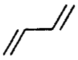
Acknowledgment. We are indebted to the Air Force Office of Scientific Research for financial support (AFOSR-83-0209) and in part to the National Science Foundation (CHE-8419089).

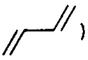
Appendix I

Reactions influencing the ES and SCP yields are

$$:SiH_2 + HC{\equiv}CH \underset{-6}{\overset{6}{\rightleftharpoons}} ES \xrightarrow{7} \text{other products}$$

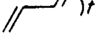
$:SiH_2 +$  $\xrightarrow{3}$ SCP

Therefore, $d(ES)/dt = k_6(:SiH_2)(HC{\equiv}CH) - (k_{-6} + k_7)(ES)$

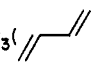
$d(SCP)/dt = k_3(:SiH_2)($  $)$

Integrating for the stirred-flow condition with $(k_{-6} + k_7) = k_{ES}$ gives

$$[ES] = k_6(:SiH_2)(HC{\equiv}CH)t - k_{ES}[ES]t$$

$[SCP] = k_3(:SiH_2)($  $)t$

From the ratio of the above one obtains

$[ES](1 + k_{ES}t)/[SCP] = k_6(HC{\equiv}CH)/k_3($  $)$

which rearranges to eq II.

Note Added in Proof. Serious questions were raised[26,27] concerning the reliability of some of the solution-phase absolute rate constants used as the basis for the absolute Arrhenius parameters suggested here. Any subsequent adjustments in these reference values will, of course, require corresponding changes in the Table VI values. The situation is further confused by some recent absolute[28] and relative rate constant measurements[29] of silylene reactions which suggest much higher values than those formerly accepted or those recommended here. An early resolution of these problems is not imminent. However, use of the Table VI parameters in modeling or in mechanistic prediction can still be made with confidence as such processes only require reliable relative rate constant input data.

Registry No. $:SiH_2$, 13825-90-6; Si_2H_6, 1590-87-0; 1,3-butadiene, 106-99-0; acetylene, 74-86-2; methanol, 67-56-1.

Mechanism of Thermal Decomposition of Bis(tricyclopentylphosphine)platinacyclopentane(II): Intramolecular β-Hydride Elimination from the Platinacyclopentane Ring Is Slow Relative to an Intermolecular Chain Reaction Involving Hydridoplatinum Intermediates[1]

Timothy M. Miller and George M. Whitesides*

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

Received January 29, 1986

The thermal decomposition of bis(tricyclopentylphosphine)platinacyclopentane(II) (1) in cyclohexane yields 1-butene and bis(tricyclopentylphosphine)platinum(0) (2) as the major products. Minor hydrocarbon products include (*Z*)- and (*E*)-2-butenes, butadiene, *n*-butane, and cyclopentene. Decomposition is first order in 1 for initial concentrations of 1 < 15 mM; at higher initial concentrations of 1 decompositions proceed more slowly and deviate from first order. This deviation appears to be due to inhibition by 2. Decomposition is slowed by added 2 and by added tricyclopentylphosphine (L). Deuterium-labeling experiments suggest that two pathways are important in these decompositions. One involves *intermolecular* transfer of hydrogen atoms: this process appears to be a chain reaction involving reduction of the carbon–platinum bond of the platinacyclopentane moiety by a reactive hydridoplatinum species. The second involves incorporation of hydrogen from tricyclopentylphosphine into the 1-butene and probably involves initial cyclometalation. This latter process may be important, inter alia, in initiating the hydride chain reaction. A mechanism involving β-hydride elimination directly from the platinacyclopentane group is not important. Free alkyl radicals also do not seem to be intermediates in these reactions.

Introduction

The objective of this paper is to rationalize the high stability of platinacycloalkanes using a bis(trialkylphosphine)platinacyclopentane as a representative. Metallacycles are important intermediates in several homogeneous transition-metal-catalyzed reactions, including olefin metathesis,[2-9] isomerization of strained carbocyclic rings,[10,11] and cyclotrimerization of acetylenes.[12-14] They are undoubtedly also involved in heterogeneous metal-

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

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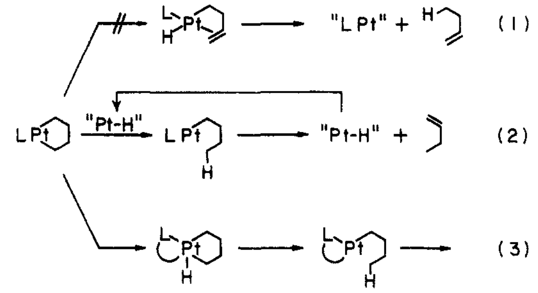
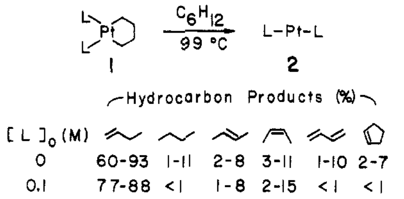
catalyzed reactions.[15] Metallacycles are often significantly more stable thermally than their acyclic counterparts.[16] We have suggested previously that this stability reflects the difficulty with which β-hydride elimination is expected to occur in the platinacyclopentane ring (eq 1).[16] The products from thermal decomposition of platinacyclopentanes are, however, the mixture of 1-butene and other C_4 products expected for simple β-hydride elimination.



We and others believe that a 0° M-C-C-H dihedral angle is optimal for β-hydride elimination.[17] The structure of the platinacyclopentane ring prohibits even a close approach to this geometry. Thermal decompositions of 3,3,4,4-tetramethylplatinacyclopentanes—compounds having no β-C-H bonds—are slower than those of unsubstituted platinacyclopentanes but not dramatically so.[18] Direct comparison of the rates of decomposition of methyl-substituted and unsubstituted platinacyclopentanes is, however, precluded by intervention of new types of decomposition pathways. The mechanism of thermal decomposition of platinacyclopentanes and similar metallacycles has remained obscure.

The objective of the work reported in this paper was to establish the mechanism of thermal decomposition of a representative platinacyclopentane, bis(tricyclopentylphosphine)platinacyclopentane (1), and particularly to determine if β-hydride elimination occurs directly from the platinacyclopentane ring. Previous studies of mechanisms of thermal decomposition of metallacycloalkanes have not dealt with this subject.[16,19-22] The choice of tricyclopentylphosphine as the stabilizing ligand in this work was based on two considerations.[23] First, because it is large, it is expected to dissociate readily. A vacant coordination site on platinum is often required for reaction. Decompositions occurring at low temperatures (<150 °C) are usually cleaner and mechanistically simpler than those requiring higher temperatures. In addition, the product bis(trialkylphosphine)platinum(0) is unstable for small trialkylphosphine ligands. Second, experience has indicated that bis(tricyclopentylphosphine)dialkylplatinum(II) complexes usually have good solubility in the alkane solvents preferred for these decomposition studies.

