Mechanism of Thermal Decomposition of Dineopentlybis(triethylphosphine)platinum(II): Formation of Bis(triethylphosphine)-3,3-dimethylplatinacyclobutane

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Abstract: The thermal decomposition of dineopentlybis(triethylphosphine)platinum(II) (1) in cyclohexane solution at 157 °C yields bis(triethylphosphine)-3,3-dimethylplatinacyclobutane (4) by a reaction which involves dissociation of 1 equiv of triethylphosphine, intramolecular oxidative addition of the C–H bond of a neopentyl methyl group to platinum (3), and reductive elimination of neopentane. Carbon–carbon bond formation resulting in production of dineopentyl is a detectable side-reaction. The overall reaction has Arrhenius activation parameters: $E_a \approx 49$ kcal mol$^{-1}$, $\log A \approx 20$. The activation energy for phosphine dissociation is 27–35 kcal mol$^{-1}$. Transfer of a hydrogen atom from the triethylphosphine group to a neopentyl moiety occurs at a rate approximately 3% that of transfer of hydrogen from the methyl of one neopentyl group to the methylene of the other. Any processes which abstract $\alpha$-methylene hydrogens from the neopentyl group occur at less than 1% the rate of processes which abstract hydrogens from the neopentyl methyl groups. Substitution of deuterium for hydrogen in either the neopentyl methyl groups or the triethylphosphine groups slows the decomposition reactions ($k_{D2}/k_O \approx 3.0$). The mechanism proposed for generation of 4 is based in part on deuterium-labeling experiments: comparison of results by using different labeling patterns for 1 demonstrates the special utility of "inverted" experiments in which hydrogen transfer from a specific site is examined in a system which is otherwise perdeuterated. The driving force for the conversion of 1 to 4 is not obvious: it may be relief of steric strain in 1, changes in electronic energy due to reorganization of ligands around platinum, or changes in entropy.

Introduction

The cleavage of unactivated aliphatic C–H bonds by reaction with transition metals occurs in a number of useful heterogeneous catalytic processes; reforming,$^2$ dehydrogenation,$^3$ and probably platinum-catalyzed oxidation$^4$ provide examples. Current efforts to develop homogeneous catalysts for C–H bond activation are justified on the basis that such catalysts might functionalize hydrocarbons selectively and that they might be amenable to detailed

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mechanistic studies. Intermolecular catalytic reactions which cleave alkane C–H bonds (apparently) homogeneously are restricted to those which result in exchange with acids in the presence of several transition-metal salts. A number of intramolecular cyclometallations break C–H bonds of ligands attached to transition-metal complexes in facile stoichiometric reactions. Although these reactions cleave C–H bonds which are "unactivated" in the sense of having no adjacent unsaturated groups of heteroatoms, their facility may in some way reflect the energetic or entropic contribution of prior coordination of the ligand to the metal center. This paper describes a study of the mechanism of one such reaction: the conversion of dineopentylbis(triethylphosphine)platinum(II) (1) to bis(triethylphosphine)-3,3-dimethylplatinanicyclobutane (4) and neopentane (Scheme I). This study establishes that a vacant coordination site on the metal facilitates cleavage of the C–H bond and suggests structural characteristics for platinum(II) complexes which might make C–H activation rapid. Although it does not rigorously establish whether the conversion of 2 to 3 or the loss of neopentane from 3 is overall rate limiting, the high entropy of activation for the reaction favors the latter possibility. In either event a rate law of the same form describes the reaction (eq 1 for 2 → 3 rate limiting, eq 2 for 3 → 4 rate limiting), provided that the steady-state assumption holds for intermediate 2 (eq 1) or intermediates 2 and 3 (eq 2).

\[
\begin{align*}
\frac{d[1]}{dt} &= \frac{k_4[2][L]}{k_2 + k_1[Et_2P]} \\
\frac{d[1]}{dt} &= \frac{k_4k_5[3]}{k_5k_4 + k_1[Et_2P]}
\end{align*}
\]

This work is based on studies of isotopically labeled compounds. These compounds are named as derivatives of the analogous nondeuterated parent: for example, bis(neopentyl)-1,1-d-[bis(triethylphosphine)platinum(II)] is represented as 1-[C,D-C(CH_3)CH_3CH_2CH_3]. This designation only labels the isotopically substituted compounds. It indicates the major isotopic species present, not the true isotopic composition. "L" refers to triethylphosphine and "P" to P(C_6D_5).

**Results**

**Preparation of 1 and Isotopic Derivatives.** The same general procedure was used to synthesize 1 and its deuterated derivatives. Scheme II outlines a synthesis of 1-[C,D-C(CH_3)CH_3CH_2CH_3]; obvious modifications of this synthesis generated other isotopic substitution patterns on the neopentyl group. Isotopically substituted triethylenes were prepared by reaction of the appropriate Grignard reagent with triethylphosphine.

**Isotopic Analyses of Hydrocarbons: Characterization of Organoplatinum Compounds.** We have relied heavily on gas chromatography/mass spectroscopy (GC/MS) for analysis of the deuterated alkanes. A number of types of error—isoeffects in reagents, adventitious isotopic exchange processes, instrumental artifacts, and competing side reactions—can be significant in these types of analyses. This section outlines methods used to estimate isotopic distributions and to evaluate their accuracy. We note at the outset that even with close attention to experimental detail, 3% uncertainty in isotopic analysis was routine, and in certain instances we were unable to establish the origin of isotopic species detected at the level of 10%.

Organoplatinum compounds were assayed for C–P bonds by treatment with DCl/D_2O and analysis of the hydrocarbons generated by GC/MS for deuterium incorporation. We preferred not to establish the isotopic yield in this deuterolysis procedure using neopentane-d from 1, since neopentane does not give a molecular ion. Instead, n-butylmetal compounds were examined: butane gives a molecular ion with abundance 50% of the base peak. Figure 1 summarizes the distribution of ion intensities observed on treating samples of n-butylmagnesium bromide (from which butane present from preparation and handling had been previously removed) with H_2 and D_2 sources; Table IA in supplementary material for this article summarizes numerical data for ion intensities. Experimentally indistinguishable data were obtained on treating di-n-butylbis(triethylphosphine)platinum(II) with H_2 or D_2. Comparison of these spectra suggests that the butane generated by deuterolysis of each organometallic compound was...
Thermal Decomposition of \((n\cdot C_{2}H_{4}I)_{n}\) (P(ET)2)\(_{3}\)Pt

A mixture of butane-\(d_1\) (96-97%) and \(-d_0\) (4-3%), on the assumption that loss of \(H^+\) (D\(^+\)) from \(C_{2}H_{4}D\) on electron impact is statistical.\(^{10}\) Proton sources present on the surface of the glassware used to manipulate samples must be eliminated by exhaustive flushing with deuterium to achieve this level of deuterium incorporation, and other precautions outlined in the experimental section must be followed.

Most of our work was concerned with analysis of mass spectra of neopentane. Neopentane does not give a molecular ion on electron impact: the base peak is \([M - \text{methyl}]^+\) (C\(_2\)H\(_5\)\(^+\), m/e 57), with smaller amounts of C\(_2\)H\(_4\)^{+} (m/e 41) (Figure 1). Isotopic analyses were based on the cluster of ions from m/e 55-58 (and corresponding clusters at higher mass for deuterated species). The spectra anticipated for neopentane-\(d_1\) and \(-d_2\) were derived from that observed for neopentane-\(d_0\) by making two assumptions: first, that there was no deuterium kinetic isotope effect on the loss of a methyl group (that is, that loss of CH\(_3\) and CH\(_2\)D\(_x\)_\(_{y}\) were equally probable); second, that the processes resulting in loss of H and D\(_2\) in addition to methyl from neopentane (that is, processes generating ions with m/e 56 and 55) also occurred in the deuterated neopentanes with no discrimination between H and D. These calculated distributions are listed in Table I A (supplementary material for this paper), together with observed distributions.

