Introduction

A problem that is encountered frequently in studies of mechanisms of reactions of transition-metal organometallic compounds is that of distinguishing between truly homogeneous reactions and heterogeneous reactions catalyzed by bulk or finely divided metal produced by decomposition of the (originally) homogeneous organometallic species. A number of methods have been proposed for detecting heterogeneous reactions catalyzed by bulk or finely divided metal produced by decomposition of the organometallic species. A number of methods have been proposed for detecting heterogeneous components in complex mechanisms, but additional complementary methods are still required.

In the course of studies of mechanisms of reactions of platinum(II) organometallic compounds, we have often encountered situations in which we wished to distinguish between homogeneous stoichiometric reactions and heterogeneous catalyzed reactions. Unwanted heterogeneous reactions have been particularly troublesome in high temperature (100–250 °C) reactions involving dihalo-2,2,3,3-tetramethylbutane and illustrate the use of this material as a reagent for the preparation of 3,3,4,4-tetramethylmetallacyclopentanes via the corresponding di-Grignard reagents.

Thermal decomposition of bis(trialkylphosphine)-3,3,4,4-tetramethylplatinacyclopentanes in hydrocarbon solvents yields two major products: 2,2,3,3-tetramethylbutane and l-methyl-1-tert:butylcyclopropane. The former appears to be generated by heterogeneous processes catalyzed by platinum(0) colloidal and/or solid formed during the decomposition; the latter is the product of a homogeneous reaction sequence. The existence of competing homogeneous and heterogeneous reaction pathways complicates the study of this thermal decomposition. The addition of mercury(0) to the system selectively suppresses the heterogeneous reaction by poisoning the bulk platinum(0). This technique has been tested in one well-defined model system—the homogeneous hydrogenation of dionpentylbis(triethylphosphine)platinum(II) to dihydridobis(triethylphosphine)platinum(II) and neopentane in the presence of the heterogeneous platinum(0)-catalyzed hydrogenation of 1-methylcyclopentene to methylcyclopentane—and found to eliminate the heterogeneous reaction while leaving the homogeneous one essentially unaffected. Application of this technique to the thermal decomposition of 3,3,4,4-tetramethylplatinacyclopentane simplifies the reaction by eliminating 2,2,3,3-tetramethylbutane as a product. Similarly, addition of mercury(0) to solutions containing H₂ and (1,5-cyclooctadiene)dimealplatinum(II) in cyclohexane suppresses the autocatalytic, heterogeneous platinum-catalyzed conversion of the organoplatinum compound to (inter alia) cyclooctane, methane, and platinum(0). In other reactions examined—especially the high-temperature thermal decompositions of (1,5-cyclooctadiene)dimealplatinum(II) and of cis-bis(cyclopentylidimethylphosphine)dimealplatinum(II) in hydrocarbon solvents—mercury poisoning does not successfully separate heterogeneous and homogeneous reactions. In the latter instance, an additional complicating process—apparent reaction of mercury(0) with the organoplatinum compound—introduces reaction paths which seem to generate methyl radicals. The paper includes a simple preparation of 1,4-dihalo-2,2,3,3-tetramethylbutane and illustrates the use of this material as a reagent for the preparation of 3,3,4,4-tetramethylmetallacyclopentanes via the corresponding di-Grignard reagents.
organometallics, Vol. 4, No. 10, 1985

The use of 

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although it may solve the problem of heterogeneous platinum-catalyzed reactions, it appears to introduce other competing and complicating processes. The purpose of this paper is to outline our experience with this technique.

The immediate focus of this study was an investigation of the mechanism of formation of 1-methyl-1-tert-butylcyclopropane (2) on thermal decomposition of bis(triethylphosphine)-3,3,4,4-tetramethylplatinacyclopentane (1) (eq 1; L = PEt3). Our interest in 1 stemmed from its structural similarity to bis(triethylphosphine)-3,3-dimethylplatinacyclobutane (5). This compound decomposes to platinum(0) and dimethylcyclopropane (eq 2; L = PEt3). The reaction of the di-Grignard reagent with tetramethylgermane, dichlorodiphenylstannane, and dichlorophenylmethylsilane, dichlorodiphenylsilane, dichlorodi-

catalyzed reaction of undetermined mechanism. Tetra-
methylcyclobutane is not an important product of decom-
position of 1.

Results

Syntheses. To study the thermal decomposition of bis(triethylphosphine)-3,3,4,4-tetramethylplatinacyclopentane, we required efficient preparations of 2,2,3,3-tetramethylbutane-1,4-diyil di-Grignard reagent and perdeuterated triethylphosphine. An improved synthesis22 of 1,4-dichloro-2,2,3,3-tetramethylbutane used 2,2'-azo-

phosphine is outlined in Scheme II. This procedure, which uses only D2O as a deuterium source, appears amenable to large-scale work. Its details are also summarized in supplementary material in the microfilm ed.

Model System: Heterogeneous Hydrogenation of 1-Methylocyclopentene in Competition with Homogeneous Hydrogenolysis of cis-Dineopentylbis(triethylphosphine)platinum(II). To test the capability of catalyst poisons such as mercury(0) to suppress a heterogeneous platinum-catalyzed reaction selectively in the presence of a competing homogeneous reaction of an organoplatinum compound, we examined a model system comprising two separate, individually well-defined components: the heterogeneous hydrogenation of 1-methylocyclopentene (MCP) catalyzed by platinum(0) (eq 3) and the homogeneous stoichiometric reaction of 4 with H2 (eq 4; L = Et3P).34


(22) Our earlier synthesis of 1,4-dichloro-2,2,3,3-tetramethylbutane by the iodine-promoted coupling of ethyl 2-methylpropionate proved difficult to scale up because dilute conditions and low temperatures were required to avoid undesired Claisen condensation of the lithium enolate and the starting aldehyde. See: Sowinski, A. F.; Whitesides, G. M. J. Org. Chem. 1979, 44, 2369–2376. Brockosm, T. J.; Petragno, N.; Rodriguez, R.; La Scala Teixeira, H. Synthesis 1975, 396–397.