Scheme I. Products of Thermal Decomposition of 1[a]



[a] Yields of products are given as percentages of one equiv/equiv of 1.

In brief, the results obtained in this work indicate that β-hydride elimination from the platinacyclopentane moiety is *not* the major pathway for thermal decomposition of 1. Instead, the decomposition follows a more complex pathway, involving two major components: an intermolecular hydride chain transfer process (eq 2) and a reaction (presumably involving initial cyclometalation) that transfers hydrogen intramolecularly from the cyclopentyl groups to the butyl moiety (eq 3).

We use the same system of nomenclature employed in previous papers in this series: L refers to tricyclopentylphosphine, and $[L]_0$ indicates the concentration of L added to a solution.

Results

Products of Thermal Decomposition of 1 in Cyclohexane. Thermal decomposition of 1 in cyclohexane at 99 °C was complete in 5 h. Solutions containing decomposition products were yellow, but no solids deposited. Decomposition yielded bis(tricyclopentylphosphine)platinum(0) (2) (97%) as the only observed phosphorus containing species. The major hydrocarbon product (Scheme I) was 1-butene. Additional hydrocarbon products included varying amounts of (*Z*)- and (*E*)-2-butene, butadiene, *n*-butane, and cyclopentene. Decomposition of 1 in cyclohexane containing 0.1 M L yielded a similar mixture of products. Again, 1-butene and 2 were the major products; the yields of butane and butadiene were reduced and cyclopentene appeared only at higher temperatures. An acceptable mass balance (>90%) was obtained on the C_4 products of decomposition. Cyclohexene, *n*-butylcyclohexane, dicyclohexyl, and *n*-octane—products whose presence would have suggested free radical intermediates—were not detected by GLC, and their yields, if they were present, must have been less than 0.5%. Compound 2 was characterized by ^{31}P and ^1H NMR spectroscopy, by independent synthesis, and by conversion to methyliodobis(tricyclopentylphosphine)platinum(II) (97% based on starting 1) by reaction with methyl iodide. The ^{31}P NMR signals due to 2, produced in the decomposition of 1, were broad. The signals were broader in decompositions carried out with added 1-octene or L. The products of thermal decomposition of 1 showed broad signals at δ 5.75 and 4.93 in the ^1H NMR spectrum at room temperature. We attributed these results to rapid exchange of coordinated and free 1-butene on the NMR time scale.[24]

In order to determine whether or not the 2-butene produced in the decomposition of 1 was a primary product, we carried out the decomposition of 1 in the presence of 1-pentene. Decomposition of 1 in cyclohexane containing

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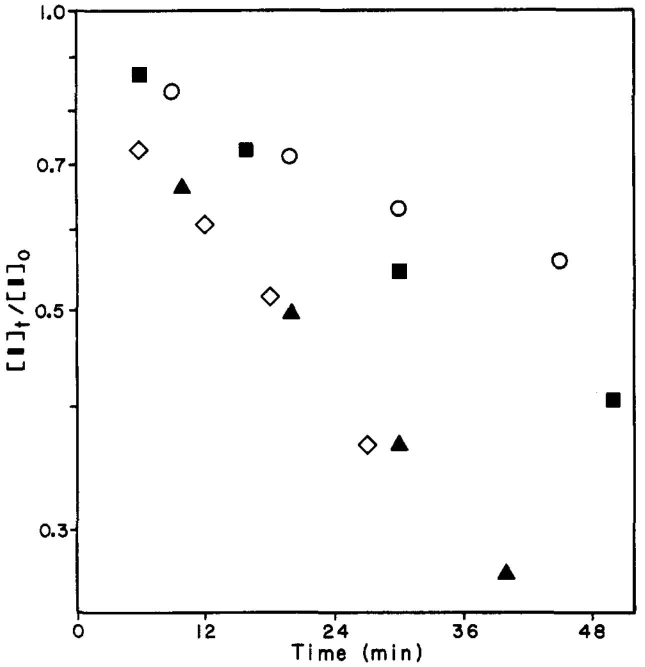
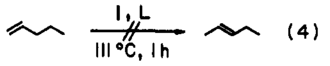


Figure 1. Thermal decomposition of 1 in cyclohexane solutions (T = 99 °C): (▲) $[1]_0$ = 8 mM; (◇) $[1]_0$ = 15 mM; (■) $[1]_0$ = 25 mM; (○) $[1]_0$ = 30 mM.

0.1 M L and 0.1 M 1-pentene resulted in isomerization of less than 0.5% of the 1-pentene to 2-pentenes (eq 4).



(4)

Decomposition of 1 with 1-pentene in cyclohexane resulted in isomerization of 1–2% of the 1-pentene to 2-pentenes. Addition of mercury(0) or the free radical trap tetramethylpiperidinyloxy (TEMPO) did not change the distribution of products from decomposition of 1.[18]

Kinetics. The kinetics of thermal decomposition of 1 were followed by ^{31}P NMR spectroscopy. Compounds 1 and 2 were the only species observed by ^{31}P NMR spectroscopy during the thermal decomposition of 1. Addition of water, powdered glass, or TEMPO or exposure to strong visible light did not significantly affect the kinetics. The kinetics of thermal decomposition of 1 were qualitatively similar in cyclohexane, THF, and toluene. The presence of platinum metal (in the form of a metallic mirror on the wall of the NMR tube) accelerated decomposition of 1.

Figure 1 shows plots of representative kinetic data obtained at different initial values of the concentration of 1 ($[1]_0$). Decomposition of 1 followed first-order kinetics for $[1]_0 \leq 15$ mM. For $[1]_0 > 15$ mM, the rate of decomposition decreased and deviation from first-order behavior increased. The apparent order in 1 at the higher values of $[1]_0$ was greater than first; evidence summarized below suggests that the deviations from first-order behavior are attributable to the influence of products of reaction (especially 2) on the rate. For the purpose of analysis first-order (eq 5) rate constants determined over the first half-life of the decomposition have been used throughout this paper.

$$-d[1]/dt = k_{\mathrm{obsd}}[1] \qquad (5)$$

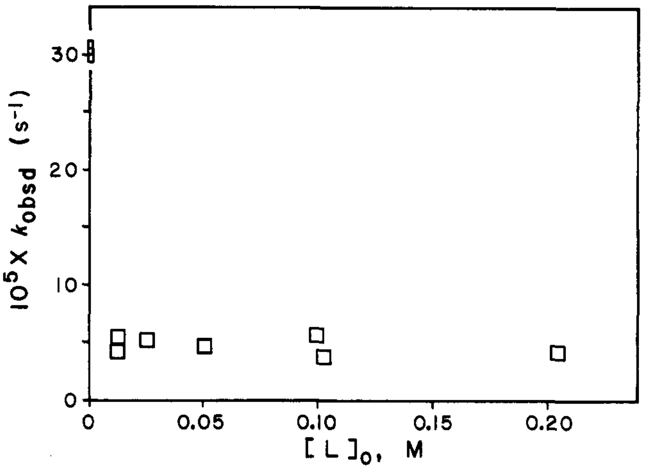


Figure 2. Observed first-order rate constant as a function of [L]: T = 99 °C; $[1]_0$ = 25 mM.