The good agreement between calculated and observed intensities for neopentanes-\(d_1\)-12 establishes that no intramolecular scrambling of hydrogen (deuterium) between carbon atoms occurs in neopentane-\(d_0\) before fragmentation. The minor discrepancies observed are compatible with a secondary isotope effect involving preferential loss of methyl radical rather than methyl-d\(_2\) radical on fragmentation.\(^{11}\) These experimental ion intensities are not useful in establishing whether the hydrogen-loss processes are also subject to kinetic isotope effects. Even with the assumption of an isotope effect of \(k_{D}/k_{H} = 6\), however, the influence of changes in the abundances of ions from such an isotope effect would sum to only ca. 9.9\% of [M - methyl]\(^+\) and would thus be smaller than the uncertainty in measuring this intensity.\(^{12}\) Detailed comparison of calculated and observed intensities for neopentanes-\(d_0\)-12 is not worthwhile, since the available experimental samples were all isotopic mixtures. The ion intensities listed in Table I A for these species are all approximate. They entirely neglect isotope effects in both methyl- and hydrogen-loss processes and are almost certainly in error to some extent. The purpose of experiments based on these species was, however, normally qualitative: that is, to establish whether hydrogen or deuterium was transferred in a particular reaction. Semi-quantitative information on concerning isotopic compositions was adequate for this purpose.\(^{13}\)

Estimation of the composition of all isotopic mixtures was based on unsophisticated analysis.\(^{14}\) The major species present were identified on the basis of knowledge of the starting material and reaction and observation of the major peaks in the mass spectrum. The calculated ion distributions listed in Table I A were used to correct the intensities of the base peaks of overlapping spectra, and the isotopic composition was inferred from the relative intensities of the base peaks.\(^{15}\)

Several other experimental details were found to be important in obtaining reproducible isotopic analysis. First, isotopic fractionation in GLC is well-known\(^{16}\) and was evident in our spectra.\(^{17}\) Isotopic analyses reported here are based on an average of approximately 50 individual spectra taken over the full width of the GLC peak. Second, injection of platinum-containing solutions onto the GLC led to the deposition of platinum in the injection port. This platinum was capable of causing isotopic scrambling. To minimize this problem, we changed injection port liners after 10 injections.

The success of these procedures can only be judged empirically. Compound I was converted to neopentane-\(d_1\) by treatment with commercial (99%) DCI/D\(_2\)O—a reaction which we believe (but have not proved) to proceed without isotopic exchange in the alkyl groups. GC/MS analysis of this neopentane indicated a mixture of \(d_1\) (97\%) and \(-d_0\) (3\%). This result is in adequate agreement with similar experiments carried out by using \(n\)-butylmetal compounds.

A second MS analysis was also essential to this work. Treatment of \(L_2Pt_3\) with cyanoen (N≡C≡C≡N) yields the coupled dimer R–R. Although the coupling of this reaction is only ~30\%, it provided a very useful method for identifying the two alkyl groups present on a single platinum atom.\(^{18}\) GC/MS analysis of the dineopentyl generated from I–\(d_0\) by treatment with cyanoen also relied on a prominent [M - methyl]\(^+\) peak (m/e 127 for \(d_0\) material): Figure 1 shows representative mass spectra, and Table I A lists ion distributions in the region used for analysis.\(^{19}\) The cyanoen-induced coupling reaction is cleanly intramolecular. Treatment of a mixture of I and I-\(CD_2C(CH_3)_2\) with cyanoen generates no significant intensity at m/e 129 above that expected for the unmixed dineopentyls (eq 3).

\[
1 + [CD_2C(CH_3)_2] \xrightarrow{N≡C≡C≡N} [(CH_3)_2CCH_2]^+ + \quad \quad \quad \quad [CH_2C(CH_3)_2CD_2C(CH_3)_2] (3) \sim 0.02
\]

Thermal Decompositions of I: Products. Most decompositions were carried out under argon in sealed tubes starting with 0.08 M solutions of I in cyclohexane containing 0.02 M triethylphosphine (eq 4); yields are based on I. Addition of triethylphosphine

\[
C_2H_5P + (CH_3)_2CCH_2 + 4 + (Et_2P)_2Pd \quad (4)
98-102\% \quad 5-10\% \quad 85-90\% \quad \text{trace}
\]

phosphine prevented a rapid increase in the rate of decomposition of I after 1.5-2.0 half-lives which was observed for reactions carried out in the absence of added triethylphosphine; it slowed the reaction (see below) but had no effect on product yields. All reaction mixtures appeared homogeneous throughout. The starting solution was colorless; the final mixture was pale yellow-orange. Hydrocarbon product yields did not change when the initial

\[(15)\] No corrections were made in the analysis of mixtures for \(^{1}H\) impurities in the deuterated starting materials.


\[(17)\] Typically, the isotopic composition of a 1:1 mixture of neopentane-\(d_0\) and neopentane-\(d_1\) would change from a 3:2 \(d_0\)-\(d_1\) at the leading edge of a GLC peak to a 2:3 \(d_0\)-\(d_1\) mixture at the tail of the peak. These changes were larger with broad peaks.

\[(18)\] This reaction probably occurs by oxidative addition of cyanoen to platinum(II) (or nonadditive oxidation), yielding a transitory dialkylplatinum(IV) species which spontaneously reductively eliminates dialkyl. For previous descriptions of reactions of neopentane with transition-metal complexes see: Tolman, C. A.; Lukosius, E. J. Inorg. Chem. 1977, 16, 940-943; Gasson, R.; Chastrette, M. J. Organomet. Chem. 1979, 163, 139-149.

\[(19)\] Analysis of isotopic mixtures of dineopentyl were performed by comparison of these mixtures with the dineopentyl obtained from reaction of cyanoen with I or I-\([CD_2C(CH_3)_2]\)
concentration of 1 was varied, when benzene-$d_{40}$ diethyl ether, or decane was substituted for cyclohexane as solvent, or when mercury(0) was added. Mercury(0) would have been expected to modify the activity of bulk or colloidal platinum(0) by amalgamation. The observation that it had no effect supports the belief that the reaction is homogeneous and not catalyzed by traces of bulk platinum metal. The distribution of hydrocarbon products was independent of the extent of decomposition.

Compound 4 was isolated as an air-stable white solid. Its assigned structure rests on a combination of spectroscopic evidence (summarized in the Experimental Section) and on the chemical transformation summarized in Scheme III. In particular, GC/MS analysis indicated that treatment of 4 with DCl introduced deuterium into the 1,3-positions of the neopentane produced; little or no 1,1-disubstitution was observed. Dimethylcyclopropane was observed as a major product on treatment of 4 with diiodine, bromine, or cyanogen. Thermolysis of 4 is complicated by the deposition of platinum metal and by reactions apparently catalyzed by this metal. Thermolysis of perdeuterated 4 generates a dark reaction mixture containing platinum(0), neopentane-$d_{10}$, and 1,1-dimethylcyclopropane-$d_{10}$, in addition to ethylene-$d_{4}$ (from triethylphosphine-$d_{4}$) and a compound tentatively identified by GC/MS as ethylcyclohexane-$d_{4}$. Thermolysis of 4 in the presence of mercury(0) results in clear reaction mixtures containing no obvious precipitated platinum(0) and a simpler spectrum of products; amalgamation of the platinum(0) with the mercury(0) suppresses platinum(0)-catalyzed reactions. Under these conditions, dimethylcyclopropane is the major product of thermal decomposition, and formation of the products (neopentane and ethylene) suggesting hydrogen transfer from the triethylphosphine ligand to the metallacycle is inhibited. In no instance do we observe 2-methylbutene, 2-methylbutane, isobutylene, isobutane, or other products, suggesting carbon skeleton rearrangement or fragmentation.

The molecular weight of 1 in benzene is consistent with a monomeric structure (calculated 501, found 515). The inference that there are no significant dimeric organometallic species in solution is reinforced by the observation that reactions which induce carbon–carbon bond formation (treatment with diycyanogen, thermolysis) generate no detectable products containing two moieties derived from neopentyl groups; in particular, 1,1,4,4-tetramethylcyclohexane or other $C_{10}$ products were not observed.

The presence of small quantities of (Et₃P)₅P⁴ among the reaction products was inferred from $^{31}P$ NMR spectroscopy. During the disappearance of 1 (0.08 M) in cyclohexane containing Et₃P (0.12 M, δ = -19.9) the $^{31}P$ NMR signal for free Et₃P broadened markedly. At the conclusion of the reaction, a new, low-intensity $^{31}P$ signal appeared at δ 41.9. This signal and the exchange broadening are consistent with the assignment of this new peak to (Et₃P)₅P⁴.

### Deuterium-Labeling Studies
Table I summarizes experiments which establish that a methyl group of the neopentyl moiety is the primary source of the hydrogen (deuterium) which is transferred to the newly formed molecule of neopentane, that there is significant incorporation of hydrogen from the alkyl group of (24) (Et₃P)₅P⁴ reported to have δ 41.9 in hydrocarbon solvents (Gerlach, D. H.; Kane, A. R.; Parshall, G. W.; Jesson, J. P.; Muetterties, L. J. Am. Chem. Soc. 1971, 93, 5343–5344).