Homogeneous Reactions of Organoplatinum Compounds

The choice of MCP as the olefinic substrate to be used in this study was based on its rate of hydrogenation; under the conditions used, the two reactions summarized in eq 3 and 4 proceeded at comparable rates. Reaction of 4 with dihydrogen at 40 °C in the presence of MCP proceeds by a first-order reaction having rate constant \( k = 10.7 \times 10^{-4} \) s\(^{-1}\) (Figure 1A). This rate constant is in good agreement with previous studies of the hydrogenolysis of 4 in the absence of olefin.\(^{24}\) Addition of a heterogeneous platinum catalyst (platinum on scintered glass) increases this rate constant by approximately 30%. This small increase appears to represent a small heterogeneous contribution of unknown character. MCP present in the reaction mixture catalyzes smoothly (Figure 1B). In the presence of 4 but in the absence of the heterogeneous platinum catalyst, no reduction of MCP occurs under these conditions (Figure 1B). Thus, neither 4 itself, nor its reaction products, are hydrogenation catalysts for MCP. The observation that MCP hydrogenates smoothly in the presence of 4 is important in indicating that neither this compound nor its reaction product dihydridobis(triethylphosphine)platinum(II) is a catalyst poison for bulk platinum(0), although free triethylphosphine is a strong catalyst poison for platinum(0).\(^{25}\)

The data given in Figure 2 summarize the course of the reactions given in eq 3 and 4 proceeding in the same reaction vessel in the presence and the absence of mercury (added in the form of a small drop of metallic mercury to magnetically stirred reaction mixtures). The rate of the stoichiometric hydrogenolysis of 4 is essentially unaffected by the presence of mercury(0); that is, it has a value indistinguishable from that in homogeneous solution (Figure 2) (the Experimental Section contains rate constants). The heterogeneous platinum-catalyzed reaction is completely suppressed in the presence of mercury (Figure 2).

We examined a number of other potential heterogeneous catalyst poisons for species which might be compatible with homogeneous organometallic reactions. Carbon monoxide\(^{26}\) (added at the start of the reaction) and triphenylphosphine gave results indistinguishable from those observed with mercury(0). Other catalyst poisons—including triphenyl and dibenzophosphine—were less successful.

Thermolysis of Bis(triethylphosphine)-2,3,4-tetramethylplatinacyclopentane (1). We have explored the influence of mercury on the products of decomposition of 1. The products of decomposition in solutions containing no mercury were a mixture of 2,2,3,3-tetramethylbutane and 1-methyl-1-tert-butylcyclopropane, in addition to other minor products (summarized in the Experimental Section) (eq 5; \( L = \text{PEt}_{3}\)). The reaction mixture is brown-black at its conclusion and shows variable densities of platinum mirror deposited on the walls of the flask. Olefins which would be expected to be products of the platinum-catalyzed ring opening of the cyclopropane (2-tert-butyl-2-ene, 2-tert-butyl-1-ene, and others) were occasionally observed as products and became major products if platinum dioxide was intentionally added to the reaction mixture.

\[ \text{Figure 1. Reaction in the absence of catalyst poisons. (A) Reaction of cis-dineopentylbis(triethylphosphine)platinum (4) (0.022 mmol in 6 mL of n-octane) with 2 atm H}_2 \text{ at 40 °C: O, in the presence of 0.030 mmol of MCP; } \square, \text{ in the presence of 10 mg of a 29% Pt on scintered glass catalyst and MCP. (B) Reaction of MCP with 2 atm H}_2 \text{ in n-octane at 40 °C: O, in the presence of 0.030 mmol of MCP; } \square, \text{ in the presence of 10 mg of a 29% Pt on scintered glass catalyst and MCP and 4 (0.022 mmol); } \blacksquare, \text{ in the presence of 4 (0.022 mmol).} \]

\[ \text{Figure 2. Reaction in the presence of catalyst poisons. (A) Reaction of 4 with 2 atm of H}_2 \text{ in n-octane at 40 °C: O, in the presence of Hg; } \Delta, \text{ in the presence of CO; } \square, \text{ in the presence of PPh}_3. \text{ Both 4 and MCP were present in the same solution for these studies; quantities are as given in Figure 1.}

\[ \text{Organometallics, Vol. 4, No. 10, 1985 1821} \]
Variability in product yields, and the obvious requirement that hydrogen atoms be transferred to the tetramethylplatinacyclobutane ring to produce tetramethylbutane (3), suggested that platinum-catalyzed heterogeneous reactions played an important role in the reaction. Decomposition of 1 containing perdeuterated triethylphosphine ligands established that significant but irreproducible quantities of deuterium were incorporated into both 2 and 3 (up to approximately 15% for 2 and up to 45% of a combination of δ1 and δ2 material for 3). Within the limits of GC detection, no tetramethylcyclobutane or 2-methylpropene was produced when decompositions were carried out in alkane solutions; tetramethylcyclobutane was formed in 17% yield when the tri-n-butylphosphine analogue was decomposed in methylene chloride at 118 °C.27

Addition of a small bead of mercury to the reaction solution before decomposition and vigorous mixing of the resulting mixture during decomposition using the apparatus in Figure 3 resulted in a qualitative change in the mixture of products obtained (eq 5). The reaction proceeded somewhat more slowly, tetramethylbutane production was completely suppressed, and the small quantities of ethane and ethylene observed essentially disappeared. The only significant hydrocarbon product was 2. The solution at the conclusion of the reaction was clear and colorless.

Although the interpretation of these facts remains unclear in detail, we propose that the formation of tetramethylbutane in these reactions is either entirely or in major part a heterogeneous reaction catalyzed by colloidal or bulk platinum(0). This heterogeneous process can be eliminated or suppressed by the addition of metallic mercury.

Reaction of (1,5-Cyclooctadiene)dimethylplatinum(II) (11) with Dihydrogen. We have also examined the influence of mercury(0) on the heterogeneous, platinum-catalyzed hydrogenation of (diene) dialkylplatinum(II) complexes (eq 6).α9,27 In the absence of added Hg(0), an initial irreproducible induction period is followed by uptake of H2 and precipitation of platinum metal (Figure 4). This autocatalytic process is entirely suppressed by addition of mercury(0).

