 g of silica gel. Ether was removed with a steady stream of nitrogen (25 °C) yielding L<sub>2</sub>PtNpCl as white crystals. L<sub>2</sub>PtNpCl was further purified by one recrystallization from methanol and two recrystallizations from petroleum ether yielding white crystals (405 mg, 50%), mp 170–171 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 2.8–2.9 (m, 6 H), 1.9–2.2 (m, 24 H), 1.78 (t of t, J<sub>H-Pt</sub> = 88 Hz, 2 H, PtCH<sub>2</sub>),<sup>42</sup> 1.6–1.8 (m, 12 H), 1.4–1.5 (m, 12 H), 1.37 (s, 9 H). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>): δ 12.66 (J<sub>P-Pt</sub> = 3040 Hz). <sup>31</sup>P NMR (C<sub>6</sub>H<sub>12</sub>): 12.66 (J<sub>P-Pt</sub> = 3060 Hz). Anal. Calcd for C<sub>35</sub>H<sub>46</sub>ClPt: C, 54.01; H, 8.42; Cl, 4.55; P, 7.96. Found: C, 54.19; H, 8.30; Cl, 4.57; P, 8.11.

L<sub>2</sub>PtNp<sup>D</sup>Cl, L<sup>D</sup><sub>2</sub>PtNpCl, L<sup>D</sup><sub>2</sub>PtNp<sup>D</sup>Cl, and 1-*d*<sub>2</sub> were prepared by procedures analogous to those used to prepare L<sub>2</sub>PtNpCl. L<sub>2</sub>PtNp<sup>D</sup>Cl: mp 169–170 °C; <sup>31</sup>P NMR (C<sub>6</sub>H<sub>12</sub>): δ 12.80 (J<sub>P-Pt</sub> = 3060 Hz). L<sup>D</sup><sub>2</sub>PtNpCl: mp 174–175 °C; <sup>31</sup>P NMR (C<sub>6</sub>H<sub>12</sub>): δ 12.05 (J<sub>P-Pt</sub> = 3054 Hz). L<sup>D</sup><sub>2</sub>PtNp<sup>D</sup>Cl: mp 174.5–175.5 °C; <sup>31</sup>P NMR (C<sub>6</sub>H<sub>12</sub>): δ 12.33 (J<sub>P-Pt</sub> = 3059 Hz). Anal. Calcd for C<sub>35</sub>D<sub>46</sub>ClPt: C, 49.88; D, 7.77; Cl, 4.21. Found: C, 50.20; D, 7.61;<sup>43</sup> Cl, 4.21. 1-*d*<sub>2</sub>: mp 172–174 °C; <sup>31</sup>P NMR (C<sub>6</sub>H<sub>12</sub>): δ 12.77 (J<sub>P-Pt</sub> = 3058 Hz). L<sub>2</sub>PtNp<sup>D</sup>Cl, L<sup>D</sup><sub>2</sub>PtNpCl, L<sup>D</sup><sub>2</sub>PtNp<sup>D</sup>Cl, and 1-*d*<sub>2</sub> all gave <sup>1</sup>H NMR spectra consistent with their assigned structures.

**(1-Norbornyl)methyl bromide** was synthesized in three steps by the methods of Wiberg and Lowry<sup>44</sup> from bicyclo[2.2.1]heptane-1-carboxylic acid with an overall yield of 60%.

**(1,5-Cyclooctadiene)bis((1-norbornylmethyl)platinum(II))** was synthesized by a procedure analogous to that used to synthesize CODPtNp<sub>2</sub>. CODPt(CH<sub>2</sub>Nb)<sub>2</sub> was obtained in 63% yield as a yellow solid, mp 72–74 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 4.69 (t, J<sub>H-Pt</sub> = 36 Hz, 4 H), 2.24 (t, J<sub>H-Pt</sub> = 110 Hz, 4 H), 1.6–2.1 (m, 22 H), 1.1–1.6 (m, 8 H).

