Thermal Decomposition of Di(cycloalkyl)bis(triethylphosphine)platinum(II) Complexes[1]

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Abstract: The thermal decompositions of three di(cycloalkyl)bis(triethylphosphine)platinum(II) complexes [cycloalkyl = cyclopropyl ($L_2Pt(c\text{-}C_3)_2$), cyclobutyl ($L_2Pt(c\text{-}C_4)_2$), cyclopentyl ($L_2Pt(c\text{-}C_5)_2$)] have been examined. The mechanisms of decomposition of $L_2Pt(c\text{-}C_4)_2$ and $L_2Pt(c\text{-}C_5)_2$ are similar to those established in greater detail for diethylbis(triethylphosphine)platinum(II). The individual steps in solutions containing low concentrations of free triethylphosphine are dissociation of triethylphosphine and creation of a vacant coordination site, β-hydride elimination, and reductive elimination of cycloalkane (Scheme I); either the first or the third of these steps may be rate limiting. At high [L], another path having two triethylphosphines on platinum in the rate-determining transition state is important. Both enthalpic and entropic terms are important in determining which mechanism for decomposition is followed. Thermal decomposition of $L_2Pt(c\text{-}C_3)_2$ is complex and is not presently understood: isomerization of *cis*-$L_2Pt(c\text{-}C_3)_2$ to *trans*-$L_2Pt(c\text{-}C_3)_2$, hydrogen transfer from L to the cyclopropyl group, and opening of the cyclopropyl ring are all competitive processes.

Introduction

The preceding paper summarizes a detailed study of the mechanism of thermal decomposition of diethylbis(triethylphosphine)platinum(II) in cyclohexane solution (Scheme I, R = H).[4] The products of this reaction are ethane and either ethylenebis(triethylphosphine)platinum(0) or tris- or tetrakis-(triethylphosphine)platinum(0), depending on the concentration of triethylphosphine present in solution. At least three different mechanisms are responsible for the production of these products. One (operating in solutions containing no added L) involves rate-limiting generation of a vacant coordination site on platinum by dissociation of L (1 → 2); a second (for [L] ~0.3 M) has reductive elimination of alkane as the rate-limiting step (3 → 4); a third (at [L] ≳1.6 M) is not entirely defined, but has a transition state with the elemental composition indicated by 5, and involves either reductive elimination of ethane or loss of ethylene as the rate-limiting step. The thermal decompositions of dipropylbis-(triethylphosphine)platinum(II)[4] and di(*n*-butyl)bis(triphenylphosphine)platinum(II)[5] appear to follow similar mechanisms, and the thermal conversion of dineopentylbis(triethylphosphine)platinum(II) to neopentane and bis(triethylphosphine)-3,3-dimethylplatinacyclobutane—a reaction involving cleavage of a γ-CH bond—also follows a related mechanistic path.[6]

The present paper describes a more qualitative survey of the thermal decompositions of di(cycloalkyl)bis(triethylphosphine)-platinum(II) complexes (cycloalkyl = cyclopropyl, cyclobutyl, and cyclopentyl). We conducted these studies for several reasons. First, in broad terms, we wish to understand the mechanisms of the elementary thermal reactions of platinum alkyls. These reactions (β-hydride elimination, olefin insertion into Pt–H bonds, reductive elimination of C–H and C–C bonds from platinum and oxidative addition of C–H bonds to platinum) are typical of important reactions in metal-catalyzed transformations of hydrocarbons. Platinum alkyls are tractable subjects for mechanistic studies, and results obtained with them are relevant to large-scale heterogeneous catalytic processes (especially re-forming) carried out over platinum metal.[7] Second, the di(cycloalkyl)platinum(II)

Scheme I. Mechanisms of Thermal Decomposition of L_2PtR_2 (L = Et_3P)
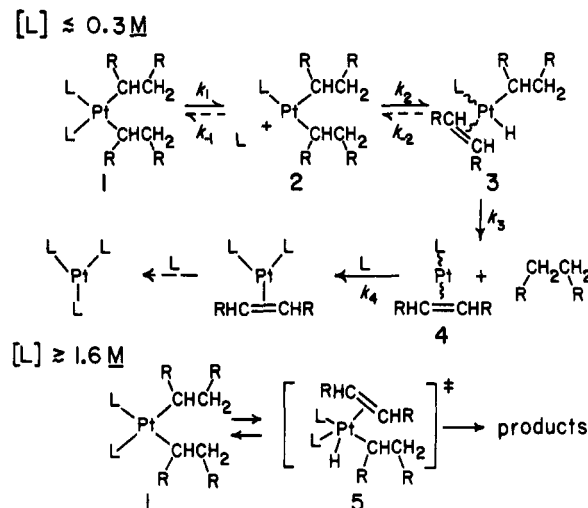
complexes have three structural characteristics which might result in mechanistically instructive differences in behavior from the di(*n*-alkyl)platinum(II) complexes examined previously: first, cycloalkyl groups are larger than *n*-alkyl groups, and might encourage phosphine dissociation;[8] second, cycloalkenes are generally poorer ligands for transition metals than ethylene,[9] and may be less successful in stabilizing intermediate metal–olefin complexes; third, cyclopropene and cyclobutene are strained olefins,[10] and their formation by β-hydride elimination at or before the rate-limiting transition state might be slow.

This study establishes that the mechanisms summarized in Scheme I for diethylbis(triethylphosphine)platinum(II) also describe the thermal decompositions of di(cycloalkyl)bis(triethylphosphine)platinum(II) complexes in which R = cyclobutyl and cyclopentyl. Thermal decomposition of di(cyclopropyl)bis(tri-

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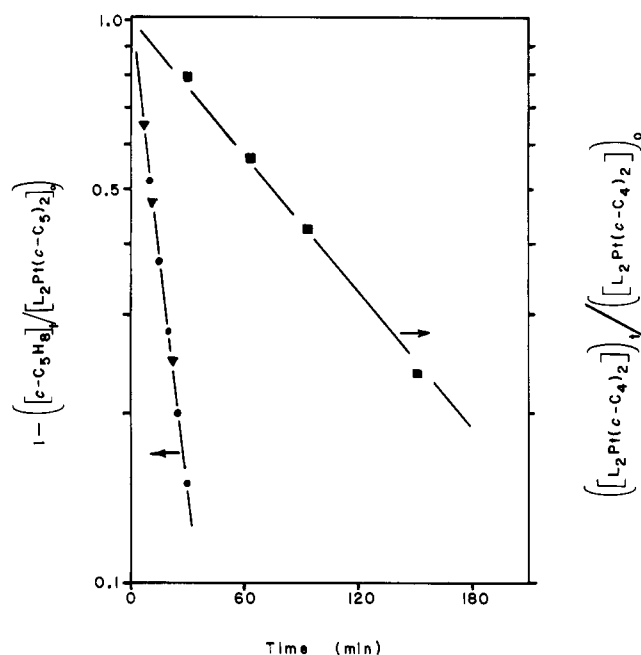
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(8) The influence of the size of nonphosphine ligands on the dissociation of phosphines has not been systematically studied. The influence of phosphine size on the properties of metal complexes has been reviewed: Tolman, C. A. *Chem. Rev.* 1977, 77, 313-348.

