

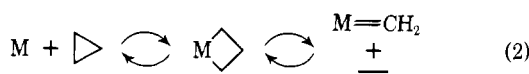
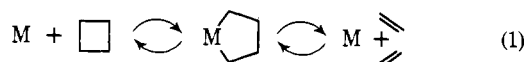
Thermal Decomposition of Bis(phosphine)platinum(II) Metallocycles¹

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Abstract: The thermal decomposition of several metallocyclic derivatives of platinum(II)—particularly $(\text{Ph}_3\text{P})_2\text{Pt}(\text{CH}_2)_4$ (**1**), $(\text{Ph}_3\text{P})_2\text{Pt}(\text{CH}_2)_5$ (**2**), and $(\text{Ph}_3\text{P})_2\text{Pt}(\text{CH}_2)_6$ (**3**)—have been examined. Compounds **1** and **2** decompose more slowly than $(\text{Ph}_3\text{P})_2\text{Pt}(\text{CH}_2\text{CH}_3)_2$ (**7**) or $(\text{Ph}_3\text{P})_2\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_2$ (**8**) by a factor of more than 10^4 ; **3**, **7**, and **8** decompose at comparable rates. Decomposition of **1** and **2** is accelerated by added phosphine; decomposition of **8** is inhibited. We propose that the high thermal stability of **1**, **2**, and derivatives reflects steric inhibition of the reaction resulting in cis elimination of platinum and β -hydrogen: the relatively rigid five- and six-membered platinocyclic rings do not permit the PtCCH dihedral angle to assume the value of 0° that seems to be optimal for this metal hydride elimination. Inhibition of platinum β -hydride elimination should permit types of reactions to occur in platinocycles that would be masked in acyclic analogues. In accord with this suggestion, 1,4-tetramethylenebis(tri-*n*-butylphosphine)platinum(II) (**9**) yields cyclobutane as a major product of thermal decomposition in methylene chloride solution; diethylbis(tri-*n*-butylphosphine)platinum(II) (**10**) generates only ethylene and ethane under similar conditions.

Transition metal metallocycles are intermediates in a variety of metal-catalyzed reactions: isomerizations of strained carbocyclic rings,³⁻⁷ olefin dimerization and related reactions,⁸⁻¹¹ and probably olefin metathesis¹²⁻¹⁷ (eq 1, 2). The



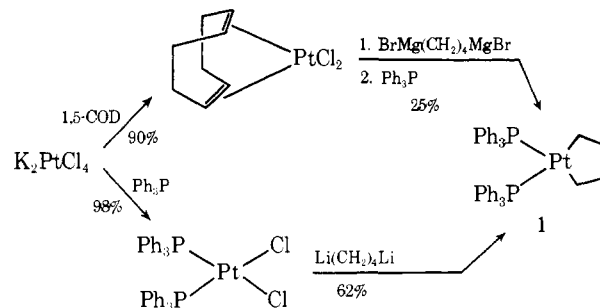
dominant thermal reaction of most acyclic transition metal alkyls is the cis elimination of metal and β -hydrogen.¹⁸⁻²⁰ We have suggested previously that this metal hydride elimination reaction should be suppressed in six-, five-, four-, (and three-)membered metallocycles, because the M-C-C-H dihedral angles in these compounds are constrained to values far from 0° .²¹ Slow thermal β -hydrogen elimination should make other types of reactions—particularly carbon-carbon bond-forming and bond-breaking reactions—relatively more important in transformations of metallocycles than in those involving acyclic metal alkyl intermediates. An understanding of the thermal chemistry of metallocycles should both contribute to the usefulness of known types of transformations in which these species are intermediates and help in predicting new types of transition metal-catalyzed processes that depend on reactions other than metal-hydrogen elimination to determine their products.

Here we describe details of an examination of the thermal stabilities and mechanisms of decomposition of bis(phosphine)platinum(II) metallocycles. This class of compounds was selected for study for two reasons. First, dialkylbis(phosphine)platinum(II) complexes are stable, well-characterized, substances whose physical properties make them particularly suitable for mechanistic examination. Second, the results of a study of the thermal decomposition of platinum metallocycles should be directly and profitably comparable with those obtained earlier from examination of a closely related acyclic complex, di-*n*-butylbis(triphenylphosphine)platinum(II).²²

Results

Synthesis. Two procedures have been used to prepare bis(phosphine)platinum(II) metallocycles: reaction of dichloro(1,5-cyclooctadiene)platinum(II) with alkane di(Grignard) reagents followed by displacement of the 1,5-cyclooctadiene ligand by phosphines, and direct reaction of

Scheme I. Preparation of 1,4-Tetramethylenebis(triphenylphosphine)platinum(II) (**1**)



dichlorobis(phosphine)platinum(II) with dilithioalkanes.^{23,24} Direct reaction of dichlorobis(phosphine)platinum(II) complexes with Grignard reagents gives a mixture of products containing large quantities of monoalkylated platinum(II) compounds, and is not a satisfactory synthetic procedure. Scheme I summarizes yields obtained on preparation of 1,4-tetramethylenebis(triphenylphosphine)platinum(II) (**1**) using these procedures. Each method has its advantages. Alkane di(Grignard) reagents are more easily prepared, less likely to form two-phase systems in ethereal solvents, and more stable than the corresponding alkane dilithium reagents, but their use generates product in lower yields and requires chromatography in purification. Moreover, the experimental procedures required in their use are complicated (see the Experimental Section). Dilithium reagents, particularly those involving a secondary center (e.g., 1,4-dilithiopentane) are insoluble in hydrocarbon solutions and unstable in diethyl ether, and thus inconvenient to use, but generate alkylplatinum complexes in higher yield than do Grignard reagents. In practice, **1** and 1,5-pentamethylenebis(triphenylphosphine)platinum(II) (**2**) were prepared from the corresponding dilithium reagents, and other compounds were obtained from di(Grignard) reagents.

Kinetics and Products of Decomposition of **1 and **2**.** The major fraction of data concerning the kinetics of thermal decomposition of dialkylplatinum(II) complexes was obtained using methylene chloride as solvent following procedures developed previously.²² The principal reasons for choosing methylene chloride are that it is an excellent solvent for the otherwise often sparingly soluble dialkylbis(triphenylphosphine)platinum(II) complexes, it seemed not to influence the kinetics of thermal decomposition (vide infra), and it had been

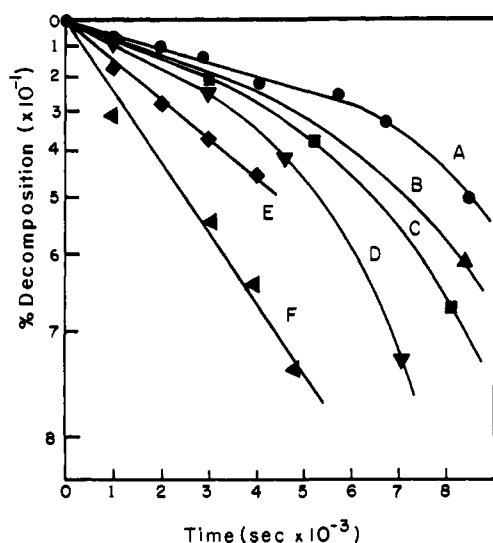


Figure 1. The apparent rate of thermal decomposition of 1,4-tetramethylenebis(triphenylphosphine)platinum(II) (**1**) depends on the concentration of triphenylphosphine in solution. Data are for runs in methylene chloride, having $[1]_0 = 0.025$ M, and these values for $[\text{Ph}_3\text{P}]_0$ (M): A, 0.0; B, 0.003; C, 0.007; D, 0.026; E, 0.13; F, 0.26. The initial rates are reproducible. The nonlinear portions of curves A through D tend to vary slightly in different kinetic runs (see the text for a discussion of this point).

the solvent used in earlier studies of the mechanism of thermal decomposition of acyclic dialkylbis(phosphine)platinum complexes.²² In order to obtain fully reproducible rates in methylene chloride, it was necessary to purify the methylene chloride carefully to remove traces of chloroform, and to take great caution in sealing evacuated sample tubes to avoid sample pyrolysis.