**Chloro(1,5-cyclooctadiene)(1-norbornylmethyl)platinum(II).** To a solution of (COD)Pt(CH<sub>2</sub>Nb)<sub>2</sub> (1.74 g, 3.34 mmol) in 25 mL of petroleum ether at room temperature in a 50-mL round-bottomed flask equipped with a magnetic stirring bar was added 0.50 mL of concentrated hydrochloric acid in one portion. The reaction was allowed to stir at room temperature for 1.5 h at which point the reaction was judged to be complete by TLC (ether/petroleum ether, 1:1). The organic layer of the reaction mixture was removed, the aqueous layer and reaction flask were washed with copious quantities of diethyl ether, and the combined organic phase was passed rapidly through 10 g of silica gel. The solvent was removed by rotary evaporation, yielding a white solid. Two recrystallizations from petroleum ether yielded CODPt(C<sub>6</sub>H<sub>12</sub>Nb)<sub>2</sub>Cl (952 mg, 64%) as a white solid, mp 118–119 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 5.41 (t, J<sub>H-Pt</sub> = 31 Hz, 2 H), 3.93 (t, J<sub>H-Pt</sub> = 73 Hz, 2 H), 2.2 (s, 1 H), 2.13 (t, J<sub>H-Pt</sub> = 31 Hz, 2 H), 1.2–2.0 (m, 18 H). Anal. Calcd for C<sub>41</sub>H<sub>58</sub>ClPt: C, 42.30; H, 5.63; Cl, 7.93. Found: C, 42.45; H, 5.44; Cl, 7.93.

**trans-Chloro(1-norbornylmethyl)bis(tricyclopentylphosphine)platinum(II) (6).** A suspension of CODPt(CH<sub>2</sub>Nb)<sub>2</sub> (410 mg, 0.92 mmol) in 12 mL of diethyl ether was cooled to –78 °C. Tricyclopentylphosphine (0.52 mL, 2.14 mmol, 2.32 equiv) was added in one portion. The reaction solution was stirred at –78 °C for 5 h, allowed to warm to room temperature over 1 h, cooled to –78 °C, and filtered. The resulting white solid was purified by dissolving it in methylene chloride and passing this solution through 2 g of silica gel. Two recrystallizations from petroleum ether yielded L<sub>2</sub>Pt(CH<sub>2</sub>Nb)<sub>2</sub>Cl (367 mg, 49%) as white crystals, mp 211–212 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 2.7–2.9 (m, 6 H), 1.3–2.2 (m, 61 H). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>): δ 14.02 (J<sub>P-Pt</sub> = 3015 Hz).

(42) The PtCH<sub>2</sub> protons are not resolved from the phosphine protons in L<sub>2</sub>PtNpCl in the <sup>1</sup>H NMR spectrum. The chemical shift and coupling constants for these protons were determined from the <sup>1</sup>H NMR spectrum of L<sup>D</sup><sub>2</sub>PtNpCl and are included here for convenience.

(43) Deuterium cannot be determined specifically by elemental analysis. Meaningful elemental analyses, however, can be obtained for deuterated compounds by calculating % deuterium as % hydrogen and by using the higher (deuterated) molecular weight.

(44) Wiberg, K. B.; Lowry, B. R. *J. Am. Chem. Soc.*, 1963, 85, 3188–3193.

$^{31}P$  NMR ( $C_6H_{12}$ ):  $\delta$  14.12 ( $J_{P-Pt} = 3035$  Hz). Anal. Calcd for  $C_{38}H_{67}ClP_2Pt$ : C, 55.90; H, 8.27; P, 7.59. Found: C, 55.82; H, 8.30; P, 7.69.

$L_2^D Pt(CH_2Nb)Cl$  was prepared in 59% yield by a procedure which was analogous to that used to prepare  $L_2Pt(CH_2Nb)Cl$ ; mp 219–220 °C.  $^{31}P$  NMR ( $C_6H_{12}$ ):  $\delta$  13.50 ( $J_{P-Pt} = 3028$  Hz).