<table>
<thead>
<tr>
<th>entry</th>
<th>(CH₃)₂C</th>
<th>CH₃Pt</th>
<th>C₂H₅Pd</th>
<th>solv</th>
<th>isotopic comp of neopentane (%)</th>
<th>inference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>D</td>
<td>D</td>
<td>D</td>
<td>D</td>
<td>D (89)</td>
<td>not solvent</td>
</tr>
<tr>
<td>2</td>
<td>D</td>
<td>*D</td>
<td>D</td>
<td>D</td>
<td>D (88)</td>
<td>little or no α</td>
</tr>
<tr>
<td>3</td>
<td>D</td>
<td>H</td>
<td>D</td>
<td>D</td>
<td>D (83)</td>
<td>γ</td>
</tr>
<tr>
<td>4</td>
<td>D</td>
<td>H</td>
<td>D</td>
<td>D</td>
<td>D (79)</td>
<td>some L (&lt;γ)?</td>
</tr>
<tr>
<td>5</td>
<td>D</td>
<td>D</td>
<td>D</td>
<td>D</td>
<td>H (79)</td>
<td>γ</td>
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<tr>
<td>6</td>
<td>D</td>
<td>H</td>
<td>D</td>
<td>D</td>
<td>H (97)</td>
<td>γ</td>
</tr>
<tr>
<td>7</td>
<td>H</td>
<td>D</td>
<td>D</td>
<td>D</td>
<td>H (98)</td>
<td>γ</td>
</tr>
<tr>
<td>8</td>
<td>H</td>
<td>H</td>
<td>D</td>
<td>D</td>
<td>H (92)</td>
<td>γ</td>
</tr>
<tr>
<td>9</td>
<td>H</td>
<td>D</td>
<td>H</td>
<td>D</td>
<td>H (99)</td>
<td>γ</td>
</tr>
</tbody>
</table>

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4 Reaction mixtures were originally 0.08 M in platinum organometallic and contained 0.02 M of the corresponding triethylphosphine. Decompositions were carried to completion at 157 °C (2 h). Isotopic compositions reported are not corrected for isotopic impurities in the starting materials and represent the absolute isotopic enrichment. The entries in this column indicate whether the indicated position is protonated or deuterated: entry 3 is (CD₂)₄CH₂I⁻[Pt(C₂D₅)₂]₂⁺ in C₂H₅I. The isotopic purities of the starting platinum complexes were analyzed by examination of the neopentanes produced by treatment with HCl/H₂O or DCI/D₂O: (CH₃)₂CCCl₂⁻ (96% $d_{2}$, 4% $d_{3}$); (CD₃)₂CCH⁻ (96% $d_{2}$, 4% $d_{3}$); CH₃Cl⁻ (93% $d_{3}$, 7% $d_{4}$); (CD₃)₂CCD⁻ (94% $d_{3}$, 6% $d_{4}$). The estimated isotopic composition was 92% $d_{3}$ and 8% $d_{4}$, as inferred from the ethyl-$d_{3}$ bromide from which it was made. The solvent used was cyclohexane or cyclohexane-$d_{12}$ (99% $d$), except entry 7 which was dodecane. These data summarize the isotopic composition of the neopentanes produced. For example, for entry 1, (CD₃)₂C (93%) and (CD₃)₂CCD (9%); CCl₂ were the two major species detected. Only these two major neopentane species are listed. These estimates are derived directly from the MS data; they are not corrected for isotopic impurities present in the starting materials. This column summarizes the conclusion drawn from the neopentane isotopic compositions concerning the origin of the hydrogen transferred to the neopentyl group: α refers to the CH₃ position of the neopentyl group; γ refers to the methyl portion of the neopentyl group.

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For the chemical reactions used in characterizing (4), the following scheme is provided:

\[
\begin{align*}
\text{C}_9 + \text{H}_2 & \rightarrow \text{C}_9 \text{H}_{12} \quad 100
d + \text{H} & \rightarrow \text{H} + \text{H} \quad 100
d + \text{H} & \rightarrow \text{H} + \text{H} \quad 100
d + \text{H} & \rightarrow \text{H} + \text{H} \quad 100
\end{align*}
\]
the triethyolphosphine, and that little or no hydrogen transfer occurs from the α-position of the neopentyl group or from solvent. Experiments designed to identify the source of hydrogen in a hydrogen-transfer reaction are commonplace in organometallic chemistry and are always almost conducted by substituting deuterium in the position to be tested and examining the products for incorporation of deuterium. While this type of experiment is a necessary one, it may yield ambiguous results. If deuterium is transferred in the isotopically labeled system, one can conclude that hydrogen is transferred in the unlabeled system; if deuterium is not transferred, one cannot conclude that hydrogen is also not transferred, because the partitioning of reactant between paths involving hydrogen abstraction from different sites can be altered by deuterium substitution. That is, deuterium substitution may suppress the reaction of interest through a deuterium isotope effect. This problem is particularly severe because the difficulties associated with the synthesis of isotopically pure organometallic species and with the GC/MS analyses of deuterated compounds produce results with only modest signal-to-background levels and require that a significant fraction of 1 equiv of deuterium/molecule can be transferred before the experimental data can be interpreted with confidence.

Since we knew neither how many reactions were competing in the production of neopentane from 1 nor the isotope effects characterizing the reactions that did occur, it was necessary to proceed by testing the potential sources of hydrogen (deuterium) in two steps. First, a site of interest was labeled with deuterium. If incorporation of this deuterium into the neopentane occurred, then that site was clearly involved in the production of neopentane in unlabeled 1. If incorporation of deuterium did not occur, it was necessary to invert the experiment: that is, to label all the other sites with deuterium and to try to detect hydrogen transfer from the site of interest. In this type of experiment, of course, a normal kinetic isotope effect would exaggerate the importance of the hydrogen-transfer path being examined, but the amplification would be useful in the qualitative detection of minor pathways.

The first two entries in Table I establish that no hydrogen comes from the solvent, since substitution of hydrogen for deuterium in the solvent results in no increase in the hydrogen content of the neopentane. The 11% hydrogen detected in entry 1 is attributable in part to hydrogen impurities in the neopentyl groups of the I-[CD₃C(CH₃)₂]₂ moieties and possibly also to chemical impurities. Entries 4 and 8 establish the γ-hydrogen of the neopentyl group as the major source of the hydrogen (deuterium) consumed in converting one neopentyl group of 1 to neopentane. Comparison of entries 2 and 5 indicates that the triethyolphosphine ligand also donate a small amount of hydrogen in a process which forms neopentane. Comparison of entries 2 and 3 suggests that hydrogen transfer from the α-position, if it occurs at all, is a minor process. The difference in the hydrogen content of the neopentane produced in entries 2 and 3 is close to experimental error. When the experiment is run in the reversed sense—that is, detecting deuterium transfer from the α-position rather than hydrogen (entries 4 and 5 or entries 7 and 9), no detectable transfer occurs. Arguments outlined below indicate that hydrogen abstraction from the methyl groups of the triethyolphosphine moieties occurs at ca. 3% the rate of abstraction from the γ-neopentyl groups. Analogous reasoning would indicate that transfer from the α-neopentyl position would be <1% that from the γ-position.

Mixtures of labeled derivatives of 1 were used to explore the molecularity of the thermal decomposition. Decomposition of a 1:1 mixture of undeuterated 1 and I-[CD₃C(CH₃)₂]₂ to ca. 45% conversion, followed by resolution of the remaining organoplatinum compounds and treatment with cyanogen, gave the results outlined in Scheme IV. Coupling of neopentyl groups originally located on different platinum atoms is a minor reaction. Thus, intermolecular scrambling of alkyl groups appears to be slow relative to thermal decomposition. Decomposition of a 1:1 mixture of 1-[LP₃] and 1-[LP₃][CD₃C(CH₃)₂] did, however, suggest significant crossover. The neopentane generated from the former platinum compound contained ca. 14% (CH₃)₂C(CH₃)₂ and that from the latter ca. 39% (CD₃)₂CCD₃ (11% would have been expected on the basis of isotopic composition of the starting material). Interpretation of these experiments is complicated by the difference in rate of decomposition of the two platinum complexes (see below). Nonetheless they suggest qualitatively that a significant minority of the reduction events leading to neopentane (10–30%) involve hydride and alkyl groups originally present on different atoms.

A separate experiment established that any interchange of the methyl and methylene groups of 1-[CD₃C(CH₃)₂]₂ occurs at a rate less than 10% of the rate of decomposition. Approximately 45% of a sample of this platinum complex was decomposed at 157 °C and the remaining material recovered and converted to di-neopentane (Scheme V). GC/MS analysis of deionpentane from the thermal decomposition and from recovered organoplatinum compound showed [M – methyl]⁺ had lost less than 4% of the CD₂ groups originally present in the starting organoplatinum complex. Thus, conversion of 5 to 6 is not important.