The rates of decomposition of metallocycles were followed using several procedures. Samples were taken periodically, and were cooled and quenched using hydrochloric acid or bromine: GLC was used to follow the appearance of butane relative to an internal standard (HCl quench), the ratio of butane to olefin products (HCl quench), or the disappearance of 1,4-dibromobutane relative to an internal standard (Br_2 quench). The results obtained using these different techniques were indistinguishable within experimental error.

The thermolyses of **1** and **2** were first order only over approximately the first 30% of decomposition. Rate constants in this region were independent of the initial concentration of platinum complex, but depended on the concentration of triphenylphosphine in solution. Figure 1 shows typical data for **1**, alone and in the presence of added triphenylphosphine. Rate constants derived from the initial linear regions of the decomposition curves observed in the absence of added triphenylphosphine for several platinum(II) metallocycles are summarized in Table I, together with yields of hydrocarbon products. These hydrocarbon yields drifted during the course of the decompositions, for reasons that have not been established. The yields of hydrocarbons reported in Table I are relative yields obtained after ca. 30% decomposition (close to the end of the kinetically linear region); the material balances observed at this point (that is, the sum of alkyl groups in the reported hydrocarbon products and in undecomposed platinum alkyl) and those obtained at the conclusion of the decomposition were both >90%.

The influence of added triphenylphosphine on the rate constant for decomposition of **1** is linear above ca. 0.007 M (Figure 2), and the overall rate constant in this region can be expressed by a two-term rate expression (eq 3),

$$-\frac{d[1]}{dt} = (k_1 + k_2[\text{PPh}_3])[1] \quad (3)$$

Table I. Rate Constants ($k \times 10^4 \text{ s}^{-1}$) and Products of Thermal Decomposition of Bis(phosphine)platinum(II) Metallocycles in Methylene Chloride^a

Compound	Rate		Relative product yields (%)			
	60°	120°	<i>n</i> -Alkane	1-Alkene	2-Alkene ^b	Diene ^c
1		0.54	0	78	20	2
2		0.40	0	75	17	8
3		1.7	0	83	17	0
4		0.17	0	83	17	0
5		1.0	0	70	25	5
6		<i>d</i>	15	28	32	25
7	4.5		50	50	0	0
8	4.1	9100 ^e	50	49	1	0

^a L = PPh₃; the initial concentration of the Pt complex was 0.025 M. Yields are relative; material balances were between 95 and 100%. Relative yields of olefins and dienes tended to drift during the course of the reaction, particularly for 4 and 6. Relative yields are derived from data collected at 30% decomposition in order to provide a meaningful comparison. ^b A mixture of *cis* and *trans* isomers. ^c Predominately α, ω . ^d Qualitative kinetics indicated that the rate of decomposition was comparable to 5. ^e Value extrapolated from measurements at lower temperatures. See the text for an explanation.

where $k_1 = 0.54 \text{ s}^{-1}$ and $k_2 = 2.8 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ at 120 °C. An experimentally significant shift in product composition accompanies an increase in triphenylphosphine concentration: the C₄-derived products consist of a mixture of 1- and 2-butene throughout, but at high triphenylphosphine concentration, the formation of 2-butene is strongly inhibited (Figure 3). To test the stability of the olefin products under the reaction conditions, a sample of **1** was allowed to decompose to ca. 70% completion in the presence of 1-pentene. The 1-pentene could be recovered quantitatively; no isomerization had taken place. Thus, equilibration of the olefinic products of the metallocycle decompositions presumably takes place by metal hydride additions and eliminations *before* the olefin is released into solution. A similar phenomenon is observed for **8**.²² It is not clear whether the shift in relative proportions of 1- and 2-olefin reflects a genuine shift in the position of the hydrogen that is lost in the initial step of the decomposition, or simply a decrease in the rate of a subsequent, intramolecular, metal hydride-catalyzed, isomerization; the deuterium labeling studies that might distinguish between these mechanisms have not been carried out.

The thermal decomposition of **2** was studied in less detail than that of **1**, but showed the same general kinetic features. The disappearance of **2** followed reproducible first-order kinetic behavior only over ca. the first 30% of the decomposition. As the extent of decomposition passed this value, the rate increased in a not entirely reproducible manner. Added triphenylphosphine accelerated the reaction, although not as strongly as it accelerated the decomposition of **1**.

These results indicate that the thermal decomposition of **1** and **2** differs from that of acyclic dialkylbis(phosphine)platinum(II) complexes in two important respects: first, the metallocycles are much more stable thermally than their acyclic analogues; second, decomposition of the metallocycles is accelerated by added phosphine, while decomposition of acyclic

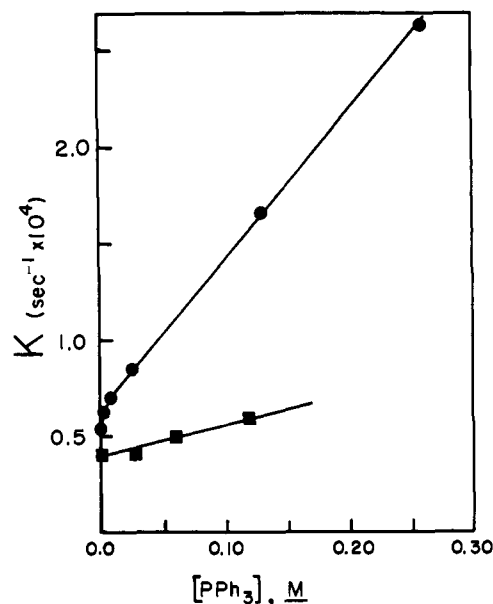


Figure 2. Rate constants for thermal decomposition of 1 (●) and 2 (■) as a function of the concentration of added triphenylphosphine. These curves are derived from the data of Figure 1.

complexes is inhibited. To test the hypothesis that dissociation of a phosphine from 1 is not necessary for its decomposition, the chelating complex 1,4-tetramethylene(1,2-diphenylphosphinoethane)platinum(II) (4) was synthesized and thermally decomposed. The equilibrium constant for dissociation of a phosphine moiety from this complex is expected to be much less than that from 1 or 2. If phosphine dissociation promotes decomposition, 4 should be appreciably more stable than 1. In fact, the rate of thermal decomposition of 4 is only ca. a factor of three less than that of 1. This factor is sufficiently small that it reinforces the conclusion (drawn from the observation that added phosphine accelerates the decomposition of 1 and 2) that a three-coordinate platinum complex is not an intermediate along the reaction coordinate for thermal decomposition.