When the hydrogenation of 11 is carried out in the presence of controlled-porosity glass beads, the induction period is much shorter and the rate of hydrogenation increases substantially. In the presence of added mercury(0), the rate of reaction decreases, but hydrogenation continues, albeit at a much slower pace. Addition of mercury(0) to the hydrogenation of 11 in the presence of controlled-porosity glass beads after 50% conversion of 11 to products confirms this result: hydrogenation is slowed, but not halted, by the presence of Hg(0) (Figure 5).

Although the course of this reaction is discussed elsewhere,27,28 the essential feature is that reaction of 11 and H2 proceeds rapidly in the presence of bulk platinum(0). The role of Hg(0) thus appears to be to poison initial traces of Pt(0) produced by unknown mechanisms.30 The failure

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of mercury(0) to halt the reaction of 11 and H₂ when the hydrogenation is carried out in the presence of glass beads may result from the inability of Hg(0) to poison the Pt(0) buried in small-diameter pores. Platinum(0) on the outer surface of the beads is, however, still susceptible to poisoning by mercury. Thus, in this system, the success of mercury(0) in poisoning a heterogeneous reaction seems to depend on physical details (distribution of platinum in pores).

Thermal Decomposition of (1,5-Cyclooctadiene)dineopentylplatinum(II) (12). We have examined the thermal decomposition of (1,5-cyclooctadiene)dineopentylplatinum(II) (12) in the presence and absence of mercury(0) in an effort to suppress the troublesome heterogeneous decomposition of this compound. Solutions of 12 in benzene-δ₉ were decomposed thermally in sealed glass tubes in the presence and absence of mercury using the off-axis stirring technique (Figure 3). Before thermolysis, these solutions were pale yellow (as is crystalline 12) and the mercury was bright and shiny. After thermolysis, the inside walls of the tubes not containing mercury were covered with a black solid and the reaction solution was brown and contained a suspended black precipitate. In contrast, the inside walls of the tubes containing mercury were clean and the reaction solutions was clear and colorless. The mercury was covered with a dusty film. Thermolyses conducted in the absence of mercury produced neopentane which was composed of 14% neopentane-δ₉. Thermolyses conducted in the presence of mercury produced only 4% neopentane-δ₉; dineopentylmercury was also produced (eq 7; yields are expressed as percent conversion since 5% 12 (without Hg) and 25% 12 (with Hg) remained at the end of these reactions). We suggest that the transfer of deuterium from benzene-δ₉ to the neopentyl moieties in the absence of added mercury is due to a heterogeneous reaction catalyzed by colloidal or bulk platinum(0). Mercury is apparently able to suppress but not to stop entirely this transfer. Thus, either the strategem of adding mercury(0) to suppress heterogeneous reactions is only partially successful in this case, or there is an independent, homogeneous reaction which incorporates deuterium from benzene-δ₉ into neopentane. The observation of dineopentylmercury(II) as product establishes that transmetalation of the dialkylmercury(II) compound may also contribute to the observed hydrocarbon products.

Thermal Decomposition of cis-Bis(cyclopentylidimethylphosphine)dimethylplatinum(II). Thermal decomposition of organoplatinum compounds at high temperature in deuterated hydrocarbon solvents often results in incorporation of small amounts of deuterium into hydrocarbon products derived from the platinum complex. This apparent "activation" of solvent-carbon–hydrogen bonds might occur either homogeneously or heterogeneously. In order to explore whether the observed hydrocarbon activation represented a homogeneous process, we examined the thermal decomposition of cis-bis(cyclopentylidimethylphosphine)dimethylplatinum(II) (33) selected because it had useful solubility in hydrocarbon solvents) in alkane solvents. The cyclopentylidimethylphosphine ligand would be expected to resist metatation: formation of a platinacyclopropane by activation of a C–H bond to phosphorus is uncommon, and metatation β or γ to

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### Table I. Thermolysis of Bis(cyclopentylidimethylphosphine)dimethylplatinum in the Presence and Absence of Mercury(0)

<table>
<thead>
<tr>
<th>organometallic components</th>
<th>rel yields (%) of products (isotopic composites)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[c-C₅H₅P(CH₂)₂]₂Pt(CH₃)₂</td>
<td>methane 74 (d₁/d₀ = 0.14)  ethane 24 (d₁/d₀ = 0)  ethylene 8 (d₁/d₀ = 0.14)</td>
</tr>
<tr>
<td>[c-C₅H₅P(CH₂)₂]₂Pt(CH₃)₂, Hg(0)</td>
<td>methane 74 (d₁/d₀ = 0.14)  ethane 24 (d₁/d₀ = 0)  ethylene 8 (d₁/d₀ = 0.14)</td>
</tr>
<tr>
<td>[c-C₅H₅P(CH₂)₂]₂Pt(CH₃)₂, Hg(0), (CD₃)₂Hg</td>
<td>methane 74 (d₁/d₀ = 0.14)  ethane 24 (d₁/d₀ = 0)  ethylene 8 (d₁/d₀ = 0.14)</td>
</tr>
<tr>
<td>(CH₃)₂Hg</td>
<td>methane 74 (d₁/d₀ = 0.14)  ethane 24 (d₁/d₀ = 0)  ethylene 8 (d₁/d₀ = 0.14)</td>
</tr>
<tr>
<td>(CH₃)₂Hg, Hg(0)</td>
<td>methane 74 (d₁/d₀ = 0.14)  ethane 24 (d₁/d₀ = 0)  ethylene 8 (d₁/d₀ = 0.14)</td>
</tr>
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37. Activation of a C–H bond of a methyl group bonded to platinum would produce a platinum carbene, e.g., L₂Pt(CH₃)₂CH₂(H) or L₂Pt(CH₃)₄ (after reductive elimination of methane). Although similar platinum–methylene species have been postulated as intermediates in heterogeneous platinum-catalyzed reactions, the only soluble platinum–carbene complexes isolated thus far contain a heteroatom-stabilized carbene moiety. See: Belluco, U. "Organometallic and Coordination Chemistry of Platinum"; Academic Press: London, 1974; pp 282-292.
38. In alkane solvents. The cyclopentylidimethylphosphine ligand would be expected to resist metatation: formation of a platinacyclopropane by activation of a C–H bond to phosphorus is uncommon, and metatation β or γ to
phosphorus would produce a (seemingly) strained compound.