(9) Hartley, F. R. *Chem. Rev.* 1973, 73, 163-190. Brown, H. C.; Rei, M. *Chem. Commun.* 1969, 1296-1297.

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Table I. First-Order Rate Constants for Thermal Decomposition of L_2PtR_2 ($[L] = 0^a$) in Cyclohexane Solution

R	T, °C	$k_{L=0}^{obsd}$, s⁻¹	k_{35C}^{rel} [b]	probable rate-limiting step (Scheme I)[c]
c-C₄	35	1.6 × 10⁻⁴	6.1 × 10²	3 → 4; reductive elimination of RH
c-C₅	35	1.0 × 10⁻³	3.8 × 10³	1 → 2; dissociation of L
CH₂CH₃	147	4.7 × 10⁻² d		1 → 2; dissociation of L
	35	2.6 × 10⁻⁷ d	1	
CH₂C(CH₃)₃ d	147	1.2 × 10⁻³ e		reductive elimination of RH
	35	3.3 × 10⁻¹² e	1.3 × 10⁻⁵	
c-C₃	147	2.4 × 10⁻⁴ f		unknown

^{a} [L] = 0 indicates that no triethylphosphine has been added to the solution. ^{b} $k_{35°C}^{rel} = k_{L=0}^{obsd}$ (L_2PtR_2, 35 °C)/$k_{L=0}^{obsd}$ (L_2PtEt_2, 35 °C). ^{c} These assignments summarize arguments in the Discussion; vide infra. ^{d} Estimated from Arrhenius parameters reported in ref 4. ^{e} Estimated from Arrhenius parameters reported in ref 6. ^{f} Observed first-order rate constant for decomposition of a solution initially containing 72% *trans*- and 28% *cis*-$L_2Pt(c-C_3)_2$.

ethylphosphine)platinum(II) appears to involve several competing reactions, and important details of these processes remain obscure.

We refer to intermediates by reference to Scheme I; for example, RCH=CHR represents cycloalkenes when discussing these decompositions. We name the platinum complexes using abbreviated structures; for example, di(cyclopentyl)bis(triethylphosphine)platinum(II) is written $L_2Pt(c-C_5)_2$. Many of the experiments were carried out in solutions containing added triethylphosphine. The concentration of triethylphosphine in solution which would be calculated to result from this added material is represented by [L]. Thus, [L] = 0 indicates no triethylphosphine was added; it does *not* indicate that there is no free triethylphosphine in solution, since some (we believe only a very small amount) is formed by dissociation from the triethylphosphine-platinum complexes.

Results

Preparation of $L_2Pt(c-C_n)_2$. These complexes were prepared from dichloro(1,5-cyclooctadiene)platinum(II), the appropriate Grignard reagent, and triethylphosphine by modifications of procedures reported previously.[11,12] $L_2Pt(c-C_3)_2$ is stable indefinitely as a solid at room temperature. $L_2Pt(c-C_4)_2$ and $L_2Pt(c-C_5)_2$ are less stable. They can, however, be handled in air at room temperature for several hours without decomposition. No decomposition was apparent after 3 months of storage at −10 °C. Efforts to prepare $L_2Pt(c-C_6)_2$ and $L_2Pt(i-Pr)_2$ led to complexes which were too unstable to be used in mechanistic studies without special effort. This effort did not seem justified and the study of these complexes was not pursued, but the qualitative observation that they are unstable relative to $L_2Pt(c-C_n)_2$ ($n = 3, 4, 5$) provides useful supporting detail for the proposed mechanism and is discussed below. Complexes were characterized by using ³¹P and ¹H NMR spectroscopy, by examining the products of thermolysis and treatment with HCl, and by performing elemental analysis.

Products of Thermal Decomposition. All thermal decompositions were homogeneous; no platinum metal was deposited, and the solutions ranged from clear to yellow at their conclusion. The rates of thermal decomposition were similar in several hydrocarbon solvents (cyclohexane, toluene, pentane, benzene); cyclohexane was used because it is easily purified, nontoxic, and available in perdeuterated form (for ¹H NMR). Reactions seemed insensitive to low concentrations of impurities.

In a representative experiment, $L_2Pt(c-C_4)_2$ (0.05 M in cyclohexane) was decomposed in a sealed tube at 40 °C for >4 h (>3 half-lives). GLC analysis showed a 1:1 mixture of cyclobutane and cyclobutene, with a yield of 96% based on alkyl groups in the starting platinum complex (Scheme II). No C₈ products were detected. The ³¹P NMR spectrum showed a single compound with $J_{P,Pt}$ = 3418 Hz, as expected[13,14] for $L_2Pt(cyclobutene)$. Decom-

Scheme II

position of $L_2Pt(c-C_5)_2$ at 35 °C also yielded the expected 1:1 mixtures of cyclopentane and cyclopentene as determined by GLC analysis. The ³¹P NMR spectrum showed *no* resonances, probably because of interchange between cyclopentene groups free in solution and those coordinated with $L_2Pt(0)$ with concomitant ³¹P line broadening.[15] Thermal decomposition of $L_2Pt(c-C_3)_2$ proceeded much more slowly than decompositions of $L_2Pt(c-C_4)_2$ or $L_2Pt(c-C_5)_2$. Thermolysis at 148 °C in cyclohexane produced homogeneous, amber solutions containing a complex mixture of platinum(0) complexes. These solutions contained $L_3Pt(0)$ as a major product. Examination by {¹H} ³¹P NMR at −55 °C of a sample decomposed in toluene showed overlapping platinum-(0)-coupled resonances ($\delta \simeq 22$–18 ppm, exchange broadened in the ambient temperature spectrum) as well as small quantities of L_4Pt^0. We have assigned one minor set of peaks to propylenebis(triethylphosphine)platinum(0);[14] the nature of other soluble platinum-containing species was not established. Analysis by GLC showed the presence of cyclopropane and propene corresponding to 1 equiv of the alkyl groups initially bound to platinum. The exact ratio of these products was found to vary unpredictably from run to run and with the duration of heating. Cyclopropane was the major component; cyclopropene, either as a platinum complex[13,16] or free in solution, was not detected. This olefin would be expected to polymerize under the thermolysis and GLC analysis conditions,[17] and it is unclear whether it would have been detected if it were a product. The formation of propene is suppressed when decompositions are carried out in the presence of added L.[18] Examination of {¹H} ³¹P NMR spectra of partially decomposed samples showed that *trans*-dicyclopropylbis(triethylphosphine)-

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(15) Exchange broadening of ³¹P NMR resonances in phosphine complexes of Pt(0) has been observed previously.[13,14] The nature of possible equilibria involved in this system has not been established.