The solvent in which decompositions of 1 and 2 were carried out influenced the composition of the decomposed mixtures, but not the kinetics of the decompositions. The decompositions of 1 and 2 in trichlorotrifluoroethane, 1,2-dichloroethane, and benzene took place at rates qualitatively comparable to those observed in methylene chloride. The products derived from the C₄ and C₅ fragments were similar in these four solvents, with the exception that a 10% yield of *n*-alkane was produced in benzene (presumably reflecting the involvement of platinum hydrides generated by oxidative addition of aromatic C-H bonds to Pt(0)), in addition to the 1- and 2-olefins and small quantities of dienes observed in chlorinated solvents. Thermal decomposition of 2 in benzene-*d*₆ resulted in production of unlabeled *n*-pentane. It seems possible that the hydrogen incorporated into this saturated product is derived from triphenylphosphine.²⁵ The decompositions of 1 and 2 in chlorinated solvents often give colorless product mixtures; in benzene, decomposition mixtures are the red color characteristic of the products of thermal degradation of bis(triphenylphosphine)platinum(0).²⁶ We assume that platinum(0) species produced initially in chlorinated solvents are rapidly oxidized to soluble, colorless, platinum(II) complexes.

To check the origin of the hydrogens in the C₄-derived products, 1 was allowed to decompose thermally in CD₂Cl₂, and 1,4-tetramethylenebis(triphenylphosphine-*d*₁₅)platinum(II) was allowed to decompose in CH₂Cl₂. Mass spectrometric analysis of the butene mixture produced early in these reactions showed ca. 5% incorporation of deuterium in each

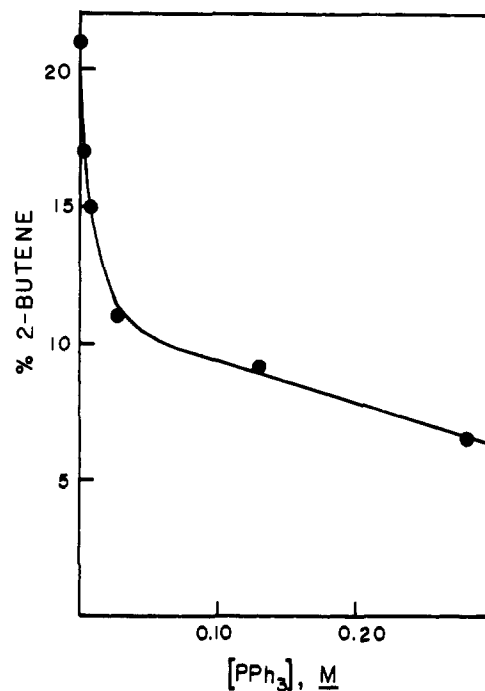


Figure 3. The formation of 2-butene on thermal decomposition of 1 is suppressed by added triphenylphosphine. The product balance in these experiments is completed by 1-butene, with small amounts (<3%) of butadiene.

instance. Thus there is little hydrogen transfer from solvent or the phenyl rings of triphenylphosphine to the products derived from the tetramethylene moiety. Later in the reactions, the deuterium incorporation increases to 10–15%.

Comparisons with the Thermal Decomposition of Di-*n*-butylbis(triphenylphosphine)platinum(II) (8) and Related Acyclic Compounds. The kinetic behavior of 8 is less complicated than that of 1 and 2. The thermal decomposition of 8 is clearly first order to greater than 80% conversion. The rate of decomposition is decreased by a factor of 60 in the presence of 0.043 M added triphenylphosphine.²² The rate of thermal decomposition of 8 is so much more rapid than that of 1 that a direct comparison is not practical. We have, instead, measured the rate of decomposition of 8 at several temperatures and extrapolated the resulting Arrhenius plot to the temperature used in studying the decompositions of the metallocycles (Figure 4). The result of this extrapolation is included in Table I.²⁷

The thermal decomposition of 8 involves dissociation of a phosphine ligand in or before the rate-determining step.²² It seemed possible that the great difference in thermal stability between 1 and 8 reflected a difference in steric interaction between the triphenylphosphine ligands and the alkyl moieties attached to platinum: the large *n*-butyl group might interact sufficiently with the phosphines to promote their dissociation strongly, while the smaller 1,4-tetramethylene moiety might not do so. To test this hypothesis, the rate of decomposition of diethylbis(triphenylphosphine)platinum(II) (7) was measured. An important contribution to the rate resulting from steric interaction between triphenylphosphine ligands and the alkyl groups would be expected to be reflected in greater stability for 7 than for 8. In fact, the rates of decomposition of these compounds are comparable. Di-*n*-octylbis(triphenylphosphine)platinum(II) was also examined qualitatively²² and found to decompose at a similar rate. Thus, the steric bulk of the alkyl moieties attached to platinum does not influence the rates of decomposition of these metal alkyls in an easily interpretable way.

Thermal Decomposition of 1,4-Tetramethylenebis(tri-*n*-butylphosphine)platinum(II) (9) Yields Cyclobutane. The ther-

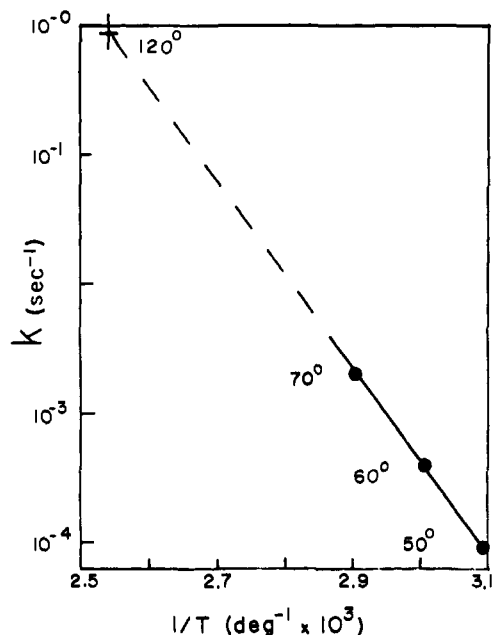
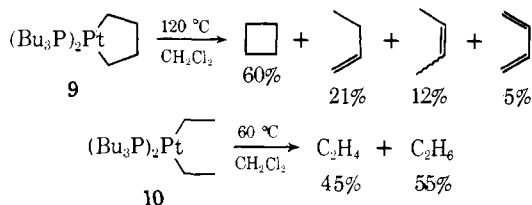


Figure 4. An Arrhenius plot describing the temperature variation in the rate of thermal decomposition of di-*n*-butylbis(triphenylphosphine)platinum(II). Experimental points were obtained at 50, 60, and 70 °C, and the resulting plot was extrapolated to 120 °C for comparison with the rate of decomposition of **1**. The activation energy estimated from this plot is $E_a \approx 33 \text{ kcal mol}^{-1}$.

mal decomposition of **1** by metal β -hydride elimination is much slower than that of **7** and **8**. We hoped that by inhibiting the metal hydride elimination reaction, other thermal decomposition paths might appear. Although there is no evidence for reactivity peculiar to metallocycles among the compounds related to **1**, unusual reactivity was observed for the analogous complex 1,4-tetramethylbis(tri-*n*-butylphosphine)platinum(II) (**9**). Thermal decomposition of **9**, as expected, takes place much



more slowly than the corresponding diethylplatinum complex **10**. The major hydrocarbon formed from **9** in methylene chloride solution is cyclobutane, the product of carbon-carbon bond formation. Decomposition of **10** yields only the expected ethane and ethylene: no (1% would have been detected) butane was formed.

