Gaussian amplitudes for all non-hydrogen atoms resulted in $R = \{\sum W |F_o| - |F_c|/k|W/|F_o|\} = 0.0588$ (3264 reflections with $l > 0$) and GOF = $\{\sum W(F_o^2 - F_c^2/k)^2/(n_o - n_p)\}^{1/2} = 1.51$, where n_o is the number of reflections and n_p is the number of parameters (4124 reflections). The parameters for the Cp* hydrogens H111–H253 and the phenyl ring H4–H8 were not refined. There was no residual electron density greater than 0.4 e⁻/Å³ remaining in the final difference Fourier map. The final values for the atom coordinates are given in Tables XI and XII; bond lengths and angles are located in Table XII.

The molecular structure of Cp*₂Nb(CH₂=CHC₆H₅)H is shown in Figure 5; a skeletal view of niobium coordination with notable bond lengths and angles is shown in Figure 6.

Registry No. 1, 93558-77-1; **2**, 95313-63-6; **3**, 113628-22-1; **4**, 113628-23-2; **5**, 113628-24-3; **6**, 11105-67-2; *endo*-**7**, 113628-25-4; *exo*-**7**, 113667-63-3; *endo*-**8**, 113628-26-5; *exo*-**8**, 113667-64-4; *endo*-**9**, 113628-27-6; *exo*-**9**, 113667-65-5; *endo*-**10**, 113628-28-7; *exo*-**10**, 113667-66-6; **11**, 11105-70-7; **12**, 95313-60-3; **13**, 66786-38-7; **14**, 100701-96-0; *endo*-**15**, 95313-62-5; *endo*-**16**, 75576-71-5; *exo*-**16**, 75599-42-7; *endo*-**17**, 113667-67-7; *endo*-**18**, 68586-68-5; *exo*-**18**, 68680-01-3; Cp₂Nb(C≡NMe)(NMe₂), 113628-29-8; *m*-(trifluoromethyl)styrene, 402-24-4; *m*-methylstyrene, 100-80-1; *m*-(dimethylamino)styrene, 5339-11-7; styrene, 100-42-5; *p*-(trifluoromethyl)styrene, 402-50-6; *p*-methoxystyrene, 637-69-4; *p*-(dimethylamino)styrene, 2039-80-7; methyl isocyanate, 593-75-9.

Supplementary Material Available: Hammett plots for Cp₂Nb(CH₂=CHC₆H₄-*p*-X)H insertion rates versus σ_+ and transition-state energies versus σ_p and σ_+, the corrected and uncorrected Eyring plots for *endo*-Cp*₂Nb(CH₂=CHC₆H₅)H, and tables of hydrogen idealized positional parameters and thermal parameters and Gaussian amplitudes for all non-hydrogen atoms (6 pages); a listing of structure factors (17 pages). Ordering information is given on any current masthead page.