Thermolysis of cis-bis(cyclopentylidimethylphosphine)dimethylplatinum(II) in cyclohexane-d\textsubscript{12} in the absence of mercury to low conversion produces methane, ethane, and ethylene (eq 8, Table I). Thermolyzed solutions are pale yellow and completely homogeneous in appearance. Methane, the major gaseous product, contains negligible deuterium.

When a bead of mercury is present, the thermolyzed solutions are colorless and the mercury looks dirty. More importantly, a significant amount (12\%\%) of the methane produced is monodeuterated (eq 8). We believe that this apparent “activation” of deuterated hydrocarbon solvent is not a homogeneous process, but a mercury-promoted side reaction.

The mechanism of this side reaction has not been defined. One possibility involves a mercury–platinum intercharge reaction yielding dimethylmercury. Dimethylmercury could then decompose to methyl radicals and generate CH\textsubscript{3}D by deuterium abstraction from solvent. Although we cannot firmly exclude such a process, we have not observed dimethylmercury as a reaction product. Moreover, the data in Table I suggest that if dimethylmercury were formed under the reaction conditions, it would decompose primarily to ethane (see below). As ethane is only a minor (1–2\%) product in the thermolysis of cis-bis(cyclopentylidimethylphosphine)dimethylplatinum(II) in the presence of mercury, the formation of dimethylmercury under the reaction conditions does not seem to be significant.

The marked difference between the products of thermal decomposition of dimethylmercury in the presence and absence of 13 suggests that the chemistry involved in these systems is complex. In the absence of 13, the major products are methane and ethylene. The first product, methane, is not unexpected; other workers\textsuperscript{27,36} have found methane to be the sole product of thermolysis of dimethylmercury in the presence of cyclopentane. We observed that much of the methane generated from the thermolysis of unlabeled dimethylmercury in C\textsubscript{6}D\textsubscript{12} is CH\textsubscript{3}D, rather than CH\textsubscript{3}H. This result, as well as the relatively high yield of ethylene, suggests that some process other than attack by methyl radicals on the solvent is important. In fact, the detection of ethylene from the thermolysis of neat dimethylmercury has been used as evidence for radical–radical recombination mechanisms of presently undefined nature and surface-mediated heterogeneous reactions.\textsuperscript{39-44} The sensitivity of this decomposition reaction to surface effects is notorious.\textsuperscript{41,43,45-50}

In the presence of 13, ethane (derived from dimethylmercury) becomes the major product. We do not presently understand the mechanistic basis for this change in product distribution. Metallic platinum is known\textsuperscript{52} to catalyze the reaction

\[
\text{Hg} + \text{R}-\text{H} \rightarrow \text{R}-\text{Hg} + \text{H} \text{.}\text{(9)}
\]

The reaction of zerovalent triphenylphosphine platinum and palladium complexes with R\textsubscript{2}Hg\textsuperscript{52,53} suggests a plausible mechanism (eq 10). Reaction of dimethylmercury with platinum(II) complexes, e.g., dichlorobis(phosphine)platinum complexes, is, however, quite slow.\textsuperscript{54}

\[
\text{(M = pr, n = 3, L = pph3)}
\]

\[
\text{L}_\text{n}M\cdot\text{Hg(O)}\rightarrow\text{R-Hg-M-R} \quad \text{(10)}
\]

\[
\text{L}_\text{n}M\cdot\text{Hg(O)} + \text{R-R} \quad \text{(10)}
\]
Although the mechanistic bases for the products observed in eq 7 are obscure, the important conclusion from the vantage of this paper is that the use of Hg(0) to simplify the thermal decomposition of 13 is clearly unsuccessful: the reaction is more complex in the presence of Hg(0) rather than less complex.

Thermal Decomposition of trans-Chloro(neopentylidimethylphosphine)dichloro(1,2-dimethylcyclopropane)platinum(II) (L₂;Pt(NP)Cl). The thermal decomposition of cyclohexane solutions of L₂;Pt(NP)Cl has in the presence of added mercury produces 1,1-dimethylcyclopropane-d₁₀, neopentane-d₁₄, and neopentane-d₁₂ in proportions nearly identical with those observed from the thermal decomposition of 14 in the absence of added mercury (Table II, eq 11, L₂ = (C₆D₉)₂P). The rate of this thermal decomposition seems to be ~5% faster in the presence of added mercury, but this difference in rates is probably not experimentally significant. Reaction solutions remain clear and appear to be homogeneous whether mercury is present or not, but reaction solutions decomposed in the presence of mercury become a pale salmon color as the reaction proceeds. (Solutions decomposed in the absence of added mercury are colorless.) Reactions performed in the presence of added mercury give minor product(s) which in total constitute ~5% (by ³¹P NMR integration) of the major phosphorus-containing product L₂;PtPDCI. These products are absent in the absence of mercury.

Mercury(0) apparently does not significantly change the course of the reaction. Thus, the reaction which abstracts hydrogen (deuterium) from cyclohexane (-d₁₀) and forms neopentane-d₁₄ appears to be a homogeneous reaction. Because the reaction which leads to neopentane is a relatively minor pathway for the decomposition of 14 (with the major pathway being decomposition to dimethylcyclopropane, probably via a 3,3-dimethylplatinacyclobutane intermediate), it is not practical to investigate the mechanism of this reaction in detail. Whatever its mechanism, it probably does not reflect heterogeneous solvent activation.

Discussion

Selective poisoning with mercury(0) is a useful but not universally applicable technique for differentiating homogeneous and heterogeneous reactions involving transition-metal organometallic compounds. The technique, when successful, probably involves formation of mercury amalgams. Mercury forms amalgams with bulk platinum in a stepwise fashion giving PtH₄, PtH₆, and PtH₉ species. Mercury may also adsorb on the surface of platinum. Similarly, mercury probably modifies the activity of colloidal platinum through amalgamation. Although the initial ratio of platinum to mercury, the experimental conditions, and the details of treatment of the metals all affect the composition of the resulting amalgam, PtH₄ is usually the final compositions. This amalgam is stable to 400 °C, at which temperature decomposition to PtH₄ and PtH₉ is observed. In general, we suspect that mercury will be most effective in poisoning systems in which amalgamation with mercury is possible. Palladium, for instance, forms amalgams of various compositions PdH₄, nickel forms NiH₂, and NiH₄ systems involving other transition metals which have not been observed to form amalgams with mercury, but which have a solubility in mercury (i.e., cobalt, ruthenium, rhodium, and iridium) may be less amenable to this poisoning scheme. In any event, mercury may adsorb on the surfaces of these metals, even if solution or amalgam formation is not possible.