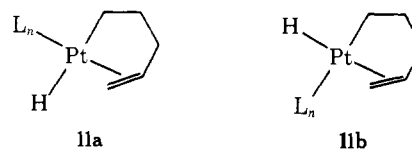
The observation of cyclobutane as a product of decomposition of **9** indicates that carbon-carbon bond formation can be an important reaction of (initially) dialkylplatinum(II) complexes, when platinum hydride elimination is slowed. We have not yet established the detailed course of decomposition of **9**.²⁸

Discussion

Five- and six-membered platinum metallocycles (**1**, **2**, **5**, and **6**), but not the seven-membered metallocycle **3**, are much more stable than the acyclic di-*n*-alkylplatinum complexes **7** and **8**. This stabilization is easily rationalized using the hypothesis that cis metal β -hydrogen elimination is inhibited in the five- and six-membered metallocycles. In **8**, metal hydride elimination is *not* the sole rate-determining step: either loss of phosphine (possibly concerted with metal hydride elimination) from **8** or reductive elimination of alkane from an intermediate

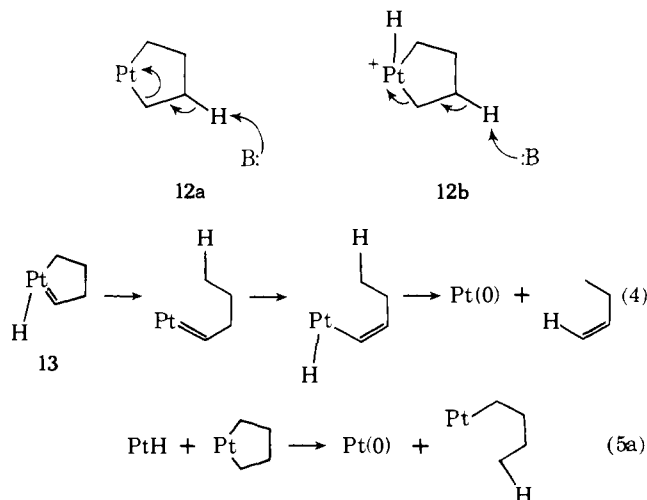
hydridoalkylplatinum(II) complex, depending on phosphine concentration, is overall rate-limiting. The mechanism(s) of decomposition of the metallocycle **1** is clearly different from those of **8**. Whether metal hydride elimination is itself the rate-limiting step in the decomposition of **1** is not evident from the available data. Nonetheless, it appears that hindering the metal hydride elimination results in a large decrease in the rate of thermal decomposition of these dialkylplatinum(II) complexes.

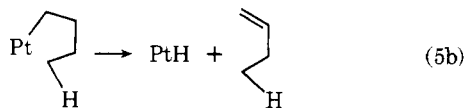
Although the details of the mechanism by which the metallocycles decompose are not clear, several observations are in keeping with (slow) metal β -hydride elimination for these compounds. First, the pronounced dependence of the rate of decomposition on ring size is compatible with the suggestion that in the relatively rigid rings that compose **1** and **2** the β -hydrogen atoms are constrained to positions far from the platinum center, but in the flexible seven-membered ring of **3**, cis elimination of metal hydride is less hindered. Second, the hydrocarbon products of decomposition are easily rationalized on the basis of metal hydride elimination followed by reductive elimination of alkene, a mechanism similar to that established for **8**.²² The small quantities of dienes produced from certain metallocycles may suggest an intermediate structure in which



a hydride and an alkyl group are coordinated trans (**11a**). Reductive elimination of alkene from this structure should be slower than from a cis isomer (**11b**).²⁹ The most unsatisfactory aspect of the metal β -hydride elimination mechanism as a rationalization for the thermal decomposition of these platinumocycles is that it is not clear that the platinum atom and a β -hydrogen atom can be brought close enough together for a concerted elimination to take place, without introducing energetically unacceptable bond angle distortions. An x-ray structure of **1** is available, but is relevant to this problem only in showing a significant distortion of the five-membered ring from planarity.³⁰ Further, the stability of the α -methyl substituted substances **5** and **6** is puzzling; hydride loss from the methyl groups would be expected to be less inhibited than hydride loss from the ring.

Several alternative mechanisms are available, a priori, for the decomposition of **1**. The metal hydride elimination step might be assisted by an external acid or base (**12**), or might require an initial α -hydride elimination (eq 4).^{18,31} The reaction might involve an intermolecular chain reaction (eq 5a, 5b).

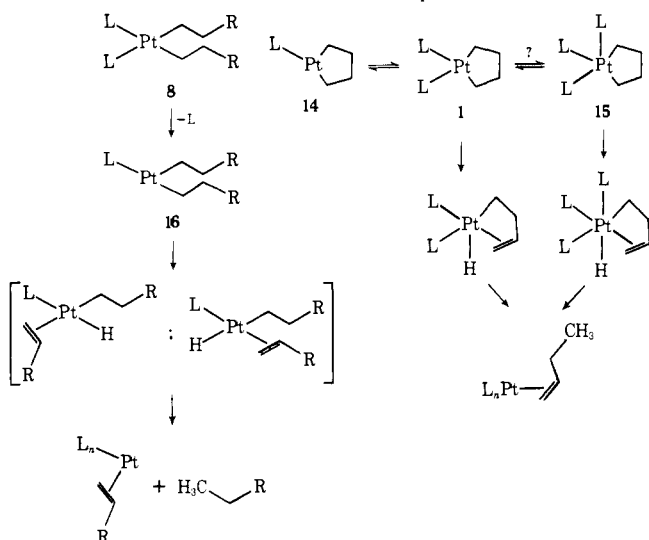




It might involve free alkyl radicals. There are objections to several of these possibilities. We have seen no evidence for acid or base catalysis: treating **1** with HCl results in protonolysis of carbon–platinum bonds and formation of butane rather than production of butene; the decomposition of **1** is not induced by very strongly basic organolithium reagents. If decomposition required a bimolecular chain reaction between a platinum hydride and a platinum alkyl, the rate would not be first order. The observation that the decomposition does follow first-order kinetics in the early stages of reaction argues against free radical chain reactions and intermolecular reactions involving a platinum hydride, although the rate acceleration and accompanying external deuterium incorporation into products that occurs later in the reaction may reflect this latter type of reaction. It is, however, difficult to exclude α -hydride elimination (**13**) on the basis of available evidence.

If we *assume* that the decomposition of **1** involves metal β -hydride elimination, it is possible to make an interesting comparison between the rates of decomposition of **1** and **8**. The decomposition of **8** normally involves generation of a three-coordinate complex by loss of phosphine in a preequilibrium or rate-limiting step (Scheme II).²² The rate inhibition ob-

Scheme II. Mechanisms of Thermal Decomposition of **1** and **8**



served for **8** on adding phosphine stands in clear contrast to the rate acceleration observed with **1**. Although this acceleration might be due either to inhibition of the formation of a three-coordinate intermediate, **14**, or to promotion of the formation of a five-coordinate intermediate, **15**, the former seems the more likely: the kinetic behavior of **8** demonstrates that dissociation of triphenylphosphine from dialkylbis(phosphine)platinum(II) complexes is energetically feasible. If we assume that decomposition of **1** proceeds through a four-coordinate complex, and take into account the rate decrease of ca. 60 observed in solutions of **8** on adding triphenylphosphine,²² we estimate the difference in rate of decomposition of **14** and **16** to be greater than 10^5 .