# Heterogeneous, Platinum-Catalyzed Hydrogenation of (Diolefin)dialkylplatinum(II) Complexes: Kinetics[1]

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Abstract: (Diolefin)dialkylplatinum(II) complexes [(Ol₂)PtR₂] are rapidly reduced by dihydrogen in the presence of platinum black catalyst: the organic groups are converted to alkanes, and the platinum(II) to platinum(0). This platinum(0) is incorporated into the surface of the platinum black catalyst. The reaction is a heterogeneous process catalyzed by platinum(0). Its rate is strongly influenced by mass transport and by the surface area of the catalyst. It is poisoned by dineopentylmercury, di-*n*-octyl sulfide, and tri-*tert*-butylphosphine. Because the catalyst surface is constantly renewed by deposition of platinum, the reaction is, however, less sensitive to poisoning than more familar platinum-catalyzed reactions such as hydrogenation of olefins. The form of the kinetic rate law observed for reduction of (1,5-cyclooctadiene)dimethylplatinum(II) (1) depends on the reaction conditions. Two limiting kinetic regimes are observed. In one, mass transport of dihydrogen to the catalyst surface is rate-limiting; in the second, a reaction occurring on the platinum surface is rate-limiting. The activation energy for reaction in the mass transport limited regime is ~3 kcal/mol and that in the reaction rate limited regime is ~15 kcal/mol. In neither regime is there a kinetic isotope effect: $v_{H_2}/v_{D_2} \approx 1.0$. Examination of the relative rates of reaction of a series of (diolefin)dialkylplatinum(II) complexes indicates that the structure of the diolefin has a greater influence on the rate of reaction than does that of the alkyl group. Competitive experiments show that rates are influenced by adsorption of the (Ol₂)PtR₂ complex to the catalyst. These studies suggest that the platinum-catalyzed reaction of (Ol₂)PtR₂ with dihydrogen takes place by a mechanism analogous to that of the platinum-catalyzed heterogeneous hydrogenation of olefins: the (Ol₂)PtR₂ complex chemisorbs on the surface of the platinum catalyst; its organic groups are converted to platinum surface alkyls; coupling of these surface alkyls with surface hydrogen atoms generates the alkane products. The platinum atom originally present in the soluble complex is incorporated into the surface of the platinum catalyst and becomes the reactive site for a subsequent cycle of chemisorption and reaction. The reaction of (Ol₂)PtR₂ complexes with dihydrogen thus provides a new method for generating platinum–surface alkyls under conditions representative of those used in heterogeneous platinum-catalyzed processes.

This and the accompanying papers[2,3] describe studies of the reaction of (diolefin)dialkylplatinum(II) complexes [(Ol₂)PtR₂] with dihydrogen in the presence of a platinum black catalyst (eq 1). We demonstrate that this process is a heterogeneous platinum-catalyzed reduction of the soluble organoplatinum compound.
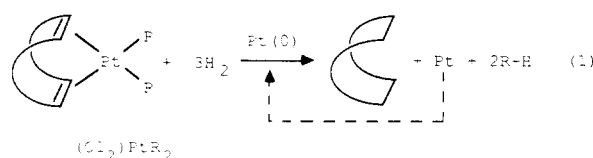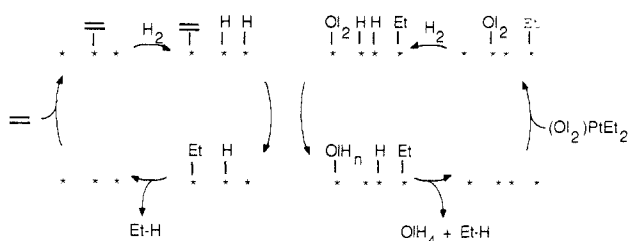

It involves steps broadly analogous to those taking place in platinum-catalyzed heterogeneous hydrogenation of olefins: chemisorption of the organoplatinum compound and dihydrogen

Pt-Catalyzed Hydrogenation of [(Ol₂)PtR₂]

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Scheme I. Proposed Analogy between the Mechanisms of Platinum-Catalyzed Hydrogenation of Olefins (Left) and of (Ol₂)PtR₂ Complexes (Right)

Table I. Organic Products and Their Absolute Yields from Reduction of **1**[a]

reaction conditions[b]	cyclooctane	bicyclo[3.3.0]- octane	methane
RRL	100 ● 3	0	200 ± 10
MTL	96 ● 3	1.3 ± 0.2	204 ± 10

[a] These yields are expressed as a percentage of 1 equiv of **1** and are the average of three determinations. [b] Reaction conditions are defined in Table II.

on the catalyst surface, generation of platinum–surface alkyls from the alkyl and diolefin groups originally present in the organoplatinum complex, and coupling of surface alkyl moieties and hydrogen yielding alkane products. The major objective of this paper is to establish the kinetic features of the reaction, especially those relevant to a study of reaction mechansim. The following paper presents deuterium-labeling evidence for the mechanism of the reaction.[2] In the third paper in this series, deuterium-labeling experiments are used to analyze the reactivity of platinum–surface alkyls.[3]

