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Suppression of Unwanted Heterogeneous Platinum(0)-Catalyzed Reactions by Poisoning with Mercury(0) in Systems Involving Competing Homogeneous Reactions of Soluble Organoplatinum Compounds: Thermal Decomposition of Bis(triethylphosphine)-3,3,4,4-tetramethylplatinacyclopentane[1]

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Thermal decomposition of bis(trialkylphosphine)-3,3,4,4-tetramethylplatinacyclopentanes in hydrocarbon solvents yields two major products: 2,2,3,3-tetramethylbutane and 1-methyl-1-*tert*-butylcyclopropane. The former appears to be generated by heterogeneous process(es) 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 heterogeneous and homogeneous 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 dineopentylbis(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 H_2 and (1,5-cyclooctadiene)dimethylplatinum(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)dineopentylplatinum(II) and of *cis*-bis(cyclopentyldimethylphosphine)dimethylplatinum(II) in hydrocarbon solvents—mercury poisoning does not successfully separate homogeneous and heterogeneous 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.

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 components in complex mechanisms,[6-15] 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 involved in studies of carbon–hydrogen bond activation.[16] We describe here a procedure which addresses the problem of distinguishing between homogeneous and heterogeneous reactions by selective poisoning. Addition of mercury(0) or other catalyst poisons to reaction mixtures suppresses the catalytic activity of the bulk platinum metal (by either physisorption or amalgamation) but, under appropriate circumstances, does not influence the homogeneous, nonheterogeneously catalyzed reactions of the organometallic species of interest. We do not yet have a sufficiently wide range of experience with this technique of selective poisoning to be able to set well-defined limits to its applicability: in some circumstances it is clearly a useful technique; in

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[3] National Institutes of Health Postoctoral Fellow, 1979—1981.

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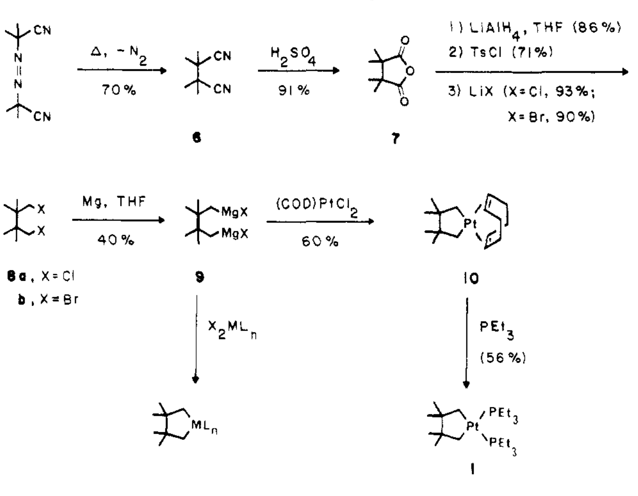
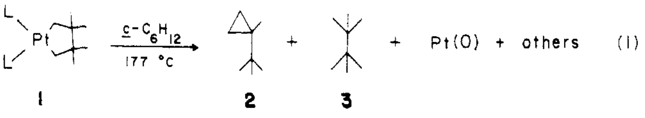
Scheme I. Preparation of Bis(triethylphosphine)-3,3,4,4-tetramethylplatinacyclopentane (1) and Related Compounds



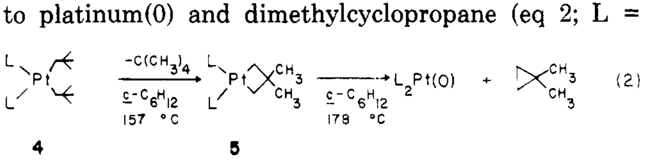
others, although it may solve the problem of heterogeneous platinum-catalyzed reactions, it appears to introduce other competing and complicating processes. The purpose of this paper is to outline our experience with this technique.

The use of mercury(0) to poison undesired heterogeneous transition-metal-catalyzed reactions is not original with us. We have not, however, been able to identify its originator(s).[17-19] This technique is, apparently, a part of the oral tradition of organometallic experimental practice but has not previously been examined independently.

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 = PEt_3). Our interest in 1 stemmed from its

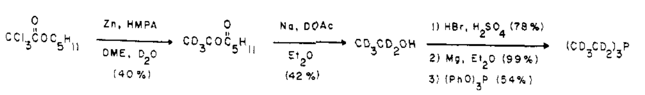


structural similarity to bis(triethylphosphine)-3,3-dimethylplatinacyclobutane (5). This compound decomposes to platinum(0) and dimethylcyclopropane (eq 2; L =



PEt_3).[21] Analogy suggested tetramethylcyclobutane as a probable product of thermal decomposition of 1. In brief, examination of the thermal decomposition of 1 in the absence and presence of mercury(0) strongly suggests that the dialkylcyclopropane 2 is the product of a true homogeneous reaction and that 2,2,3,3-tetramethylbutane 3 is an artifact resulting from a heterogeneous, platinum-catalyzed reaction of undetermined mechanism. Tetramethylcyclobutane is not an important product of decomposition of 1.

Scheme II. Preparation of Perdeuterated Triethylphosphine



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-diyl di-Grignard reagent and perdeuterated triethylphosphine. An improved synthesis[22] of 1,4-dichloro-2,2,3,3-tetramethylbutane[23] used 2,2′-azobis(2-methylpropionitrile) (AIBN) as starting material (Scheme I). Organometallic compounds were prepared using the di-Grignard reagent. Metallacyclopentanes were obtained from the reaction of the di-Grignard reagent with *cis*-dichloro(1,5-cyclooctadiene)platinum(II), dichlorodimethylsilane, dichlorodiphenylsilane, dichlorodiphenylgermane, dichlorodiphenylstannane, and dichlorophenylphosphine. Details of the first of these reactions are summarized in the Experimental Section; the other preparations are described in supplementary material to this paper contained in the microfilm edition. No isolable products were obtained from reaction with dichlorobis(triphenylphosphine)palladium(II), bis(benzonitrile)dichloropalladium(II), or dichlorobis(triphenylphosphine)nickel(II). Reaction with dichlorobis(cyclopentadienyl)zirconium and dichlorobis(cyclopentadienyl)hafnium yielded thermally unstable, air-sensitive complexes which were not carefully characterized. The reaction of the di-Grignard reagent with palladium, zirconium, nickel, and hafnium complexes was not pursued thoroughly and more persistent efforts might result in the successful synthesis of the corresponding metallacyclopentanes.

A straightforward synthesis of perdeuterated triethylphosphine is outlined in Scheme II. This procedure, which uses only D_2O as a deuterium source, appears amenable to large-scale work. Its details are also summarized in supplementary material in the microfilm edition.

Model System: Heterogeneous Hydrogenation of 1-Methylcyclopentene 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-methylcyclopentene (MCP) catalyzed by platinum(0) (eq 3) and the homogeneous stoichiometric reaction of 4 with H_2 (eq 4; L = Et_3P).[24]

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[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. Brocksom, T. J.; Petragnani, N.; Rodriguez, R.; La Scalla Teixeira, H. *Synthesis* **1975**, 396–397.

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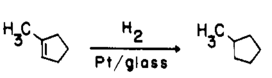
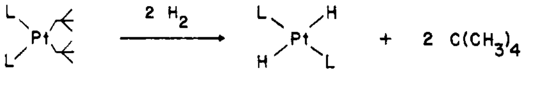


(3)

MCP



(4)

4

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 containing the heterogeneous platinum catalyst hydrogenates 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 thiophene and dibenzothiophene—were less successful.