It is evident that the technique has limitations. In reactions involving hydrogen abstraction from solvent during thermal decomposition of bis(cyclopentylidimethylphosphine)dihaloplatinum(II), it seems possible that free methyl radicals derived from organomercury compounds may be involved. Both insertion of mercury into Pt–C bonds and transmetalation of mercury with platinum alkyls (driven by heat of amalgamation) seem possible reaction pathways. In other systems, in which the thermal decompositions generating platinum(0) are rapid, it may be impossible to suppress heterogeneous processes following from the initial nucleation of platinum colloids in solution.

This work leaves unresolved the question of the detailed mechanism of conversion of 1 to 2. We offer two speculative and schematic pathways for the reaction. One (eq 12) involves an internal cyclometalation reaction. In this equation, the other ligands present on platinum are not indicated, but by analogy with previously studied systems, at least one vacant coordination site would probably be required for this reaction to proceed. The obvious difficulty with this scheme is the large strain which would appear to be involved in forming compound 15. The conversion of 16 to 2 has excellent precedent in the thermal decomposition of 3,3-dimethylplatinacyclobutane to dimethylcyclopropane. An alternative route for this transformation would involve a chain reaction with a platinum hydride of uncharacterized structure as the chain carrier (eq 13).
bottle techniques. Lab Glass septa for use in the pressure bottles were extracted with toluene until the washings were colorless and then washed with hexane, methanol, and finally water. The septa were dried by heating them to 110 °C in a slow stream of argon and were stored at room temperature under argon before use. Olefins were removed from alkanes by stirring over concentrated sulfuric acid for 48 h, followed by a washing with a saturated sodium bicarbonate solution and water. Some batches were also treated with concentrated aqueous potassium permanganate solution. All were filtered through alumina and/or distilled under inert gas immediately before use. Diethyl ether and THF were dried by standing over sodium metal and were stored at −15 °C. 1-Methylcyclopentene (Chem. Samples Co.) was distilled from calcium hydride (Alfa Products, 40 mesh) under argon. Dihydrogen was Matheson U.H.P. (99.999%). Hexamethylphosphoric acid triamide (HMPA) was distilled from CaH2 under reduced pressure. Dimethylacetamide (DMA) was distilled from CaH2 under reduced pressure and redistilled from molten sodium under reduced pressure and redistilled from molten sodium under reduced pressure. Tosi chloride was recrystallized according to the procedure of Fieser. Dichlorodiphenylstannane, dichlorodimethylstannane, dichlorodiphenylsilane, dichlorodimethylsilane, and dichlorodiphenylgermane were obtained from Alfa and used as received. Dichlorophenylphosphine was distilled prior to use and dichlorodiphenylgermane were obtained from Alfa and used as received. Dichlorodiphenylstannane, dichlorodimethylstannane, dichlorodiphenylsilane, dichlorodimethylsilane, and dichlorodiphenylgermane were obtained from Alfa and used as received. Dichlorophenylphosphine was distilled prior to use and dichlorodiphenylgermane were obtained from Alfa and used as received. Dichlorodiphenylstannane, dichlorodimethylstannane, dichlorodiphenylsilane, dichlorodimethylsilane, and dichlorodiphenylgermane were obtained from Alfa and used as received.

Melting points were determined in open capillary tubes on a Thomas-Hoover apparatus and are uncorrected. Chemical shifts are reported relative to internal Me4Si. Yields of Grignard reagents were determined by using the Eastham method. cis-Dichloro(1,5-cyclooctadiene)platinum(II) cis-dineopentylbis(triethylphosphine)platinum(II), and (1,5-cyclooctadiene)dimeopentylplatinum(II) were synthesized according to literature procedures. Unlabeled dimethylmercury was purchased from Strem and used without further purification. Perdeuterated dimethylmercury was prepared from perdeuterated methyllithium and mercuric chloride. Neopentane, 2,3-dimethylbutane (internal standard), and 1-methyl-2,2,3,3-tetramethylsuccinic acid anhydride (7) were synthesized according to literature procedures. Anal. calcd for C14H16O4: C, 58.44; H, 6.22. Found: C, 58.24; H, 6.12.

To a 1-L, three-necked round-bottomed flask equipped with a condenser, addition funnel, and magnetic stirring bar was added 600 mL of THF. Lithium aluminum hydride (LAH) (18.6 g, 0.48 mol) was added in portions with stirring. The resulting mixture was heated at reflux. A solution of the anhydride (15.3 g, 0.36 mol) in THF (180 mL) was added dropwise to the refluxing suspension. After the addition was complete, the reaction mixture was heated at reflux for 9 h. The reaction flask was immersed in an ice bath, and ethyl acetate (~25 mL) was cautiously added to destroy the excess LAH. Water (75 mL) was added to ensure that all of the LAH had been destroyed (Caution). The reaction mixture was decanted into 500 mL of 2 N H2SO4 with cooling to maintain its temperature between 10–15 °C. The organic phase was washed with two 100-mL portions of ether. The combined organic extracts were washed with 400 mL of water and then with 40 mL of saturated aqueous NaHCO3. The organic phase was dried over anhydrous Na2SO4 and filtered. The solvent was removed under reduced pressure. Benzene (250 mL) was added to the resludde to the result. The resulting suspension was filtered. It was recrystallized from the reaction mixture and was separated by filtration. It was recrystallized from 325 mL of ethanol to give 134 g (85 mol, 91%) of the anhydride 7 as a white solid: mp 151–153 °C (subl. lit. mp 147–148 °C[72]; 152.8 °C[70]; H NMR (CDCl3) δ 1.27 (s).