**trans-Chlorohydridobis(tricyclopentylphosphine)platinum(II)** (**5**) is the major organometallic product of decomposition of  $L_2PtNpCl$ . As part of our proof of its structure, we synthesized  $L_2PtHCl$  independently by the thermal decomposition of *trans*-chloroethylbis(tricyclopentylphosphine)platinum(II) to  $L_2PtHCl$  and ethylene.<sup>45</sup> Samples of  $L_2PtHCl$  produced by these two methods were indistinguishable; mp 131–132 °C.  $^1H$  NMR ( $C_6D_6$ ):  $\delta$  2.36 (m, 6 H), 1.88 (m, 24 H), 1.68 (m, 12 H), 1.5 (m, 12 H), –17.80 (t of t,  $J_{H-Pt} = 1215$  Hz,  $J_{H-P} = 11.5$  Hz, 1 H).  $^{31}P$  NMR ( $C_6H_{12}$ ):  $\delta$  44.03 ( $J_{P-Pt} = 2876$  Hz). IR ( $CHCl_3$ ):  $\nu_{Pt-H} = 2240$  cm<sup>–1</sup>. Anal. Calcd for  $C_{30}H_{55}ClP_2Pt$ : C, 50.88; H, 7.83; Cl, 5.01. Found: C, 50.73; H, 7.77; Cl, 4.87.  $L_2^D PtHCl$  gives a similar  $^{31}P$  NMR spectrum ( $C_6H_{12}$ ):  $\delta$  43.03 ( $J_{P-Pt} = 2867$  Hz).  $L_2PtDCl$ : IR ( $CHCl_3$ )  $\nu_{Pt-D} = 1615$  cm<sup>–1</sup>.

**Sample Preparation.** Two procedures were used to prepare solutions of **1** in cyclohexane. **Procedure A** was used in the deuterium-labeling experiments to decrease contamination by water. In a typical experiment, a 5-mm NMR tube which was joined to a 6-mm o.d. Pyrex glass tube (5 cm long) was charged with 25 mg of  $L_2PtNpCl$  (**6**) and attached to a vacuum transfer manifold by an O-ring connector. The sample was placed under vacuum for 4–12 h. Cyclohexane ( $d_0$  and  $d_{12}$ ) was stored over LiAlH<sub>4</sub> in Schlenk flasks and was purged of volatile impurities by at least three freeze–pump–thaw degassing cycles before use. Cyclohexane (0.4–0.8 mL)<sup>46</sup> was added to the sample tube by trap-to-trap distillation. The resulting solution was freeze–pump–thaw degassed three more times, and the NMR tube was sealed under vacuum. **Procedure B** was used in kinetic studies when an accurate determination of  $[1]_0$  was necessary or when cyclohexane solutions containing **L** were used. Cyclohexane used here was distilled from Na/K alloy immediately prior to its use. A 5-mm Wilmad NMR tube was sealed to a ground glass joint and checked for leaks with use of a Tesla coil. The assembly was washed with distilled water, acetone, and ether and attached to a vacuum line via its ground glass joint. The assembly was flame-dried, cooled under vacuum, and filled with argon, and 23.3 mg of  $L_2PtNpCl$  (0.030 mmol) was added while the tube was flushed with argon. The sample was dried under vacuum for at least 4 h, and solvent (0.5 mL) was added by syringe while the tube was flushed with argon. The solution was taken through three freeze–pump–thaw degassing cycles, and the NMR tube was sealed under vacuum (0.005 torr).