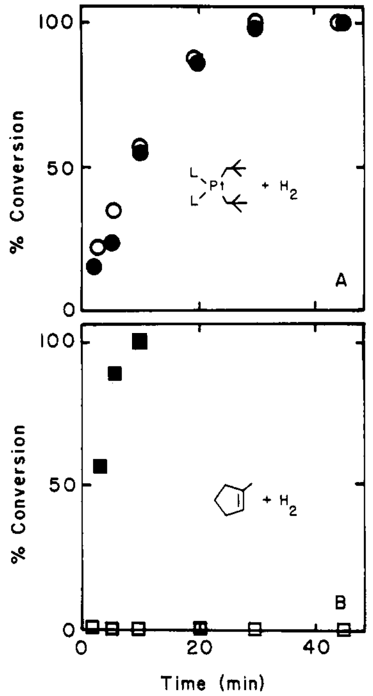


Figure 1. Reaction in the absence of catalyst poisons. (A) Reaction of *cis*-dineopentylbis(triethylphosphine)platinum (4) (0.022 μmol in 6 mL of *n*-octane) with 2 atm H_2 at 40 °C: ○, in the presence of 0.030 mmol of MCP; ●, in the presence of 10 mg of a 29% Pt on scintered glass catalyst and MCP. (B) Reaction of MCP (0.030 mmol in 6 mL of *n*-octane) with 2 atm H_2 at 40 °C: □, in the presence of 10 mg of a 29% Pt on scintered glass catalyst and 4 (0.022 mmol); ■, in the presence of 4 (0.022 mmol).

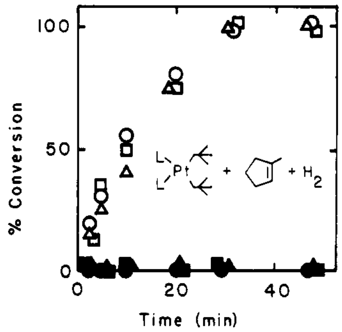
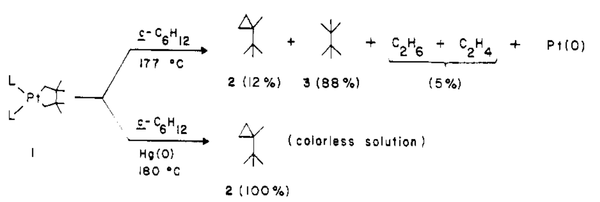


Figure 2. Reaction in the presence of catalyst poisons. (A) Reaction of 4 with 2 atm of H_2 in *n*-octane at 40 °C: ○, in the presence of Hg; △, in the presence of CO; □, in the presence of PPh_3. (B) Reaction of MCP with 2 atm H_2 in *n*-octane at 40 °C: ●, in the presence of Hg; ▲, in the presence of CO; ■, inthe presence of PPh_3. Both 4 and **MCP** were present in the same solution for these studies; quantities are as given in Figure 1.

Thermolysis of Bis(triethylphosphine)-3,3,4,4-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 = 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*-butylbut-2-ene, 2-*tert*-butylbut-1-ene, and others) were occasionally observed as products and became major products if platinum dioxide was intentionally added to the reaction mixture.



(5)

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[25] Phosphines, as a group, are strong poisons for heterogeneous catalysis: Maxted, E. B. *Adv. Catal.* **1951**, *3*, 129–177. Baltzly, R. *Ann. N. Y. Acad. Sci.* **1967**, 31–45.

[26] Although no insertion of carbon monoxide into platinum–carbon bonds was observed in this case, carbonylation of M–C bonds could be an important side reaction in other systems. See, for example: Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980.

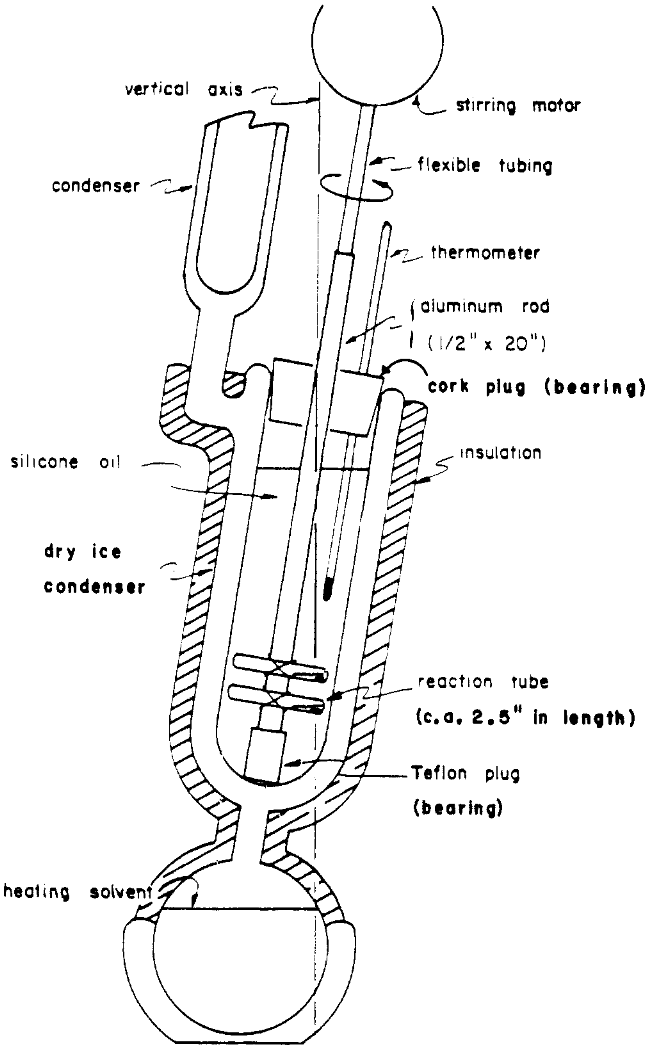


Figure 3. Apparatus used for thermal decomposition of 1 in the presence of mercury(0). To achieve intimate contact of the solution with the surface of the mercury bead, the sample solutions were positioned perpendicular to a shaft positioned ca. 20° from the vertical in sealed reaction tubes and rotated at 60 rpm. Rotation caused the mercury bead to roll from one end of the reaction tube to the other and ensured efficient mixing.

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 d_1 and d_2 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.

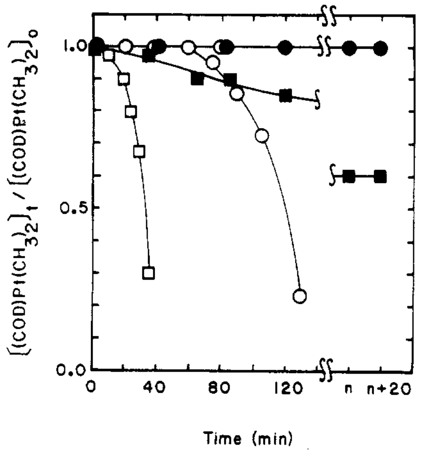
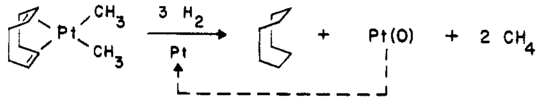


Figure 4. Reaction of CODPt$(CH_3)_2$, 11, with H_2 (1.3 atm) in *n*-heptane (5 mL, 27 °C): ○, 15 mg of CODPt$(CH_3)_2$; ●, 15 mg of CODPt$(CH_3)_2$ and 3.5 g of mercury(0), n = 1500; □, 15 mg of CODPt$(CH_3)_2$ and 10 mg of controlled-pore glass (see Experimental Section); ■, 15 mg of CODPt$(CH_3)_2$, 10 mg of controlled pore glass, and 3.5 g of mercury(0), n = 1030.

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 (diolefin)dialkylplatinum(II) complexes (eq 6).[28,29] In the absence of added Hg(0), an initial irreproducible induction period is followed by uptake of H_2 and precipitation of platinum metal (Figure 4). This autocatalytic process is entirely suppressed by addition of mercury(0).



(6)

11

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,[28,29] the essential feature is that reaction of 11 and H_2 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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[27] Sowinski, A. F. Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA, 1980.

[28] McCarthy, T. J.; Shih, Y. S.; Whitesides, G. M. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 4649–4651.

[29] McCarthy, T. J. Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA, 1982.