(16) Several transition metal–cyclopropene complexes have been reported: Fredericks, S.; Thomas, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 350–351; Visser, J. P.; Schipperijn, A. J.; Lukas, J. *J. Organomet. Chem.* **1973**, *47*, 433–438.

(17) Closs, G. L. In "Advances in Alicyclic Chemistry", Hart, H.; Karabatsos, G. J., Eds.; Academic Press: New York, 1966; pp 53–127 and references cited therein.

(18) A separate experiment, in which $L_2Pt(c-C_3)_2$ was heated in the presence of cyclopropane without decomposition, showed that the starting complex does not catalyze the isomerization of cyclopropane to propene. The chemistry underlying its formation is not understood.

Figure 1. Thermal decomposition of $L_2Pt(c\text{-}C_n)_2$ (n = 4, 5) in cyclo-hexane solution (T = 35 °C). Kinetics for decomposition of $L_2Pt(c\text{-}C_4)_2$ was obtained by following the disappearance of starting material by {^1H} ^{31}P NMR; the kinetics of the decomposition of $L_2Pt(c\text{-}C_5)_2$ as obtained by following the appearance of cyclopentane by GLC: for ▼, $[L_2Pt(c\text{-}C_5)_2]_0$ = 0.01 M; for ●, $[L_2Pt(c\text{-}C_5)_2]_0$ = 0.02 M.

Figure 2. Corrected rate constants k_L plotted according to eq 1 for the thermal decomposition of $L_2Pt(c\text{-}C_5)_2$ in cyclohexane solution at 35 °C.

platinum(II) (δ 14.1, $J_{Pt,P}$ = 3111 Hz) is formed during the decomposition at a rate greater than that of decomposition. At lower temperatures (125 °C), ~75% of $cis\text{-}L_2Pt(c\text{-}C_3)_2$ is converted to $trans\text{-}L_2Pt(c\text{-}C_3)_2$ without significant further decomposition to hydrocarbons and platinum(0) products.

Kinetics. The disappearance of $L_2Pt(c\text{-}C_3)_2$ and $L_2Pt(c\text{-}C_4)_2$ were followed by {^1H} ^{31}P NMR spectroscopy; the appearance of cyclopentene from $L_2Pt(c\text{-}C_5)_2$ was followed by GLC. Decompositions of $L_2Pt(c\text{-}C_4)$ and $L_2Pt(c\text{-}C_5)_2$ follow first-order kinetics to greater than 3 half-lives (eq 1, Figure 1). Observed rate

$$-d\left[L_2Pt(c\text{-}C_n)_2\right]/dt = k_L^{obsd}\left[L_2Pt(c\text{-}C_n)_2\right] \qquad (1)$$

$$k_L^{obsd} = \frac{k_1 k_2 k_3}{k_{-1}(k_2 + k_3)[L] + k_2 k_3} + k' \qquad (2)$$

$$k_L^{-1} = (k_L^{obsd} - k')^{-1} \simeq [L]\left(k_{-1}(k_2 + k_3)/k_1 k_2 k_3\right) + 1/k_1 k_2 \qquad (3)$$

constants at a given concentration of added triethylphosphine, k_L^{obsd}, were independent of the concentration of the starting platinum complex. Table I lists rate constants obtained at [L] = 0, together with rate constants from other work for comparison. The listing of probable rate-limiting steps at [L] = 0 is based on arguments developed below.

Addition of triethylphosphine to solutions of $L_2Pt(c\text{-}C_5)_2$ inhibits the decomposition of this substance, as it does for L_2PtEt_2, $L_2Pt(CH_2C(CH_3)_3)_2$, and other complexes. Analysis of the kinetic data obtained by adding L followed the procedure outlined previously;[4] numerical values for the rate constants are summarized in the Experimental Section. Assuming **3** → **4** (Scheme I) to be rate limiting, eq 2 holds.[4,6] In this equation, k_L is the rate constant for the phosphine-dependent path for decomposition (1 → **4** → products, Scheme I) and k' is the rate constant for the decomposition pathway observed at high values of [L], where rate is independent of [L] (1 ⇌ **5** → products, Scheme I). Figure 2 shows the rate data for $L_2Pt(c\text{-}C_5)_2$ plotted according to eq 3; k' was taken as 1.5 × 10^{-4} s^{-1} from the plateau observed for [L] ≥ 0.3 M on a plot of k_L^{obsd} as a function of [L].
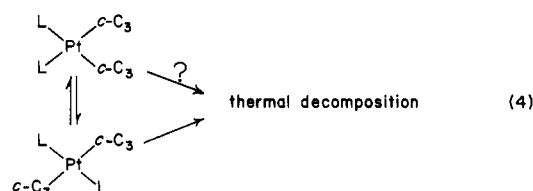
complete; the trans isomer is the major product, constituting 72–75% of the reaction mixture. No equilibration in the ratio of cis to trans isomers was observed at ambient temperatures over several months. Isomerization of cis- to $trans\text{-}L_2Pt(c\text{-}C_3)_2$ follows first-order kinetics to ~35% remaining starting material; at higher conversion the rate decreases sharply suggesting an approach to equilibrium. The observed rate of isomerization at 138 °C with [L] = 0.65 M is indistinguishable from that found in the absence of added L. At 147 °C, significant decomposition to Pt(0) and hydrocarbons occurs. Figure 3 shows kinetics plots for decomposition of four samples: two originally containing pure $cis\text{-}L_2Pt(c\text{-}C_3)_2$, [L] = 0.00 M; a third pure $cis\text{-}L_2Pt(c\text{-}C_3)_2$, [L] = 0.20 M; and the fourth a mixture of 28:72 cis:trans, [L] = 0.00 M. Kinetics for decomposition of the mixture are first order to greater than 2 half-lives. Decomposition of solutions containing pure cis complex [L] = 0.00 M does not follow a simple first-order rate law; a slow initial rate increases to a limiting value indistinguishable from that found for the 28:72 cis:trans mixture. As shown in Figure 3, this increase in rate occurs during the part of the decomposition characterized by isomerization of cis- to $trans\text{-}L_2Pt(c\text{-}C_3)_2$. The disappearance of $cis\text{-}L_2Pt(c\text{-}C_3)_2$ thus appears to occur in two stages: an initial, rapid isomerization of $cis\text{-}L_2Pt(c\text{-}C_3)_2$ to $trans\text{-}L_2Pt(c\text{-}C_3)_2$, followed by thermal decomposition of the trans isomer. It is unclear whether the cis isomer is itself decomposing under these conditions.[19]

Arrhenius activation parameters were determined for isomerization of $L_2Pt(c\text{-}C_3)_2$, and for decomposition of $L_2Pt(c\text{-}C_4)_2$ ([L] = 0.0 M) and $L_2Pt(c\text{-}C_5)_2$ ([L] = 0.0 and 0.55 M). The last value of [L] lies within the range in which the rate of decomposition of $L_2Pt(c\text{-}C_5)_2$ is independent of [L]. Figure 4 shows Arrhenius plots; Table II summarizes the activation parameters.