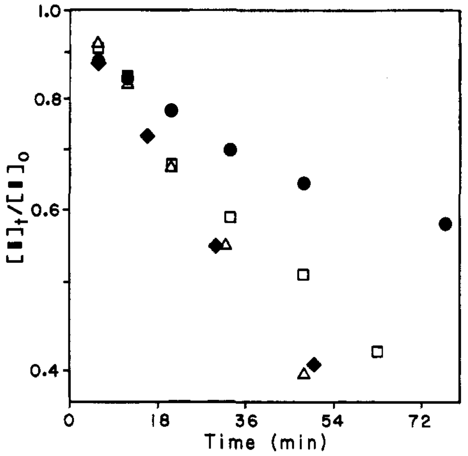


Figure 3. Thermal decomposition of 1 in cyclohexane containing added 2 (T = 99 °C): $[1]_0$ = 25 mM; (◆) $[2]_0$ = 0 mM; (△) $[2]_0$ = 10 mM; (□) $[2]_0$ = 30 mM; (●) $[2]_0$ = 60 mM.

Our examination of the influence of reaction products on rates was qualitative and focused on L, 1-butene, and 2. Changing the concentration of $[L]_0$ from 0 to 0.013 M decreased the rate of decomposition by a factor of 6. Further change (from 0.013 to 0.2 M) had no significant effect (Figure 2). For technical reasons we chose not to add 1-butene itself to the reaction because its volatility makes it inconvenient to handle, but we established that the rate of decomposition of 1 was independent of the concentration of 1-octene from 0 to 0.16 M. Addition of 2 slowed the decomposition (Figure 3).

In the absence of added L, rates of decomposition over the first $^1/_2$ to 1 half-life were reproducible (±10–20%). After the first half-life, rates varied by factors of ±1.5–2.0. The length of time for which 1 had been stored before use (0 °C, dark, in air) did not influence the kinetics. Compound 1, when in solution, slowly decomposed on exposure to dioxygen. If traces of dioxygen had been the cause of irreproducibility, we would have expected that added L should increase reproducibility (by scavenging dioxygen). Rates of decomposition in the presence of L were *less* reproducible than those in its absence.

The quality of the kinetic data does not permit detailed mechanistic interpretation but is adequate for qualitative mechanistic studies. The product distribution is changed by the addition of L (Scheme I), and thus one or more of the pathways followed in the absence of L are slowed. This effect accounts for some of the rate decrease on addition of L. We suggest below that a major decomposition pathway is an intermolecular process and the overall rate of decomposition is probably strongly related to the concentration of one or more reactive species. It appears that 1-octene and by analogy 1-butene are not responsible for the deviations from first-order behavior. We believe the deviations are due to the build-up of 2 over the course of the decomposition. Species 2 may be inhibiting reaction by increasing the concentration of free L or more probably

Table I. Isotopic Composition of 1-Butene Derived from Thermal Decomposition of 1 in Cyclohexane

1	second component (concn, mM)	$[L]_0$	isotopic compositn of 1-butene compd (%)[a]	inference
1^b	C_6D_{12}	0.0	d_0 (>98)	no solvent involvement
1^c	C_6D_{12}	0.1	d_0 (>98)	
$1\text{-}d_8{}^b$		0.0	d_8 (60), d_7 (40)	cyclometalation of L occurs
$1\text{-}d_{54}{}^b$		0.0	d_0 (94), d_1 (6)	
$1\text{-}d_8{}^c$		0.1	d_8 (87), d_7 (13)	cyclometalation of L is reduced by added L
$1\text{-}d_8{}^d$	1 (13)	0.1	d_8 (25), d_7 (24), d_1 (19), d_0 (32)	crossover occurs in the decomposition of 1
$1\text{-}d_8{}^c$	1-butene (30)	0.1	d_0 (66), d_1 (<2), d_7 (3), d_8 (32)	
$1\text{-}d_4{}^b$		0.0	d_4 (71), d_3 (27), d_5 (2)	
$1\text{-}d_4{}^c$		0.1	d_4 (51), d_3 (33), d_5 (19)	

[a] The methods used to determine these values are described in the Experimental Section. The values are not corrected for isotopic impurities in the starting materials. [b] $[1]_0$ = 25 mM; T = 99 °C; after 1 h. [c] $[1]_0$ = 25 mM; T = 110 °C; after 2 h. [d] $[1]_0$ = 13 mM; T = 110 °C; after 2 h.

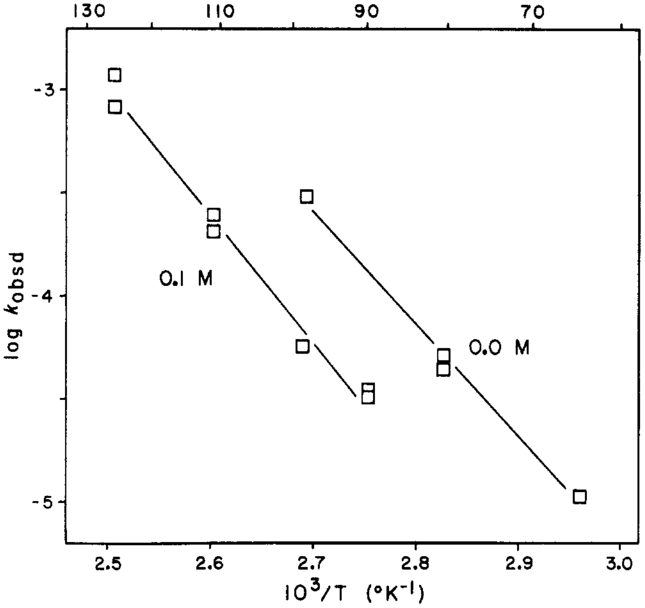


Figure 4. Arrhenius plots for decomposition of 1 with two concentrations of L (indicated in the figure): $[1]_0$ = 25 mM.

by consumption of the species mediating the intermolecular process.

Activation Parameters. The temperature dependence of the rate of decomposition of 1 was studied under two different reaction conditions. Linear Arrhenius plots were obtained by using k_{obsd} (eq 5) at two different values of added L: $[L]_0$ = 0 M and 0.1 M. For [L] = 0 M, log $A \simeq 11$ and $E_a \simeq 25$ kcal/mol. For [L] = 0.1 M, log $A \simeq 12$ and $E_9 \simeq 28$ kcal/mol (Figure 4).