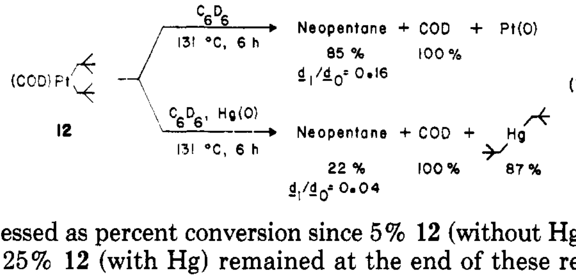
Table I. Thermolysis of Bis(cyclopentyldimethylphosphine)dimethylplatinum in the Presence and Absence of Mercury(0)

	rel yields (%) of products (isotopic compositns)		
organometallic components[a]	methane	ethane	ethylene
$[c\text{-}C_5H_9P(CH_3)_2]_2Pt(CH_3)_2$	95 ($d_1/d_0 = 0$)	4^b	4 ($d_1/d_0 = 0$)
$[c\text{-}C_5H_9P(CH_3)_2]_2Pt(CH_3)_2$, Hg(0)	74 ($d_1/d_0 = 0.14$)	2^b	24 ($d_1/d_0 = 0$)
$[c\text{-}C_5H_9P(CH_3)_3]_2Pt(CH_3)_2$, Hg(0), $(CD_3)_2Hg$	16 ($d_1/d_0 = 0.28$, $d_1/d_0 = 0$)[c]	76^d	8 ($d_1/d_0 = 0.14$)
$[c\text{-}C_5H_9P(CH_3)_2]_2Pt(CH_3)_2(CD_3)_2Hg$	10 ($d_4/d_3 = 0.76$, $d_1/d_0 = 0$)[e]	88^d	2 ($d_1/d_0 = 1.11$)
$(CH_3)_2Hg$	65 ($d_1/d_0 = 0.35$)	1^b	34 ($d_1/d_0 = 0$)
$(CH_3)_2$ Hg, Hg(0)	77 ($d_1/d_0 = 0.52$)	1^b	22 ($d_1/d_0 = 0$)

[a] Thermolyzed in sealed tubes containing $c\text{-}C_6D_{12}$ for 4 h at 181 °C. [b] Only C_2H_6 was observed. [c] Of the methane produced, 12% was d_0. [d] Only C_2D_6 was observed. [e] Of the methane produced, ca. 4% was d_0.

of mercury(0) to halt the reaction of **11** and H_2 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 thermolysis 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.[29] Solutions of **12** in benzene-d_6 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-d_1. Thermolyses conducted in the presence of mercury produced only 4% neopentane-d_1; 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-d_6 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-d_6 into neopentane. The observation of dineopentylmercury(II) as product establishes that transmetalation can occur under these conditions. Thermal decomposition of the dialkylmercury(II) compound may also contribute to the observed hydrocarbon products.



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(7)

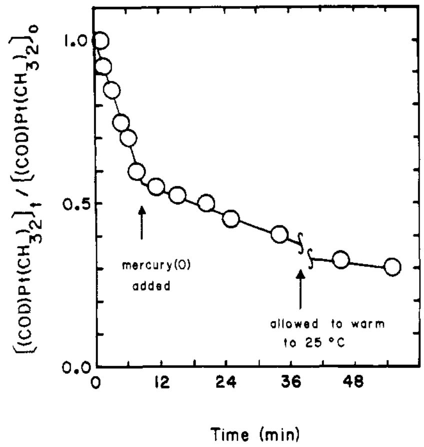

Figure 5. Poisoning of Pt(0)/glass catalyst by mercury(0). Reaction of 15 mg of $CODPt(CH_3)_2$, **11**, with H_2 (1.3 atm) in *n*-heptane (5 mL) at 0 °C in the presence of 8.6 mg of Pt(0)/glass catalyst (see Experimental Section). Mercury(0) (9.0 g) was added after 7.5 min.

Thermal Decomposition of *cis*-Bis(cyclopentyldimethylphosphine)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.[31,32] In order to explore whether the observed hydrocarbon activation represented a homogeneous process, we examined the thermal decomposition of *cis*-bis(cyclopentyldimethylphosphine)dimethylplatinum(II)[33] (selected because it had useful solubility in hydrocarbon solvents) in alkane solvents. The cyclopentyldimethylphosphine ligand would be expected to resist metalation: formation of a platinacyclopropane by activation of a C–H bond α to phosphorus is uncommon,[34] and metalation β or γ to

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(30) The initial traces of platinum(0) may result from a glass- or light-catalyzed reaction or from a homogeneous process of which we are unaware.

(31) Clarke, J. K. A.; Rooney, J. J. *Adv. Catal.* **1976**, *25*, 125–183. Somorjai, G. A. "Chemistry in Two Dimensions: Surfaces"; Cornell University Press: Ithaca, NY, 1981; Chapter 9, pp 479–515.

(32) Activation of a C–H bond of a methyl group bonded to platinum would produce a platinum carbene, e.g., $L_2Pt(CH_2)(CH_3)(H)$ or $L_2Pt(CH_2)$ (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. Hartley, F. R. "The Chemistry of Platinum and Palladium"; Wiley: New York, 1973; pp 101–102, 348–350.

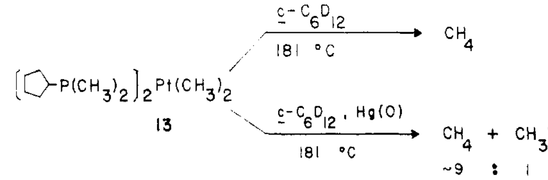
(33) Although formation of three-membered metallocycles by other routes, such as reduction of metal–halide bonds, is a well-known reaction, only one case of phosphine metalation to produce a platinacyclopropane has been reported. See: Bresciani, N.; Caligaris, M.; Delise, P.; Nardin, G.; Randaccio, L. *J. Am. Chem. Soc.* **1974**, *96*, 5642–5643.

(34) Metalation of tricyclopentylphosphine by platinum has been observed, but whether metalation results from oxidative addition of a ligand C-H bond or from a radical reaction is unclear. See ref 55.

phosphorus would produce a (seemingly) strained compound.[35]

Thermolysis of *cis*-bis(cyclopentyldimethylphosphine)dimethylplatinum(II) in cyclohexane-d_{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.



(8)

The mechanism of this side reaction has not been defined. One possibility involves a mercury–platinum interchange reaction yielding dimethylmercury. Dimethylmercury could then decompose to methyl radicals and generate CH_3D by deuterium atom abstraction from solvent. Although we cannot firmly exclude such a process, we have not observed dimethylmercury as a reaction product.[36] 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(cyclopentyldimethylphosphine)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 di(methyl-d_3)mercury 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[37,38] 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_6D_{12} is CH_4, rather than CH_3D. 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.[39–44] The sensitivity of this decomposition reaction to surface effects is notorious.[41,43,45–50]

Table II. Thermal Decomposition of *trans*-((C_5D_9)$_3$P)$_2$Pt($CD_2C(CD_3)_3$)Cl (14) in Cyclohexane[a]

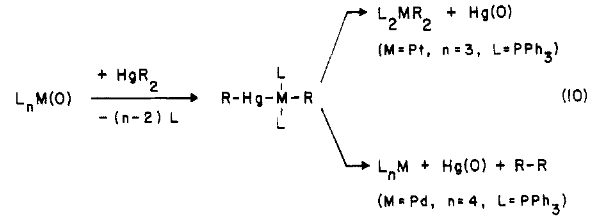
solv	Hg (mg) added	$(CD_2)_2C$-$(CD_3)_3$[b]/ Np^D-H + Np^E-D	% Np^D-D[c]	$10^6 k^{obsd,d}$ $M^{1/2}$ s^{-1}
C_6H_{12}		6.8	14	1.74 ± 0.07
C_6H_{12}	740	7.0	15	1.78 ± 0.07
C_6D_{12}		5.2	98	1.71 ± 0.03
C_6D_{12}	590	7.2	96	1.80 ± 0.09