This observation provides no evidence for the reversible interconversion of 1 and 5 (here, 1-[CD₃C(CH₃)₂]₂ and 5) but does not rigorously exclude it: in principle, the geometry of 5 might be such that only H–CH₂ bond formation could occur. 25 Kinetic Studies. These were conducted by using ¹H or ³¹P NMR spectroscopy or GLC,26 for ¹H NMR work, 1-[P(C₃D₆)₂]₂ was

(25) A geometrical requirement for reductive elimination is known for six-coordinate platinum (IV) complexes; Ruddick, J. D.; Shaw, B. L. J. Chem. Soc. A 1969, 2969−2972. Compound 5, at least as generated initially, should be five-coordinate and might be expected to interconvert stereoisomers rapidly.
Table II. Rate Constants (Eq 6-10) for Decomposition of 1-d₆ and Appearance of Products: \( \text{L} = \text{P(C}_2\text{H}_4\text{)}_3, \ \text{L} \text{D} = \text{P(C}_2\text{D}_4\text{)}_3 \)

<table>
<thead>
<tr>
<th>entry</th>
<th>R₂PtL₂</th>
<th>conc, M</th>
<th>R₂PtL₂</th>
<th>Lᵇ</th>
<th>T, °C</th>
<th>( k_{\text{obsd}} ), s⁻¹</th>
<th>( k_{\text{NH(D)}} ), \text{M}⁻¹ s⁻¹</th>
<th>( k_{\text{LD(H)}} ), \text{M}⁻¹ s⁻¹</th>
<th>( k_{\text{NNN}} ), \text{M}⁻¹ s⁻¹</th>
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<tbody>
<tr>
<td>1</td>
<td>(CD₃)₂CCD₂-</td>
<td>L_D</td>
<td>0.077</td>
<td>0.054</td>
<td>157</td>
<td>62.2 (G)</td>
<td>3.35</td>
<td>2.94 (D)</td>
<td>0.42</td>
</tr>
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<td>2</td>
<td>(CD₃)₂CCD₂-</td>
<td>L</td>
<td>0.082</td>
<td>0.056</td>
<td>157</td>
<td>56.9 (G)</td>
<td>3.19</td>
<td>2.24 (D)</td>
<td>0.45</td>
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<td>3</td>
<td>(CH₃)CH₂-</td>
<td>L</td>
<td>0.084</td>
<td>0.056</td>
<td>157</td>
<td>167.0 (G)</td>
<td>9.35</td>
<td>8.71 (H)</td>
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<td>4</td>
<td>(CH₃)CH₂-</td>
<td>L</td>
<td>0.088</td>
<td>0.022</td>
<td>138</td>
<td>29.7 (N)</td>
<td>0.65</td>
<td>0.063 (H)</td>
<td>0.25</td>
</tr>
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<td>5</td>
<td>(CD₃)₂CCD₂-</td>
<td>L_D</td>
<td>0.084</td>
<td>0.022</td>
<td>118</td>
<td>1.23 (N)</td>
<td>0.027</td>
<td>0.024 (H)</td>
<td>0.0008</td>
</tr>
<tr>
<td>6</td>
<td>(CD₃)₂CCD₂-</td>
<td>L</td>
<td>0.081</td>
<td>0.036</td>
<td>157</td>
<td>27.4 (N)</td>
<td>9.86</td>
<td>8.90 (H)</td>
<td>0.35 (D)</td>
</tr>
<tr>
<td>7</td>
<td>(CD₃)₂CCD₂-</td>
<td>L</td>
<td>0.081</td>
<td>0.120</td>
<td>157</td>
<td>71.0 (N)</td>
<td>8.52</td>
<td>7.68 (H)</td>
<td>0.48 (D)</td>
</tr>
<tr>
<td>8</td>
<td>(CD₃)₂CCD₂-</td>
<td>L</td>
<td>0.084</td>
<td>0.054</td>
<td>157</td>
<td>145.0 (N)</td>
<td>7.83</td>
<td>7.02 (H)</td>
<td>0.43 (D)</td>
</tr>
<tr>
<td>9</td>
<td>(CD₃)₂CCD₂-</td>
<td>L_D</td>
<td>0.081</td>
<td>0.022</td>
<td>118</td>
<td>409.0 (N)</td>
<td>9.00</td>
<td>8.05 (H)</td>
<td>0.50 (D)</td>
</tr>
<tr>
<td>10</td>
<td>L</td>
<td>L</td>
<td>0.087</td>
<td>0.000</td>
<td>118</td>
<td>15 (N)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a The experimental accuracy for \( k_{\text{obsd}} \) is estimated at ±8%. b The concentration of \( L \) added to the solution of \( R_2\text{PtL}_2 \). c Method refers to the technique used to determine the rate constants: G = GLC; N = NMR. d The quantity \( k_{\text{NH(D)}} + k_{\text{LD(H)}} \) was measured experimentally by following the rate of appearance of neopentane. Its separation into component parts followed arguments discussed in the text. e (H) and (D) refer to the predominant isotope being transferred to neopentane and are included to facilitate comparisons. f \( k_{\text{NH(D)}} \) and \( k_{\text{LD(H)}} \) are not separable; the reported number is their sum. g This rate constant is inaccurate: the hydrogen content of the \( (CD₃)_2CCD_2 \) moieties (~10%) makes accurate determination of hydrogen transfer from \( P(C_2H_4)_3 \) difficult.

Figure 2. First-order plots for decomposition of 1-L₂[2] at 157 °C in cyclohexane solution (0.08 M) containing added L₂ (0.055 M): • = fractional decomposition of 1-L₂[2]; □ = fractional appearance of neopentane (NH) and dinoepentyl (NN) (based on 1-L₂[2] originally present). Data indicated with filled symbols were collected by ²⁹P NMR (O) or ¹³C NMR (□); open symbols (□) are based on GLC data.

Figure 3. Kinetic plots for thermal decomposition of 1 (●, ▲ = two separate runs) and 1-[CD₃C(CD₃)]₂[2] (O) in cyclohexane solution at 138 °C. The observed uncorrected (see text) value for \( k_{\text{NH}}/k_{\text{LD}} \) is 2.5.

Since we could follow independently the disappearance of 1-d₆, the appearance of neopentane and dinoepentyl, and the isotopic compositions of these hydrocarbons, we were able to estimate kinetic orders, rate constants, and deuterium kinetic isotope effects for several of the three competing processes inferred from the product studies: in solutions containing triethylphosphine, these processes were described accurately by rate equations containing a term in the reciprocal of the phosphine concentration (eq 6–9):

\[
\frac{d[I]}{dt} = k_1[I][L]^{-1}
\]

(5)

(26) An entire kinetic run could be carried out by NMR by using a single tube but was limited to those compounds having distinct, characteristic resonances. GLC required multiple tubes and had greater experimental uncertainty but allowed more compounds to be followed.

(27) When the decomposition of 1-[CD₃₂CD₂]₂P was followed by ¹H NMR, the appearance of neopentane and dinoepentyl could not be separated because the methyl resonances overlapped. Their concentrations at any given time were calculated by using height of methyl/height of Me₄Si = (12/neopentane) + 18(dinoepentyl)/12(Me₄Si) and determining the ratio of neopentane to dinoepentyl at the termination of the kinetic run by GLC (this ratio was constant throughout the decomposition). Analysis specifically for the appearance of neopentane or dinoepentyl was performed by GLC.

(28) The uncertainty in \( k_{\text{LD}} \) is appreciable, as judged by the variation in the values of this constant in Table II. The value used in estimating \( k_{\text{NH}}/k_{\text{LD}} \) was the one we believed subjectively to be most likely correct.
abstraction from triethylphosphine and solve the statistically corrected eq 10.29 Comparison of entries 2 and 8 and, less as
\[
\frac{9k_{1,1}}{18k_{ND}} = \frac{\text{yield of neopentane-}d_{11}}{\text{yield of neopentane-}d_{12}} = \frac{10}{90}
\]
(10)
accurately, entries 1 and 3 of Table II indicates that the kinetic isotope effect observed on the rate of formation of neopentane when deuterium is substituted for hydrogen in the neopentyl methyl groups is \(k_{ND}/k_{SH} \approx 3\) for decompositions performed in the presence of added triethylphosphine.

In the absence of added triethylphosphine the kinetic isotope effect inferred from the rates of decomposition of 1 and 1-[CD\(_{3}\)C(CD\(_{3}\))\(_{2}\)]\(_{2}\) as determined by \(^{31}\)P NMR by following the rate of disappearance of 1 is \(k_{SH}/k_{ND} \approx 2.5\) (Figure 3). This observed kinetic isotope effect is not corrected for formation of dinoethyl (ca. 5%) from 1 and 1-[CD\(_{3}\)C(CD\(_{3}\))\(_{2}\)]\(_{2}\) or for transfer of hydrogen from the triethylphosphine to the perdeuterioethyl group in 1-[CD\(_{3}\)C(CD\(_{3}\))\(_{2}\)]\(_{2}\) (ca. 10%).28 After subtracting the contributions from these side reactions from the rates of decomposition and replotted the data, the corrected kinetic isotope effect in the absence of triethylphosphine becomes \(k_{SH}/k_{ND} \approx 2.9\). This isotope effect is indistinguishable from that observed in the presence of added triethylphosphine and indicates that the decomposition of 1 in the absence of added triethylphosphine does not involve rate-limiting loss of this ligand.