Deuterium Labeling Studies. Heating a benzene-d_6 solution of $cis\text{-}L^D_2\text{-}Pt(c\text{-}C_3\text{-}1\text{-}d_1)$ (L^D = $Et_3P\text{-}d_{15}$) at 147 °C for 10 min results in the formation of the trans complex without evident scrambling of the deuterium label (Figure 5). At 139 °C, there is no detectable deuterium kinetic isotope effect (k_H/k_D = 1.1 ± 0.3) on the conversion of cis- to $trans\text{-}L_2Pt(c\text{-}C_3)_2$; this process occurs equally rapidly with cyclopropyl and cyclopropyl-d_5 ligands. At

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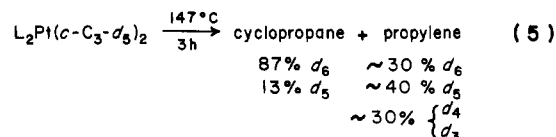(19) The details of the dependence(s) of the rates of thermal decomposition of $L_2Pt(c\text{-}C_3)_2$ on [L] have not been established.
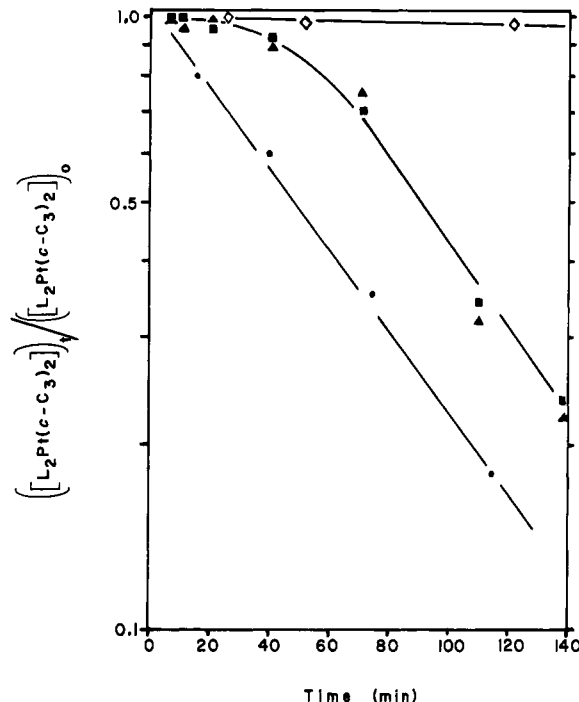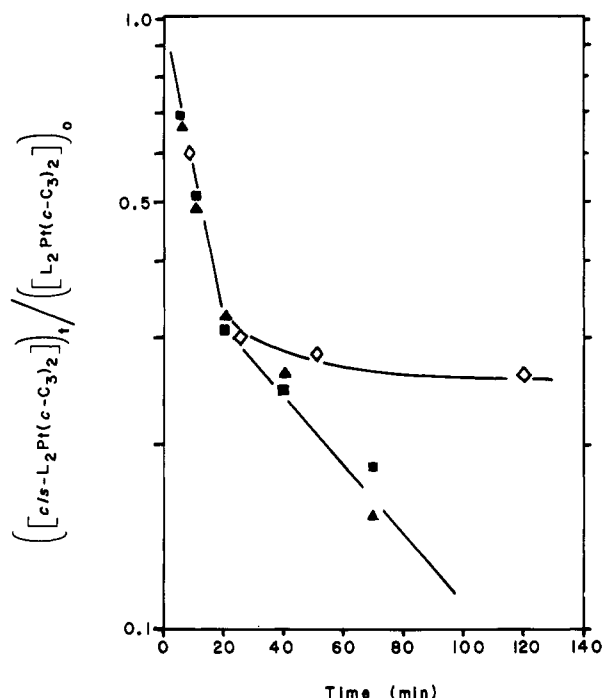
Figure 3. Kinetics for the isomerization and thermal decomposition at 147 °C: ■, ▲ initially cis-$L_2Pt(c\text{-}C_3)_2$, $[L]$ = 0.00 M; ◊ initially cis-$L_2Pt(c\text{-}C_3)_2$, $[L]$ = 0.20 M; ● initially 28:72 $cis\text{-}:trans\text{-}L_2Pt(c\text{-}C_3)_2$. In the above plots $[L_2Pt(c\text{-}C_3)_2]_t = [cis\text{-}L_2Pt(c\text{-}C_3)_2]_t + [trans\text{-}L_2Pt(c\text{-}C_3)_2]_t$.

Table II. Arrhenius Activation Parameters for Thermal Decompositions (TD) and Isomerizations (I) of L_2PtR_2 [a]

R	reaction	[L], M	$\log A$ [b]	E_a, kcal mol⁻¹ [b]
c-C₄	TD	0.00	20 ± 2	33 ± 3
c-C₅	TD	0.00	13 ± 2	22 ± 2
	TD	0.55	14 ± 2	24 ± 3
CH₂CH₃ [c]	TD	0.00	14 ± 1	29 ± 2
	TD	0.30	22 ± 2	46 ± 3
	TD	1.64	16 ± 1	37 ± 3
CH₂C(CH₃)₃ [d]	TD	0.00	20 ± 1	44 ± 2
c-C₃	I	0.00	16 ± 1	36 ± 1

[a] All reactions were carried out in cyclohexane solution using $[L_2PtR_2]_0 \simeq 0.05\text{-}0.10$ M. The isomerization refers to cis-$L_2Pt(c\text{-}C_3) \rightarrow trans$-$L_2Pt(c\text{-}C_3)_2$. [b] Errors were determined from standard deviations of least-squares slopes and intercepts by methods identical with those described earlier.[4] [c] Data from ref 4. [d] Data from ref 6.

147 °C the platinum complexes decompose irreversibly. Under these conditions, $k_H/k_D \simeq 1.3$ (again measured using cyclopropyl- and cyclopropyl-d_5 ligands with initial ratios of cis:trans equal to 28:72). Thermolysis of $L_2Pt(c\text{-}C_3\text{-}d_5)_2$ in C_6H_{12} yields the isotopic distributions shown in eq 5.

$$L_2Pt(c\text{-}C_3\text{-}d_5)_2 \xrightarrow[\text{3h}]{147\,°C} \text{cyclopropane} + \text{propylene} \quad (5)$$

87% d_6 ~30 % d_6
13% d_5 ~40 % d_5
        ~30% {d_4 d_3}

Control experiments using $L_2Pt(c\text{-}C_3)_2$ in cyclohexane-d_{12} and $L^D_2Pt(c\text{-}C_3)_2$ in cyclohexane-d_0 established the triethylphosphine ligands as the origin of the hydrogen appearing in the cyclopropane of eq 5.[20] Thermal decomposition of $L_2Pt(c\text{-}C_3\text{-}l\text{-}d_1)_2$ gives cyclopropane with an isotopic composition of >90% d_1.