Kinetic Isotope Effect. The kinetic isotope effect on the rate of thermal decomposition was determined by decomposition of 1, bis(tricyclopentylphosphine)platinacyclopentane-d_8 (1-d_8), and bis(tricyclopentylphosphine)platinacyclopentane-*3,3,4,4*-d_4 (1-d_4) in separate NMR tubes. The kinetic isotope effects were $k(1)/k(1\text{-}d_8) = 2.3 \pm 0.4$ and $k(1)/k(1\text{-}d_4) = 1.2 \pm 0.1$ (Figure 5). The difference in the magnitude of these kinetic isotope effects indicates that the rate of decomposition does not depend only on the rate of breaking a C–H(D) bond in the β-position of the platinacycle.

Deuterium-labeling experiments were used to establish the origin of the hydrogen atoms in the hydrocarbon products (Table I).[25,26] When cyclohexane-d_{12} was the solvent, no deuterium was incorporated in the 1-butene. Decomposition of 1-d_8 or bis(perdeuteriotricyclopentylphosphine)platinacyclopentane (1-d_{54}) (in the absence of added L) resulted in significant (0.06–0.4 equiv) but less than stoichiometric transfer of H(D) from L to 1-butene. In the decomposition of 1 in the presence of 0.1 M L, only 0.1 equiv of H was transferred from L to butene.

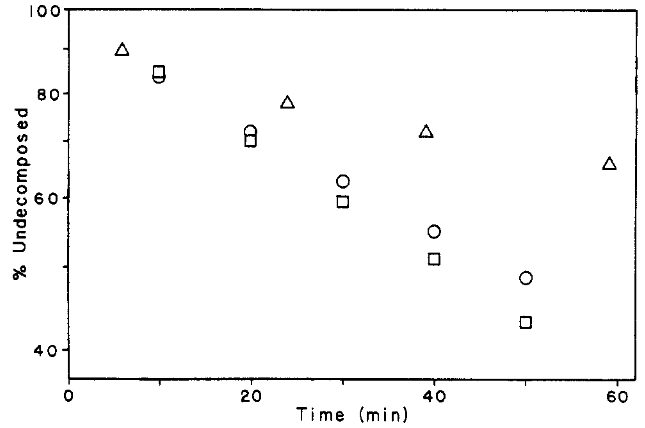
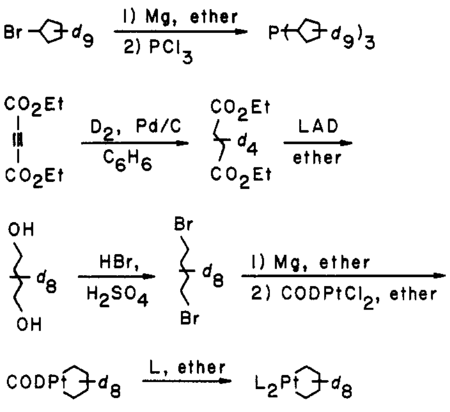
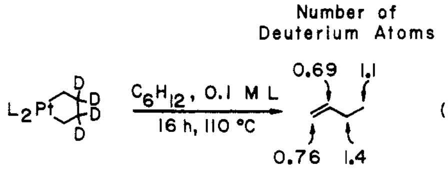


Figure 5. Thermal decomposition of 1 (□), 1-d_4 (○), and 1-d_8 (△) in cyclohexane: T = 99 °C; $[1]_0 = [1\text{-}d_4]_0 = [1\text{-}d_8]_0$ = 25 mM.

Scheme II. Synthesis of Deuterated Analogues of 1



Decomposition 1-d_4 yielded 1-butene having deuterium on all carbons (eq 6). The ^{2}H NMR spectrum of this



(6)

1-butene yielded the relative numbers of deuterium atoms at each position. The process which produces 1-butene is accompanied by transfer of deuterium atoms from the

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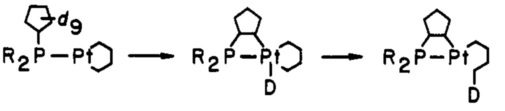
[25] Merck, Sharp, and Dohme sells cyclopentyl-d_9 bromide.

[26] A similar synthesis of deuterium-labeled metallacyclopentanes has appeared recently. Yank, G. K.; Bergman, R. G. *Organometallics* **1985**, *4*, 129–138.

β-position of the platinacyclopentane to the 1- and 4-positions of 1-butene. We expected transfer of deuterium from the β-position of the platinacyclopentane to the 4-position but not the 1-position of 1-butene. A reversible β-hydride elimination from an intermediate *n*-butylplatinum species provides the simplest rationalization of deuterium atoms in the 1-position of 1-butene and the observation of 2-butenes as primary reaction products (Scheme I).

Decomposition of 1-d_8 and 1 in the presence of 0.1 M L yielded a mixture of 1-butenes containing 8, 7, 1, and 0 (Table I) deuterium atoms. We demonstrated that the crossover of hydrogen isotopes was a primary reaction by the absence of 1-butene-d_1 in the decomposition of 1-d_8 and 1-butene. The appearance of 1-butene-d_5 in the decomposition of 1-d_4 also supports crossover. Transfer of deuterium from the β-position of the platinacyclopentane to the 4-position of 1-butene and crossover imply that there is no preference for *intramolecular* transfer.

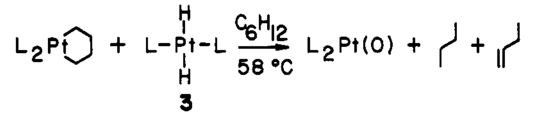
We were unable to determine whether hydrogen transfer from coordinated L into 1-butene was inter- or intramolecular, because exchange of phosphine moieties between platinum centers was much faster than decomposition: the ^{31}P NMR spectrum of a mixture of 1 and 1-d_{54} taken immediately upon dissolution showed a statistical mixture of 1-d_{54}, 1-d_{27}, and 1. An intramolecular hydrogen transfer accompanying cyclometalation has, however, ample precedent[27-29] (eq 7; in this equation, any of the C–D bonds of the cyclopentyl-d_9 moiety might, in principle, add to platinum). It thus seems unnecessary to invoke intermolecular reaction.



(7)

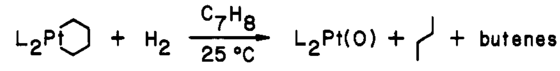
The intermolecular hydrogen transfer between C_4 moieties is a more interesting reaction. We hypothesized that this transfer might occur via an intermediate platinum hydride (eq 2). A mechanism of this type has not been established for platinum, but related processes have been investigated for cobalt and osmium.[30,31] To provide evidence for a reactive hydridoplatinum(II) intermediate in the decomposition of 1, we allowed 1-d_8 (1.0 equiv) to decompose in the presence of $L_2Pt(CH_3)_2$ (1.0 equiv); this latter compound is itself thermally stable under these reaction conditions. The methane obtained (ca. 0.1 equiv) was 90% d_1.