We are developing this reaction as a new approach to the study of the mechanisms of heterogeneous platinum-catalyzed reactions, especially hydrogenation of olefins. The extensive prior work in this subject includes studies of well-defined single-crystal surfaces[4-10] and metal clusters,[11-14] studies of the kinetics of olefin hydrogenation[15-18] and accompanying isotopic exchange and olefin isomerization,[16,19,20] and the influence of catalyst morphology on the reaction.[10,18,21-24] Over group VIII metals, olefin and dihydrogen adsorb at the surface before they react;[16] over platinum the reaction is insensitive to the atomic morphology,[21-24] and reduction is generally accompanied by isotopic exchange and olefin isomerization.[16,19,20] A mechanistically useful parallel between the hydrogenation of olefins and (Ol₂)PtR₂ complexes is suggested by Scheme I (with ethylene and (Ol₂)PtEt₂ as examples). The essential point to note in this scheme is that both catalytic sequences involve generation of platinum–surface alkyls as reactive intermediates.

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Reaction starting from (Ol₂)PtR₂ offers several advantages in studying the mechanism of platinum-catalyzed reactions of hydrocarbons. First, because the structure of the platinum–surface alkyl is determined, at least initially, by the structure of the (Ol₂)PtR₂ complex rather than by the structure of an olefin, it is possible to generate a surface alkyl with a well-defined pattern of isotopic labeling and with known regio(stereo)chemistry of bonding to the platinum surface. Moreover, it is possible with this reaction to generate surface alkyls (methyl, phenyl, neopentyl, butane-1,4-diyl) that cannot be generated by hydrogenation of olefins. Second, the reaction takes place near room temperature and under 0.1 to 3.0 atm of dihydrogen in conventional solvents with commercially available platinum catalysts; it is, thus, convenient to study experimentally. Finally this reaction continually generates a fresh platinum surface and is therefore not readily susceptible to poisoning by small quantities of poisons.

We have previously reported experiments based in isotopic exchange suggesting that reaction of (Ol₂)PtR₂ complexes with hydrogen was a heterogeneous platinum-catalyzed process involving platinum–surface alkyls as intermediates.[25] A second report concerned the ability of Hg(0) to selectively poison heterogeneous processes while leaving homogeneous processes unaffected.[26] (1,5-Cyclooctadiene)dimethylplatinum (**1**) was reported to react autocatalytically with an irreproducible initiation period with dihydrogen. The presence of controlled-pore glass shortened the initiation period, but the presence of Hg(0) prevented reaction. If a platinum supported on controlled-pore-glass catalyst was present, Hg(0) slowed reduction of **1** but did not stop it. One of the conclusions from this work was that reaction of **1** with dihydrogen did not proceed at a significant rate in the absence of bulk platinum(0).

Results and Discussion

General Methods. Organoplatinum complexes were prepared by well-established procedures. The (Ol₂)PtR₂ complexes have the attractive features that they contain no components (halide ions, carbonyl groups, phosphines) that might act as catalyst poisons and that many of them are reasonably stable thermally and resistant to reaction with dihydrogen in the absence of platinum metal. The course of the reactions seemed to be independent of the previous history of the (Ol₂)PtR₂ complexes, and the reactions appeared to be insensitive to trace impurities present in them.

We chose platinum black as the catalyst principally for convenience. It is commercially available in large quantities (>1 g) from several sources. The studies in this work were carried out over fuel-cell grade platinum black purchased from Johnson Matthey Inc. We found this catalyst to be reasonably reproducible (±20%) in surface area and in catalytic activity.

Reactions were generally carried out in 20-mL pressure bottles that were capped with neoprene septa. *n*-Heptane (3–4 mL) was the usual solvent although diethyl ether was used for (Ol₂)PtR₂ compounds having poor solubilities in heptane. The catalyst and solvent were saturated with dihydrogen prior to beginning reductions. Dihydrogen pressures of less than 1 atm were maintained by using a mixture of 10% dihydrogen in argon.