**Kinetics of Thermal Decomposition.** Sealed NMR tubes containing solutions of **1** (**or 6**) in cyclohexane were immersed in a solvent-vapor bath, removed at regular intervals, and immersed in water. The temperatures of the solvent–vapor baths were determined with a calibrated thermometer and were found to be constant to  $\pm 0.7$  °C (95% confidence). The mole fraction of  $L_2PtNpCl$  remaining at each interval was calculated from  $^{31}P$  NMR data and was set equal to the integral of the signal due to **1** divided by the sum of the integrals of the signals due to **5** and **6**. Reactions were typically followed to ca. 75% completion (25% undecomposed  $L_2PtNpCl$ ).

**Thermal Decomposition of  $L_2Pt(CH_2Nb)Cl$ .** Solutions of **6** in cyclohexane were prepared by using procedure A. The extent of decomposition was determined by  $^{31}P$  NMR spectroscopy. The mole fraction of **6** remaining was set equal to the integral of the signal due to **6** divided by the sum of the integrals of the signals due to **5**, **6**, and **7**. IR,  $^1H$  NMR, and  $^{31}P$  NMR spectra of  $L_2PtHCl$  produced in the decomposition of **6** were indistinguishable from spectra of **5** from other sources (thermolysis of  $L_2PtNpCl$  or *trans*- $L_2PtEtCl$ ); no olefinic hydrogens were observed by  $^1H$  NMR.

(45) The thermal decomposition of  $L_2PtEtCl$  to  $L_2PtHCl$  and ethylene is related to the thermal decomposition of *cis*-( $Et_3P$ )<sub>2</sub>PtEtCl which has been studied extensively.<sup>13</sup>

(46) The volume of the solution was determined by comparing the height of the solution in the NMR tube against the height of a column of water weighed into an identical NMR tube. Determined in this way, the volume of the solution was within 1% of the true value.

**The cyclometalated compound 7** is produced as a major product in the thermal decompositions of  $L_2Pt(CH_2Nb)Cl$ , *trans*- $L_2PtMeCl$ , and *trans*- $L_2Pt(CH_2Ad)Cl$  (**L** = tricyclopentylphosphine; Ad = 1-adamantyl).<sup>28</sup>  $^1H$  NMR ( $C_6D_6$ ):  $\delta$  2.77 (m), 2.6 (m), 2.2–2.5 (m), 2.1 (m), 1.9 (m), 1.75 (m), 1.30 (m).  $^{31}P$  NMR ( $C_6H_{12}$ ):  $\delta$  40.49 (t of d,  $J_{P-Pt} = 3061$ ,  $J_{P-P} = 393$  Hz), 26.43 (t of d,  $J_{P-Pt} = 2972$ ,  $J_{P-P} = 393$  Hz).

**Preparation of Cyclohexane Solutions Containing Tricyclopentylphosphine.** A Schlenk flask calibrated to 2.0 and 4.0 mL was charged with tricyclopentylphosphine (516 mg, 2.17 mmol) and filled with cyclohexane to 4.0 mL. A portion of this 0.54 M solution (0.5 mL) was withdrawn by syringe and used in the preparation of a sample in an NMR tube. The remaining solution was reduced to 2.0 mL via cannula and diluted with fresh cyclohexane to the 4.0-mL mark, yielding a 0.27 M solution of tricyclopentylphosphine. This successive dilution technique was repeated, yielding 0.135, 0.068, and 0.34 M solutions of tricyclopentylphosphine. We estimate the error in concentration of the 0.54 M solution to be  $\pm 3\%$  ( $0.54 \pm 0.02$  M) and the error in each successive dilution to be  $\pm 5\%$ :  $0.27 \pm 0.02$  M ( $\pm 8\%$ ),  $0.135 \pm 0.02$  M ( $\pm 13\%$ ),  $0.07 \pm 0.01$  M ( $\pm 18\%$ ),  $0.03 \pm 0.01$  M ( $\pm 23\%$ ). Similarly, tricyclopentylphosphine (26.9 mg, 0.113 mmol) in a second Schlenk flask calibrated to a 5.0 and 10.0 mL was dissolved in cyclohexane to make a 0.011 M solution (10.0 mL). Successive dilution yielded 0.0056 and 0.0028 M solutions. We estimate the error in the concentrations of each of these solutions to be  $\pm 0.0005$  M.