Figure 4 illustrates the decrease in rate of decomposition of 1-[P(C\(_{6}H\(_{11}\))\(_{3}\)]\(_{2}\) on adding P(C\(_{6}H\(_{11}\))\(_{3}\)). The invariance of the rate constants to these changes in phosphine concentration (Table II) justifies the form of eq 6.

Analysis of the temperature dependence of the rate of appearance of neopentane (i.e., \(k_{SH} - k_{SH}, Table II\)) at three temperatures in the presence of 0.022 M added triethylphosphine gave a linear Arrhenius plot: \(E_a = 49\) kcal/mol, log \(A = 20\); with no added triethylphosphine, the corresponding values were \(E_a = 46\) kcal/mol, log \(A = 21\) (Figure 5). The close similarity between activation parameters in the presence and absence of added triethylphosphine suggests that the same mechanism describes de-compositions in both kinds of solutions.

The rate of decomposition of 1 showed some sensitivity to solvent. Although rates of decomposition of 1 in benzene, diethyl ether, cyclohexane, and decane were all similar, a solution of 1 (0.11 M) in neat triethylphosphine (ca. 6.8 M) decomposed approximately 65 times more rapidly than expected on the basis of

\[\text{(29) In making this statistical correction, we assume that } \text{LPr}_R \text{ is the critical intermediate involved and that the three methyl groups of both neopentyl moieties have equal access to the vacant coordination site. Unpublished results indicate processes such as } i = ii \text{ (or some equivalent process which renders the } R \text{ groups equivalent) are fast compared with the rate-limiting step in a } \beta \text{ hydride elimination reaction (McCarthy, T. J.; Nuzzo, R. G., unpublished results).}\]


\[\text{(32) Evidence for a change in mechanism at high concentrations of added phosphines is clear for the decomposition of diethylphosphine(tributylphosphine)-platinum(II). At sufficiently high concentrations of phosphine, the } \beta \text{-hydride elimination reaction occurs with a rate-limiting transition state having two phosphines associated with platinum rather than one. The same explanation is compatible with the kinetic behavior observed in this work for 1, but this kinetic regime has not been explored in any detail. T. J. McCarthy and R. G. Nuzzo, unpublished results.}\]

\[\text{(33) This latter estimate is derived from comparison of the data at 157 } ^\circ \text{C for } k_{SH} \text{ (entry 6 of Table II) with the rate constant for decomposition in the absence of added triethylphosphine at 157 } ^\circ \text{C, } k_{SH} = 3.0 \times 10^{-7} \text{ s}^{-1}, \text{ which is obtained from extrapolation of the Arrhenius plot for decomposition of 1 with no added phosphine.}\]
Table III. Photolysis of Dineopentylmercury and 1 in Cyclohexane

<table>
<thead>
<tr>
<th>MN₂ (conc, M)</th>
<th>phosphine (conc, M)</th>
<th>cyclohexane</th>
<th>% decomp (time, h)b</th>
<th>rel product yieldsc</th>
<th>NHD</th>
<th>N-N</th>
<th>N-S</th>
<th>S-S</th>
<th>others</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(CH₃)₅C₅H₅]₂He (0.39)</td>
<td>0</td>
<td>C₅D₁₅</td>
<td>19 (48)</td>
<td>1 (69%, d₁)</td>
<td>0.80</td>
<td>0.67</td>
<td>0.44</td>
<td>d</td>
<td></td>
</tr>
<tr>
<td>(0.39)</td>
<td>L_D (0.054)</td>
<td>C₅D₁₅</td>
<td>24 (48)</td>
<td>1 (76%, d₁)</td>
<td>0.93</td>
<td>0.71</td>
<td>1.0</td>
<td>d</td>
<td></td>
</tr>
<tr>
<td>1 (0.080)</td>
<td>L (0.056)</td>
<td>C₅H₁₂</td>
<td>100 (48)</td>
<td>1</td>
<td>0.11</td>
<td>0.12</td>
<td>0.07</td>
<td>e</td>
<td></td>
</tr>
<tr>
<td>(0.082)</td>
<td>(0.056)</td>
<td>C₅H₁₂</td>
<td>100 (48)</td>
<td>1</td>
<td>0.11</td>
<td>0.12</td>
<td>0.07</td>
<td>e</td>
<td></td>
</tr>
<tr>
<td>1 (0.080) + 1 [CD₂C(CH₃)₂]₁ (0.04)</td>
<td>(0.056)</td>
<td>C₅H₁₂</td>
<td>100 (8)</td>
<td>1</td>
<td>0.13f</td>
<td>0.15</td>
<td>0.07</td>
<td>e</td>
<td></td>
</tr>
</tbody>
</table>

* Photolyses were carried out at 60 °C, using Pyrex tubes and 3500 and 2537-A lamps. b % decomposition was calculated on the basis of the sum of the yields of the observed products. c NH(D) = neopentane (D), N-N = dineopentyl, N-S = neopentylcyclohexane, and S-S = dicyclohexyl. Cyclohexene overlapped with cyclohexene in the GLC trace and would not have been detected. Cyclohexene and a trace of ethylene were observed. Ethylene (−0.1 mol/mol of I) was observed. d, d₁ = 26%, d₂ = 51%, and d₃ = 23%.

than in cyclohexene (cf. Experimental Section).

Phosphorus NMR spectroscopy provides additional evidence confirming the compatibility of a dissociative equilibrium generating LPrR₂ (eq 11, R = CH₃C(CH₃)₃) with the kinetic data.

\[
\text{d}[1-\{\text{P(CD₃)₃}\}] / \text{dt} = \\
(7.7 \times 10^{-5} \text{ s}^{-1}) [1-\{\text{P(CD₃)₃}\}] [\text{P(CD₃)₃}]^{3\text{obs}} (12)
\]

describing the disappearance of 1-d₃₀ at 30 °C (representative spectra and individual rate constants are given in the Experimental Section). Although the error in the exponent of the term in the concentration of P(CD₃)₃ is large, this rate law indicates that the interchange of phosphines on 1 occurs by an Sₚ1 process: rate-limiting dissociation of phosphine from 1, followed by recombination of a new phosphine with the resulting LPrR₂ intermediate. Thus, ³¹P NMR spectroscopy provides direct evidence for dissociation of phosphine ligands from 1 at a rate significantly faster than the rate of decomposition of 1.

Analysis of the dependence of k₅ on triethylphosphine concentration indicated qualitatively that the rate of phosphine dissociation inferred from this dependence is compatible with the rate determined by ³¹P NMR. Substitution of eq 5 into eq 1 and inversion of eq 13; similar manipulation of eqs 2 into eq 14. In either event, a plot of (k₅obs)⁻¹ vs. [L] should generate a straight line, with the intercept [L]₀ = 0 being the reciprocal of the phosphine-dissociation rate (k₅)⁻¹. This plot (from entries 6–9 of Table II) is shown in Figure 6. The intercept is not accurately defined from the plot, and only a lower limit for k₅ can be extracted: k₅ ≥ 1.3 \times 10^{-3} s⁻¹. This rate constant is estimated from data collected at 157 °C and cannot be compared directly with that from the ³¹P NMR observations at 30 °C. This latter rate can, however, be extrapolated approximately to 157 °C by first assuming reasonable values of the Arrhenius preexponential factor and calculating values of the activation energy for phosphine dissociation: for A = 10^{16} (assumed), Eₐ = 27 kcal mol⁻¹, and k₅ (extrapolated) = 10² s⁻¹; for A = 10^{10} (assumed), Eₐ = 33 kcal mol⁻¹, and k₅ (extrapolated) = 10³ s⁻¹. These estimates of rates are compatible with that estimated by extrapolating the line in Figure 6 to [L] = 0 but are much more reliable quantitatively. Because the quality of the latter data are such that they lead only to a lower limit for k₅, we will use the estimate from ³¹P NMR as the basis for further discussion. The exchange of (C₅H₅)_₂P into 4-[1(C₅H₅)₂P] was measured by ³¹P NMR and was calculated to have a half-life of ca. 15 min (k = 10^{-3} s⁻¹, 30 °C, cyclohexane, assuming an Sₚ1 mechanism). With the assumption that 1 and 4 follow the same mechanism for phosphine exchange, compound 4 exchanges ~10 times faster than 1.

Radical Mechanisms. A comparison of the products of thermal decomposition of 1 with those of a reaction which generates authentic neopentyl radicals—photolysis of dineopentylmercury—indicates that it is very unlikely that the former reaction involves neopentyl radical intermediates. Table III lists products of photolysis of dineopentylmercury and 1 in cyclohexane and in cyclohexane containing triethylphosphine. The array of products observed on photolysis is that expected for a radical reaction. In particular, the products are derived in major part from attack on the cyclohexane solvent. This distribution is clearly very different from that observed in thermal decomposition of 1.