Regardless of whether the decomposition of **1** proceeds through elimination of an α - or β -hydride, and regardless of uncertainties concerning the role of added phosphine in this decomposition, the important fact remains that **1** and related metallocycles are particularly thermally stable substances. The production of cyclobutane from decomposition of **9** provides evidence that when β -hydride elimination is blocked, other types of reaction, normally masked in acyclic dialkyl platinum

complexes by the facility of this elimination, become important. The particular structural features favoring carbon–carbon bond formation have not been explored here, but a related examination of the decomposition of nickel(II) metallocycles suggests several possibilities.^{28,32}

The major point of this work—that suppression of β -hydride elimination by incorporation of alkyl groups into metallocyclic moieties increases thermal stability and permits new types of reactions—is fully supported by the results reported here and in the accompanying paper concerning related titanium(IV) metallocycles.³³ The importance of four- and five-membered metallocyclic intermediates in transition metal catalysis is easily documented, and the unusual chemistry that characterizes these intermediates probably reflects, at least in part, the inhibition of metal β -hydride elimination. An unexpected result from this work is that a six-membered platinum metallocycle shows the same thermal stability as its five-membered analogue. There are presently no clear examples of important catalytic reactions that depend on six-membered intermediates, presumably because such species are difficult to form.³⁴ The unusual chemistry characteristic of stable metallocycles suggests that a search for reactions generating such species might lead to useful reactions.

Experimental Section

General Methods. All reactions involving organometallic compounds were carried out under prepurified nitrogen or welding-grade argon using standard techniques³⁵ for handling air-sensitive compounds. Solvents for use in organometallic reactions were distilled under an inert atmosphere. Diethyl ether was distilled from lithium aluminum hydride, and tetrahydrofuran from sodium benzophenone dianion. Hexane was stirred over concentrated sulfuric acid for several days, then distilled from the darkened acid and redistilled from a suspension of sodium benzophenone ketyl. Methylene chloride for use in kinetic runs was distilled from barium oxide under nitrogen, then redistilled through a 60-cm platinum spinning band column. A center cut (ca. 30%) was collected for use. The methylene chloride employed in recrystallizations was reagent grade, as were other solvents, unless otherwise noted. Absolute ethanol was used in synthetic work. The platinum alkyls in this study are not very sensitive to air or water. Reaction workup, recrystallization, and spectral measurement could be performed in the atmosphere without special precautions. Thermal decompositions were, however, carried out under anhydrous, oxygen-free, conditions (see below). A number of organoplatinum compounds decomposed slowly in chloroform at 25 °C even though they were quite stable in other solvents.³⁶ Chloroform-*d*₁ could, however, be satisfactorily employed for spectral measurements provided the solutions were quite fresh. Platinum alkyls show slight sensitivity to light, and should be stored in the dark. Melting points were obtained using a Thomas-Hoover capillary melting point apparatus and are uncorrected. The observed melting points (actually decomposition points) of the platinum alkyls are usually higher in a sealed evacuated tube, indicating some sensitivity to air above 100 °C; values given here were taken in evacuated capillaries, unless noted otherwise. Infrared spectra were taken on a Perkin-Elmer Model 237 instrument. NMR spectra were run on a Varian T-60 or Perkin-Elmer R20B spectrometer. Chemical shifts are reported in parts per million downfield from Me₄Si. Microanalyses were performed by Midwest Microlab, Inc., Indianapolis, Ind. Solutions were analyzed by gas chromatography on Perkin-Elmer Model 990 or Hewlett-Packard 810 instruments equipped with flame ionization detectors. Products were identified by comparison of retention times to those of authentic samples. Identity was considered established by equal retention times on at least two columns with different stationary phases. Product yields were determined by response relative to an internal standard. Response factors were obtained from authentic samples.

Dichloro(1,5-cyclooctadiene)platinum(II) ((COD)PtCl₂).³⁷ Potassium tetrachloroplatinate (K₂PtCl₄, 2.5 g, 6.0 mmol) was dissolved in 40 ml of water and filtered. To the deep red filtrate were added 60 ml of glacial acetic acid and 2.5 ml (20 mmol) of 1,5-cyclooctadiene (technical grade, used without purification). The reaction mixture was stirred rapidly and heated to about 90 °C on a steam bath. Over 30 min the deep red solution slowly became pale yellow and fine

crystals were deposited. The volume of the solution was reduced to 30 ml by evaporation under reduced pressure. The light yellow needles were collected and washed in succession with 50-ml portions of water, ethanol, and ether. After being dried at 100 °C for 60 min, the product weighed 2.16 g (96%) and decomposed without melting between 250 and 280 °C (lit.³⁷ dec 220–278 °C). The dichloro(1,5-cyclooctadiene)platinum(II) was used without recrystallization in the syntheses of the alkylplatinum complexes.

Butane-1,4-Pentane-1,5-, Pentane-1,4-, and Hexane-1,6-di(magnesium bromide). The di(Grignard) reagents were prepared from the corresponding dibromides (purified by distillation from calcium hydride) and triply sublimed magnesium turnings in diethyl ether according to the procedure of Nenitzescu and Necsoiu.^{38,39} During the formation of the di(Grignard) reagents the reaction mixture separated into two liquid layers. The upper ether layer was removed by forced siphon under nitrogen pressure using a cannula and discarded. Adding distilled tetrahydrofuran to the oily lower layer gave a homogeneous solution. To estimate the amount of the Grignard reagent present, 2 ml of the tetrahydrofuran solution was quenched in ca. 5 ml of water, and the aqueous solution titrated with hydrochloric acid to give the total base present. The saturated solutions of Grignard reagents in the mixed diethyl ether-THF solutions, formed by adding just enough THF to the separated lower layer of the two-phase ether system to give a homogenous solution, were found to have the following normalities: BrMg(CH₂)₄MgBr, 0.19 N; BrMg(CH₂)₅MgBr, 0.78 N; BrMgCH(CH₃)(CH₂)₃MgBr, 0.60 N; BrMg(CH₂)₆MgBr, 0.80 N.

Preparation of Bis(triphenylphosphine)platinum(II) Metallo-cycles by Reaction of Dichloro(1,5-cyclooctadiene)platinum(II) and Di(Grignard) Reagents: General Remarks. Attempts to prepare the platinocycles by adding THF-diethyl ether solutions of di(Grignard) reagents to (COD)PtCl₂ suspended in ether were unsatisfactory both because the di(Grignard) reagents precipitated from the ether medium and because they formed intractable gums when they underwent reaction with (COD)PtCl₂. Tetrahydrofuran was an equally unsatisfactory reaction solvent, because, even at low temperatures, the reaction of (COD)PtCl₂ and the di(Grignard) reagents gave dark brown solutions and low yields of metalocyclic products.⁴⁰ By adding only enough tetrahydrofuran to keep the di(Grignard) reagents from precipitating from the ether reaction medium, a successful reaction occurred. The (COD)PtCl₂ could react more completely in the mixed solvent and the 1,5-cyclooctadieneplatinocycles formed seemed to be more stable than in tetrahydrofuran alone. The yields of platinocycles were highest when the reactions were stirred as rapidly as possible.

Reactions were carried out in 40-ml centrifuge tubes capped with No-Air stoppers and equipped with Teflon-coated stirrer bars. The temperature of the reaction mixtures was regulated by immersing the centrifuge tubes in a Dewar containing a mixture of isopropyl alcohol and dry ice. Unlike the solvent composition, the temperature did not seem to be a critical parameter. The temperature was regulated in each case so that the reaction of (COD)PtCl₂ with the di(Grignard) reagents was complete after 1.5 h, and the reaction solution was only a light brown. At temperatures much above 0 °C, the reaction solutions turned dark brown in a few minutes, indicating that the platinocycle had decomposed.

