THE MECHANISMS OF THERMAL DECOMPOSITION OF DIALKYLBIS(TRIETHYLPHOSPHINE)-PLATINUM(II) COMPLEXES.

George M. Whitesides

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 USA

Abstract - The thermal decomposition of dialkylbis(triethylphosphine)platinum(II) complexes provide examples of reactions in which unactivated C-H bonds react at a metal center of well-defined structure. An examination of a number of these reactions suggests a surprising similarity in mechanism: in most instances, the reactions proceed by initial dissociation of a phosphine and creation of a vacant coordination site, subsequent oxidative addition of a C-H bond to platinum, and final reductive elimination of alkane. The rate-limiting step can be either phosphine dissociation or reductive elimination of alkane; it does not seem to be the oxidative addition of a C-H bond to platinum. The implication that these intramolecular oxidative addition reactions are intrinsically rapid stands in clear contrast with the observation that intermolecular C-H addition to platinum is slow. Possible reasons for this difference are discussed.

INTRODUCTION

A number of synthetically important processes involving hydrocarbons (especially hydrogenation and reforming) are catalyzed heterogeneously by platinum metal. These reactions are generally believed to involve platinum surface alkyls, but neither structures nor reactivities of the intermediates involved in catalysis have been established. For a number of technical reasons, it is presently very difficult either to examine the mechanisms of heterogeneous reactions or to identify intermediates in these reactions. Their rationalization nonetheless is (or should be) a central concern in mechanistic chemistry, because they are of very great practical and economic importance. Since direct exploration of the chemistry of platinum surface alkyls is presently so difficult, in approaching the mechanistic problem of catalysis by platinum we have elected to examine instead the characteristics of soluble, complexed, platinum alkyls. We have placed particular emphasis on the study of the important class of reactions which break (and make) carbon-hydrogen bonds by oxidative addition to (and reductive elimination from) platinum, because these reactions are a part of many of the interesting catalytic processes. The relevance of these studies to any concerns in heterogeneous catalysis involving platinum of course remains to be established. They do, in any event, provide a body of information which clarifies the mechanisms of reaction types which are widely represented in homogeneous catalysis by transition metals (although not especially by platinum, whose utility in homogeneous catalysis is limited). In addition, they provide information which will be helpful in interpreting studies of the heterogeneous catalytic reactions involving platinum, as these are finally carried out.

RESULTS

The dialkylbis(phosphine)platinum(II) complexes (abbreviated L_2PtR_2 in this paper) were prepared by standard procedures outlined in Fig. 1. They are, in many but not all cases,
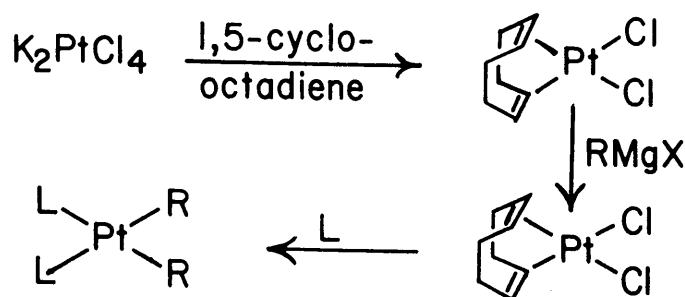
$$K_2PtCl_4 \xrightarrow{\text{1,5-cyclo-octadiene}}$$

Fig. 1. Preparation of dialkylbis(phosphine)platinum(II) complexes.
L_2PtR_2 (L = PEt_3 unless indicated otherwise).

air-stable substances which can be characterized by conventional techniques. When heated, those compounds having β-C-H bonds decompose by initial β-hydride elimination, generating an intermediate hydridoplatinum(II) alkyl moiety, followed by reductive elimination of alkane. Compounds containing neopentyl or other groups not subject to β-hydride elimination undergo a related type of reaction involving cleavage of a C-H bond from some accessible part of the molecule (either alkyl group or phosphine), followed by reductive elimination of alkane. In both types of reactions, the platinum(II) atom is transformed into a platinum(0) species.