(34) The ³¹P NMR (C₅D₅)_2 chemical shift for (C₅D₅)_2P is 2.4 ppm upfield from (C₅H₅)_2P (−19.9 ppm). When they are complexed, as in 1-[1(C₅D₅)₂P] and 1, they differ by 1.6 ppm in the same sense. The mixed complex 1-[1(C₅D₅)₂P]-[(C₅H₅)_2P] shows half of an AB pattern (only H was decoupled; phosphines coupled to deuterium are broadened) with Jₚ₋ₚ = 12 Hz.


(36) A = 10¹⁴ was chosen as typical of a unimolecular dissociation; A = 10¹⁶ is the value estimated from the Sₚ1 mechanism.

(37) This activation energy is comparable to values obtained for (F₃P₃)₄P (24 kcal/mol) which also exchanges phosphines by an Sₚ1 mechanism. Johnston, R. D.; Basolo, F.; Pearson, R. G. Inorg. Chem. 1971, 10, 247–251.

**Figure 6.** Plot of (k₅obs⁻¹) vs. (k₅obs - k₅N)⁻¹ vs. the concentration of added P(CD₃)₃. Rate constants were obtained at 157 °C in cyclohexane solution by ³¹P NMR spectroscopy.
noplatinum complexes has not been established, but the products of this reaction can plausibly be derived, at least in part, from neopentyl radicals. The distribution of a 1:2:1 mixture of di-neopentyls-D$_2$, -t-$d_3$, and -t-$d_4$ from photolysis of a mixture of 1 and 1-[CD$_5$C(CH$_3$)$_2$]$_3$ is compatible with this path. The relatively low incorporation of deuterium into neopentane in C$_5$D$_{12}$ suggests, however, that another, more selective, nonradical path may also be important. In any event, these product distributions are so different from those observed in thermal decomposition of 1 as to exclude radical paths for the thermal decompositions, even though the reaction conditions in the thermolysis and photolyses are quite different.

Discussion

Six lines of evidence support the mechanism outlined in Scheme I for the thermal decomposition of 1: (1) the platincyclobutane 4 and neopentane are the major products; (2) the decomposition involves an intramolecular transfer of hydrogen from a methyl group of one neopentyl moiety to the methylene group of a second; (3) a kinetic isotope effect of $k_{H}/k_{D} \approx 3.0$ is observed for the transferred hydrogen; (4) dissociation of triethylphosphine and formation of a three-coordinate intermediate LPr$_2$ is required for the reaction; (5) neopentyl radicals are not intermediates; (6) the methyl and methylene groups of the neopentyl moieties do not interchange during the reaction.

The most important question unresolved by these data is the overall rate-limiting step: carbon–carbon bond breaking (2 $\rightarrow$ 3) and carbon–hydrogen bond making (3 $\rightarrow$ 4) is both compatible with the kinetic isotope effect and the observation that the methyl and methylene groups of 1 do not equilibrate during decomposition does not exclude reversible formation of 3. A second question is that of the timing of neopentane loss and triethylphosphine addition involving 3 (eq 15). The large Arrhenius preexponential factor ($\log A \approx 20$) is most compatible with a mechanism in which reductive elimination (3 $\rightarrow$ 7) is overall rate limiting. This mechanism would involved a transition state in which three particles (L, 7, and neopentane) are generated in the transition state from one particle (I) in the ground state and would be expected to be characterized by a large, favorable, entropy of activation.38 In the absence of clear models for such a process and with the fact that relief of steric crowding (see below) may be accompanied by an increase in entropy of unpredictable magnitude, this mechanistic proposal should be considered tentative. We note that the observed isotope effect ($k_{H}/k_{D} \approx 3$) is similar to that observed for reductive elimination of methane from bis(triphenylphosphine)hydridometalylplatinum(II) ($k_{H}/k_{D} \approx 3.5$).39 On the assumption that neopentane loss is rate limiting, phosphine association must follow neopentane loss: that is, the reaction path must be 3 $\rightarrow$ 7 $\rightarrow$ 4.

Comparison of the results of this study with that for cis-di-n-butylbis(triphenylphosphine)platinum(II) and cis-diethylbis(triethylphosphine)platinum(II) suggests the parallel that a three-coordinate complex LPr$_2$ is an important reactive species in each case. These studies indicate that the relative rates of intramolecular loss of different types of hydrogen by processes involving additions to platinum are $\beta$-CH ($\beta$-hydrate elimination) $>$ $\gamma$-CH (cycloolactallation) $>$ $\alpha$-CH (carbene formation). Note, however, that this order is not necessarily the same as the order of the addition reactions themselves since C–H bond cleavage is rate limiting in none of these reactions. The requirement for phosphine dissociation in these reactions rationalizes the observation that organoplatinum compounds are more stable as solids than in solution and that solution stability is increased by adding phosphines.

The side-reactions accompanying the transformation of 1 to 4—that is, neopentane production by abstraction of hydrogen from triethylphosphine and dineopentane production—are interesting in that they seem similar in kinetic behavior. The first of these reactions is probably a competitive cyclometallation, and the kinetic similarity is not surprising (eq 16). The second reaction forms a carbon–carbon bond and is a different type of process. The reaction proceeds in this system in a yield which is too low to make detailed mechanistic study practical (although it is approximately 40% for didecyldiphenyl(tetraphenylphosphine)platinum(II) in some conditions). We note, nonetheless, that the reaction need not proceed by reductive elimination from a di-neopentylplatinum(II) species (eq 17a) but may reflect an alternative mode of decomposition of the platinum(IV) species 3 (or some derivative) (eq 17b). Reductive elimination with carbon–carbon bond formation and platincyclobutane ring opening has been observed.40 There is, to date, no well-established example of carbon–carbon bond formation by reductive elimination from a dialkylplatinum(II) group.

The mechanism of decomposition of 1 suggests hypotheses (although not yet firm answers) for two general questions. First, why does the reaction 1 $\rightarrow$ 4 + neopentane occur? Second, if addition of C–H bonds from neopentyl moieties and from triethylphosphine occurs readily, why is solvent not attacked? The simplest thermodynamic analysis of the overall reaction identifies no obvious driving force for the reaction (eq 18): it simply interchanges Pt–C and C–H bonds. Three factors seem capable, in principle, of making the reaction exergonic: first, since two particles are produced from one, $\Delta S$ for the reaction should be positive; second, there may be some special stability associated with a platincyclobutane ring; third, the reaction may relieve unfavorable steric interactions in the starting material. Further work will be required to evaluate these possibilities, but on the basis of our current knowledge we would suggest the third as the most important. The favorable $\Delta S$ will probably not be large enough to account for the apparent irreversibility of the reaction,44 it is not obvious why a metallocyclobutane should be especially stable; 1 is, however, probably significantly more strained by interaction of the bulky ligands than is 4. If this analysis is correct, then, in principle, it should be possible to find instances in which solvent C–H bonds add to platinum. In the particular case of 1, it

(38) A related mechanism with a similar value for $A$ has been inferred for the decomposition of diethylbis(triethylphosphine)platinum(II).
appears that the second most reactive C–H bonds in the system are those of the triethylphosphine moieties; this reactivity certainly reflects the favorable influence of high local concentration and may reflect electronic factors as well. Further, if the cyclohexane solvent was to add, it would probably increase rather than decrease the unfavorable steric interactions around the metal: the solvent molecule added should, at minimum, be smaller than the alkyl group it replaces to encourage addition.

**Experimental Section**

**General Data.** Organometallic reactions were carried out under argon or purified nitrogen by using standard anerobic techniques. Melting points were obtained in open tubes and are uncorrected. Mass spectra were obtained by using a Hewlett-Packard 5990A GC/MS, with a 5973 N electron ionizing voltage. 3P NMR spectra were taken by using a JEOL FX 90 Q spectrometer and are referenced to 85% H3PO4 (external). Grignard reagents were titrated by the procedure of Eastham. 43 Ethereal solvents were dried by distillation from disodium benzophenone diiuan. Bulb-to-bulb distillations and gas transfers were carried out by using a calibrated volume vacuum line equipped with a mechanical pump to maintain a 0.002 torr vacuum. Sealed tubes for kinetic studies were prepared by using this same line. Photolyses were carried out in Pyrex tubes by using a Rayonet reactor containing eight 350-nm and eight 253.7-nm mercury lamps.

Cycloocta-1,5-diene (Tchel, Aldrich) and cyclooctene (Matheson, tex) were used without purification. Acetonitrile-d3 (99.5%, Stohler Isotope Chemicals, LiAlH4 (99.9% D), Stohler Isotope Chemicals, D2O (99.7% D, Merck), and DCl (38% in D2O, 99.6% D, Stohler Isotope Chemicals) were used as received; cyclohexane-d8 was purified by distillation from P2O5; TiCl4 (Alfa) was distilled before use.