**Gas Chromatographic and GC/MS Analysis of Reaction Mixtures.** Reaction mixtures in sealed NMR tubes which had been thermally decomposed until ca. 25% of the starting material remained (**1** or **6**) were cooled with liquid nitrogen to condense volatiles, opened, and capped with a septum. The liquid phase of each sample was analyzed by GC and GC/MS.

The absolute yields of 1,1-dimethylcyclopropane, neopentane, and cyclopentene were determined by comparing their GC integrals with that of an internal standard of *n*-pentane (4-m 4% UCW-98 GC column at room temperature), but in routine analyses, the relative amounts of 1,1-dimethylcyclopropane and neopentane were determined by direct comparison of their GC integrals. Cyclohexene was separated from cyclohexane on a 7-m 25%  $AgNO_3$  GC column at room temperature. The absolute yield of cyclohexene was determined by comparison with an internal standard of cycloheptane, but because of the difficulty associated with separating small quantities of cyclohexene from cyclohexane, the reported values for the amount of cyclohexene produced are probably not highly accurate. Dineopentyl was analyzed by comparison with an internal standard of *n*-dodecane (4-m UCW-98 GC column at 70 °C).

Mass spectra were obtained by using a Hewlett-Packard 5990A GC/MS, with a 70-eV ionizing voltage. For a given injection into this instrument, each GC peak was sampled six to eight times over a broad range of retention times. The resulting spectra were statistically weighted according to their base peak abundance to produce one composite mass spectrum.

The relative quantities of neopentane- $d_0$  vs. - $d_1$  and neopentane- $d_{11}$  vs. - $d_{12}$  were determined by comparing the relative abundance of the ( $M - methyl$ )<sup>+</sup> peaks of the product neopentane ( $m/e$  57, 58, 65, 66) with the ( $M - Methyl$ )<sup>+</sup> peaks of authentic neopentane- $d_0$  (57/100%, 58/4.7%), neopentane- $d_1$  (57/35%, 58/100%),<sup>47</sup> neopentane- $d_{11}$  (65/100%, 66/39%), and neopentane- $d_{12}$  (65/11.4%, 66/100%).<sup>48,49</sup> The relative quantities of 1-methylnorbornane- $d_0$  and 1-methylnorbornane- $d_1$  were de-

(47) Neopentane- $d_1$  was produced by using two different methods. (i) Addition of DCl in  $D_2O$  (99 atom %) to a solution of *cis*-( $Et_3P$ )<sub>2</sub>PtNp-**11** in dry methylene chloride produced neopentane- $d_1$ . (ii) A sample of neopentyl magnesium bromide which had been dried under vacuum was quenched with  $D_2O$  to produce neopentane- $d_1$ . These methods produced samples of neopentane- $d_1$  which gave similar mass spectra.

(48) Two ethereal solutions of (neopentyl- $d_{11}$ )magnesium bromide (used in the synthesis of  $L_2^D PtNp^DCl$  and  $L_2^D PtNpDCl$ ) were dried under high vacuum and were quenched with  $H_2O$  and  $D_2O$  to produce samples of neopentane- $d_{11}$  and neopentane- $d_{12}$ .

(49) The mass spectra of the reference samples were redetermined periodically to minimize errors which could arise from variations in the performance of the GC/MS. These variations were never very large and would, at most, contribute only 1–2% error in the determination of %  $d_0$ , %  $d_1$ , and % neopentane- $d_1$ .

terminated by comparing the relative abundance of the  $m/e$  81, 82, 110, and 111 peaks of the product 1-methylnorbornane with the relative abundance of the same peaks of authentic 1-methylnorbornane- $d_0$  (81/100%, 82/9.5%, 110/10%, 111/0.9%) and 1-methylnorbornane- $d_1$  (81/17.5%, 82/100%, 110/1.8%, 111/11%).<sup>50</sup>

The measured isotopic composition of neopentane and 1-methylnorbornane did not depend on the history of the injection port liner. Several solutions derived from the decomposition of  $L^{D_2}PtNp^{DCl}$  in cyclohexane which contained mixtures of neopentane- $d_{11}$  and neopentane- $d_{12}$  were analyzed by GC/MS using an injection port liner which had been in use for ca. 3 months without cleaning and by GC/MS using a new injection port liner. The mass spectra obtained under these two conditions were very similar.