We have restricted detailed mechanistic studies to reactions in which this platinum(0) complex, or some derivative formed from it in the reaction mixture, is soluble and stable under the reaction conditions: when deposition of platinum(0) occurs, or when a platinum(0) colloid forms, the reactions often become difficult to reproduce kinetically, and may show isotopic scrambling reflecting heterogeneous catalysis by this platinum metal.

Almost all of the β-hydride and intramolecular C-H oxidative addition reactions we have studied fit a common mechanistic pattern, exemplified in Fig. 2 by the most thoroughly studied example; viz., the β-hydride elimination reaction of $L_2Pt(CH_2CH_3)_2$. This mechanism
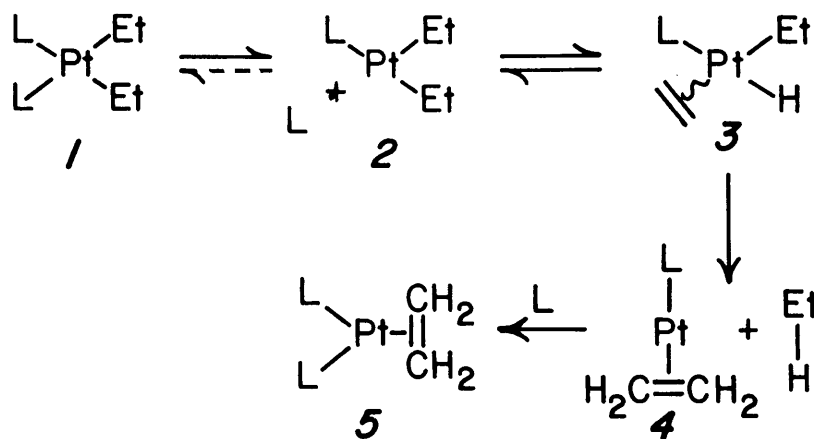
Fig. 2. Mechanism of thermal decomposition of L_2PtEt_2 in cyclohexane solution (T = 141 °C). Analogous mechanisms apply to other β-hydride elimination reactions.

has three important features. In describing these features, we refer to the concentration of triethylphosphine which has been added to the solution by [L]. Thus, [L] = 0 indicates that no triethylphosphine has been added; it does not indicate that there is no uncoordinated triethylphosphine in solution, since some (we believe only a small amount) dissociates from the phosphine-platinum complexes present in the reaction mixture. The inferred transition-state structures are summarized in Fig. 3.

i) When [L] = 0 M, the rate-limiting step is the dissociation of L from L_2PtEt_2.

ii) When [L] ∿ 0.3 M, the rate-limiting step appears to be the loss of ethane from the intermediate $LPt(H)(C_2H_4)Et$.

iii) When [L] is large (∿1.6 M) another mechanism becomes important in which the rate-limiting transition state has the elementary composition $L_2Pt(H)(C_2H_4)Et$. The details of the bond-breaking and bond-making involved in this transition state are not entirely clear, but we believe that loss of either ethane or ethylene is rate-limiting.