**Neopentylmagnesium bromide** was prepared in 80% yield by reaction of neopentyl bromide with Rieke magnesium44 in ether, followed by centrifugation to remove precipitated magnesium salts. cis-Dichloro-1,5-cyclooctadiene (without melting 255-280 °C dec) was obtained in 96% yield by reaction of K2PcCl4 with 1,5-cyclooctadiene in acetic acid-water.45

**Dioxanemethylen** was prepared from mercuric chloride and neopentylmagnesium bromide by following a literature procedure.46 It had mp 95 °C (lit. 93-95 °C) and bp 78 °C (0.1 torr); +5.1° m (C,H2Cl2).47

**Pinacol-d5** ([CD3]C3H7OH)48, 49 To a 3-L Erlenmeyer flask equipped with a stopper and thermometer was added HgCl2 (13.2 g, 0.05 mol), dry tetrahydrofuran (THF, 300 mL), and magnesium powder (45.6 g, 1.87 g/atom, 40 mesh). The reaction mixture was allowed to stir for 2 h, and the supernatant solution was removed from the dark magnesium amalgam by cannula. Dry THF (1.8 L) was added, and the mixture was cooled to −30 °C in a dry ice-acetone bath. Titanium tetrachloride (178 g, 104 mL, 0.94 mol) was added slowly while this temperature was maintained. After the addition had been completed, the yellow-green solution was warmed to −5 °C in an ice-acetone bath and stirred for 1 h. To the mixture was added 40 mL of acetone-d6 in 5-g aliquots while keeping the temperature below 0 °C (this reaction is extremely exothermic, with variable induction periods). A blue-black mixture resulted which was allowed to stand for 8 h and was quenched with a saturated solution of K2CO3 in water. The solution was separated from solids by centrifugation, acidified (pH 6) with 0.1 M H2SO4, and extracted with four 100-mL portions of CH2Cl2. The ether was removed on a rotary evaporator at room temperature, and the residual oil was poured on a column containing silica gel, 200-400 mesh. The column was eluted with pentane to give 1.11 g (91% yield) of pinacol-d5.

**Pinacol-d4** ([CD3]2C3H6O)49 To a 3-L Erlenmeyer flask equipped with a stopper and thermometer was added HgCl2 (13.2 g, 0.05 mol), dry tetrahydrofuran (THF, 300 mL), and magnesium powder (45.6 g, 1.87 g/atom, 40 mesh). The reaction mixture was allowed to stir for 2 h, and the supernatant solution was removed from the dark magnesium amalgam by cannula. Dry THF (1.8 L) was added, and the mixture was cooled to −30 °C in a dry ice-acetone bath. Titanium tetrachloride (178 g, 104 mL, 0.94 mol) was added slowly while this temperature was maintained. After the addition had been completed, the yellow-green solution was warmed to −5 °C in an ice-acetone bath and stirred for 1 h. To the mixture was added 40 mL of acetone-d6 in 5-g aliquots while keeping the temperature below 0 °C (this reaction is extremely exothermic, with variable induction periods). A blue-black mixture resulted which was allowed to stand for 8 h and was quenched with a saturated solution of K2CO3 in water. The solution was separated from solids by centrifugation, acidified (pH 6) with 0.1 M H2SO4, and extracted with four 100-mL portions of CH2Cl2. The ether was removed on a rotary evaporator at room temperature, and the residual oil was poured on a column containing silica gel, 200-400 mesh. The column was eluted with pentane to give 1.11 g (91% yield) of pinacol-d5.
were purified by three trap-to-trap fractions through a 0 °C trap.
cis-Diopentyl-1,5-cyclooctadieneplatinum(II). To a stirred suspension of 3.5 g (9.4 mmol) of cis-dichloro-1,5-cyclooctadieneplatinum(II) in 200 mL of dry ether at −90 °C was added over a period of 1 h 270 mL (20 mmol) of 0.075 M solution of neopentylmagnesium bromide in tetrahydrofuran. The mixture was allowed to stir for 8 h while being warmed to room temperature, quenched with 100 mL of NaCl-
H₂O (50% saturated), and diluted with 150 mL of pentane. The aqueous portion (sometimes black) was extracted with two 150-mL portions of pentane and combined with the organic layer. The organic portion was dried over Na₂SO₄, filtered, and concentrated at room temperature by using a rotary evaporator. The product was an oily solid, which was recrystallized by dissolving in 25 mL of acetone and cooling to −15 °C. A light yellow crystalline product (1.4 g) was obtained; an additional 1.3 g was obtained from the mother liquor by adding 1 mL of water and cooling to −20 °C. mp 105 °C. [α]D₂₀ = 2.8° (CH₂Cl₂), [α]D₂₀ = 1.81 ± 0.92 °(br, 8 H, CH₂-CH₂-), 2.16 (t, 1:41: J = 9 H, J) = 92 Hz, PCl₂CH₂-), 4.74 (t, br, 4:1, 4 H, J) = 38 Hz, CH₂CH₂-). IR (KB pellet): 2900 (vs), 2795 (vs), 1470 (s), 1455 (s), 1425 (s), 1370 (s), 1350 (vs), 1335 (m), 1230 (s), 1140 (s) cm⁻¹.

Anal. Ca₁₀H₈₂Pt₄: C, 48.54; H, 7.64. Found: C, 48.65, H, 7.82.

Deuterated analogues of CDPβ(CH₃CH₂CH₂)₃ were prepared by using the same procedure: all had mp 107 °C and 3H NMR spectra consistent with the assigned structures.

cis-Diopentylbis(triethylphosphine)platinum(II). To a 10-mL solution of 1.1 M cis-diopentyl-1,5-cyclooctadieneplatinum(II) in ether was added triethylphosphine (0.27 mL, 2.00 mmol). The mixture was allowed to stand for 10 h. The solution was passed through a column of activity I alumina (3 cm × 1 cm) and eluted with additional ether to remove any unreacted triethylphosphine and phosphine oxide.

The solvent was removed under vacuum to leave an off-white crystalline solid. The solid was dissolved in a minimum of pentane (≈20 mL) by gently warming and cooled to −10 °C. Material was used for NMR studies. The kinetic studies were recrystallized again from pentane: mp 130–132 °C. [2]P NMR (CD₂Cl₂, HPO₂ external reference) d = 2.1 (t, 1:41, J = 1638 Hz); [3]H NMR (CD₂Cl₂) d = 0.25–0.76 (6 line m, 36 H), 0.76–1.64 (7 line m, 16 H). IR (KB pellet) 2880 (vs), 1450 (br s), 1430 (s), 1370 (s), 1345 (s), 1230 (s), 1025 (s), 750 (s), 710 (s) cm⁻¹.


Deuterated analogues of 1 were prepared by analogous procedures. All had melting points with decomposition in the range 127–133 °C.

Quantitative Protolysis of 1. Into a 1-mL centrifuge tube was weighed 12.8 mg (0.022 mmol) of 1. A No-Air stopper was fitted to the tube, and the solid was dissolved in 0.3 mL of a standard solution of 0.1 M cyclooctane (as a GC internal standard) in cyclohexane. The solution was treated with 0.1 mL of HCl (38% in H₂O). HCl (concentrated), or trifluoromethanesulfonic acid and was shaken for 2 min. The organic layer was analyzed by GLC with the use of a cold clean injection port (50 °C) to obtain 100% of the theoretical 2 equiv of neopentane.

This procedure was not used for deuterium incorporation experiments of alkyl complexes.

Cryoscopic Molecular Weight Determination of 4. Using a modification of a standard procedure,27 0.0150 g (0.030 mmol) of 4 was weighed into a flame-dried 6 × 30 mm disposable culture tube. The tube was capped with a rubber septum and 0.511 g (6.55 mmol) of distilled benzene added by syringe. The contents of the tube were mixed thoroughly and then frozen at −78 °C, and the tube was attached to a Beckman thermometer and suspended in a Dewar of ice-water being stirred slowly at 0 °C. The temperature of the bath was allowed to increase at −0.05 °C/min, and the temperature at which the solution first began to melt was recorded. A second determination was performed, and the molecular weight was determined from the measured time of benzene added to the tube and the melting points determined with respect to a tube of pure benzene.

Workup of the data in the usual manner yielded a molecular weight for 4 of 515 (calculated 501).

Reactions of 4 with DCI, Br₂, and I₂. Into a flame-dried 1.0-mL centrifuge tube was weighed 15 mg (0.030 mmol) of 4. The tube was capped with a rubber septum and flushed with argon. To the tube was added 0.25 mL of a 0.1 M solution of cyclooctane (GC internal standard) in cyclohexane followed by 0.05 mL of DCI (3% in D₂O, 99% D), and the tube was shaken for 0.5 h. HCl analysis showed a 98% yield of neopentane which was determined to be 99% (CH₃)₂CHD₂ and 1% (CH₃)₂CCl₂D by GC/MS.

With use of a similar procedure, reaction of 4 with 1 equiv of I₂ dissolved in cyclohexane at 25 °C yielded 98% 1,1-dichloro-2,2-dimethylpropane and 2% 1,3-diido-2,2-dimethylpropane. Reaction of 2 equiv of Br₂ was carried out in a similar manner.