[a] The volume of solution was ca. 0.5 mL. The concentration of $L^D{}_2PtNp^DCl$ was 0.029–0.042 M. Reaction solutions were thermalized at 133 °C until ~25% starting material remained (~15 h). [b] Relative quantities of 1,1-dimethylcyclopropane and neopentane were determined by GC. The experimental accuracy of the yield of 1,1-dimethylcyclopropane produced is estimated at ±4%. Thus, all variations listed here are within experimental error. [c] Experimental accuracy estimated at ±3%. Np^D-D is neopentane containing a deuterium distribution compatible with replacement of the $N_p{}^D$-Pt bond of **14** by Np^D-D on decomposition. % Np^D-D = (Np^D-D/(Np^D-D + Np^D-H)) × 100%; Np^D = $CD_2C(CD_3)_3$. [d] The thermal decomposition of **14** occurs by a mechanism which is half-order in **14**.[55] This kinetic order is consistent with the postulated mechanism for the decomposition of **14** in which reversible phosphine dissociation precedes the rate-limiting step. The error limits for these half-order rate constants are reported at 95% confidence levels.

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[51] to catalyze the reaction

$$R_2Hg \xrightarrow{Pt(0)} R\text{-}R + Hg(0) \quad (9)$$

The reaction of zerovalent triphenylphosphine platinum and palladium complexes with R_2Hg[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.[54]



(10)

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(35) The liquid phase of the reaction mixture (ca. 0.5 mL) was analyzed by gas chromatography (9-ft 20% SE-30 column on 80/100 Chromasorb P). All components of the reaction mixture eluted before cyclohexane-d_{12}. Spiking the reaction mixture with dimethylmercury (1 μL, 3 mg, 13 μmol, ca. 26 μM) produced an additional peak which eluted after C_6D_{12}.

(36) Russell, M. E.; Bernstein, R. B. *J. Chem. Phys.* **1959**, *30*, 607–612, 613–617.

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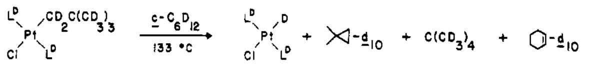
Although the mechanistic bases for the products observed in eq 7 are obscure, the important conclusion from the vantage of this paper is that the use of Hg(0) to simplify the thermal decomposition of **13** is clearly unsuccessful: the reaction is *more* complex in the presence of Hg(0) rather than less complex.

Thermal Decomposition of *trans*-Chloro(neopentyl-d_{11})bis(tri(cyclopentyl-d_{27})phosphine)platinum(II) ($L^D{}_2PtNp^DCl$, 14). The thermal decomposition of cyclohexane solutions of $L^D{}_2PtNp^DCl$[55] in the presence of added mercury produces 1,1-dimethylcyclopropane-d_{10}, neopentane-d_{11}, and neopentane-d_{12} in proportions nearly identical with those observed from the thermal decomposition of **14** in the absence of added mercury (Table II, eq 11, $L^D = (C_5D_9)_3P$). 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 ^{31}P NMR integration) of the major phosphorus-containing product $L^D{}_2PtDCl$. These products are absent in the absence of mercury.



(11)

14

7 : 1

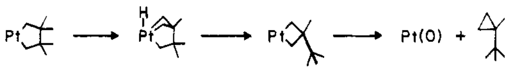
Mercury(0) apparently does *not* significantly change the course of the reaction. Thus, the reaction which abstracts hydrogen (deuterium) from cyclohexane (-d_{12}) and forms neopentane-d_{12} appears to be a homogeneous reaction. Because the reaction which leads to neopentane is a relatively minor pathway 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 $PtHg_4$, $PtHg_2$, and PtHg species.[56-58] Mercury may also adsorb on the surface of platinum.[59] Similarly, mercury probably modifies the activity of colloidal platinum through amalgamation.[28] Although the initial ratio of platinum to mercury, the experimental conditions,[56] and the details of treatment of the metals all affect the composition of the resulting amalgam, $PtHg_4$ is usually the final compositions. This amalgam is stable to 400 °C, at which temperature decomposition to $PtHg_2$ and PtHg is observed:[60] 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 Pd_nHg_m; nickel forms $NiHg_4$ and $NiHg_3$.[56,61] 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)[56] 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.

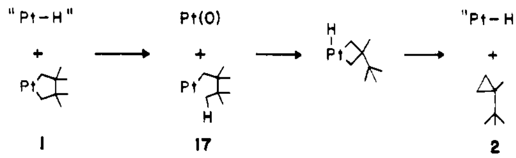
It is evident that the technique has limitations. In reactions involving hydrogen abstraction from solvent during thermal decomposition of bis(cyclopentyldimethylphosphine)dimethylplatinum(II), it seems possible that free methyl radicals derived from organomercury compounds may be involved. Both insertion 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,[19,62] 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.[21] An alternative route for this transformation would involve a chain reaction with a platinum hydride of uncharacterized structure as the chain carrier (eq 13).[24]



(12)

1 **15** **16** **2**



(13)

1 **17** **2**

Experimental Section

General Data. All reactions requiring anhydrous or anaerobic conditions were performed by using standard Schlenk or pressure

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[54] The synthesis of $L^D{}_2PtNp^DCl$, and a detailed mechanistic study of its thermal decomposition, will be described elsewhere: Brainard, R. L.; Miller, T. M.; Whitesides, G. M., in progress.

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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 distilled from disodium benzophenone under argon. 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 CaH_2 under reduced pressure. Dimethylacetamide (DMA) was distilled from CaH_2 under reduced pressure and redistilled from molten sodium under reduced pressure. Tosyl chloride was recrystallized according to the procedure of Fieser.[63] Dichlorodiphenylstannane, dichlorodimethylstannane, dichlorodiphenylsilane, dichlorodimethylsilane, and dichlorodiphenylgermane were obtained from Alfa and used as received. Dichlorophenylphosphine was distilled prior to use and stored in a flask equipped with a Teflon stopcock. Magnesium turnings were supplied by J. T. Baker. Triply distilled mercury was used in poisoning experiments without further purification. Melting points were determined in open capillary tubes on a Thomas-Hoover apparatus and are uncorrected. Chemical shifts are reported relative to internal Me_4Si. Yields of Grignard reagents were determined by using the Eastham method.[64] *cis*-Dichloro(1,5-cyclooctadiene)platinum(II),[65] *cis*-dineopentylbis(triethylphosphine)platinum(II),[19] and (1,5-cyclooctadiene)dimethylplatinum(II)[66] and (1,5-cyclooctadiene)dineopentylplatinum(II)[19] 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.[67] Neopentane, 2,3-dimethylbutane (internal standard), methylcyclopentane, 1-methylcyclopentene, and *n*-octane were separated by using a 2-ft Hi Plate 600 SE-30 on Chromosorb W column (Analabs) in a temperature-programmed run. Methane, ethane, and ethylene were analyzed on a 2-ft 4% Apiezon on alumina column in a temperature-programmed run. Analyses of 1-*tert*-butyl-1-methylcyclopropane and 2,2,3,3-tetramethylbutane were carried out by using a 20-ft 4% SE-30 column at 60 °C. Characterization of products was based on co-injection with authentic materials and on GC/MS analysis.

2,2,3,3-Tetramethylsuccinic Acid Dinitrile (6).[68-70] To a 1-L, three-necked round-bottomed flask equipped with a magnetic stirring bar, reflux condenser, and thermometer was added 230 mL of heptane. A second flask containing 220 g (1.3 mol) of solid 2,2′-azobis(2-methylpropionitrile)[71] was connected to the reaction flask with Gooch tubing. The reaction flask was heated to 90–95 °C, and portions of the AIBN were added to the hot heptane over 15 h. The reaction mixture was filtered to remove a small amount of insoluble polymeric material and allowed to cool. The product crystallized from the reaction mixture and was separated by filtration. It was recrystallized from 325 mL of ethanol to give 128 g (0.94 mol, 72%) of the dinitrile **6** as colorless prisms: mp 157–160 °C (lit.[70] (165 °C); ^{1}H NMR ($CDCl_3$) δ 1.53 (s) (lit. δ 1.45 (s)); IR (KBr) 3034 (s), 2980 (m) 2926 (m), 2278 (s), 1482 (s), 1407 (s), 1206 (s), 1170 (s), 1133 (m), 928 (m), 355 cm^{-1}.