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Table II. Standard Conditions Used in Kinetics Experiments

variable	RRL[a]	MTL[b]	Remarks
$(Ol_2)PtR_2$	40 μmol (10 mM)	50 μmol (12 mM)	CODPtMe$_2$, 1
solvent (mL)	3–4	3–4	n-heptane, n-hexane, diethyl ether
reaction vessel			20-mL glass pressure tube
T (°C)	–20	40	
catalyst (mg)	31	40	platinum black
S_{Pt} (μg-atom)[c]	8.7	11	
P_{H_2} (atm)	2.4	0.17	
agitation (RPM)	1800	1800	rate of rotation (ω) of egg-shaped (10 × 6 mm) magnetic stirring bar
analytical methods	GC and UV	GC and UV	

[a]RRL = reaction rate limited. [b]MTL = mass transport limited. [c]S_{Pt} ≡ μg-atom of accessible platinum.

We mention a useful and interesting feature observed with platinum black and highly loaded supported platinum catalysts in nonpolar solvents. After these catalysts had been handled in air and suspensed in a nonpolar solvent, they are finely divided, easily stirred, highly dispersed powders. When the catalysts were stirred under dihydrogen, they became aggregated, "clumpy" masses. During reduction of a (diolefin)dialkylplatinum complex or an olefin, the catalyst returned to finely divided, easily stirred, highly dispersed powders. When the substrate was consumed, the catalysts reaggregated. End points of reaction could be roughly determined by observing reaggregation. We attribute this aggregation and dispersion to the species covering the surface: the working catalyst is plausibly covered with a layer of surface alkyls and other adsorbed species. We believe that these materials act as surfactants and lower the catalyst–solvent interfacial free energy.[27]

Stoichiometry of Reduction of 1. The hydrocarbon products of reaction were almost independent of the reaction conditions (Table I) and consisted of the alkanes derived from reduction of the diolefin groups and the platinum–carbon bonds. In the reduction of 1 under mass transport limited (MTL) conditions, we observed small quantities (<5% of the quantity of cyclooctane) of cyclooctene at small conversions of 1; free 1,5-cyclooctadiene in solution was not detected. The reaction generated small quantities (<2%) of cis-bicyclo[3.3.0]octane under MTL conditions; this compound is also formed in the reduction of 1,5-cyclooctadiene (COD) under MTL conditions. The platinum atoms in 1 were quantitatively (>97%, as measured by gain in weight) incorporated into the initial catalyst.

We determined the stoichiometry in dihydrogen by monitoring (by UV, see below) the concentration of 1 as a function of the quantity of hydrogen added to the reactor. Three (3.0 ± 0.3) equivalents of dihydrogen reduced 1.0 equiv of 1. This stoichiometry was expected from the products of reaction.

Kinetic Methods, Standard Conditions for Kinetics Experiments. In studying the kinetics of these and other heterogeneous reactions, extensive properties of the system (e.g., absolute volumes of solution and flask) are important, as well as intensive properties (molarities, temperature, pressure). Table II gives the standard conditions used for reductions established by the evidence that follows to be mass transport limited (MTL) or reaction rate limited (RRL).

A kinetics experiment was carried out by placing the catalyst, solvent, and magnetic stirring bar in a reactor, flushing the system with dihydrogen or dihydrogen in argon, and stirring for >5 min at the desired temperature. In this initial activation, the catalyst aggregated during the first 10–20 s. Stirring was halted and a solution of $(Ol_2)PtR_2$ was added. An initial aliquot (60–80 μL) of the reaction mixture was immediately withdrawn and the

magnetic stirrer was restarted at t = 0. Subsequent aliquots were removed periodically by stopping the stirring, allowing the catalyst particles to settle for 3–6 s, and withdrawing an aliquot. To maintain a constant concentration of dihydrogen in the vapor phase over the course of a reduction under MTL conditions, the reactors were provided with a continuous slow (5 mL/min) leak of gas.