The method used to quench the solution mixtures was, however, critical. If triphenylphosphine was added directly to one of the light brown reaction mixtures above, the bis(triphenylphosphine)platinocycles later isolated were contaminated with L₂PtCl₂ and partially substituted L₂PtRCl which were difficult to remove. If the reaction mixture was quenched by adding it directly to ice water before adding triphenylphosphine, very little bis(triphenylphosphine)platinocycle was isolated because the intermediate (COD)Pt(CH₂)_n apparently decomposed. The most satisfactory method involved the preparation under nitrogen of a short chromatography column containing silica gel in pentane. The entire column was cooled to 0 °C in a refrigerator before use, and the reaction mixture was quickly flushed through under a pressure of nitrogen. The silica gel retained the brown decomposition products, and if the quenching procedure had been carried out correctly, a clear ether solution resulted. If the resulting ether solution was still brown, however, a pinch of activated charcoal completely decolorized the solution. Although 1,5-cyclooctadieneplatinocycles were never isolated, their ether solutions appeared to be air stable. The ether solutions were therefore filtered in the air into a flask containing solid triphenylphosphine, giving a clear solution. Letting the solution stand at room temperature caused the 1,5-cy-

clooctadiene in (COD)Pt(CH₂)_n to be replaced by two triphenylphosphine ligands. During the replacement reaction, the clear solution often turned a light yellow, but the color change did not complicate the isolation of white crystalline platinocyclic products.

1,4-Tetramethylenebis(triphenylphosphine)platinum(II) (1). To a stirred solution of (COD)PtCl₂ (0.187 g, 0.5 mmol) in 30 ml of diethyl ether and 5 ml of tetrahydrofuran at -50 °C was added 5.5 ml (0.53 mmol) of a tetrahydrofuran solution (0.19 N) of butane-1,4-di(magnesium bromide). The reaction mixture was allowed to warm slowly to -20 °C over 30 min and then stirred an additional 60 min between -25 and -15 °C to give a brown solution. The reaction mixture was transferred by cannula under nitrogen to a 2-cm chromatography column, containing 10 cm of a pentane slurry of silica gel (Merck, No 60) at 0 °C. The reaction mixture was forced through the column with a positive pressure of nitrogen. The column was washed with 40 ml of ether. A pinch of activated charcoal decolorized the resulting clear, light brown, solution, which was then filtered in the air into a 100-ml flask containing solid triphenylphosphine (0.26 g, 1.0 mmol). The solution was allowed to stand at ambient temperature for 30 min; 10 ml of absolute ethanol was added, and the solution concentrated to 10 ml by evaporation at reduced pressure. The white solid which precipitated from the concentrated solution was collected with a fritted-glass disk and washed once with 10 ml of absolute ethanol and twice with 10-ml portions of ether to yield 0.155 g of white crystals (40% based on (COD)PtCl₂); mp 190 °C (dec, the crystals had turned a salmon color by ca. 145 °C and golden-brown by ca. 175 °C). The metalocycle was recrystallized by dissolving it in 20 ml of methylene chloride and adding 15 ml of absolute ethanol, and evaporating the methylene chloride by heating the solution on a steam bath until white crystals appeared. Cooling the solution slowly to room temperature and then to -20 °C gave more white crystals which were collected and washed with 10 ml of absolute ethanol and 10 ml of ether. After air drying, the product weighed 0.125 g. An additional crop of crystals weighing 0.015 g was recovered when the volume of the mother liquor was further reduced to 10 ml. Any solvent of recrystallization was removed by pumping on the product overnight at 0.01 Torr in an Abderhalden apparatus containing refluxing methylene chloride. The purified product has mp 197 °C (dec; the crystals turned a salmon color ca. 145 °C and a gold-brown color ca. 180 °C); NMR (2:1 mixture of CD₂Cl₂ and pyridine-*d*₅) δ 1.0–2.0 (m peaking at δ 1.55, 4 H, -(CH₂)₄-), 7.0–7.77 (m with two prominent peaks at δ 7.22 and 7.40, 15 H, aromatic); ir (CH₂Cl₂) 2875 m, 2820 m, 1476 m, 1430 and 1418 md, 993 cm⁻¹.

Anal. Calcd for C₄₀H₃₈P₂Pt: C, 61.93; H, 4.94. Found: C, 61.69; H, 5.15. Mol wt. Calcd: 775.74. Found: 750 (CHCl₃).

1,5-Pentamethylenebis(triphenylphosphine)platinum(II) (2). To a stirred suspension of (COD)PtCl₂ (0.187 g, 0.5 mmol) in 25 ml of ether and 15 ml of tetrahydrofuran at -50 °C was added 1.35 ml (0.53 mmol) of a tetrahydrofuran solution (0.78 N) of pentane-1,5-di(magnesium bromide). The reaction mixture was allowed to warm slowly to 0 °C over 30 min and then stirred an additional 60 min between -10 and 0 °C to give a brown solution. The reaction mixture was worked up and added to triphenylphosphine following procedure analogous to that used to make **1** to give 0.177 g of white crystals (45% based on (COD)PtCl₂). The metalocycle was recrystallized by dissolving it in 15 ml of methylene chloride, adding 10 ml of absolute ethanol, and evaporating the methylene chloride by boiling the solution on a steam bath until white crystals appeared. The solution was cooled slowly to room temperature and then to -20 °C to give more white crystals which were collected and washed with 10 ml of absolute ethanol and then 10 ml of chilled ether. After air drying, the product weighed 0.15 g. By concentrating the mother liquor to 8 ml, an additional 0.012 g of white crystals was recovered. Any solvent of recrystallization was removed by pumping on the product overnight at 0.01 Torr in an Abderhalden apparatus containing refluxing acetone. The purified product had mp 188 °C (dec; the crystals turned pink by ca. 160 °C and golden-brown by ca. 180 °C); NMR (CD₂Cl₂) δ 0.66–1.67 (m with two overlapping broad peaks at δ 0.88 and 1.5, 1 H, -(CH₂)₅-), 6.9–7.6 (m with two prominent peaks at δ 7.20 and 7.35, 3 H, aromatic); ir (CHCl₃) 3000 mb, 2880 mb, 2815 mb, 1475 s, 1430, 1091 s cm⁻¹.

Anal. Calcd for C₄₁H₄₀P₂Pt: C, 62.35; H, 5.11. Found: C, 62.48; H, 5.29. Mol wt. Calcd: 789.76. Found: 880 (CHCl₃).

The metalocycle was purified further by using preparative thin-layer chromatography. Elution of the pentamethylene metalocycle (0.1 g) with methylene chloride on a 1000 μ thick silica gel plate gave

one band (R_f 0.8) which was scraped from the plate. The product was removed from the silica gel using a 1:1 solution of methylene chloride and methanol. Two recrystallizations from methylene chloride-ethanol solutions yielded 0.6 g of pure sample having mp 187 °C (dec).

Anal. Calcd for $C_{41}H_{40}P_2Pt$: C, 62.35; H, 5.11. Found: C, 62.16; 62.43; H, 5.01, 5.05. Mol wt. Calcd: 789.76. Found: 800 ($CHCl_3$).