2,2,3,3-Tetramethylsuccinic Acid Anhydride (7).[70] The dinitrile **6** (128 g, 0.94 mol) was slowly dissolved in a mixture of 195 mL of water and 455 mL of concentrated H_2SO_4. The resulting mixture was gradually heated to 100–110 °C at which point a vigorous exothermic reaction occurred. The temperature of the reaction mixture rose quickly to ca. 150 °C. After the initial reaction had subsided, the mixture was heated at 130–150 °C for an additional 2 h. The reaction mixture was allowed to cool to room temperature and was then extracted with three 400-mL portions of ether. The combined organic extracts were washed with 400 mL of water and then with 40 mL of saturated aqueous $NaHCO_3$. The organic phase was dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure. Benzene (250 mL) was added to the residue and then removed under reduced pressure. The residue was dried in vacuo to give 134 g (0.85 mol, 91%) of the anhydride **7** as a white solid: mp 151–153 °C (subl) (lit. mp 147,[70] 145–146,[72] 152,[68] 140 °C[73]); ^{1}H NMR ($CDCl_3$) 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)[74] (18.6 g, 0.48 mol) was added in portions with stirring. The resulting mixture was heated at reflux. A solution of the anhydride (55.7 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 8 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 H_2SO_4 with cooling to maintain its temperature between 10–15 °C. The organic phase was removed, and the aqueous phase was extracted with two 100-mL portions of ether. The combined organic extracts were washed with 100 mL of water and two 100-mL portions of saturated aqueous $NaHCO_3$. The organic phase was dried over anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure. Dissolution of the residue in benzene followed by removal of the solvent in vacuo gave 45.1 g (0.31 mol, 86%) of the diol as a colorless solid: mp 206–207 °C (lit. 209.5–211.5 °C;[23] ^{1}H NMR ($CDCl_3$) δ 0.86 (s, 12 H), 3.40 (s, 4 H), 4.55 (br s, 2 H); IR ($CDCl_3$) 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-ditosylate. The ditosylate was prepared as described previously.[22]

1,4-Dichloro-2,2,3,3-tetramethylbutane (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.[22]

Procedure B. A solution of the ditosylate (45.4 g, 0.1 mol) in 400 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.

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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 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 $MgSO_4$ 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 ^{1}H NMR and IR spectra of the dichloride were indistinguishable from those obtained by procedure A.[22]

1,4-Dibromo-2,2,3,3-tetramethylbutane (8b). The dibromide was prepared in 90% yield using the HMPA procedure described previously[22] except that LiBr was substituted for LiCl: mp 51–52 °C; ^{1}H NMR ($CDCl_3$) δ 1.06 (s, 12 H), 3.51 (s, 4 H); IR (14 Br) 2970 (s), 1470 (s), 1438 (s), 1395 (s), 1380 (s), 1250 (s), 1125 (s), 988 (s), 664 (s), 520 (s) cm^{-1}.

(2,2,3,3-Tetramethylbutane-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 × 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-2,2,3,3-tetramethylbutane (9.2 g, 35 mmol) in 20 mL of THF. The solution was added at 75 °C over a 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. Aliquots (1 mL) were removed by syringe and titrated against 0.14 M 2-butanol in xylene[64] 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-tetramethylene-1,4-diyl)bis(magnesium chloride) (**9a**) gave consistently higher yields of metallacycles.

(1,5-Cyclooctadiene)-3,3,4,4-tetramethylplatinacyclopentane (10). To a three-necked 500-mL flask equipped with a 250-mL addition funnel, a glass stopper, a No-Air septum, and a Teflon-coated stirrer was added (1,5-COD)$PtCl_2$ (2.24 g, 6.0 mmol) and diethyl ether (50 mL). The mixture was chilled to −50 °C, and a solution of 2,2,3,3-tetramethylbutane-1,4-diyl)-bis(magnesium chloride) (0.070 M, 100 mL, 7 mmol) was added dropwise over 3 h. The mixture was allowed to warm slowly to ambient temperature. Reaction appeared to commence at −25 to −15 °C. The mixture was stirred for 12 h at 20 °C, and the resulting red-brown solution was subjected to forced column chromatography over silica gel/charcoal at 0 °C, and the column was washed with diethyl ether (ca. 200 mL). The pale yellow solution was concentrated to an oil under reduced pressure on a rotary evaporator; the oil solidified after evacuation to 0.05 torr for 30 min. The produce was recrystallized from a solution of methanol (4 mL) and ether (15 mL) by solvent evaporation in a nitrogen stream at 0 °C, yielding white flakes (1.54 g, 62%): mp 97.3–99.0 °C; IR (CCl_4) 2998 (w), 2940 (s), 2870 (s), 2795 (m), 1475 (m), 1455 (m), 1440 (w), 1428 (m), 1375 (m), 1368 (s), 1353 (s), 1338 (m), 1310 (m), 1235 (m), 1130 (m), 1123 (s), 991 (m), 970 (m), 855 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.79 (4 H, 1:4:1 "t", $^2J_{\text{Pt-H}}$ = 44 Hz, C*H*=C*H*), 2.25 (8 H, CH_2C=), 1.92 (4 H, 1:4:1 "t", $^2J_{\text{Pt-H}}$ = 92 Hz, $PtCH_2$–), 0.90 (12 H, "t", J = 1 Hz, CCH_3). Anal. Calcd for $C_{16}H_{28}Pt$: C, 46.23; H, 6.79. Found: C, 46.32; H, 6.91.

Bis(triethylphosphine)-3,3,4,4-tetramethylplatinacyclopentane (1). A solution of impure (1,5-COD)Pt(CH_2CMe_2)$_2$ (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, granular solid precipitated and was recovered by decanting the supernatant and drying in vacuo. The crude product (0.54 g, 56%) was recrystallized from ether (3 mL) and methanol (2 mL) by preparing a saturated solution as above and chilling slowly to −78 °C: mp 90.5–95.5 °C; IR (KBr) 2990–2870 (vs, br), 1452 (m, sh), 1455 (s), 1430 (br, sh), 1380 (m, sh), 1375 (m), 1363 (m, sh), 1351 (m, sp), 1251 (br, w), 1240 (sh, br, w), 1178 (w), 1122 (w), 1039 (s), 1028 (sp, sh, m), 765 (s, br), 718 (s), 630 (br, m); ^{1}H NMR ($CDCl_3$) δ 2.0–1.4 (ca. 16 H, br multiplet, –CH_2–), 1.4–0.85 (ca. 30 H, multiplet consisting of small s (1.4–1.0 ppm) and large s (0.95 ppm), –CH_3); ^{31}P NMR δ 11.5 ($^1J_{\text{Pt-P}}$ = 1798 Hz). Anal. Calcd for $C_{20}H_{46}P_2Pt$: C, 44.17; H, 8.53. Found: C, 46.11, H, 8.76. The unacceptable elemental analysis for this compound appears to result from the use of impure CODPt(C_8H_{16}). Despite several recrystallizations, a sharp melting point and acceptable analysis were not obtained. The recrystallized compound prepared from this same precursor complex showed an impurity in its ^{1}H NMR (1.3 ppm (br s, ca. 4 H)).