Triethylphosphine Exchange in $L_2Pt(c\text{-}C_3)_2$ Is Associative. In an attempt to confirm that the dissociation of L is faster for complexes containing bulky secondary alkyl groups than for those

(20) Attempts made to examine the reversibility of phosphine dissociation for $L_2Pt(c\text{-}C_5)_2$, $[L]$ = 0.0 M, have been unsuccessful. Reaction of $L_2Pt(c\text{-}C_5\text{-}l\text{-}d)_2$ with bromine gives cyclopentyl-d_1 bromide with deuterium scrambled. For the rationale underlying these experiments, see ref 4.
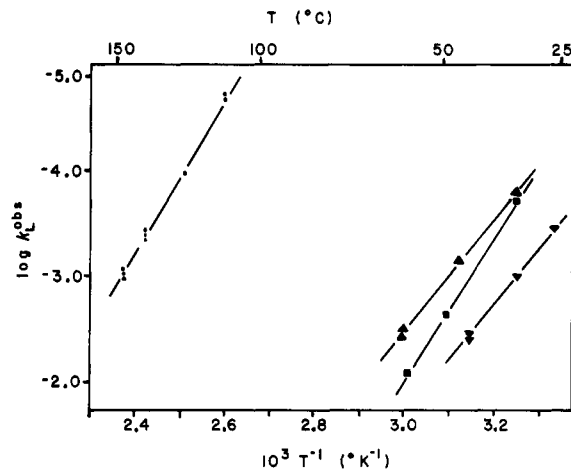
Figure 4. Arrhenius plots for thermal decompositions of $L_2Pt(c\text{-}C_4)_2$, $[L]$ = 0.0 M (■); $L_2Pt(c\text{-}C_5)_2$, $[L]$ = 0.55 M (▲); $L_2Pt(c\text{-}C_5)$, $[L]$ = 0.0 M (▼); and isomerization of cis-$L_2Pt(c\text{-}C_3)_2$ (●).

with smaller primary alkyl groups, we examined the rate of exchange of L^D for L in cis-$L_2Pt(c\text{-}C_3)_2$ and L for L^D in cis-$L^D_2Pt(c\text{-}C_3)_2$. $L_2Pt(c\text{-}C_3)_2$ was used for these experiments since it is the most stable thermally of the secondary alkyl complexes. Exchange of L for L^D in cis-$L_2Pt(c\text{-}C_3)_2$ at $[L^D] \simeq 0.8$ M is approximately 200 times faster than dissociation of L from L_2PtEt_2;[4] this conclusion was also confirmed by studying exchange of L for L^D in cis-$L^D_2Pt(c\text{-}C_3)_2$. These exchange reactions occur *without* conversion of cis-$L_2Pt(c\text{-}C_3)_2$ to $trans$-$L_2Pt(c\text{-}C_3)_2$. The rate of exchange of cis-$L^D_2Pt(c\text{-}C_3)_2$ increases, however, with increasing [L]. Thus, a solution with $[L] \simeq 0.4$ M, $[L^D_2Pt(c\text{-}C_3)_2] \simeq 0.5$ M exchanges at approximately half the rate as one with $[L]$ = 0.8 M. These results indicate that exchange of phosphine in $L_2Pt(c\text{-}C_3)_2$ occurs at least in part by a S_N2 (associative) mechanism. As a consequence, the rate of dissociation of phosphine ligands from this secondary alkyl complex can not be inferred from the rate of exchange of coordinated and noncoordinated phosphine. Exchange of L in $trans$-$L_2(c\text{-}C_3)_2$, $[L^D] \simeq 0.4$ M, occurs at a rate at least 100 times faster than that observed for the cis complex. We have not examined the kinetic order of this exchange.
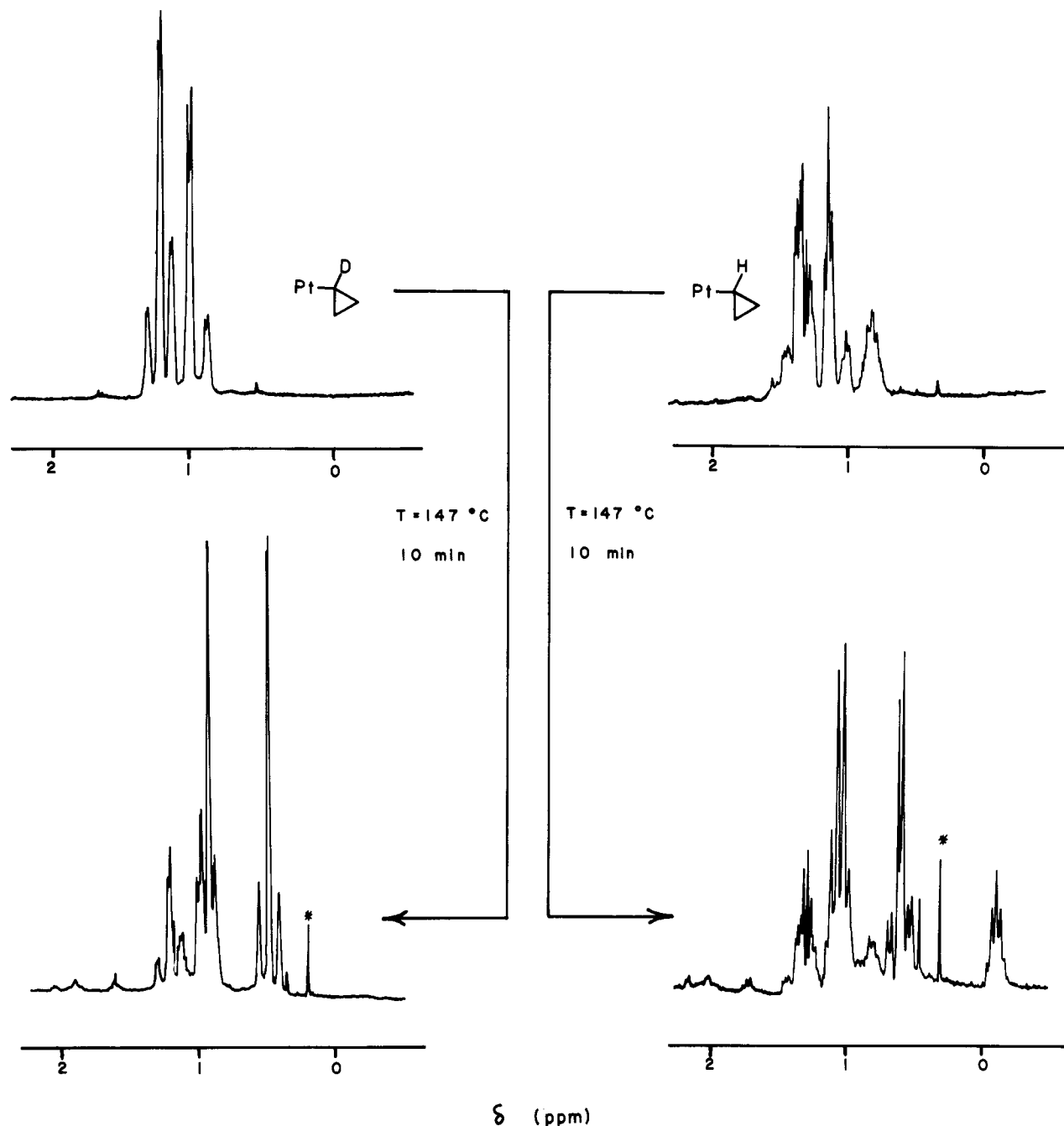
Figure 5. The 250-MHz NMR spectra of $L^D_2Pt(c\text{-}C_3\text{-}l\text{-}d_1)_2$ and $L^D_2Pt(c\text{-}C_3)_2$ in benzene-d_6 and the solutions produced contain the trans isomer as the major component; the asterisk indicates cyclopropane formed from partial decomposition of the starting complex (and/or products). The multiplet at -0.21 ppm in the spectrum of isomerized $L^D_2Pt(c\text{-}C_3)_2$ is the resonance for the c-C₃ hydrogen in the trans complex α to platinum. This resonance is absent in the deuterated complex indicating that the cis to trans isomerization does not equilibrate the position of ^2H in the c-C₃ moieties.