We have carried out two additional experiments which demonstrate that both a stable platinum(II) hydride species and a platinum(II) hydride generated *in situ* can react with 1. In the first, we found that *trans*-bis(tricyclopentylphosphine)dihydridoplatinum(II) (3) reacted with 1. In the absence of dioxygen, 3 is itself thermally stable. When an equimolar solution of 1 and 3 was prepared in a sealed NMR tube and heated to 58 °C, 1 and 3 yielded 2 and a mixture of *n*-butane and 1-butene (2.2:1.0) (eq 8). Approximately 1.5 mol of 1 reacted with 1.0 mol of 3 at a rate more than 30 times faster than the rate of decomposition of 1 in the absence of 3. Complex 3 not only reacted stoichiometrically with 1 but also catalyzed the decomposition of 1. We hypothesize that the catalysis occurs by generation of a new hydridoplatinum species in the reaction of 1 and 3 which competitively reacts further with a second molecule of 1. This species may or may not be the species mediating the intermolecular pathway observed in the decomposition of 1 itself.



(8)

In the second experiment, a solution of 1 (52 μmol) in toluene was exposed to 26 μmol of dihydrogen at room temperature. Within 1 h, 0.6 equiv of 1 yielded 2 and a mixture of *n*-butane and butenes (4.8:1.0) (eq 9). The reaction of bis(trialkylphosphine)dialkylplatinum complexes with an excess of dihydrogen has been investigated previously, and the observed products were always alkane and *trans*-bis(trialkylphosphine)dihydridoplatinum(II).[32] Here, there is an excess of 1, and reaction of an intermediate in the hydrogenolysis of 1 with a second molecule of 1 is apparently competitive with unimolecular decomposition of this intermediate.



(9)

Discussion

We summarize the mechanistically important results from this study.

(i) The major hydrocarbon products from thermal decomposition of 1 are butenes; in the absence of added L, butane and butadiene appear as minor components of the reaction mixture.

(ii) The decomposition is first-order in 1. The kinetics are not sufficiently reproducible to permit detailed analysis, but the sources of this irreproducibility probably rest in mechanistically uninteresting phenomena (e.g., the influence of products such as L_2Pt^0 on the reaction). Activation parameters and kinetic isotope effects derived from these studies are not mechanistically useful.

(iii) Several different experiments demonstrate deuterium crossover and intermolecular reaction: decomposition of a mixture of $L_2Pt(C_4D_8)$ and $L_2Pt(C_4H_8)$ yields a mixture of 1-butene-d_0, -d_1, -d_7, and -d_8; decomposition of $L_2PtCH_2CD_2CD_2CH_2$ yields a significant quantity of 1-butene-d_5; decomposition of a mixture of $L_2Pt(C_4D_8)$ and $L_2Pt(CH_3)_2$ yields CH_3D as the principal product.

(iv) L_2PtH_2 reacts rapidly with 1 and yields butane; H_2 reacts with 1 and yields both butane and 1-butene.

(v) Deuterium present in 1-butene derived from $L_2PtCH_2CD_2CD_2CH_2$ is extensively scrambled. The processes responsible for this scrambling may contribute to the difference in deuterium kinetic isotope effects observed for $L_2PtCD_2CD_2CD_2CD_2$ (k_H/k_D = 2.3) and $L_2PtCH_2CD_2CD_2CH_2$ (k_H/k_D = 1.2).

The immediate conclusion from these studies is that the thermal decomposition of 1 to 2 and 1-butene does *not* proceed exclusively by simple β-hydride elimination from the metallacyclopentane ring followed by intramolecular reductive elimination (eq 1), as we[16] and others have tacitly assumed. This and other types of intramolecular reaction

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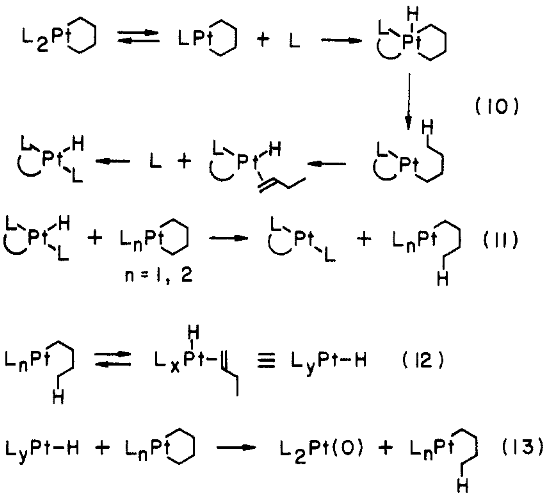
are effectively excluded by the extensive intermolecular deuterium transfer observed between C_4 moieties. A plausible vehicle for this (these) intermolecular process(es) is a platinum hydride of undefined structure. Independent experiments establish that 1 reacts readily with authentic L_2PtH_2.

If the thermal decomposition of 1 does not proceed entirely by β-hydride elimination followed by reductive elimination of butene, what *is* the major pathway for decomposition? The insensitivity of the reaction to TEMPO and the absence of products characteristic of free radicals effectively exclude a free radical process. The observation that hydrogen transfer between C_4 moieties proceeds by an intermolecular process, and the implication of platinum hydrides as intermediates is compatible with a hydride chain process of the form outlined in eq 2 and eq 10–13.



The series of reactions represented by eq 10 rationalize an initial generation of a hydridoplatinum(II) species by a process that does not require β-hydride elimination within a platinacyclopentane. These reactions also rationalize the observation of significant hydrogen transfer (ca. 0.05–0.1 equiv) of hydrogen from L to 1-butene. Cyclometalation reactions of the type indicated in eq 10 have abundant precedent.[27-29] We write the initial cyclometalation as involving a three-coordinate platinum complex, both by analogy with previously studied reactions[24,27,32] and because the rate of the thermal decomposition of 1 is lowered by added L (and by the presence of species such as 2 which could plausibly serve as a source of L). In candor, however, we have no direct experimental evidence bearing on the extent of coordination of any of the species in this mechanism.

Equation 11 postulates an initiation step for the following hydride chain reaction. Reduction of a platinum(II)–alkyl bond by a hydridoplatinum species has ample precedent both here and in other systems,[32] but an obscure mechanism. We intentionally leave the degree of coordination and formal oxidation state of platinum unspecified in these and the following equations, but we note that, in principle, one of the ligands for the platinum hydride moiety might be platinum: that is, di- or polyplatinum species might be intermediates in these reactions.