2,2,3,3-Tetramethylbutane-1,4-diol. To a 1-L, three-necked round-bottomed flask equipped with a condenser, addition funnel, and magnetic stirring bar was added 600 mL of THF. Lithium aluminum hydride (LAH) (18.6 g, 0.48 mol) was added in portions with stirring. The resulting mixture was heated at reflux. A solution of the anhydride (15.3 g, 0.36 mol) in THF (180 mL) was added dropwise to the refluxing suspension. After the addition was complete, the reaction mixture was heated at reflux for 9 h. The reaction flask was immersed in an ice bath, and ethyl acetate (~25 mL) was cautiously added to destroy the excess LAH. Water (75 mL) was added to ensure that all of the LAH had been destroyed (Caution). The reaction mixture was decanted into 500 mL of 2 N H2SO4 with cooling to maintain its temperature between 10–15 °C. The organic phase was washed with two 100-mL portions of ether. The combined organic extracts were washed with 400 mL of water and then with 40 mL of saturated aqueous NaHCO3. The organic phase was dried over anhydrous MgSO4, filtered, and evaporated under reduced pressure. Dissolution of the residue in benzene was followed by removal of the solvent in vacuo gave 45.1 g (90 mol, 86%) of the diol as a colorless solid: mp 114–116 °C (lit. 114–116 °C[70]). 2,2,3,3-Tetramethylbutane-1,4-diol was obtained by using the Eastham method. The reaction mixture was heated at reflux. A solution of the anhydride (15.3 g, 0.36 mol) in THF (180 mL) was added dropwise to the refluxing suspension. After the addition was complete, the reaction mixture was heated at reflux for 9 h. The reaction flask was immersed in an ice bath, and ethyl acetate (~25 mL) was cautiously added to destroy the excess LAH. Water (75 mL) was added to ensure that all of the LAH had been destroyed (Caution). The reaction mixture was decanted into 500 mL of 2 N H2SO4 with cooling to maintain its temperature between 10–15 °C. The organic phase was washed, and the aqueous phase was extracted with two 100-mL portions of ether. The combined organic extracts were washed with 400 mL of water and then with 40 mL of saturated aqueous NaHCO3. The organic phase was dried over anhydrous MgSO4, filtered, and evaporated under reduced pressure. Dissolution of the residue in benzene was followed by removal of the solvent in vacuo gave 45.1 g (90 mol, 86%) of the diol as a colorless solid: mp 114–116 °C (lit. 114–116 °C[70]). H NMR (CDCl3) δ 0.86 (8, 12 H), 3.40 (s, 4 H), 4.55 (br s, 2 H); IR (CDCl3) 3250 (s) (br), 2980 (s), 2880 (s), 1460 (s), 1365 (m), 1270 (w), 1145 (w), 1050 (s), 1010 (m), 805 (w) cm⁻¹.

2,2,3,3-Tetramethylbutane-1,4-diol (8a). Procedure A. The dichloride (24.2 g, 0.13 mol, 93%) was prepared by the reaction of 19.5 g (0.46 mol) of lithium chloride with the ditosylate in HMPA as described.

Procedure B. A solution of the ditosylate (45.4 g, 0.1 mol) in 100 mL of dimethylacetamide was prepared in a 1-L, three-necked round-bottomed flask equipped with a reflux condenser, thermometer, and magnetic stirring bar. Lithium chloride (12.6 g, 0.3 mol) was added to the solution. The reaction mixture was heated at 110 °C for 48 h and allowed to cool to room temperature.
The reaction mixture was decanted into a mixture of 750 mL of water and 200 mL of pentane. The organic phase was removed, and the aqueous phase was extracted three 200-mL portions of pentane. The combined organic extracts were washed in succession with three 100-mL portions of water and 100 mL of saturated aqueous NaCl. The organic phase was dried over MgSO₄ and filtered. The solvent was removed in vacuo to give the dichloride (bp 106–107 °C (17 torr); 13.0 g, 0.071 mol). The ¹H NMR and IR of the dichloride were indistinguishable from those obtained by procedure A."}

"(2,2,3-Tetramethylbutylene-1,4-diyl)bis(magnesium bromide) (9b). A 300-mL pressure bottle equipped with a magnetic stirring bar was charged with magnesium turnings (8.0 g, 0.33 mol), capped, and flame-dried under a stream of argon. After the apparatus had cooled, THF (ca. 50 mL) was added, followed by 1,2-dibromoethane (1 mL). The mixture was stirred vigorously for 40 min to ensure complete reaction of the dibromoethane. The solvent and suspended magnesium salts were removed via cannula, and the activated magnesium turnings were washed with 3 x 25 mL of THF. Fresh THF (80 mL) was added, and a pressure-adjusted dropping funnel equipped with a Leur trip and needle was attached to the pressure bottle. The funnel was charged with a solution of 1,4-dibromo-2,3,3-trimethyl-1-butene (9.2 g, 35 mmol) in diethyl ether (15 mL) was introduced in a dropwise fashion over 2 h period to the stirred suspension of magnesium. Heating continued for an hour after addition was complete. The mixture was then allowed to cool to room temperature. Allgouts (1 mL) were removed by distilling and titrated against 0.14 M 2-butanol in xylenes with 2,2'-biquinoline as the indicator. The concentration of the di-Grignard reagent was 0.15 M (43% yield, assuming the concentration of the di-Grignard reagent to be half the concentration of titratable organomagnesium moieties). Use of diethyl ether as solvent, or more concentrated solutions of the dibromide, gave significantly lower yields. At concentrations above 0.15 M in di-Grignard reagent, a precipitate formed upon cooling of the reaction mixture. Although the di-Grignard reagent could be prepared in slightly higher yield (as estimated by titration) from the dibromide than from the dichloride, (2,2,3,3-Tetramethyl-1,4-diyl)bis(magnesium chloride) (9a) gave consistently higher yields of metallocycloalkanes.