Trapping Platinum Hydride Intermediates in the Thermal Decomposition of $L_2Pt(c\text{-}C_5)_2$. Decomposition of $L_2Pt(c\text{-}C_5)_2$ in cyclohexane under ethylene yields the platinum-containing products shown in eq 6. A similar decomposition of $L_2Pt(c\text{-}C_5)_2$

$$L_2Pt(c\text{-}C_5)_2 \xrightarrow[\substack{c\text{-}C_6H_{12} \\ 40\,psi\,C_2H_4}]{25\,°C,\,1h} L_2Pt\!\!\begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array} + L_2PtEt_2 \quad (6)$$
$$ 20\% \qquad 80\%$$
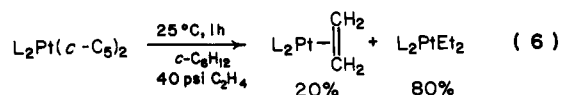
in the presence of a tenfold excess of 1,5-cyclooctadiene (6 °C, 48 h)[21] generated 74% cyclopentene and 26% cyclopentane (again based on two cyclopentyl groups), cyclooctene (96% based on the

quantity of hydrogen lost from the cyclopentyl groups), a 1:1 mixture of 1,3- and 1,4-cyclooctadiene, and a solution whose {¹H} ³¹P NMR spectrum showed the presence of a soluble platinum-(0)–phosphine complex whose structure we did not establish. When a similar experiment was carried out in the presence of 0.50 M L, the isomerization of 1,5-cyclooctadiene was blocked, and a 1:1 mixture of cyclopentane and cyclopentene formed. All of these observations are compatible with insertion of olefins into Pt–H bonds formed by β-hydride elimination from cyclopentyl-platinum moieties.

Discussion

Each of the complexes examined here decomposes by a mechanism having interesting features. We discuss each in turn.

$L_2Pt(c\text{-}C_5)_2$. This decomposition follows mechanisms closely analogous to those inferred previously for $L_2Pt(CH_2CH_3)_2$ (Scheme I). The experimental evidence supporting the proposed

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(21) Decomposition of $L_2Pt(c\text{-}C_5)_2$ in the presence of 1,5-COD was carried out at 6 °C in an attempt to characterize unstable Pt(II) alkyls which may have formed as intermediates. Analysis of these solutions by {¹H} ³¹P NMR showed only uncharacterized Pt(0) products.

Thermal Decomposition of (c-alkyl)₂L₂Pt

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mechanism comprises (i) the formation of equal quantities of cyclopentane, cyclopentene, and a platinum(0) complex as products of decomposition; (ii) first-order kinetics for decomposition; (iii) a linear dependence of $(k_L)^{-1}$ on [L]; (iv) the independence of k_L^{obsd} on [L] for large [L] (>0.3 M); (v) an Arrhenius preexponential factor at values of [L] for which k^{obsd} is independent of [L] (log $A = 14 \pm 2$, [L] > 0.5 M) which is similar to that for L_2PtEt_2 in the same kinetic regime (log $A = 16 \pm 1$, [L] > 1.64 M); (vi) the trapping of intermediate platinum hydrides with ethylene and other olefins; (vii) an Arrhenius preexponential factor (log $A = 13 \pm 2$) and activation energy $E_a = 22 \pm 2$) at [L] = 0 consistent with rate-limiting phosphine dissociation. All of these observations parallel observations made for L_2PtEt_2, and their interpretation is also parallel.

We note that there are two qualitative differences between the kinetic behavior of these compounds. First, the decomposition of $L_2Pt(c\text{-}C_5)_2$ is 10^3–10^4 faster than that of L_2PtEt_2 at all values of [L]. Second, the rate of decomposition of $L_2Pt(c\text{-}C_5)_2$ becomes independent of [L] at values less than one-third those required to reach the same kinetic regime for L_2PtEt_2. We hypothesize that the high rate of decomposition of $L_2Pt(c\text{-}C_5)_2$ in the kinetic regime in which rate depends on [L] ($0 \leq$ [L] ≤ 0.3 M) is due to an increased rate and extent of dissociation of L. The same effect should be important for other bulky secondary alkyl groups, and the low stabilities of $L_2Pt(c\text{-}C_6)_2$ and $L_2Pt(i\text{-}Pr)_2$ are qualitatively in accord with this suggestion. The increased rate of decomposition of $L_2Pt(c\text{-}C_5)_2$ relative to L_2PtEt_2 at high concentrations of added L ([L] > 2 M) presumably reflects the same underlying structural origin, viz., relief, in the transition state, of steric congestion in the ground state. Here, however, detailed analysis is more difficult, since the structure of the transition state in this regime is still unclear. We cannot presently rationalize the value of [L] at which the rate becomes independent of [L]. The rate-limiting step is almost certainly (by analogy with L_2PtEt_2) decomposition of 5 ($L_2Pt(R)(H)(olefin)$), either by loss of RH or by loss of olefin. Until the transition state is defined more clearly it is useless to speculate on its response to steric effects.

$L_2Pt(c\text{-}C_4)_2$. At [L] = 0, this complex decomposes more rapidly than L_2PtEt_2, but the high value of log $A = 20 \pm 2$ suggests that reductive elimination of cyclobutane (3 → 4) is the probable rate-limiting step, rather than the dissociation of phosphine observed for L_2PtEt_2 and $L_2Pt(c\text{-}C_5)_2$. Since $L_2Pt(c\text{-}C_4)_2$ decomposes approximately 600 times *more* rapidly than L_2PtEt_2, while the activation energy ($E_a = 33$ kcal/mol) is *greater* than that for L_2PtEt_2 ($E_a = 29$ kcal/mol), this substance is apparently one in which the endothermicity of the cyclobutene olefinic link is more than offset by a combination of a high dissociation constant for L (relieving steric strain in the ground state) and a favorable entropy of activation (reflecting the formation of three particles rather than two in the transition state).