Bis(tri(ethyl-*d*$_5$)phosphine)-3,3,4,4-tetramethylplatinacyclopentane was prepared in analogous fashion in 62% yield from a pure sample of (1,5-COD)Pt(CH_2CMe_2)$_2$. It exhibited the following properties: mp 95.5–97.0 °C; IR (KBr) 2955 (s), 2920 (s), 2860 (s), 2800 (m), 2220 (s), 2190 (w), 2140 (w), 2120 (w), 2080 (m), 1125 (m), 1060 (s), 1045 (m), 1038 (m), 891 (m), 878 (m), 790 (s), 642 (m), 632 (m), 622 (m); ^{1}H NMR (CD_2Cl_2) δ 1.45 (4 H, 1:4:1 "t" of "q", $^2J_{\text{Pt-H}}$ = 64 Hz, $PtCH_2$–), 0.80 (12 H, br s, CCH_3).

1,1,2,2-Tetramethylcyclobutane (TMC). An impure sample of TMC was prepared for use as a GLC standard by stoichiometric coupling of (2,2,3,3-tetramethylbutane-1,4-diyl)bis(magnesium chloride) using silver(I) according to published procedures.[75] Silver triflate (2.80 g, 10.9 mmol) and diethyl ether (10 mL) were combined in a 250-mL, three-necked flask that was equipped with an 80-mL addition funnel and a Teflon-coated stirrer. The solution of $[Me_2CCH_2MgCl]_2$ in THF (0.13 M, 70 mL, 9.1 mmol) was added over 70 min to the vigorously stirred solution at −5 °C. Reaction appeared to occur instantaneously: black solids were deposited immediately after addition began. The mixture was allowed to warm to ambient temperature over a 12-h period. The solids were removed by filtration and the supernatant was washed with two 30-mL portions of water. The solution was dried over magnesium sulfate and was subjected to careful distillation through a 10-in. stainless-steel spinning band. Fractions boiling below 98 °C at 760 torr were discarded, and the concentrated solution was distilled through a short-path apparatus. The product fraction (98–120 °C) was found to consist of 2,2,3,3-tetramethylbutane (**3**) and 1,1,2,2-tetramethylcyclobutane (1:4.5, respectively; ca. 0.16 g (16%) of TMC by ^{1}H NMR and GLC). It was not possible to purify the product by distillation; hence an elemental analysis was not performed. The impure colorless wax exhibited the following properties: mp ca. 50 °C; IR (CCl_4) 2960 (br, s), 2860 (s), 1465 (m), 1450 (m), 1384 (m), 1379 (m), 1367 (m), 1177 (m), 1146 (m); ^{1}H NMR (CD_2Cl_2) δ 1.60 (4 H, s, –CH_2–), 0.97 (12 H, s, –CH_3), 0.86 (ca. 4 H, s, 3 –CH_3).

1-*tert*-Butyl-1-methylcyclopropane (TBC). The three-membered ring was prepared by a Simmons–Smith reaction.[76] The zinc–copper couple was prepared by a reported procedure.[77] The zinc–copper couple (19.0 g, 0.19 mol) was suspended in diethyl ether (100 mL) in a 500-mL, three-necked flask that was equipped with a 250-mL addition funnel, condenser, and mechanical stirrer. Neat methylene iodide (74.0 g, 0.28 mol) was added rapidly to the refluxing slurry. A crystal of iodine was introduced, and a slow, mildly exothermic reaction ensued. The mixture was refluxed for 12 h, giving a gray-black supernatant and a reddish suspension. A solution of 2,3,3-trimethyl-1-butene (7.7 g, 0.080 mol) in ether (40 mL) was introduced in a dropwise fashion over 40 min, and the resulting mixture was stirred at reflux for 11 h.

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(77) This catalyst was found to give reproducibly 3.5 × 10^{-5} mol of Pt/g of catalyst.

Table III. Hydrogenolysis of *cis*-Dineopentylbis(triethylphosphine)platinum(II) (4) in the Presence of 1-Methylcyclopentene (MCP)[a]

$10^4\ k^{obsd}$ (s^{-1}) for hydrogenolysis of 4	max convn % of MCP[b]	poison	Pt cat.[c] present
10.7	<1	none	no
14.0	100.0	none	yes
11.0	<1	Hg	yes
11.0	<1	CO	yes
11.2	<1	PPh_3	yes

[a] Experiments were carried out in *n*-octane under 2 atm of H_2 at 40 °C. [b] Determined by GLC analysis on a 2-ft HiPlate 600 SE-30 on Chromosorb W column (Analabs). [c] The heterogeneous platinum catalyst consisted of 10 mg of a 29% Pt on scintered 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 (CCl_4) 3080 (s), 3010 (s), 2960 (br, s), 2870 (s), 1480 (s), 1460 (br, s), 1428 (m), 1382 (s), 1365 (s), 1188 (s), 1105 (s), 1092 (m), 1010 (s), 930 (m), 855 (m); ^1H NMR (CD_2Cl_2) δ 0.98 (3 H, s, CH_3), 0.93 (9 H, s, $C(CH_3)_3$), 0.45 (2 H, multiplet, $-CH_2-$), 0.02 (2 H, multiplet, $-CH_2-$). Anal. Calcd for C_8H_{16}: C, 85.63; H, 14.38. Found: C, 85.48; H, 14.60.

Preparation of Supported Platinum Catalysts.[28] (1,5-Cyclooctadiene)dimethylplatinum(II) (1 g) was reduced with dihydrogen (2 atm) onto controlled porosity glass (1.5 g) (Sigma PG-120-200) from *n*-pentane solution at 25 °C. The number of active platinum atoms per gram of catalyst was subsequently obtained by dioxygen–dihydrogen titration.[78,79] A typical catalyst loading was 29% platinum.

Concurrent Hydrogenolysis of 4 and Hydrogenation of 1-Methylcyclopentene. A 1.5 cm × 2.5 cm heavy-walled pressure tube equipped with a Teflon coated, football-shaped, magnetic stirring bar was charged with the 29% platinum on glass catalyst (10 mg, 5.7×10^{-4} mmol of platinum) and 4 (10 mg, 0.018 mmol). The pressure tube was capped, evacuated to 0.01 torr, charged with dihydrogen (30 psig), and immersed in a thermostated ethylene glycol/water bath (1/1, v/v) at 40 °C. A solution of *n*-octane (6 mL) which contained 2,3-dimethylbutane (0.015 mmol) (internal standard) and 1-methylpentene (0.030 mmol) was added, and stirring was begun. Reaction samples (~5 μL) were taken periodically for GLC analysis. Reactions carried out in the presence of poisons followed the same procedure, except that small quantities of the indicated materials were added: mercury(0)—a small bead (~1 g, 0.005 g atom) of triply distilled mercury was added at the same time as the catalyst; carbon monoxide—the reaction tube was pressurized to 7.5 psig before it was pressurized with H_2; triphenylphosphine—5 mg (0.018 mol) of triphenylphosphine was added at the same time as the platinum catalyst. Observed first-order rate constants are summarized in Table III, together with qualitative observations concerning the poisoning of the heterogeneous reactions.

Thermolysis of Bis(triethylphosphine)-3,3,4,4-tetramethylplatinacyclopentane (1). An 11.5 cm × 0.6 cm Vycor thermolysis tube charged with 1 (15 mg, 0.024 mmol) was evacuated to <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 μL) 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-methylcyclopropane (2) as the only detectable product.

Qualitative examination of products from the thermolysis of 1 in the presence of added Pt(0) (as platinum/glass and PtO_2) charcoal, glass, and water indicated that 2 and 3 were the major products in all instances. In mixtures containing suspended PtO_2, 10–30% yields of 2-*tert*-butylbut-2-ene and 2-*tert*-butylbut-1-ene were detected. Yields of ethane and ethylene ranged from 0% (mol/mol Pt) in the presence of Hg(0) to 5% in solutions containing no additives to 36% (with glass) to 60% (with Pt/glass) and to 87% (with charcoal).