The evidence supporting these three mechanistic proposals is too lengthy to detail here, and has been described elsewhere (ref.1); only a summary is warranted. Similar, although less complete, arguments have been used to support an analogous mechanism for the decomposition
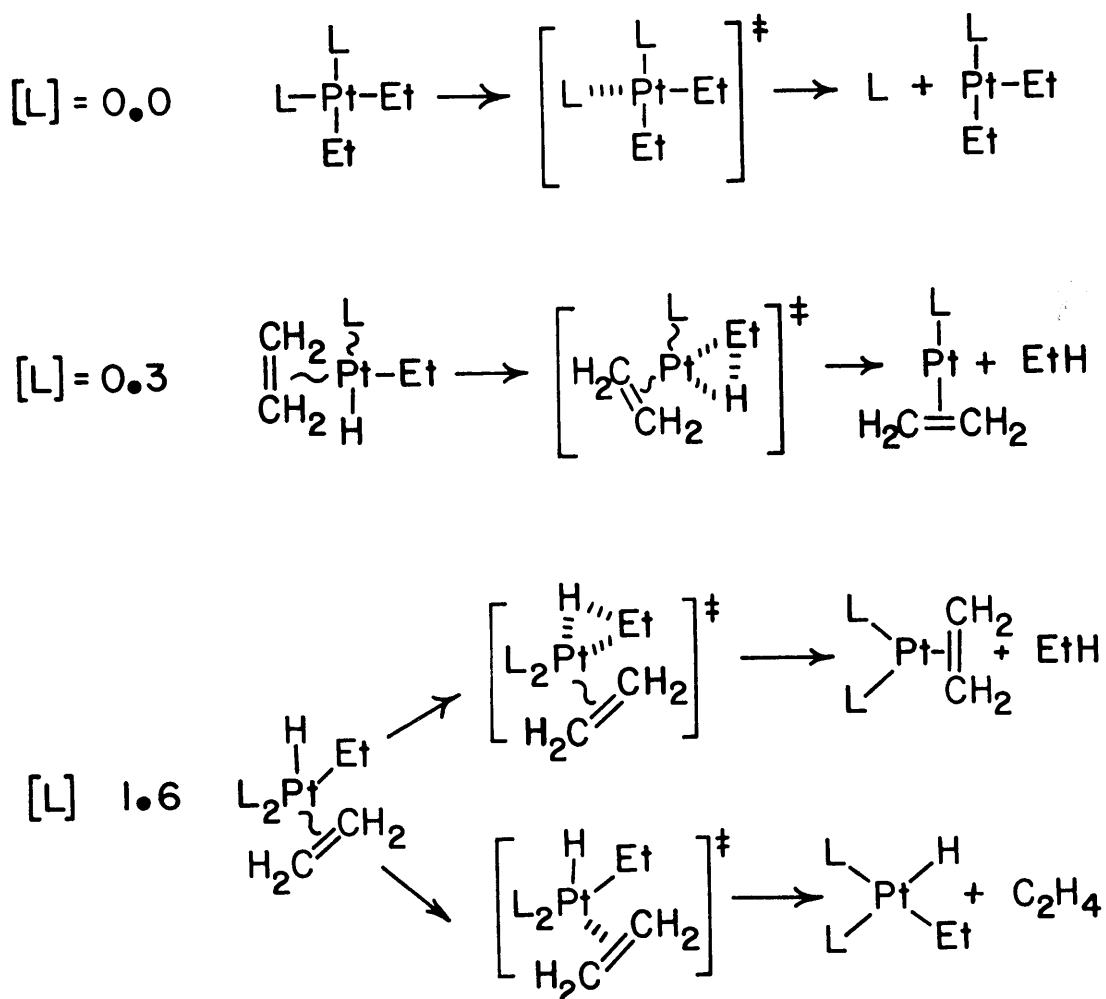

Fig. 3. Transition state structures for the decomposition of L_2PtEt_2 at different values of the concentration of added triethylphosphine [L].

of $(Bu_3P)_2PtBu_2$ (ref. 2), and several complexes of the structure $L_2Pt(cycloalkyl)_2$ (ref. 3). In brief, the assignment of mechanism in studies of $(Et_3P)_2PtEt_2$ rests on four types of experimental evidence:

i)   The dependence of its rate of decomposition on [L].

ii) The extent of scrambling of deuterium label in products and in recovered starting material in decompositions of $L_2Pt(CH_2CD_3)_2$.

iii) The magnitude of the deuterium kinetic isotope effect on the rate of decomposition of $L_2Pt(CD_2CD_3)_2$.

iv) The magnitude of the Arrhenius preexponential factor A for the decomposition.

The interpretation of the first three types of experimental data is straightforward, but that of the last deserves brief comment. We believe, from comparisons of a number of reactions of these types of organoplatinum compounds, that a value of log A = 14-16 indicates that two particles are being created from one in the transition state, and that log A ≃ 20 indicates that three particles are being formed from one. These interpretations, as all interpretations of thermodynamic terms of entropic origin, require a certain element of faith. We note, however, that the solvent reorganization that complicates the interpretation of entropic terms in reactions involving polar media should be largely absent in the cyclohexane solutions used in this work. Similar interpretations have been offered for other non-polar reactions (ref. 4).