$L_2Pt(c\text{-}C_3)_2$. This compound is significantly more stable than the analogous c-C_4, c-C_5, and Et complexes.[22] We have not been able to elaborate the mechanism of its decomposition in detail, but several features of the mechanism emerge nonetheless. First, at [L] = 0, phosphine dissociation is probably not rate limiting.[23] Second, isomerization of *cis*-$L_2Pt(c\text{-}C_3)_2$ to give *trans*-$L_2Pt(c\text{-}C_3)_2$ is faster than the rate of decomposition of either the cis or trans isomer. Third, the kinetic data suggest that reaction of the trans compound makes an important contribution to the observed rate of decomposition.[24] We note that although we have not observed cis to trans equilibration with other dialkylplatinum complexes, and although the rate of isomerization of *cis*- to *trans*-$L_2Pt(c\text{-}C_3)$ is much slower than the rate of decomposition of these other

dialkylplatinum complexes,[4–6] we cannot rigorously exclude isomerization as an important part of these thermal decompositions. Fourth, addition of triethylphosphine inhibits decomposition. Thus, intermediates formed via phosphine dissociation are probably important in the decomposition of $L_2Pt(c\text{-}C_3)_2$. Finally, the transfer of deuterium from one cyclopropyl-d_5 group to another with the formation of cyclopropane-d_6 and the transfer of hydrogen from one cyclopropyl-1-d_1 group to another with formation of cyclopropane-d_1 suggest a significant contribution to the decomposition from β-hydride elimination. Thus, one mechanism for decomposition of $L_2Pt(c\text{-}C_3)_2$ probably involves a sequence closely analogous to other β-hydride eliminations (Scheme I). This process is obscured by the competing (or subsequent) reactions which generate propylene and which transfer hydrogen from the triethylphosphine ligands into the product hydrocarbons. We suggest that the enthalpy of formation of the double bond of cyclopropene,[10] even as a platinum-bound complex, is sufficiently high that the normal decomposition via β-hydride elimination is so slowed that these other types of reactions become competitive.

We conclude from these studies that the β-hydride elimination mechanisms outlined here and in previous papers for complexes of the structure L_2PtR_2 are described by the series of individual steps in Scheme I. Only in the slowest reactions (i.e., $L_2Pt(c\text{-}C_3)_2$) do other types of reactions compete. The location of the rate-limiting step depends on contributions to the entropy and enthalpy of activation from a number of independent factors. Either the initial dissociation of triethylphosphine (1 → 2) or reductive elimination of alkane (3 → 4) can be rate limiting at low concentrations of added triethylphosphine: we have not so far characterized a system in which β-hydride elimination is rate limiting. The process involving rate-limiting reductive elimination (1 ⇌ 3 → 4) has a higher enthalpy of activation than triethylphosphine dissociation, but a more favorable entropy of activation. The relative rates of the two processes thus reflect a balance between enthalpic and entropic terms. The steric crowding in the starting L_2PtR_2 complexes, the energy required to form the metal–olefin complex by β-hydride elimination, and the stabilization of intermediates by platinum–olefin bonding are all determined (albeit in unrelated ways) by the structure of the alkyl group and are reflected predominantly in enthalpic terms. The concentration of free triethylphosphine in solution is the major variable determining the relative entropies for these two processes.

Experimental Section

(22) This stability has been noted previously by others: Phillips, R. L.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans* **1978**, 1732–1735.

(23) Thermal decomposition of $L_2Pt(c\text{-}C_3)_2$ at 147 °C is at least two orders of magnitude slower than the slowest phosphine dissociation rate we have yet observed (Table I). From this observation, and from the relative stabilities of $L_2Pt(c\text{-}C_4)_2$ and $L_2Pt(c\text{-}C_5)_2$ compared to $L_2Pt(c\text{-}C_3)_2$, we infer that dissociation of L is not the rate-limiting step in this decomposition.

(24) An unspecified autocatalysis by materials formed slowly in the decomposition is also consistent with the kinetic data. Although we cannot rigorously exclude such a possibility, we believe it to be unlikely.

(25) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165–169.

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spectra were obtained using a Hewlett-Packard Model 5990 GC/MS spectrometer.

$L_2Pt(c-C_3)_2$. CODPtCl$_2$ (0.5 g, 1.33 mmol) and a small stirring bar were placed in a dry, 100-mL, round-bottomed flask. The flask was capped with a serum-stopper and flushed with argon. Diethyl ether (40 mL) and 7.0 mL of 0.76 M cyclopropylmagnesium bromide (5.3 mmol) were added at −50 °C. The solution was allowed to warm to −20 °C over 2 h and stirred at this temperature for 6 h. The entire reaction mixture was passed through a 1 × 6 cm column of silica gel (Fischer, 200 mesh) mixed with 5% activated charcoal (Fisher, Darco) at 0 °C. The solution thus obtained was treated with 0.4 mL (2.75 mmol) of triethylphosphine at 0 °C. The ether was removed partially (in vacuo). Methanol (∼20 mL) was added and the solution cooled to −78 °C. The resulting white powder was recrystallized from ether–methanol to give $L_2Pt(c-C_3)_2$ (0.45 g, 66%) as a white, crystalline solid, mp 88–90 °C: ^{31}P NMR (cyclohexane), δ 8.0, $J_{P,Pt}$ = 1790 Hz.

$L_2Pt(c-C_4)$ was prepared in 56% yield by an analogous procedure: mp 87-88 °C; ^{31}P NMR (cyclohexane) δ 6.3, $J_{P,Pt}$ = 1647 Hz.

$L_2Pt(c-C_5)_2$. Into a 250-mL round-bottomed flask was weighed 0.50 g (1.34 mmol) of (COD)PtCl$_2$. The flask was fitted with a stirring bar, sealed with a rubber septum, and flushed thoroughly with argon. Degassed ether (100 mL) was added to the flask and the mixture was cooled to −50 °C. To the stirred mixture was added 10.0 mL of 0.60 M cyclopentylmagnesium bromide in THF. The reaction was stirred vigorously at −50 °C for 4 h, warmed slowly to −20 °C, and stirred for an additional 4 h. The reaction was quenched by addition of 10 mL of 20% methanol in water by syringe. The ether layer was decanted into a 100-mL flask and the ether removed at −20 °C under reduced pressure to a volume of ca. 10 mL. To this solution was added 30 mL of cold methanol containing 1.00 mL (0.810 g, 6.86 mmol) of triethylphosphine. The solution was stirred for 3 h at −20 °C during which time a white crystalline solid precipitated. The solution was further concentrated by removal of the remaining ether under reduced pressure, cooled to −30 °C, and filtered rapidly on a coarse frit. The product was washed with 2 × 3 mL portions of cold (−30 °C) methanol and dried in vacuo to give an off-white solid in 43% overall yield, mp 59–61 °C dec: ^{31}P NMR (cyclohexane) δ 9.0, $J_{P,Pt}$ = 1616 Hz.