Mercury Poisoning of the Hydrogenolysis of CODPt(CH_3)$_2$. 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(CH_3)$_2$, and glass, 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 N_2. *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(CH_3)$_2$ by UV spectrophotometry (280 nm (ϵ 1700)). For the experiment shown in Figure 5, the catalyst was activated with two conditioning runs involving the hydrogenolysis of 15 mg of CODPt(CH_3)$_2$. Complex and mercury(0) were added to the reactor via syringe. In the reactor containing only CODPt(CH_3)$_2$, 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 m^2, about the same as the surface area of reactor exposed to solution), a smokey 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(CH_3)$_2$ and mercury(0) was allowed to stir for 5 days under 2.3-atm pressure of H_2. The solution was clear; a mirror formed on the reactor walls. Mercury adhered strongly to this mirror. The CODPt(CH_3)$_2$ 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 absorbed into the mercury bead. The surface of the mercury bead became dirty gray with black flecks. When mercury(0) was added to an active Pt(0)/glass catalyst, most of the catalyst was absorbed into the mercury bead. After less than 1 min of vigorous stirring only a very small amount (ca. 1 mg) of very fine catalyst particles remained "loose". Even after weeks of stirring, these particles remained loose. The mercury(0) bead in this experiment was a dull gray color. Although soft as a whole, the surface appeared "crusty" and the bead held shapes and contours.

Thermal Decomposition of (1,5-Cyclooctadiene)dineopentylplatinum(II) (12). A sample of 10 mg of CODPt($CH_2C(CH_3)_3$)$_2$ (12) (0.022 mmol) and ~400 mg of mercury in a 6-mm o.d. Pyrex tube was dried under vacuum (<0.015 torr, 3 h) and then dissolved in 0.30 mL of freshly distilled benzene-d_6. The solution was freeze–pump–thawed three times and sealed under vacuum (0.015 torr) so that the tube was not longer than 6 cm. A similar tube was prepared which did not contain mercury. These tubes were attached to an off-axis stirrer (Figure 3) with Teflon tape and stirred at ca. 15 rpm at 131 °C for 6 h. The tubes differed markedly in appearance due to added mercury (see Discussion). Tubes were cooled with liquid nitrogen, opened, and analyzed by GC and GC/MS. 1,5-Cyclooctadiene, dineopentylmercury, and neopentane were identified by comparing the GC retention times of the products with those of authentic samples. No 1,1-dimethylcyclopropane was observed by GC. The relative amounts of neopentane-d_0 and neopentane-d_1 were determined by comparing the relative abundance of the *m/e* 57 and 58 peaks of the product neopentane with the *m/e* peaks of authentic neopentane-d_0 (57/100%, 58/4.7%) and neopentane-d_1 (57/35%, 58/100%).[80,81] The relative concentrations of 1,5-

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[78] For titration method see: Carballo, L.; Serrano, C.; Wolf, E. E.; Carberry, J. J. *J. Catal.* **1978**, *52*, 507–514.

[79] The mass spectra of the reference samples were redetermined periodically to minimize errors which could arise from variations in the performance of the GC/mass spectrometer. These variations were never very large and would, at the most, only contribute 1-2% error to the determination of % neopentane-d_1 or % neopentane-d_{12}.

cyclooctadiene, neopentane, dineopentylmercury, and 12 from the thermal decomposition of 12 in the presence of mercury were determined by ^{1}H NMR integration to be δ 1.0, 0.43, 0.87, and 0.33, respectively, and in the absence of mercury were determined to be δ 1.0, 1.7, 0.0, and 0.05, respectively.[82] These relative concentrations were determined by comparing one or two well-resolved proton resonances from each compound: 1,5-cyclooctadiene (5.57 (s, CH), 2.20 ppm (s, CH_2)), neopentane (0.90 ppm (s)), and 12 (4.70 (t, CH),[83] 1.33 (s, CH_3)).

Cyclopentylmagnesium Bromide. A solution of the Grignard reagent in diethyl ether was prepared from cyclopentyl bromide (50 mL, 69 g, 0.46 mol) and magnesium turnings (24.3 g, 1.00 mol). Titration of the dark yellow supernatant indicated a concentration of 1.2 M (quantitative yield).

Cyclopentyldimethylphosphine. A three-necked 500-mL flask was equipped with pressure-adjusted dropping funnel, a stirring bar, and a Friedrich condenser topped by an argon inlet. The reaction flask was charged with cyclopentylmagnesium bromide (1.2 M, 65 mL, 78 mmol); a solution of chlorodimethylphosphine (6.0 mL, 6.0 g, 63 mmol) in 75 mL of diethyl ether was placed in the dropping funnel. The latter was added to the Grignard reagent at −78 °C over a 1-h period. After 30 min at room temperature, the reaction mixture (colorless supernatant, white precipitate) was refluxed for 2 h. The mixture was cooled to −78 °C before 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 white residue in the reaction flask was washed twice with ether; the rinses were filtered and combined with the supernatant. Solvent was removed by distillation through a 6-in. Vigreaux column topped by a short-path still head. The Vigreaux column was removed prior to fractional distillation of the product as a colorless oil, bp 160–162 °C. The yield was 4.56 g (55%): ^{1}H NMR (C_6D_6) δ 1.5 (br m, 9 H), 0.86 (d, J_{P-H} = 2.3 Hz, 6 H); ^{31}P NMR (C_6D_6) δ 40.3.

***cis*-Bis(cyclopentyldimethylphosphine)dimethylplatinum(II) (13).** A 25-mL recovery flask equipped with a stirring bar was charged with (1,5-cyclooctadiene)dimethylplatinum (0.8232 g, 2.47 mmol). The flask was capped with a septum and evacuated–back-filled with argon twice. The platinum compound was dissolved in 10 mL of diethyl ether. To this colorless solution was added cyclopentyldimethylphosphine (1.0 mL, 0.955 g, 7.34 mmol) in 5 mL of ether. The colorless solution was stirred overnight. Solvent was removed by rotary evaporation; the residual white paste was recrystallized from pentane at −80 °C and dried over potassium hydroxide in vacuo. The yield of colorless plates, mp 64–65 °C, was 45%: ^{1}H NMR (C_6D_6) δ 2.05 (s, br, 2 H), 1.68 (s, br, 4 H), 1.55–0.95 (m, 30 H); ^{31}P NMR (C_6D_6) δ 8.9 (s with Pt satellites, J_{Pt-P} = 1800 Hz). Anal. Calcd for $C_{16}H_{36}P_2Pt$: C, 39.58; H, 7.47; P, 12.76. Found: C, 39.86; H, 7.47; P, 13.03.

Thermal Decomposition of Bis(cyclopentyldimethylphosphine)dimethylplatinum(II). Thermolyses were conducted in 5-mm o.d. NMR tubes that had been flame-dried under vacuum and then allowed to cool in dry, oxygen-free argon. The tubes were removed from the vacuum manifold and charged with *cis*-bis(cyclopentyldimethylphosphine)dimethylplatinum(II) (ca. 20 mg, 41 μmol). Mercury(0) (ca. 0.3 g) was added if necessary.

Table IV. Mass Spectral Data of Methane and Deuterated Analogues[a]

	m/e								
	13	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**
CH_4[b]	10.0	20.2	95.0	100.0	1.9				
CH_3D	5.5	9.5	22.5	82.1	100.0	1.4			
CH_2D_2[c]		6.0	10.0	31.0	62.0	100.0			
CHD_3	1.3	6.1	5.3	9.1	44.3	39.8	100.0	1.0	
CD_4		8.4		15.5	1.1	90.1	2.8	100.0	0.7

[a] Analyzed on a Hewlett-Packard 5992A GC/MS using a 6-ft column of 4% Apiezon on 80/100 alumina. [b] Obtained from Matheson Gas Products. [c] From: "Index of Mass Spectral Data"; Kuentzel, L. E., Ed.; American Society for Testing and Materials: Ann Arbor, MI, 1963.

The tube was reevacuated for at least an hour before C_6D_{12} (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.