1,4-Tetramethylenebis(triphenylphosphine)platinum(II) (1) and 1,5-pentamethylenebis(triphenylphosphine)platinum(II) (2) were prepared using similar procedures, illustrated here for **1**. Bis(triphenylphosphine)platinum(II) dichloride (0.802 g, 1.01 mmol) was stirred in 40 ml of diethyl ether at 0 °C. An ether solution of 1,4-dilithiobutane (1.5 mmol) was added by syringe and the solution stirred for 10 min at 0 °C, then allowed to warm to room temperature over an additional 20 min. A white precipitate was collected after adding water to the reaction mixture. The precipitate was washed with water and ethanol. Recrystallization⁴¹ from EtOH- CH_2Cl_2 gave white crystals, 0.48 g (62%) of **1**, mp (dec in vacuo) 235–237 °C.

Metallocycle **2** was prepared in an analogous manner in 70% yield.

1,6-Hexamethylenebis(triphenylphosphine)platinum(II) (3). To a stirred suspension of (COD)PtCl₂ (0.187 g, 0.5 mmol) in 25 ml of distilled, anhydrous tetrahydrofuran at 5 °C was added 1.3 ml (0.54 mmol) of a tetrahydrofuran solution (0.80 N) of hexane-1,6-di(magnesium bromide). After 1.5 h, the solution contained a brown-black precipitate and had itself turned light brown. The reaction mixture was worked up and added to the triphenylphosphine following a procedure analogous to that used to make **1**, except that the filtered reaction solution was evaporated to dryness to yield a light yellow solid. Pentane (50 ml) was added and the flask heated on a steam bath until the pentane boiled. The yellow solid was scraped from the walls of the flask, and with vigorous stirring, the pentane extracted the yellow impurities leaving behind a white solid. The white product was collected in a funnel with a fritted-glass disk and washed four times with 20-ml portions of warm pentane to remove any unreacted triphenylphosphine. After air drying, it weighed 0.047 g. The white solid was stirred with 20 ml of acetone and filtered to give a clear solution which, upon evaporation, yielded 0.026 g of the desired metallocycle (3.2% based on (COD)PtCl₂). The metallocycle was recrystallized by dissolving it in 10 ml of acetone, adding 10 ml of absolute ethanol, and slowly evaporating the acetone at reduced pressure. This procedure gave 0.020 g of microcrystalline white powder having mp 135 °C (dec), the white solid had turned dark red ca. 120 °C): NMR ($CDCl_3$) δ 0.6–1.8 (m peaking at δ 1.0, 2 H, $-(CH_2)_6-$) 7.0–7.7 (m with two prominent peaks at δ 7.30 and 7.47, 5 H, aromatic); ir ($CHCl_3$) 3025 mb, 2910 s, 1476 s, 1105 s cm^{-1} .

Anal. Calcd for $C_{42}H_{42}P_2Pt$: C, 62.75; H, 5.27. Found: C, 63.00; H, 5.41. Mol wt. Calcd: 803.79. Found: 800 (acetone).

1,4-Tetramethylene(1,2-diphenylphosphinoethane)platinum(II) (4) was prepared from **1** by displacement of PPh₃ by diphos. A 0.13-mmol sample of **1** was dissolved in 10 ml of CH_2Cl_2 with 0.064 g (0.16 mmol) of diphos. The reaction was monitored by NMR. Free PPh₃ could be detected after 15 min. The one unobscured peak due to complexed PPh₃ at δ 7.22 had disappeared after 24 h. No further change in the spectrum was observed after 40 h. The solvent was removed at reduced pressure leaving a clear oil. Addition of absolute ethanol caused the oil to solidify. The solid was collected and washed thoroughly with ethanol. Recrystallization from EtOH- CH_2Cl_2 yielded 0.043 g (53%) of product having mp 242–247 °C and NMR ($CDCl_3$) δ 7.4, 7.3 (m, 20 H, Ph), 2.0–0.5 (m, 12 H).

Anal. Calcd for $C_{30}H_{32}P_2Pt$: C, 55.47; H, 4.96. Found: C, 55.23; H, 5.11.

1-Methyl-1,4-tetramethylenebis(triphenylphosphine)platinum(II) (5). To a stirred suspension of (COD)PtCl₂ (0.187 g, 0.5 mmol) in a solution of 30 ml of ether and 5 ml of tetrahydrofuran at –30 °C was added 2.0 ml (1.2 mmol) of a 0.60 N tetrahydrofuran solution of pentane-1,4-di(magnesium bromide). The reaction mixture was stirred for 1 h as the bath temperature slowly warmed to 10 °C. The light brown reaction mixture was worked up and added to triphenylphosphine following a procedure analogous to that used to make **1**, except that the resulting ether solution was evaporated without adding any absolute ethanol to give a clear, colorless viscous oil. The oily product was dissolved in 5 ml of methylene chloride and 40 ml of absolute ethanol was added. Complete evaporation of the methylene chloride at reduced pressure and a slow cooling to 0 °C gave white crystals which were collected, washed with 10 ml of absolute ethanol

and three 10-ml portions of pentane, and air-dried to give 0.24 g of product. Further concentration of the mother liquor to 20 ml by evaporation at reduced pressure yielded another 0.034 g for a total of 0.274 g (69% based on (COD)PtCl₂) of white crystalline product. The metallocycle was recrystallized by dissolving it in 5 ml of methylene chloride, adding 15 ml of absolute ethanol and evaporating the methylene chloride with gentle heating on a steam bath. Cooling slowly to room temperature and then to –30 °C gave white crystals which were collected, washed with absolute ethanol and pentane, and air-dried to give 0.24 g of product. Any solvent of recrystallization was removed by pumping on the crystalline product at 0.01 Torr in an Abderhalden apparatus containing refluxing acetone. The purified metallocycle has mp 176 °C (dec); the crystals turned a salmon color by ca. 140 °C, and deep red by ca. 170 °C): NMR ($CDCl_3$) δ 0.75–2.0 (m with three small sharp peaks at δ 0.88, 1.02, and 1.13 and with a larger peak at δ 1.55, 1 H, aliphatic), 6.8–7.6 (m, 3 H, aromatic); ir ($CHCl_3$) 3052 and 3005 md, 1478 s, 1433 s, 1153 w, 1090 s cm^{-1} .

Anal. Calcd for $C_{41}H_{40}P_2Pt$: C, 62.35; H, 5.11. Found: C, 62.41; H, 5.30. Mol wt. Calcd: 789.76. Found: 780 ($CHCl_3$).

Hexane-2,5-di(magnesium bromide). A portion of a 50-ml ether solution of 2,5-dibromohexane (6.6 g, 27 mmol) was added to a flame-dried flask containing 3.6 g of Mg turnings. After the reaction had initiated the remaining solution was added. The solution was stirred for 30 min until spontaneous refluxing had ceased, then refluxed an additional hour to ensure completion of the reaction. Two layers formed. The upper layer was reduced in volume by a stream of N₂ until the total volume was 20 ml. The solution was diluted with 130 ml of tetrahydrofuran. The Grignard reagent was filtered through a plug of Celite into an air-tight storage tube. Titration of a water quenched aliquot gave a total base concentration of 0.186 N (50%).