The extent of reaction was usually determined by monitoring the decrease in concentration of $(Ol_2)PtR_2$, measured by the UV absorbance of a solution prepared by dilution of 50 μL of an aliquot into 2.0 or 5.0 mL of n-heptane under air. Since the products of reaction are alkanes and insoluble Pt(0), the only component of the reaction mixture that has significant UV absorbance was the $(Ol_2)PtR_2$ complex. Monitoring the concentration of $(Ol_2)PtR_2$ by UV spectrophotometry was particularly convenient experimentally: neither unsettled catalyst particles nor traces of dioxygen introduced into the reaction on sampling caused problems. The only disadvantages of this technique are that stirring must be stopped periodically, and that several manipulations are required to prepare the sample. Under certain circumstances, the aliquots were analyzed by gas chromatography and the concentration of product cyclooctane or other hydrocarbon determined.

In order to produce interpretable kinetic information for a heterogeneous catalytic reaction, it is essential to relate the rate of reaction to the number of catalytic sites. The simplest experiments can be carried out when the number of catalytic sites remains constant during a kinetic experiment. It is possible to obtain useful information even when the catalyst activity changes during reaction, so long as the change is relatively slow and reproducible. We have characterized the catalyst used here by three criteria: catalytic activity, as determined by successive replicate kinetic runs with 1 as substrate; surface area, as measured by dihydrogen–dioxygen titration;[28,29] and physical morphology, as inferred from scanning electron microscopy (SEM).

The change in activity of a catalyst on repeated use in a series of kinetic runs is discussed in detail in the following sections on kinetics. Correlations between activity and surface area were based on measurements of platinum–surface area with dihydrogen–dioxygen titration. This titration was carried out by modification of the procedures of Carbello et al.[28] and Freel et al.[29] Passage of pulses of dihydrogen over samples of platinum catalyst having high surface area gave peaks as detected by thermal conductivity that tailed badly. This tailing precluded accurate determination of the amount of dihydrogen not adsorbed by the catalyst.[28] Instead, the number of surface platinum atoms was determined by saturating a known weight of catalyst with dihydrogen and measuring the amount of dioxygen required to saturate the catalyst with oxygen. This method assumes a stoichiometry of one atom of dioxygen adsorbed per platinum surface atom.[28–30] Thus, each platinum surface atom consumed 1.5 equiv of "O" or 0.75 equiv of O_2 on conversion from "Pt$_S$H" to "Pt$_S$O".

Reaction Rate Limited (RRL) Kinetics. The most serious technical problem foreseen at the outset of this work was that of measuring the kinetics of a heterogeneous catalytic reaction in which the surface area and activity of the catalyst might change during the course of the reaction, due to deposition of platinum derived from the $(Ol_2)PtR_2$ onto the catalyst surface.

We have examined the dependence of the catalyst surface area (S_{Pt} ≡ μg-atom of accessible platinum) on the quantity of platinum(0) deposited on the catalyst during reduction of 1 under RRL conditions. Figure 1 shows a plot of S_{Pt} of the catalyst measured after reduction of varying quantities of 1 on it. Six reductions were performed with varying amounts of 1 on six 31-mg samples of one batch of catalyst; the surface areas of these catalyst samples were measured after the reductions and plotted in Figure 1. Reduction of the first 30 μmol of 1 resulted in a reduction in S_{Pt} by 20%, but reductions of larger quantities of 1 resulted in no