The importance of this interpretation lies in the assignment of the rate-limiting step for [L] = 0.3 M. At this concentration of added triethylphosphine, the kinetic dependence of rate on [L] indicates that dissociation of L preceeds the rate-limiting transition state. The observed kinetic isotope effect (k_H/k_D ≃ 3) is compatible either with C-H bond-breaking or bond-forming in the transition state. We conclude that C-H bond-forming (i.e. reductive elimination of ethane from $LPt(H)(C_2H_6)Et$) is rate-limiting from the large value of the preexponential factor (log A ∿ 20). This conclusion is supported by the observation of extensive scrambling of deuterium in both products and starting materials derived from $L_2Pt(CH_2CD_3)_2$.

Application of these techniques to several other dialkylplatinum(II) complexes capable of β-hydride elimination yields data which form the basis for the mechanistic conclusions summarized in Table I. The rate-limited steps are assigned by analogy with the structures in Fig. 2; the extension of the structures in this scheme to those appropriate for other alkyls is obvious. The variation in the rate-limiting step in this series of dialkyl-

Table I. Activation Parameters and Mechanisms for Decomposition of L_2PtR_2 ([L] = 0.0 M, 35 °C).

L_2PtR_2	Rel Rate	E_a	log A	Mechanism	Rate-Limiting Step
$L_2Pt(C_2H_5)_2$	1.	29	14	Fig. 2	1 → 2
$(dmpe)Pt(C_2H_5)$				Unknown	
$L_2Pt(c\text{-}C_3H_5)_2$				Unknown	
$L_2Pt(c\text{-}C_4H_7)_2$	6×10^2	33	20	Fig. 2	3 → 4
$L_2Pt(c\text{-}C_5H_9)_2$	4×10^3	22	13	Fig. 2	1 → 2
$L_2Pt(CH_2C(CH_3)_3)_2$	1×10^{-5}	46	21	Fig. 4	8 → 9
$L_2Pt(CH_2C(CH_3)_2CH_2CH_3)_2$	4×10^{-1}	38	20	Fig. 4	8 → 9
$L_2Pt(CH_2C(CH_3)_3CH_2CH_2CH_3)_2$	4×10^{-2}	38	19	Fig. 4	8 → 9

platinum compounds seems to reflect the aggregate effect of two major influences: larger alkyl groups promote phosphine dissociation and accelerate decomposition; strained olefins form slowly.   The decomposition of $L_2Pt(\underline{c}-C_3H_5)_2$ probably also proceeds by a mechanism analogous to that in Fig. 2; its mechanism is, however, obscured by the instability of cyclopropene under the reaction conditions.   The mechanism of decomposition of $dmpePtEt_2$ is not understood.   The observation that a cyclohexane solution of this compound is more stable (by a factor of $\sim$ 4000) than a triethylphosphine solution of $(Et_3P)_2PtEt_2$ suggests that some factor more complex than the equilibrium constant for dissociation of a phosphine-platinum bond is responsible for the observed difference in rate of decomposition.   We suggest that the inability of the P-Pt-P bond angle of (dmpe)platinum to spread during the step which transforms platinum(II) to platinum(0) contributes to the stability of $(dmpe)PtEt_2$.

The decomposition of platinum complexes containing neopentyl and related alkyl groups follows a mechanistic pattern which is very similar to that observed in L_2PtEt_2 (ref. 5, 6).   Fig. 3 outlines the mechanism for $L_2Pt(CH_2C(CH_3)_3)_2$; Table I contains activation parameters.   The type of cyclometallation reaction shown in Fig. 4 proceeds readily for a number of related
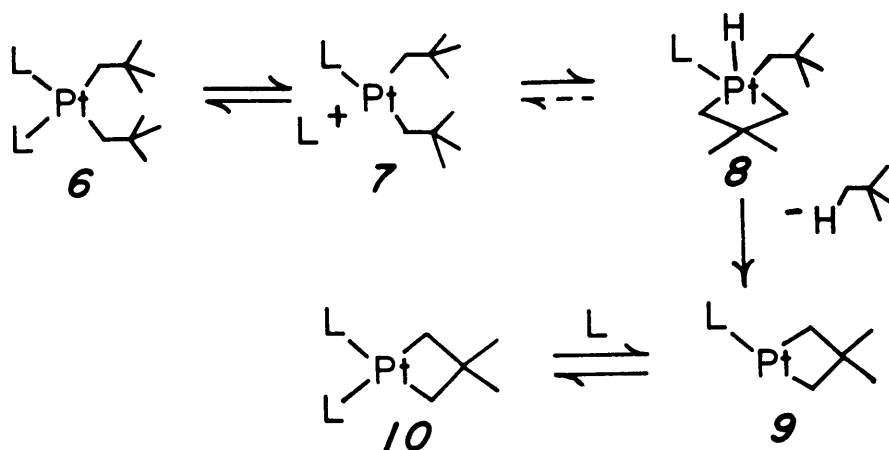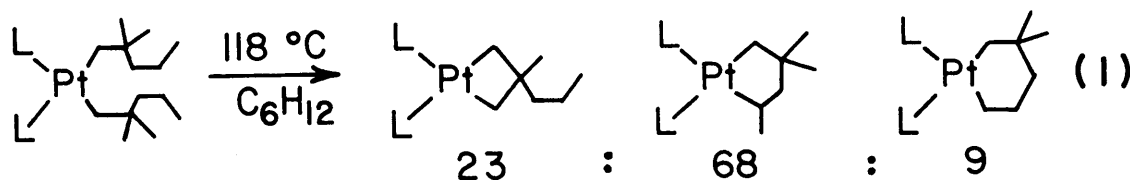