**Error Analysis.** Standard deviations from least-squares analyses of kinetic plots were adjusted to 95% confidence levels ( $t$  values for  $N - 2$  degrees of freedom). When several values were averaged (e.g., kinetic isotope effects, rate constants),  $t$  values for  $N - 1$  degrees of freedom were used. When error bars (95% confidence limits) were used, the error in slope and intercept were determined by drawing two lines through the error bars having the largest and smallest reasonable slopes. This method produced

error limits which were comparable with those determined by least-squares analysis.

**Acknowledgment.** We thank Marifaith Hackett and Chris Roberts for allowing us to use their vacuum lines and Professor Joseph San Filippo, Jr., for helpful discussions. The NMR spectrometers used at Harvard were purchased in part through NSF CHE 8008891 and through NIH BRS Shared Instrument Grant Program 1 S10 RR01748-01A1.

**Registry No.** 1, 102307-54-0; 1- $d_2$ , 102307-61-9; 5, 102307-55-1; 6, 102307-56-2; 11, 75110-84-8;  $(CD_3)_3CCD_2OH$ , 75160-19-9;  $PCl_3$ , 7719-12-2;  $(COD)PtNp$ , 75101-19-8;  $(COD)PtCl_2$ , 12080-32-9;  $(COD)PtNp^{D_2}$ , 102307-57-3;  $(COD)PtNpCl$ , 102307-58-4;  $(COD)PtNp^{DCl}$ , 102307-59-5;  $L_2PtNp^{DCl}$ , 102342-12-1;  $L^D_2PtNpCl$ , 102307-60-8;  $L^{D_2}PtNp^{DCl}$ , 97921-41-0;  $(COD)Pt(CH_2Nb)_2$ , 102307-62-0;  $(COD)Pt(CH_2Nb)Cl$ , 102307-63-1;  $L^D_2Pt(CH_2Nb)Cl$ , 102307-64-2; *trans*- $L_2PtEtCl$ , 102307-65-3; *trans*- $L_2PtMeCl$ , 102307-66-4; *trans*- $L_2Pt(CH_2Ad)Cl$ , 102307-67-5; tricyclopentylphosphine- $d_{25}$ , 102307-68-6; (cyclopentyl- $d_9$ )magnesium bromide, 102307-69-7; tricyclopentylphosphine, 7650-88-6; cyclopentylmagnesium bromide, 33240-34-5; pivalic- $d_9$  acid, 42983-07-3; neopentyl- $d_{11}$  bromide, 75160-21-3; neopentyl- $d_{11}$  tosylate, 102307-70-0; (neopentyl- $d_{11}$ )magnesium bromide, 102307-71-1; neopentylmagnesium bromide, 33974-41-3; neopentane- $d_1$ , 4741-94-0; neopentane- $d_{11}$ , 102307-72-2; neopentane- $d_{12}$ , 5152-54-5; 1-methylnorbornane- $d_1$ , 102307-73-3; dueterium, 7782-39-0.

(50) A reference sample of 1-methylnorbornane- $d_1$  was made by allowing a cyclohexane solution of  $CODPt(CH_2Nb)_2$  to react with  $DCl$  in  $D_2O$  (99 atom %). Similarly, 1-methylnorbornane- $d_0$  was made by allowing a solution of  $CODPt(CH_2Nb)_2$  to react with  $HCl$  in  $H_2O$ .