Equations 12 and 13 represent the propagation reactions in the proposed hydride chain. In eq 12, an *n*-butylplatinum species yields butenes and a platinum hydride by reversible β-hydride elimination from a non-metallacyclic species. Reversible β-hydride elimination in eq 12 rationalizes transfer of deuterium from the β-position of the ring in 1-d_4 to the 1-position of 1-butene and observation of the product 2-butene. In eq 13 reaction of the platinum hydride with the platinacyclopentane ring regenerates the butylplatinum species of eq 12 and yields 2. Because alkylhydridoplatinum(II) species are not explicitly generated in this sequence (although they may be intermediates in eq 13), the most common reaction of hydridoplatinum(II) moieties in the chemistry of L_2PtR_2 complexes—reductive elimination of alkane—does not occur.

We demonstrated that 3 reacts stoichiometrically with 1. This observation is compatible with our hypothesis that a soluble platinum hydride carries the chain in the decomposition of 1 (eq 10 and 11). We also found that 3 or a species derived from reaction of 1 and 3 and a species derived from reaction of 1 and dihydrogen catalyze the decomposition of 1. The identity of these species is not known; however, the facility with which these intermolecular reactions take place in dilute solutions is remarkable.

Because we do not have experimental evidence relevant to many of the processes in this complex sequence, it is not useful to speculate further about its details. Although the details of the proposed sequences are only partly understood, the central proposal—that the decomposition proceeds by a chain reaction carried by a reactive intermediate hydridoplatinum species (most economically summarized by eq 1)—is supported by all the available experimental evidence. This evidence is clearly incompatible with a simple β-hydride elimination/reductive elimination mechanism (eq 1). The proposed sequence of reactions represents both a previously unrecognized decomposition path for metallacycles and a procedure of interest as a method for generating hydridometal species. By establishing that rates of decomposition of platinacyclopentanes do not represent β-hydride elimination but only a lower limit for such a process, we also raise the estimates of the stability conferred on alkylplatinum compounds having β-C–H bonds by incorporation of the alkyl groups into five- (and by inference six- and seven-) membered rings.

Experimental Section

General Information. All reactions and transfers involving organometallic compounds were carried out under argon. Cyclohexane and perdeuteriocyclohexane were stirred over a mixture of nitric acid in sulfuric acid for 1 week and washed in sequence with water, dilute sodium bicarbonate, and saturated aqueous sodium chloride. They were then passed through a column of silica gel and distilled from liquid Na/K alloy under argon immediately prior to use. Ether, tetrahydrofuran and benzene were distilled from disodium benzophenone dianion under argon. Toluene was stirred with sulfuric acid for 1 h, washed with water, aqueous NaOH, and water, dried over calcium chloride, passed through silica gel, and distilled from Na prior to use. Toluene-d_8 was distilled from lithium aluminum hydride prior to use. Dichloro(1,5-cyclooctadiene)platinum(II),[16] *trans*-dichlorobis(tricyclopentylphosphine)platinum(II),[33] tricyclopentylphosphine,[34] tricyclopentyl-d_{27}-phosphine[34] and (1,5-cyclooctadiene)dimethylplatinum(II)[35] were prepared by previously described procedures. 1-Octene and methyl iodide were passed through a column of alumina immediately prior to use. 1-Pentene was distilled from CaH_2 under argon. Yields of Grignard reagents were estimated by titration against 2-butanol in xylenes with 2,2′-biquinoline as an indicator.[36] Other commercial reagents were used without further purification. ^{1}H NMR spectra were run on Bruker AM 300 or WM 300 instruments. Proton-decoupled

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^{31}P NMR spectra were run on a Bruker WM 300 instrument at 121.513 MHz. Chemical shifts are reported downfield from 85% H_3PO_4. Melting points were determined in open capillary tubes on a Thomas-Hoover apparatus and are uncorrected. Mass spectra were recorded on a Hewlett-Packard 5990A GC/MS instrument. Gas chromatograms were recorded on a Perkin-Elmer Model 3920B instrument. Satisfactory elemental analyses were obtained on all nondeuterated compounds from Galbraith Laboratories, Inc., Knoxville, TN.

Dimethyl Succinate-d_4. A 360-mL pressure bottle was charged with 0.25 g of 5% Pd/Alumina, flushed with argon, and charged with 150 mL of benzene and 21.5 mL (0.175 mol) of dimethyl acetylenedicarboxylate.[26] Reduction with D_2 (40 PSIG) at room temperature for 6 h yielded, after distillation, 24 g (94%) of dimethyl succinate-d_4 (44–46 °C, 0.05 torr). ^1H NMR ($CDCl_3$): δ 3.61 (s, 6 H).

1,4-Butanediol-d_8. To a dry 300-mL round-bottomed flask equipped with a condenser and an addition funnel was added 7.0 g (0.17 mol) of lithium aluminum deuteride and 100 mL of ether. A solution of 24 g (0.16 mol) of dimethyl succinate-d_4 in 100 mL of ether was added dropwise over 1 h at 0 °C. The reaction mixture was stirred overnight and allowed to warm to room temperature. Workup yielded 12.4 g (81%) (65–68 °C, 1.0 torr) of 1,4-butanediol-d_8. Carrying out the reduction with lithium aluminum hydride yielded 1,4-butanediol-d_4.

1,4-Dibromobutane-d_8. The procedure of Gilman was used to convert 1,4-butanediol-d_8 to 1,4-dibromobutane-d_8 and 1,4-butanediol-d_4 to 1,4-dibromobutane-d_4 in 85% yield.[37]

Preparation of Di-Grignard Reagents. (1,4-Butane)-, (1,4-butane-d_4)-, and (1,4-butane-d_8)dimagnesium bromide were prepared according to a previously described procedure.[16]

(1,5-Cyclooctadiene)platinacyclopentane(II). A 100-mL round-bottomed flask equipped with a stirring bar and a rubber septum was charged with 1.25 g (3.34 mmol) of dichloro(1,5-cyclooctadiene)platinum(II). Ether (60 mL) was added and the suspension cooled to −78 °C, and 22 mL (0.17 M, 3.7 mmol) of di-Grignard reagent in THF was added dropwise over 10 min. The reaction was allowed to warm to room temperature over 6 h, and a brown suspension resulted. The reaction was cooled to 0 °C, and 0.5 mL of saturated aqueous NH_4Cl was added. After the solution was warmed to room temperature, Na_2SO_4 and decolorizing charcoal were added and the mixture was stirred for a short period before filtration through Celite. Concentration by rotary evaporation yielded 936 mg (78%) of a tan solid. This material was used without further purification. ^1H NMR (C_6D_6): δ 4.61 (s, 4 H, J_{Pt-H} = 40 Hz), 2.40 (m, 4 H, J_{Pt-H} = 92 Hz), 1.98 (m, 4 H, J_{Pt-H} = 93 Hz), 1.60–1.95 (m, 8 H). (1,5-Cyclooctadiene)platinacyclopentane-d_8 and -d_4 (II) were prepared analogously.