"(1,5-Cyclooctadiene)-3,3,4,4-tetramethylplatinacyclopentane (1). A solution of impure (1,5-COD)Pt(CH₂CMe₂)₂ (0.693 g, 1.66 mmol) in diethyl ether (15 mL) was chilled to 0 °C. Neat triethylphosphine (0.50 mL, 0.39 g, 3.32 mmol) was added by syringe, producing a pale yellow solution. The mixture stood at 0 °C for 12 h. Methanol (8 mL) was added, and the solvents were slowly evaporated in a nitrogen stream at 0 °C. A light yellow precipitate was extracted with three 200-mL portions of pentane. The combined organic extracts were washed in succession with three 100-mL portions of water and 100 mL of saturated aqueous NaCl. The organic phase was dried over MgSO₄ and filtered. The solvent was removed in vacuo to give the dichloride (bp 106–107 °C (17 torr); 13.0 g, 0.071 mol). The ¹H NMR and IR of the dichloride were indistinguishable from those obtained by procedure A."

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The heterogeneous platinum catalyst consisted of 10 mg of a 29% Pt on scinttered glass catalyst.

The solids were removed by filtration, and the supernatant was treated with two 50-mL volumes of saturated ammonium chloride and with water (50 mL). After the solution was dried over magnesium sulfate, the solvent was removed by distillation through a 10-in. Vigreaux column. The yellow residue (ca. 10 mL) was distilled through a 10-in. stainless-steel spinning band column. The fractions boiling at 103-104 °C at 760 torr were combined, giving a clear, colorless, low-melting wax (0.2 g, ca. 3%): IR (CCl4) 3080 (s), 3010 (s), 2960 (br, s), 2870 (s), 1480 (s), 1460 (br, s), 1428 (m), 832 (s), 1365 (s), 1188 (s), 1105 (s), 1092 (m), 1090 (s), 930 (m), 855 (m); 1H NMR (CD2Cl2) δ 0.98 (3 H, s, CH3), 0.93 (9 H, s, C(CH3)2) (0.022 mmol) and -400 mg of mercury in a 6-mm ID glass tube was dried under vacuum (<0.015 torr, 3 h) and sealed. The tube was heated to 780 °C at 0.02 torr for 24 h. A small bead of mercury (~0.5 g) was subsequently added, and the tube was again evacuated for 2 h. After the addition of dry cyclohexane (100 mL) via bulb to bulb vacuum transfer, the tube was sealed and affixed to the apparatus illustrated in Figure 3 which permitted agitation of the reaction mixture at 177 °C for 36 h. Analysis of the colorless solution by GC gave 1-tert-butyl-1-methycyclopropane (2) as the only detectable product.

Qualitative examination of products from the thermolysis of 1 in the presence of added PtO2 (as platinum foil and PtO2 charcoal, glass, and water) indicated that 2 and 3 were the major products in all instances. In mixtures containing suspended PtO2, 10-30% yields of 2-tert-butyl-2-ene and 2-tert-butyl-1-ene were detected. Yields of ethane and ethylene ranged from 0% (mol/mol Pt) in the presence of HgO to 5% in solutions containing no additives with (glass) to 60% (with Pt/glass) and 87% (with charcoal) with PtO2.

Mercury Poisoning of the Hydrogenolysis of CODPt(CH2)3. These experiments were performed in 25-mL tubes capped with butyl rubber septa and crown caps. A 10 × 5 mm football-shaped stirring bar, 15 mg of CODPt(CH2)3, and mercury, or catalyst, as appropriate, were weighed into the tube which was then capped and taken through three cycles of evacuation (<5 × 10⁻³ torr) and flushing with N2. n-Heptane (ca. 5 mL) was added via syringe. For the experiments shown in Figure 4, the reactor was flushed with hydrogen gas and magnetically stirred. Sample aliquots were withdrawn by cannula (ca. 100 µL) and analyzed for CODPt(CH2)3 by UV spectrophotometry (280 nm ± 1700). For the experiment shown in Figure 5, the catalyst was activated with two conditioning runs involving the hydrogenolysis of 15 mg of CODPt(CH2)3. Complex and mercury were added to the reactor via syringe. In the reactor containing only CODPt(CH2)3, hydrogen gas, and solvent, a shiny platinum mirror formed over the surfaces (glass and stirring bar) exposed to the solution. Growth of the mirror could be visually observed to commence at the vapor/liquid/wall interface and grow from there. After ca. 50% completion the mirror began to flake off from the surface of the tubes. In the presence of 10 mg of porous glass (having a surface area of ca. 0.34 m², about the same as the surface area of reactor exposed to solution), a smoky black mirror formed on the reactor walls exposed to solution, and the glass particles turned first brown and then black as platinum was deposited on them. The reactor containing CODPt(CH2)3 and mercury(0) was allowed to stir for 5 days under 2.5-atm pressure of H2. The solution was clear; a mirror formed on the reactor walls. Mercury adhered strongly to this mirror. The CODPt(CH2)3 was less than 50% consumed. In the reactors containing glass, platinum complex, and mercury, the glass particles became black from platinum deposition, but few, if any, of the particles were detected. Yields of ethane and ethylene ranged from 0% (mol/mol Pt) in the presence of HgO to 5% in solutions containing no additives with (glass) to 60% (with Pt/glass) and 87% (with charcoal) with PtO2.

Thermal Decomposition of (1,5-Cyclooctadiene)dineopentylmercury(II) (11). A sample of 10 mg of CODPt(CH2)3, hydrogen gas, and mercury was allowed to stir for 5 days under 2.5-atm pressure of H2. The solution was clear; a mirror formed on the reactor walls. Mercury adhered strongly to this mirror. The CODPt(CH2)3 was less than 50% consumed. In the reactors containing glass, platinum complex, and mercury, the glass particles became black from platinum deposition, but few, if any, of the particles were detected. The glass particles turned first brown and then black as platinum was deposited on them. The reactor containing CODPt(CH2)3 and mercury(0) was allowed to stir for 5 days under 2.5-atm pressure of H2. The solution was clear; a mirror formed on the reactor walls. Mercury adhered strongly to this mirror. The CODPt(CH2)3 was less than 50% consumed. In the reactors containing glass, platinum complex, and mercury, the glass particles became black from platinum deposition, but few, if any, of the particles were detected. Yields of ethane and ethylene ranged from 0% (mol/mol Pt) in the presence of HgO to 5% in solutions containing no additives with (glass) to 60% (with Pt/glass) and 87% (with charcoal) with PtO2.
Homogeneous Reactions of Organoplatinum Compounds

The thermal decomposition of 12 in the presence of mercury were determined by H NMR integration to be 1.0, 0.43, 0.87, and 0.33, respectively, and in the absence of mercury were determined to be 1.1, 0.1, and 0.05, respectively. These relative concentrations were determined by comparing one or two well-resolved proton resonances from each compound: 1.5-cyclooctadiene (5.5 ppm, CH₂), 2.2 ppm (s, CH₃), neopentane (0.90 ppm (a)), and 12 (4.70 ppm, CH₃) in the presence of mercury.