When dimethylmercury was involved in the thermolysis, the procedure was slightly modified. The argon-filled tube was removed from the manifold, charged with the necessary Pt(II) complex and/or Hg(0), and capped with a septum. The dimethylmercury (0.2 mL) was added by syringe, and the contents were quickly reattached to the vacuum line. The solution was allowed to thaw; it was subjected to one freeze–pump–thaw cycle before solvent was distilled into the tube. It was sealed under vacuum, as described above.

The tubes were heated in the vapors of refluxing *o*-dichlorobenzene (181 °C) for 4 h. Analysis by ^{31}P 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 0-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 CH_4, CH_3D, CHD_3, and CD_4 and the literature values for CH_2D_2.[84] Unlabeled methane was obtained from Matheson Gas Products; methane-d_1 was prepared by quenching an aliquot of CH_3MgBr, which had been freeze–pump–thawed twice, with D_2O. Methane-d_3 and methane-d_4 were obtained similarly by quenching aliquots of CD_3MgBr with H_2O and D_2O, 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 CH_4, CH_3D, CH_2D_2, CHD_3, and CD_4. In no case was CH_2D_2 observed.

The ethane produced was either completely unlabelled or perdeuterated, as determined by comparison with literature values for C_2H_6 and C_2D_6.[84] (Mass spectral data for C_2H_5D etc. are not available, but in all cases the *m/e* values obtained experimentally were in excellent agreement with those of C_2H_6 or C_2D_6.) 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 C_2H_4, C_2H_3D, $C_2H_2D_2$ (cis and trans), C_2HD_3, and C_2D_4.[84]

Thermal Decomposition of *trans*-Chloro(neopentyl-d_{11})bis(tri(cyclopentyl-d_{27})phosphine)platinum(II) ($L^D{}_2PtNp^DCl$, 14). To 14 mg of $L^D{}_2PtNp^DCl$ (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-d_0 by vacuum transfer. The solution was freeze–pump–thawed three times and

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(80) Neopentane-d_1 was produced using two different methods. (i) Addition of DCl in D_2O (99 atom %) to a solution of *cis*-dineopentylbis(triethylphosphine)platinum(II)[19] in dry methylene chloride produced neopentane-d_1. (ii) A sample of neopentylmagnesium bromide which had been dried under vacuum was quenched with D_2O to produce neopentane-d_1. Both methods produced samples of neopentane-d_1, which gave similar mass spectra.

(81) The relative concentrations of the products of decomposition of 12 in the presence of mercury are probably accurate to ±5%, while in the absence of mercury are probably only accurate to ±20%. The heterogeneous nature of the solutions produced by thermolysis in the absence of added mercury probably caused this discrepancy in error limits.

(82) Platinum is composed of one-third ^{195}Pt (spin $^1/_2$) and two-thirds other isotopes (spin 0). A characteristic coupling pattern is the 1:4:1 platinum "triplet".

(83) Juentzel, L. E., Ed. "Index of Mass Spectral Data"; American Society for Testing and Materials: Ann Arbor, MI, 1963.

(84) Authentic samples of neopentane-d_{11} and neopentane-d_{12} were prepared by quenching samples of neopentylmagnesium bromide-d_{11} (used to make $L^D{}_2PtNp^DCl$) which had been dried under vacuum with H_2O and D_2O, respectively.

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 ^{31}P NMR resonances of $L^{D}_{2}PtDCl$ and starting material. The kinetics at decomposition were half-order in $L^{D}_{2}PtNp^{D}Cl$.[55] Solutions were thermally decomposed for 15 h or until ~25% of $L^{D}_{2}PtNp^{D}Cl$ 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%).[80,85]

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-hexamethylsilacyclopentane; 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.

Reactivity and Conformation of a Phosphine-Substituted Dihalocarbene Complex. X-ray Crystal Structures of $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(CF_2)][BF_4]$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CCl_2)][BCl_4]$

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The difluorocarbene complex $[CpFe(CO)(PPh_3)(CF_2)][BF_4]$ (1) was prepared by halide abstraction from $CpFe(CO)(PPh_3)(CF_3)$ using BF_3. The structures of this compound and $[CpFe(CO)_2(CCl_2)][BCl_4]$, 2, determined by single-crystal X-ray diffraction, show the effect of ligand asymmetry on the dihalocarbene orientation. For 1 the plane of the CF_2 ligand is tilted 18° away from coplanarity with the CO. Complex 2 adopts a vertical conformation with the plane of the CCl_2 ligand bisecting the OC–Fe–CO angle. The orientations of CX_2 in 1 and 2 agree with the conformations predicted by the MO treatment of Hoffmann and co-workers; however, low-temperature NMR measurements of 1 indicate that the CF_2 group is rapidly rotating in solution, so the energy barrier between the various conformers is low. The reaction of $CpFe(CO)(PPh_3)(CF_3)$ with BCl_3 at low temperatures was followed by low temperature NMR, which indicates the successive formation of CF_2, CFCl, and CCl_2 complexes. These results substantiate a previously postulated mechanism for halide exchange. Crystal data for 1: space group, monoclinic, $P2_1/c$; $a = 9.035$ (3) Å, $b = 24.390$ (11) Å, $c = 10.745$ (5) Å, $\beta = 102.20$ (3)°; $Z = 4$. Crystal data for 2: space group, monoclinic, $P2_1/c$; $a = 12.238$ (4) Å, $b = 9.444$ (4) Å, $c = 13.440$ (4) Å, $\beta = 113.55$ (3)°; $Z = 4$.

Introduction

Dihalocarbene transition-metal complexes are versatile precursors to other ligands.[1-8] For example, dihalocarbenes react with nucleophiles to form substituted carbenes as well as nitriles, isonitriles, and thiocarbonyls[2,4-6,8] (eq 1–3). An unusual difluorocarbene of Ru(0), $[Ru(CF_2)(CO)_2(PPh_3)_2]$, also reacts with electrophiles.[7] One convenient method of synthesizing cationic dihalocarbene complexes and neutral trihalomethyl complexes is halogen exchange and halide abstraction of trifluoromethyl complexes using boron trihalides (eq 4–6).[1,2]

$$IrCl_2(CCl_2)(PPh_3)_2 + H_2S \rightarrow IrCl_2(CS)(PPh_3)_2 + 2HCl \quad (1)$$

$$RuCl_2(CCl_2)(CO)(PPh_3)_2 + H_2NCH_3 \rightarrow RuCl_2(CNCH_3)(CO)(PPh_3)_2 + 2HCl \quad (2)$$

$$RuCl_2(CCl_2)(CO)(PPh_3)_2 + HSCH_2CH_2SH \rightarrow RuCl_2(CSCH_2CH_2S)(CO)(PPh_3)_2 + 2HCl \quad (3)$$

$$CpFe(CO)_2(CF_3) + 2BCl_3 \rightarrow [CpFe(CO)_2(CCl_2)][BCl_4] + BF_3 \quad (4)$$

$$CpFe(CO)_2(CF_3) + BF_3 \rightarrow [CpFe(CO)_2(CF_2)][BF_4] \quad (5)$$

$$CpFe(CO)_2(CF_3) + BCl_3 \rightarrow CpFe(CO)_2(CCl_3) + BF_3 \quad (6)$$

In the proposed mechanism for the reaction in eq 6 halogen exchange proceeds through dihalocarbene intermediates. However, a concerted mechanism could not be ruled out.[1] Ligand substitution of carbene complexes alters both the reactivity and geometric conformation of the complex. The carbene ligand behaves as a π-acid. Since PPh_3 donates more electron density to the metal center than does CO, one would expect phosphine substitution to facilitate halide abstraction and stabilize the carbene. In this paper a comparison of the reactivities of $CpFe(CO)(PPh_3)(CF_3)$ and $CpFe(CO)_2(CF_3)$ with BCl_3 demonstrates this stabilization of the carbene and provides evidence for the carbene exchange mechanism.

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