Bis(tricyclopentylphosphine)platinacyclopentane (1). A 25-mL round-bottomed flask equipped with a stirring bar and a rubber septum was charged with 1.01 g (2.81 mmol) of (1,5-cyclooctadiene)platinacyclopentane(II) and ether (9.0 mL). The resulting solution of platinum complex was cooled to 0 °C, and tricyclopentylphosphine (1.48 mL, 1.48 g, 6.19 mmol) was added dropwise and the reaction allowed to warm to room temperature. The reaction was stirred overnight. A white precipitate (1.69 g, 82%) formed and was separated from the reaction mixture by filtration. One slow recrystallization from toluene under argon yielded material suitable for kinetic studies: 865 mg (42%); mp 121–123 °C dec. ^1H NMR (C_6D_6): δ 2.2–2.5 (m, 10 H), 1.3–2.2 (m, 52 H). ^{31}P NMR (C_6D_6): δ 19.6 (J_{Pt-P} = 1760 Hz). 1-d_4, 1-d_8, and 1-d_{54} were prepared by analogous procedures. 1-d_4: ^1H NMR (C_6D_6) δ 2.2–2.5 (m, 10 H), 1.3–2.0 (m, 48 H); ^{31}P NMR (C_6D_6) δ 19.6 (J_{Pt-P} = 1758 Hz); mp 118–120 °C dec. 1-d_8: ^1H NMR (C_6D_6) δ 2.2–2.5 (m, 6 H), 1.3–2.0 (m, 48 H); ^{31}P NMR (C_6D_6) δ 19.7 (J_{Pt-P} = 1752 Hz); mp 120–123 °C dec. 1-d_{54}: ^1H NMR (C_6D_6) δ 2.37 (4 H, J_{Pt-H} = 67 Hz), 2.04 (4 H, J_{Pt-H} = 84 Hz); ^{31}P NMR (C_6D_6) δ 18.5 (J_{Pt-P} = 1760 Hz); mp 117–121 °C dec. Anal. Calcd: C, 56.10; H, 8.59; P, 8.51. Found: C, 56.30; H, 8.40; P, 8.73.

***cis*-Bis(tricyclopentylphosphine)dimethylplatinum(II).** A 10-mL round-bottomed flask equipped with a stirring bar and a rubber septum was charged with 122 mg (0.366 mmol) of (1,5-cyclooctadiene)dimethylplatinum(II) and ether (2.0 mL). The resulting solution was cooled to 0 °C, and 225 μL (0.92 mmol) of tricyclopentylphosphine was added and the reaction allowed to warm to room temperature. The reaction was stirred overnight. The reaction mixture was passed through ca. 1 g of silica gel, and the silica gel was washed with ether. The volatiles were removed, and recrystallization from ether–methanol yielded 105 mg (41%) of white crystals, mp 120–125 °C dec. ^1H NMR (C_6D_6): δ 2.20–2.43 (m, 6 H), 1.20-2.00 (m, 48 H), 1.05 (t with Pt sat., J_{Pt-H} = 66.8 Hz, 6 H). ^{31}P NMR (C_6D_6): δ 19.6 (J_{Pt-P} = 1852 Hz). Anal. Calcd: C, 54.76; H, 8.62; P, 8.83. Found: C, 54.71; H, 8.31; P, 9.04.

***trans*-Bis(tricyclopentylphosphine)platinum(II) Dihydride (3).** A suspension of 210 mg (289 μmol) of 1 in 14 mL of ether in a pressure bottle was treated with dihydrogen (45 PSIG).[32] A slightly yellow solution resulted after 4 h. The solution was transferred to a round-bottomed flask, and the volume was reduced by one-half. Eight milliliters of degassed absolute ethanol were added, and the solution was cooled to 0 °C. A white crystalline solid precipitated (134 mg, 69%) over 1 day. The crystals were washed with ethanol and dried under vacuum. This compound in solution and as a solid is slightly sensitive to atmospheric oxygen or visible light and exposure to both was minimized when handling it; mp (under argon) 169–171 °C. ^{31}P NMR (C_6D_6): δ 61.9 (J_{Pt-P} = 2895 Hz); ^1H NMR (C_6D_6) δ 1.20–2.30 (m, 54 H), −2.89 (t of t, 2 H, J_{Pt-H} = 782 Hz, J_{P-H} = 17 Hz). *Anal.* Calcd: C, 53.47; H, 8.38; P, 9.19. Found: C, 53.39; H, 8.17; P, 8.90.

Products of Thermal Decomposition. Thermolysis reactions were carried out in sealed tubes prepared in the following manner. Pyrex tubing (6-mm o.d., medium walled, ca. 20 cm) was sealed at one end and sealed to a ground glass joint at the other. The tube and ground glass joint assemblies were tested for leaks with a Tesla soil and washed with distilled water, acetone, and reagent diethyl ether. The tube was attached to the vacuum line via its ground glass joint, flame dried, and allowed to cool under vacuum. The assembly was filled with argon, and 9.1 mg (13 μmol) of 1 was added while the tube was flushed with argon. The assembly and 1 were kept under vacuum at least 1 h prior to adding solvent (0.5 mL) via syringe while the tube was flushed with argon. The suspension of 1 in cyclohexane was freeze–pump–thaw degassed at least two times prior to sealing under vacuum (0.005 torr). Care must be taken to ensure that 1 is not left on the tube at the sealing point because pyrolysis of 1 generates platinum metal which catalyzes decomposition. Dissolution of 1 was accomplished by gentle warming with a heat gun and vigorous agitation of the sealed tube. Tubes were heated by suspension in the vapors of a refluxing solvent: 2,3-dimethylbutane (58 °C), methanol (65 °C), cyclohexane (80 °C), *n*-heptane (99 °C), toluene (110 °C), or *n*-octane (128 °C). After decomposition the tube was cooled to −196 °C, opened, and capped with a rubber septum. Volatile products were identified and their relative ratios determined by gas chromatography by sampling the liquid phase immediately upon warming the tube to room temperature. Retention times were compared with those of authentic materials on columns having two different liquid phases. Chemical identity was further confirmed by comparison of mass spectra to those of authentic material. The absolute yield of 1-butene was determined by quenching a reaction solution with an excess of bromine and comparison of the 1,2-dibromobutane obtained to an internal standard by GPC. To determine the absolute yield of 1-butene in solutions containing L, the volatiles were transferred under vacuum into a trap and quenched with bromine. A sealed tube containing 1 and $L_2Pt(Me)_2$ which had been heated for 2 h at 99 °C was broken inside a heavy glass vessel capped with a rubber septum to which 0.04 mL (STP) of ethane had been added. The yield of methane (0.12 equivs of $L_2Pt(Me)_2$) was determined by GPC of the gas phase inside the glass vessel.