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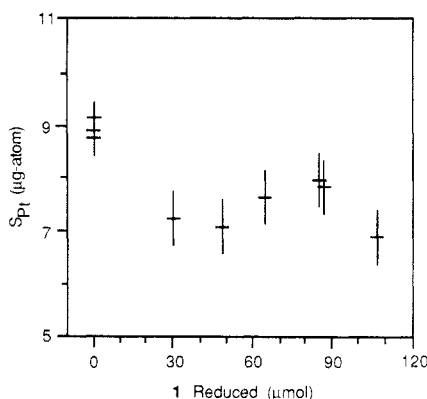
Figure 1. Surface area (S_{Pt}) of the platinum catalyst as measured by dihydrogen–dioxygen titration after reduction of various quantities of 1 under RRL conditions. The values of S_{Pt} at 1 reduced = 0 are the surface areas of three samples of the catalyst (31 mg) as received.
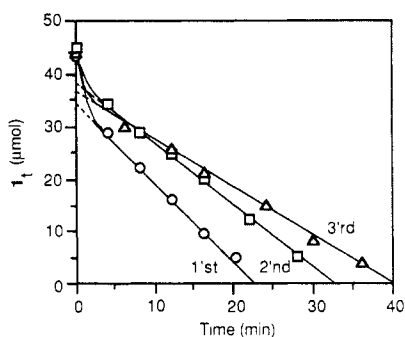
Figure 2. Plots of successive reductions of 1 on the same sample of catalyst under RRL conditions. Reductions proceed successively more slowly.

significant further change in S_{Pt}. We conclude that S_{Pt} diminishes on reduction of 1 but that the change in S_{Pt} is independent of the quantity of 1 reduced. Examination by SEM of the surface of the platinum black catalyst as received and after reduction under RRL conditions of 108 μmol of 1 on 31 mg of catalyst ($S_{Pt,0}$ ~ 9 μg-atom) showed no detectable change in morphology.

As a check on the dependence of S_{Pt} on the quantity of 1 reduced (and the quantity of platinum deposited) on the catalyst, we determined the constancy of rates of successive reductions of 1 on the same sample of catalyst. The data in Figure 2 show that successive reductions proceed successively more slowly in agreement with the S_{Pt} determinations. The form of these plots suggests immediately that the reduction of 1 is kinetically zero-order in [1]. These data also suggest that the reaction shows a pronounced initial kinetic burst. This phenomenon is discussed in the following section; we note here that its origin is probably initial reaction of 1 with a catalyst whose surface is saturated with adsorbed hydrogen.

We systematically varied reaction conditions about those given in Table II to establish an empirical rate law for the reduction of 1 under RRL conditions. Figure 3 confirms both that the kinetic order in 1 is zero over the range of initial concentration of 1 from 8.0 to 27.5 mM and the occurrence of a kinetic burst at the start of each reaction. Typically, in reductions of olefins over heterogeneous catalysts, the order in olefin is zero.[16-18] A zero-order dependence on substrate is usually interpreted to mean that all of the catalytic sites are saturated with adsorbed olefin. We believe that an analogous explanation holds true for 1; that is, that the catalyst is saturated with adsorbed 1 or fragments derived from it.

Figure 4 shows data for the dependence of velocity as defined in eq 2 on the quantity of catalyst and indicates an approximately

$$v = -d(Ol_2)PtR_2/dt \qquad (2)$$

first-order dependence of velocity on S_{Pt}. The size of the burst in these experiments is proportional to the quantity of catalyst
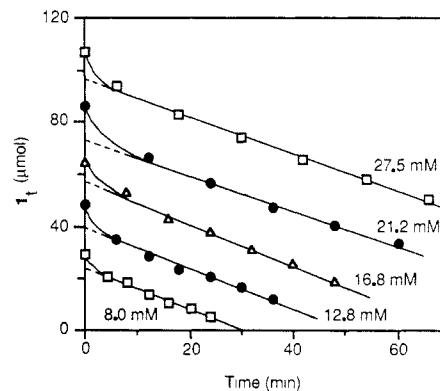
Figure 3. The rate of disappearance of 1 with time under RRL conditions is zero-order in 1. The initial concentration of ($[1]_0$) is given beside each curve.
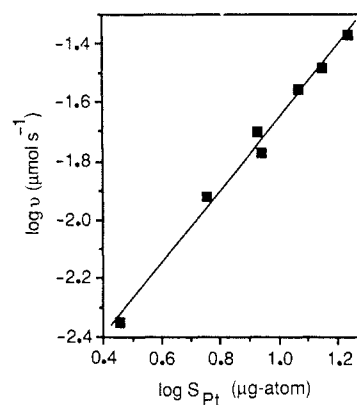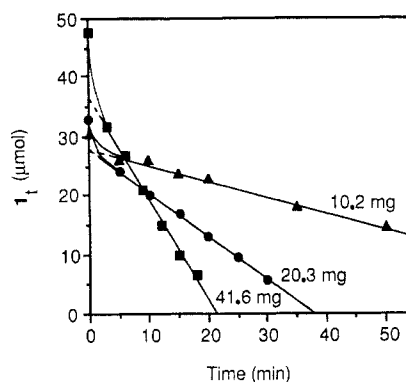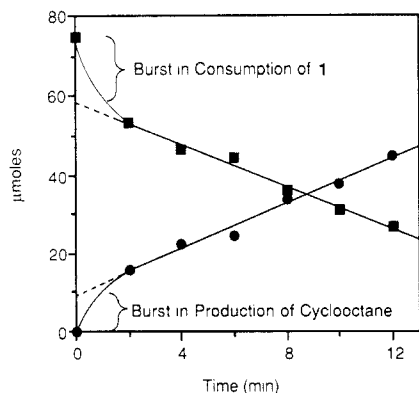