Isolation of 4[P(C₆H₅)₃]₃. In a Pyrex tube was placed 0.28 g (0.6 mmol) of I₃[P(C₆H₅)₂] and 7 mL of a 0.051 M solution of cyclooctane in cyclohexane. The compound tube were degassed, and to the tube was sealed and heated at 150 °C for 24 h at a pressure of −196 °C, and analyzed for neopentane by GLC and GC/MS. The analysis showed that the thermolysis was 97% complete with 98% neopentane-de₃ produced. A 3P NMR spectrum (CD₂Cl₂, external HPO₂ reference) of the decomposition solution showed only one major phosphine-containing product: δ +10 (t, 1:4: J, 1H, J₃P) = 1826 Hz). The solvent was removed

(55) The Hewlett-Packard 5990A GC/MS can be set to accumulate and average eight consecutive spectra automatically and to store these spectra in an external memory. Another series of scans was initiated manually only as the previous one was completed. In the completion of a peak, the series of these-scan averages (typically 48 spectra) was averaged manually.

(56) The 1H NMR spectra of Pt₄ complex properly considered as part of an AMM'X₂5'2 system. The approximately triplet splitting due to coupling between 2H and 3P does not reflect J₃P-H accurately and should be considered only as an empirical parameter. The reported J values are the separation between the outer lines of these triplets. Shokemaker, D. P.; Garland, C. W.; Steinfield, J. L. "Experiments in Physical Chemistry," 3rd ed; McGraw-Hill: New York, 1974; pp 174–185.
in a stream of argon, and the residual oil was taken up in 2 mL of acetonitrile to precipitate unreacted 1-[PC(C(6)H_{11})_3]_2. The acetonitrile solution was separated and acetonitrile removed under vacuum. Using an oil which could not be made to crystallize. Volatile proton-containing materials were removed from the oil by adding and evaporating several 2-mL portions of C6D6. The {superscript}1H NMR spectrum (see the text) indicated the presence of ca. 10% impurity resonance {delta} 1.35 ppm (the {superscript}13C NMR spectrum was identical with that of the crude reaction solution, with the addition of a small new resonance at 3.8 ppm). The complex was very soluble in all organic solvents but insoluble in water. It decomposed on a silica gel column when eluted with ether; further attempts to purify the air-stable oil were not made. The {superscript}1H NMR spectrum of 4-(1-[PC(C(6)H_{11})_3]_2)P, showed two types of protons: {delta} (CDCl_{3}) 0.73 (t, 1H, J = 1-4 Hz, J = 74 Hz, "J" = 12, 12. PCH(1)) and 1.31, (t, J = 74 Hz. "P" = 3 Hz, CH(2)CH(2)).

The proton-decoupled {superscript}31P spectrum showed one type of phosphorus: {delta} (CDCl_{3}, 85% H3PO4 external reference) +9.0 (t, 1-4, J = 1862 Hz).

Reactions of 4-[PC(C(6)H_{11})_3]_2 and 4-d_0 with DCl, HCI, and HCCN. Compound 1-[PC(C(6)H_{11})_3]_2 (29.4 mg, 0.048 mmol) was placed in an NMR tube containing 10 mL of tetramethylammonium, 2 mL of (CD_3)P, and 0.6 mL of C6D6. The tube was degassed, sealed, and heated at 157 °C until neopentane production stopped (ca. 3 h). The tube was opened and fitted with a No-Air stopper, and 0.5 mL of a 0.093 M solution of cyclohexane (GLC standard) in cyclohexane was added. GLC analysis showed 105% yield of neopentane and 7% yield of dieneophyl based on initial 1-d_0. The solvents were removed in a stream of argon, and the residual oil was dissolved in 0.5 mL of a 0.093 M solution of cyclohexane in cyclohexane. This solution was added in 0.005 mL portions of DCl (38% in D_2O) to yield neopentane (85% based on initial 1-d_0) which was monitored using GLC analysis with fragmentation pattern: m/e (%): 56 (4.8), 57 (15.9), 58 (100), 59 (81.5), 60 (4.0). A 100% mass balance of neopentane groups was obtained based on 1-d_0. Reactions with HCl and cyanogen were carried out by using similar procedures.

Sealed-Tube Reactions, General Methods. Reaction vessels used for thermolysis reactions were made from 6-mm o.d. medium-walled Pyrex tubing with a length of 15 cm. A constricted was placed 6.5 cm from a sealed end. These tubes were washed with acetone, distilled water, acetone (reagent), and cyclohexane reagent, stored at 125 °C, and flame dried under vacuum just before use. Hydrocarbons used as solvents (cyclohexane, benzene, toluene, 5-mm NMR tube, diene), were distilled under vacuum into a box covered with Petri dishes and stored at room temperature. A 0.05 M solution of phosphorus pentoxide in methanol was stirred with concentrated H_2SO_4 for 1 week, decanted, and washed several times with P_2O_5 in 3 days, and then dried under argon. GLC showed no detectable impurities. In general, it is important to keep reagents as dry as possible in these experiments. Into a tube cooled to room temperature was weighed the platinum complex. The tube was filled with a No-Air stopper, and the powder was taped to the bottom. The tube was flushed with argon by inserting a 2-in., 16-gauge syringe needle (to act as vent) and a 20-gauge (8-in.) syringe needle attached to an argon line through the 16-gauge syringe needle down into the tube as far as possible. Care was taken not to disturb the solid. After flushing for 5 min, the needles were removed and 0.3 mL of a solution of trimethylphosphine in cyclohexane was added by syringe. The tube was placed in a vacuum desiccator for 1-2 days. The tube was attached to a vacuum line by means of a 5-cm, 0.25-in. i.d. rubber vacuum tubing, degassed, and sealed off to the No-Air stopper. A stream of nitrogen emerging from the piece of rubber tubing (the rubber tube was washed with cyclohexane and pumped on for 3 days before use). The tubing was wired firmly to the sample tube. The contents of the tube were isolated from the vacuum system by pinching the rubber tubing. The tube was placed in a 100 °C oven and degassed three times to 0.005 torr, and sealed. It is important that the platinum complex was not deposited at the construction and pyrolyzed during sealing. The pyrolyses were performed in a constant-temperature bath (made from a Dry Ice condenser, wash which was filled with oil) heated by refluxing solvent: water (100 °C), acetic acid (118 °C), p-xylene (138 °C), and bromobenzene (157 °C). The tubes were placed in the vacuum desiccator and opened in cyclohexane or of excess 1-d_0 and a 0.34 M solution of trimethylphosphine in cyclohexane (both containing cyclohexane as a GLPC internal standard) was frozen, evacuated and sealed in Pyrex tubes, and shaken at 22 °C for 24 h. The tubes were placed in the vacuum desiccator and opened in cyclohexane. A saturated solution of 1-d_0 in cyclohexane at 22 °C is 0.051 M and in cyclohexane containing 0.34 M Et_3P, 0.059 M.

Measurement of K_p by {superscript}31P NMR Spectroscopy. Into each of four NMR tubes was weighed 32.8 mg (0.054 mmol) of 1-[PC(C(6)H_{11})_3]_2. The tubes were fitted with No-Air stoppers and treated with argon, and 10-mL aliquots of (CH_2O)_2PO (12.5 mg, 0.089 mmol) and 0.0 mL of C_6H_5I were added. A temperature of 155 °C was held for 1.5-2.0 h. The phosphorus pentoxide was added to a tube. The No-Air stopper was sealed with wax, and a {superscript}31P NMR spectrum was immediately taken. The peak temperature was regulated to 303 ± 0.5 K. Proton-decoupled spectra were recorded over intervals of 30 min until no change in peak heights was observed. The use of solubility measurements of this type to differentiate between associated and dissociative equilibria is discussed in: Whitides, G. M.; Gaasch, J. F.; Stedronsky, E. R. J. Am. Chem. Soc. 1972, 74, 5258-5270.
the exchange was followed by observing the decrease of free \((\text{C}_2\text{H}_2)_3\text{P}\) and yields a first-order rate constant of \(1.0 \times 10^4 \text{ s}^{-1}\). With the assumption that the exchange was first-order in \((\text{C}_2\text{H}_2)_3\text{P}\), the calculated second-order rate constants would be 0.4, 0.9, 5.6, and \(9.1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}\).

Photolyses of dineopentylmercury and 1 were carried out at ambient temperature by using cyclohexane as solvent. The progress of the photolysis of 1 was monitored by \(^{31}\text{P}\) NMR spectroscopy. During the reaction, the resonance of 1 and free triethylphosphine disappeared and were replaced by a 1:4:1 triplet at \(\delta +41 \left(\text{Et}_3\text{P}\right)\text{P}^0, J_{\text{P-P}} = 4226 \text{ Hz}\).

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Supplementary Material Available: Table IA of mass spectral data used in analyzing isotopic compositions (3 pages). Ordering information is given on any current masthead page.