1,4-Dimethyltetramethylenebis(triphenylphosphine)platinum(II) (6). (Cyclooctadiene)platinum dichloride (0.28 g, 0.75 mmol) was suspended in 25 ml of diethyl ether at –50 °C by rapid stirring. Hexane-2,5-di(magnesium bromide) (0.8 mmol in 9 ml of tetrahydrofuran-ether) was introduced by syringe and the solution was stirred for 1 h at –20 °C. The solution was passed through a short silica gel column at –10 °C and the column washed with an additional 25 ml of Et₂O. The solution was decolorized with a small amount of charcoal, then filtered onto 0.40 g (1.55 mmol) of triphenylphosphine. After 30 min the solvent was removed at reduced pressure leaving a yellow solid which was washed with ethanol and pentane. The weight of crude product was 0.27 g. Recrystallization⁴¹ from EtOH- CH_2Cl_2 gave 0.20 g (33%) of colorless crystals having mp (dec in vacuo) 189–194 °C: NMR ($CDCl_3$) δ 7.47–7.26 (m, 30 H, P-Ph), 2.3–1.0 (m, 6 H, PtCHCH₂), 0.80 (m, 6 H, CH-CH₃). The multiplet at 0.80 has roughly the appearance of a triplet, but is in fact two overlapping doublets ($J = 7$ Hz) due to the presence of two isomers, epimeric with respect to the methyl groups; $J_{P-H} = 64$ Hz is also observed for the methyl groups.

Diethylbis(triphenylphosphine)platinum(II) (7), prepared by the method of Chatt and Shaw,⁴² was recrystallized⁴¹ from EtOH- CH_2Cl_2 , yielding product having mp (dec) 153–154 °C (lit. mp⁴³ 147–148 °C): NMR ($CDCl_3$) δ 7.4, 7.2 (m, 30 H, P-Ph), 1.7–0.2 (m, 10 H, $-CH_2CH_3$).

Anal. Calcd for $C_{40}H_{40}P_2Pt$: C, 61.77; H, 5.10. Found: C, 62.05; H, 5.20.

Di-*n*-butylbis(tri-*n*-butylphosphine)platinum(II) (8) was prepared as described previously.²²

1,4-Tetramethylenebis(tri-*n*-butylphosphine)platinum(II) (9). A 1.201-g (0.54 mmol) sample of (COD)PtCl₂ was stirred in 35 ml of ethyl ether and 10 ml of tetrahydrofuran. Seven milliliters of 0.095 M butane-1,4-di(magnesium bromide) was added at –50 °C. The solution was stirred for 40 min while warming to –15 °C. The reaction mixture was passed through a silica gel column at 0 °C. The column was washed with several additional volumes of ether. Tri-*n*-butylphosphine, 0.25 ml (1.1 mmol), was added by syringe and the solution was allowed to stand at 25 °C for 1 h. After decolorization with activated charcoal, the solvent was removed at reduced pressure leaving a light yellow oil. The oil was taken up in 10 ml of methanol. Water was added until a slight cloudiness persisted. Cooling overnight to –25 °C yielded 0.06 g (17%) of white needles, having mp 79–80 °C: NMR ($CDCl_3$) δ 2.4–1.0 (m, ~42 H, a broad unresolved signal with a maximum at 1.57), 1.1–0.7 (m, ~20 H, sharp signal at 0.98 due to $PC_3H_6-CH_3$).

Anal. Calcd for $C_{28}H_{62}P_2Pt$: C, 51.20; H, 9.51. Found: C, 51.38;

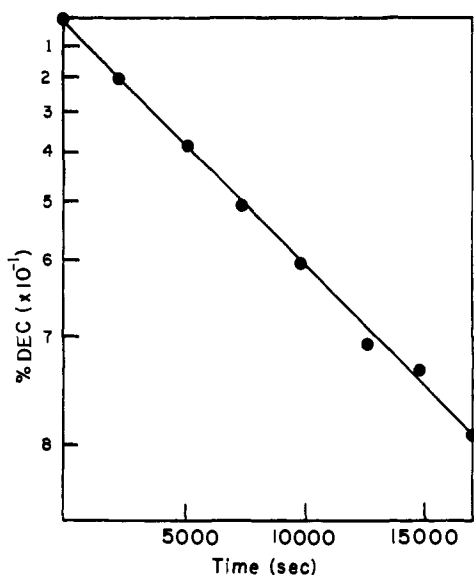


Figure 5. The thermal decomposition of **8** in methylene chloride at 50 °C.

H, 9.76.

Diethylbis(tri-*n*-butylphosphine)platinum(II) (10). A 0.375-g (1.0 mmol) sample of (COD)PtCl₂ was suspended in 25 ml of diethyl ether, -20 °C, by rapid stirring. An ether solution of EtMgBr (2.5 mmol) was added and the reaction mixture stirred for 45 min until a clear homogeneous solution of (COD)PtEt₂ was obtained. Tri-*n*-butylphosphine (0.5 ml, 2.2 mmol) was added and the solution was stirred an additional hour at 0 °C and the reaction quenched with water. The organic phase was dried and the solvent removed at reduced pressure leaving a yellow oil. The oil was dissolved in 10 ml of hot methanol which was quickly cooled to -70°, precipitating a white semisolid material after 30 min. The methanol was discarded. Fresh methanol (15 ml) was added to the solidified oil. Cooling to -25 °C with vigorous scratching caused crystallization to commence. The crystals grew at the expense of the oil during 24 h. The white needles were washed with pentane at -25 °C, and dried by pumping at 0.02 Torr. The compound is an oil at 25 °C, having mp 5 °C.

Thermolysis Reactions and Kinetics. Methods. Thermal decompositions employed 0.025 M solutions in methylene chloride or other solvent as noted. Internal standards were included in the stock solutions. Pyrex tubes of 6-mm o.d. were cut into 18-cm lengths, sealed at one end, washed with acetone and distilled water, and dried in an oven at 120 °C for at least 24 h. The tubes were cooled under dry nitrogen. About 0.3 ml of the solution to be thermolyzed was added to each tube by syringe. Care was taken to avoid contact of the solution with the upper part of the tube: otherwise pyrolysis products generated during sealing caused erratic results. The tubes were connected to a vacuum line (<0.005 Torr) and degassed through three freeze-thaw cycles. The sample was refrozen and the tube sealed under vacuum. The samples were then immersed in a thermostated oil bath constant to ±0.2 °C. The tubes were removed at intervals and quenched by immersion in liquid nitrogen. Chemical quenching was accomplished by opening the tubes and adding 0.3 ml of concentrated HCl or a fivefold excess of Br₂ (based on Pt) as appropriate, and closing with a No-Air stopper. Samples containing ethane or ethylene were stored at -78 °C until analyzed. The cold solutions were drawn into a 10-μl syringe and injected quickly into the gas chromatograph. First-order rate constants for decomposition of **8** on which Figure 4 is based are: *k*, s⁻¹ (temp, °C); 9.3 × 10⁻⁵ (50); 4.1 × 10⁻⁴ (60); 2.0 × 10⁻³ (70). Figure 5 gives a representative kinetic plot obtained in this work.

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- (40) (COD)PtCl₂ and BrMg(CH₂)₆MgBr react in tetrahydrofuran alone without showing signs of extensive decomposition.
- (41) Recrystallizations from CH₂Cl₂-EtOH were carried out in the following manner. A 1-g sample was dissolved in 15 ml of CH₂Cl₂ and placed on a steam bath. As the solvent boiled away, it was replaced by EtOH from a dropper to maintain the solution volume. This process was continued until the first sign of crystallization. The sample was allowed to slowly cool to 25 °C and then stored overnight at 3 °C.
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