The reaction was quenched with 2 mL of degassed aqueous ammonium chloride (50/50 v/v distilled water/saturated aqueous ammonium chloride). After the mixture had warmed to room temperature, the supernatant was filtered through a medium-porosity frit into an argon-flushed flask. The colorless oil, bp 160-162 °C, was removed prior to fractional distillation of the product as a colorless oil. The yield was 4.18 e 65Vo). ¹H NMR (CD₂Cl₂), δ 1.5 (br m, 9 H), 0.86 d, J(¹H-¹H) 2.5 Hz, 6 H; ¹³P NMR (CeDo), δ 40.3.

cis-Bis(cyclooctadiene)dichloro(dimethylphosphinolate)(II) (13). A 25-mL recovery flask equipped with a stirring bar was charged with (1,5-cyclooctadiene)dimethylplatinum(II) (0.8232 g, 2.47 mmol). The flask was capped with a septum and evacuated-back-filled with argon (previously subjected to three freeze-pump-thaw cycles) and was frozen in liquid nitrogen and the tube was sealed under vacuum, taking care to avoid a platinum mirror at the seal.

The tubes were heated in the vapors of refluxing o-dichlorobenzene (181 °C) for 4 h. Analysis by ¹P NMR indicated that the only phosphorus-containing species present was the starting material. Prior to gas analysis, the tubes were attached to one end of a brass valve by means of a rubber O-ring and a Swagelok fitting. The other end of the valve was fitted with an adapter which contained two rubber septa. The valve was evacuated through the septa (via syringe needle), the tube was broken by closing the valve, and the vapor phase was sampled with a gas-tight syringe. The gaseous products were analyzed by GC/MS and GC, using a 6-ft 4% apiezon on 80/100 alumina column. Results are presented in Table I.

The isotopic composition of the methane produced was determined by comparing the mass spectral data of the product with data obtained from authentic samples of CH₃H, CH₃D, CH₂D₂, and CD₄ and the literature values for CH₂D₂. Unlabeled methane was obtained from Matheson Gas Products; methane-d₁ was prepared by quenching an alkylidene of CD₃MeBr, which had been freeze–pump–thawed twice, with D₂O. Methane-d₁ and methane-d₂ were obtained simultaneously by quenching alkylidene of CD₃MeBr with H₂O and D₂O, respectively. Results of the GC/MS analyses are presented in Table IV. The relative abundance of the m/e 16, 17, 18, 19, and 20 peaks of the methane product were then compared with those of CH₄, CH₃D, CH₂D₂, CHD₃, and CD₄. In no case was CH₄D₂ observed.

The ethane produced was either completely unlabelled or perdeuterated, as determined by comparison with literature values for C₂H₆ and C₂D₆. Mass spectral data for C₂H₅D etc. are not available, but in all cases the m/e values obtained experimentally were in excellent agreement with those of C₂H₆ or C₂D₆. The isotopic composition of the ethylene produced was determined by comparison of the m/e 28, 29, 30, 31, and 32 peaks with literature values of the corresponding peaks of C₂H₄, C₂H₃D, C₂H₂D₂, C₂H₃D₂, and C₂D₄. The thermal decomposition of trans-Chloro(neopentylidene)bis(tri(cyclooctadiene)dichlorophosphine)(II) (L²PnPNCI¼Cl₂). To 14 mg of L²PnPNCI¼Cl₂ (0.017 mmol) and 740 mg of mercury dried under vacuum in a 5-mm NMR tube on a vacuum line was added 0.5 of cyclohexane-d₆ by vacuum transfer. The solution was freeze–pump–thawed three times and

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The tube was reevacuated for at least an hour before C₂D₃₁₂ (previously subjected to three freeze–pump–thaw cycles) was vacuum distilled into the tube. The contents of the tube were frozen in liquid nitrogen and the tube was sealed under vacuum, taking care to avoid a platinum mirror at the seal.

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sealed under vacuum (<0.015 torr). The other three reaction solutions shown in Table II were prepared in a similar fashion. Solutions were decomposed thermally in a constant temperature oil bath at 133 ± 0.5 °C with no stirring. The extent of decomposition was determined by comparing the integrals of the 31P NMR resonances of $^{19}$PtDCl and starting material. The kinetics at decomposition were half-order in $^{19}$PtNpDCl. Solutions were thermally decomposed for 15 h or until ~25% of $^{31}$PtNpDCl remained. After the volatiles were condensed by cooling with liquid nitrogen, tubes were opened and sealed with a septum. The liquid phase of each tube was analyzed by GC and GC/MS. The relative amounts of neopentane-$d_{11}$ and neopentane-$d_{12}$ were determined by comparing the relative abundance of the m/e 65 and 66 peaks of the product neopentane with the m/e peaks of authentic samples of neopentane-$d_{11}$ (65/100%, 66/39%) and neopentane-$d_{12}$ (65/11.4, 66/100%).

**Supplementary Material Available:** Synthesis and characterization of triethylphosphine-$d_{15}$ and several 3,3,4,4-tetramethylmetallacyclopentanes (bis(tri-n-butylphosphine)-3,3,4,4-tetramethylplatinacyclopentane; bis(triethylphosphine)-3,3,4,4-tetramethylplatinacyclopentane; 1-phenyl-3,3,4,4-tetramethylphospholane oxide; 1-phenyl-3,3,4,4-tetramethylphospholane; 1,1-diphenyl-3,3,4,4-tetramethylsilacyclopentane; 1,1,3,3,4,4-hexamethyilsilacyclopentane; 1,1-diphenyl-3,3,4,4-tetramethylstannacyclopentane; and 1,1-diphenyl-3,3,4,4-tetramethylgermacyclopentane) (11 pages). Ordering information is given on any current masthead page.