Fig. 4. Mechanism of thermal decomposition of dineopentylbis(triethyl-phosphine)platinum(II).

alkyls (ref. 6). A particularly interesting example is sketched in eq. 1. The significance of the products observed in this decomposition rests on the mechanistic inference that the

rate-limiting (and product-determining) transition states leading to these compounds (e.g. 11) already contain the platinacyclic rings which appear in the products. The relative
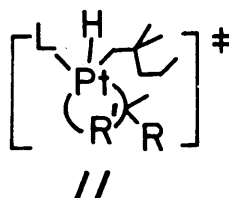
yields of products should therefore be closely related to the relative strain energies in these rings. Although quantitative estimates of ring strains based on these yields is not justified for several reasons, the qualitative observation that analogous platinacyclo-butanes, platinacyclopentenes, and platinacyclohexanes are generated in similar yields suggests that the spread in the values of ring strain in this series is less than 5 kcal mol^{-1}, and thus much less than the spread in the corresponding cycloalkanes ($\sim$ 27 kcal mol^{-1}). The inference that the platinacyclobutane ring has a low strain energy is helpful in rationalizing the relatively common occurence of metallocyclobutanes in organometallic reactions (ref. 7-9).

A current objective of work in transition metal catalysis is to clarify the processes by which metal surfaces cleave unactivated C-H bonds, and to suggest why analogous reactions are seldom observed using soluble metal complexes in solution. The facile cyclometallation reactions have the potential to contribute to this problem, because they do, in fact, cleave unactivated C-H bonds (albeit intramolecularly, rather than intermolecularly). It is particularly instructive to consider the conversion of a di(neopentyl)platinum(II) moiety into neopentane and a 2,2-dimethylplatinacyclobutane ring (6 → 10 + neopentane). This process proceeds in high yield. We cannot presently measure the magnitude of $\Delta G°$ for the reaction quantitatively, but qualitatively we have seen no evidence of its reversibility. A first step in understanding this reaction must be to rationalize the fact that it proceeds in the direction 6 → 10, and not vice versa. We suggest that, at present, it is not obvious what combination of factors provides the driving force for the reaction. As a first approximation, the sum of the bond energies remains unchanged during the reaction. Ring strain should favor 6, although we believe that ring strain is small (ref. 6). The observation that apparently similar cyclometallation reactions produce six-, five-, and four-membered platinacycles suggests that no particular stability is associated with the 2,2-dimethylplatinacyclobutane ring. What then remains? We note that at least three factors might contribute to the reaction:

  i)   the increase in entropy, reflecting the generation of two particles
       from one;

  ii) relief in non-bonded steric strain, resulting from expulsion of the
       large neopentyl moiety from the crowded molecule of 1;

  iii) favorable changes in local electronic energies, as the P-Pt-P bond
       angle spreads during reaction.

The origin of the driving force thus cannot be identified at present, but further study of this subject is warranted by its potential utility in clarifying the mechanistic origin of the difference between the rapid intermolecular cleavage of C-H bonds which occurs at a platinum surface, and the analogous, slow (in fact, unknown) reaction involving soluble platinum ions.

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