Attempted Preparations of $L_2Pt(c-C_6)$ and $L_2Pt(i-Pr)_2$. These reactions were carried out by a procedure analogous to that used to prepare $L_2Pt(c-C_5)_2$. In no instance was it possible to isolate stable complexes as solids from the solutions. The reaction products also decomposed when subjected to column chromatography at −78 °C on silica gel. GLC analysis indicated the presence of olefin and alkane products in the solution, but their origin was not rigorously established. Since diisopropyl(1,5-cyclooctadiene)platinum(II) is a stable compound,[26] we assume the failure to isolate a stable phosphine complex reflects its stability and not that of some earlier intermediate.

Kinetics. The kinetics of decomposition of $L_2Pt(c-C_3)_2$ was obtained by {^{1}H} ^{31}P NMR spectroscopy using the method described previously.[4] The kinetics of decomposition of $L_2Pt(c-C_4)_2$ was followed by a modification of this method. Decompositions were carried out in sealed tubes in the NMR probe. Short pulse sequences were used, and the midpoint of the interval used in pulsing was considered the time of sampling. Triethyl phosphate was used as the internal standard, and measurements were based on peak heights. GLC was used to follow the decomposition of $L_2Pt(c-C_5)_2$. Aliquots (50 μL) were quenched with concd HCl (100 μL), and n-pentane was used as an internal standard.

Rate constants obtained for $L_2Pt(c-C_5)_2$ as a function of [L] are: [L] (M), $10^4 k_L^{obsd}$ s^{-1}, $10^4 k_L$ s^{-1}; 0.0, 10.0, 8.5; 0.009, 4.3, 2.8; 0.018, 2.5, 1.0; 0.036, 2.1, 0.60; 0.135, 1.7, 0.20; 0.322, 1.5, 0.0; 0.500, 1.5, 1.0. Kinetics of the exchange of triethylphosphine in cis-$L^D_2Pt(c-C_3)_2$ was measured by {^{1}H} ^{31}P NMR. Cyclohexane solutions of platinum complexes (0.05–0.10 M) containing the appropriate amount of L or L^D, and sealed in NMR tubes as described earlier,[4] were used. Changes in peak height were measured relative to triethyl phosphate as an internal standard. Similar procedures were employed with $trans$-$L^D_2Pt(c-C_3)_2$. In these studies, samples enriched in the trans isomer were prepared by heating a cyclohexane solution of cis-$L^D_2Pt(c-C_3)_2$ at 140 °C for 1.5 h. The tubes were opened under an argon stream, triethylphosphine (d_0 or d_{15}) sufficient to reach the desired concentration added by syringe, and the tubes were resealed under vacuum as described above. These samples were stored in liquid nitrogen prior to use to prevent exchange.

Conversion of $L_2Pt(c-C_5)_2$ to L_2PtEt_2. Into a 20-mL pressure tube (Lab Glass) containing a stirring bar was weighed 40 mg (70 μmol) of $L_2Pt(c-C_5)_2$. The tube was capped, flushed with argon, and cooled to 0 °C in an ice bath. Degassed cyclohexane (1.00 mL, containing 0.20 M triethyl phosphate as ^{31}P internal standard) was added by syringe. A 0.3-mL aliquot was analyzed by ^{31}P NMR. The ice bath was removed, the system charged to 45 psi with ethylene, and the solution stirred for 24 h at room temperature. The tube was vented and analyzed by {^{1}H} ^{31}P NMR. This analysis indicated a mixture of 80% L_2PtEt_2 and 20% $L_2Pt(ethylene)$ with >80% conversion based on $L_2Pt(c-C_5)_2$.

Bromocyclopropane-d_5 was prepared from styrene-$α,β,β$-d_3 by the method reported by Lambert.[27] Styrene-$α,β,β$-d_3 was prepared from phenylacetylene by exchange (n-butyllithium, then deuterium oxide) and reduction (Lindlar catalyst, dideuterium) in 81% yield.

Cyclopropane-1-d-carboxylic Acid. Into a 200-mL flask under argon were placed 18.0 mL (20.8 g, 0.201 mol) of 4-chlorobutyronitrile, 0.30 g of tetra-n-butylammonium bisulfate, 100 g of D$_2$O, and 50 mL of ether. The pD of the aqueous phase was adjusted to ∼14 with 40% NaOD and the mixture stirred for 24 h. The organic phase was separated, the aqueous phase extracted with 2 × 25 mL portions of Et$_2$O, the organic layers were combined, and the ether was removed by distillation to give ∼18 g of 4-chlorobutyronitrile (>85% d_2). This material (15.0 g, 142 mmol) was dissolved in 30 g of Me$_2$SO-d_6,[28] and 7.9 g (146 mmol) of NaOMe was added slowly with vigorous stirring. The reaction was diluted with 200 mL of H$_2$O, extracted with 3 × 25 mL portions of CH$_2$Cl$_2$, and dried over MgSO$_4$. Cyclopropyl-1-d_1 cyanide was isolated by distillation (bp 135–138 °C). This material was treated directly with 30 g of 50% NaOD at 90 °C. Over a period of several hours, 50 mL of D$_2$O was added in 5-mL increments; a homogeneous mixture resulted. The reaction was cooled in an ice bath and the pD adjusted to <1.0 by addition of D$_2$SO$_4$. The mixture was extracted with ether and the product isolated by distillation (bp 110–116 °C (70 mm)) to give 8.1 g (66%) of cyclopropane-1-d_1-carboxylic acid.

Bromocyclopropane-1-d_1. This compound was prepared in 41% yield from the corresponding deuterated acid by literature procedures.[29]

Preparation of $L_2Pt(c-C_3$-1-$d_1)$ and $L_2Pt(c-C_3$-$d_5)$. The procedures employed were analogous to that described for $L_2Pt(c-C_3)_2$.

(26) Muller, J.; Göser, P. *Angew. Chem., Int. Ed. Engl.* **1967**, 6, 364–365.

(27) Kobayashi, K.; Lambert, J. B. *J. Org. Chem.* **1977**, 42, 1254–1256.

(28) On small scale it is not necessary to preexchange the nitrile because this exchange occurs rapidly with ring closure in Me$_2$SO-d_6. We preexchange the material to reduce the amount of deuterated solvent (Me$_2$SO-d_6) necessary for this step. The isotopic purity of the product is also further enhanced in this step.

(29) Meek, J. S.; Osuga, D. T. "*Org. Syntheses*"; Wiley: New York, 1973; Collect. Vol. 5, pp 126-130.