Characterization of 2. To 24.2 g of 1% sodium amalgam in a round-bottomed flask was added 30 mL of a THF solution of 1.00 g (1.35 mmol) of *trans*-dichlorobis(tricyclopentylphosphine)platinum(II).[38] The mixture was warmed to 60 °C and stirred overnight. Transfer of the solution via cannulae to a Schlenk flask followed by removal of volatiles in vacuo afforded a mixture of 2 and starting material. The spectral parameters

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of 2 obtained by this procedure were identical with those of 2 obtained from thermolysis of 1. We could not crystallize 2. ^{1}H NMR (C_7D_8): δ 1.40–2.30 (m, 54 H). ^{31}P NMR (C_6H_{12}): δ 66.5 (J_{Pt-P} = 4221 Hz). To a solution of 2 in cyclohexane prepared by complete decomposition of 27.3 mg (37.5 μmol) of 1 was added 0.25 mL (4.0 mmol) of methyl iodide in a glovebox. Removal of volatiles yielded *trans*-iodomethylbis(tricyclopentylphosphine)platinum(II) (39.5 mg, 36.2 μmol, 97%). ^{1}H NMR (C_6D_6): δ 2.76–3.05 (m, 6 H), 1.77–2.07 (m, 24 H), 1.58–1.77 (m, 12 H), 1.35–1.58 (m, 12 H), 1.00 (t with Pt sat.; 3 H, J_{P-H} = 6.2 Hz, J_{Pt-H} = 82.5 Hz). ^{31}P NMR (C_6D_6): δ 1.42 (J_{Pt-P} = 2785 Hz).

Kinetics of Thermal Decomposition of 1. The kinetics of thermal decomposition of 1 were followed in sealed, 513A-PP Wilmad, 8-mm, 9-in. NMR tubes prepared as follows. A restriction was placed about 3 cm from the open end of an NMR tube. It was then sealed to a ground glass joint and checked for leaks with a Tesla coil. The assembly was washed with distilled water, acetone, and reagent diethyl ether. Sealed 10- or 20-μL capillary tubes were prepared containing 6.6 M H_3PO_4. A capillary was placed in the NMR tube and the assembly attached to the vacuum line via its ground glass joint. The assembly was flame dried, cooled under vacuum, and filled with argon, and 27.3 mg (37.5 μmol) of 1 was added while the tube was flushed with argon. The assembly was evacuated for at least 1 h before solvent (1.5 mL) was added. The suspension of 1 in solvent was freeze–pump–thaw degassed at least two times prior to sealing under vacuum at the restriction. Gentle warming and agitation were again required for dissolution. Before heating, three successive ^{31}P NMR spectra were taken and the ratio of the areas of the central peak of 1 to the peak for phosphoric acid found by electronic integration. The NMR tube was then heated as above for a specified period of time and thermally quenched in a room-temperature water bath. The resulting concentration of 1 was determined from duplicate ^{31}P NMR spectra. ^{31}P NMR spectra were recorded by using a 90° pulse width and a relaxation delay of greater than $5T_1$ for both the phosphoric acid and 1. The concentration of 1 was varied by changing the amount of 1 placed in the NMR tube assembly. The concentration of 1-octene and tricyclopentylphosphine was varied by preparation of a standard solution of reagent in cyclohexane and then performing successive dilutions in volumetric Schlenk ware. A stock solution of 2 (60 mM) in cyclohexane was prepared by complete decomposition of 1, removal of volatiles, and addition of cyclohexane. Varying amounts of the stock solution and cyclohexane were used as solvent to prepare three tubes containing 60, 30, and 10 mM $[2]_0$. The kinetic isotope effect on decomposition was determined by preparation and thermolysis of separate tubes containing 1, 1-d_4, and 1-d_8.

Deuterium Labeling Experiments. The preparation, cleaning, sealing, and thermolysis of tubes containing 1-d_8, 1-d_4, or 1-d_{54} were the same as for the product studies. Deuterium incorporation in 1-butene was determined by two different methods. In the first method a thermolysis tube was cooled to −196 °C, opened, and warmed to room temperature. An aliquot was removed from the liquid phase and analyzed by GC/MS. Because of significant isotopic fractionation across the width of GC peaks, eight to ten mass spectra were recorded and weighted averages of these spectra were calculated and used to determine isotopic content. The parent ion (70 eV) of 1-butene was used, and corrections were applied for ^{13}C isotopic content and hydrogen or deuterium losses. It was assumed that the isotopic effect on the loss of hydrogen or deuterium was one. In the second method, bromine was added to the tube after being opened and the 1,2-dibromobutane analyzed by GC/MS. The M − Br peak was used, and corrections were applied for ^{13}C isotopic content. The results from the two methods were indistinguishable with experimental error. The isotopic composition of the methane produced in the decomposition of 1-d_8 and $L_2Pt(Me)_2$ was determined by the following method. After decomposition, a sealed tube was fitted to one end of a brass valve with a rubber 0-ring and a Swagelok nut. The other end of the valve was fitted with a rubber septum. The valve was evacuated and the tube broken with the plunger of the valve. The gas phase was analyzed by GC/MS, and the isotopic composition of the methane obtained compared with authentic samples of methane and methane-d_1.

Acknowledgment. Dr. Jean-Paul Lavalleye provided (1,4-butane-d_8)dimagnesium bromide and Dr. Robert L. Brainard provided perdeuteriotricyclopentylphosphine. We thank Dr. Allan F. Sowinski for some preliminary studies of platinacyclopentanes. The NMR spectrometers were purchased in part through NSF CHE 80-08891 and through NIH BRS Shared Instrument Grant Program 1 S10 RR01748-01A1.

Registry No. 1, 102286-26-0; 2, 102286-27-1; 3, 102286-28-2; dimethyl succinate-d_4, 30994-23-1; dimethyl acetylenedicarboxylate, 762-42-5; 1,4-butanediol-d_8, 74829-49-5; 1,4-dibromobutane-d_8, 68375-92-8; (1,5-cyclooctadiene)platinacyclopentane(II), 60161-34-4; dichloro(1,5-cyclobutadiene)platinum(II), 12080-32-9; 1,4-dibromobutane, 110-52-1; *cis*-bis(tricyclopentylphosphine)dimethylplatinum(II), 102286-29-3; (1,5-cyclooctadiene)dimethylplatinum(II), 12266-92-1; *trans*-dichlorobis(tricyclopentylphosphine)platinum(II), 102306-94-5; 1-butene, 106-98-9.