Figure 4. (Upper) A plot of 1_t versus time with three different initial quantities of catalyst (given in the plot) under RRL conditions. The velocity of reduction of 1 and the burst in consumption of 1 increase with increasing quantities of catalyst. (Lower) The order in S_{Pt} for the reduction of 1 under RRL conditions is 1.2 ± 0.2.

used. A plot of v versus S_{Pt} intercepted the origin and demonstrated (as we have found previously) that reaction of 1 with dihydrogen does not proceed at a significant rate in the absence of catalyst.[26] The velocity of reduction of 1 under RRL conditions is independent of the stirring rate, ω, and increases with increasing dihydrogen pressure. The order in dihydrogen pressure is 0.38 ± 0.04.

Combination of all of these data yields the rate law given in eq 3.[31] This rate law is similar to those determined for hydro-

$$-d1/dt = 0.014 \pm 0.003 \ (\mu\text{mol s}^{-1} \ \text{atm}^{-0.38} \ (\mu\text{g-atom})^{-1.2}) \times$$
$$(\omega^{0.0\pm0.3})(S_{Pt}^{1.2\pm0.2})(P_{H_2}^{0.38\pm0.04})([1]^{0.0\pm0.2}) \quad (3)$$

(31) Note that this rate equation is unusual in that the rate is defined in terms of μmol s^{-1} as opposed to the usual μM s^{-1} because of the zero-order dependence on [1].

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Figure 5. A plot of 1, (■) and cyclooctane, (●) produced under RRL conditions (Table I) except that $S_{Pt} = 17.1$ μg-atom.

Figure 6. A plot of 1, versus time. The catalyst poisons (20 μmol of each) (△) tri-*tert*-butylphosphine, (■) di-*n*-octyl sulfide, (●) and dineopentylmercury were added at $t = 16$ min.

genations of olefins over platinum catalysts.[16-18] A rate expression of this form is compatible with a mechanism in which the rate-determining step takes place on the surface of the catalyst. The nature of this step is not greatly restricted by the rate law in the absence of other experimental data: it might involve one or both reactants (1 and H_2) adsorbed on the catalyst surface. Interpretation of the exponent for P_{H_2} is particularly complicated since at least three different groups are being reduced (the two olefinic moieties of COD and the Pt–CH$_3$ bonds).

Burst Kinetics in the RRL Regime. Figures 3 and 4 present evidence for an initial burst of reaction on addition of **1** to a suspension of catalyst saturated with hydrogen. The magnitude of the burst was independent of the source of **1** and of the solvent in which reductions were performed; bursts were observed for all of the $(Ol_2)PtR_2$ substrates examined except for (norbornadiene)dimethylplatinum (NBDPtMe$_2$). When rates of reduction were measured on platinum black and platinum oxide from other sources (Aldrich, Alfa), bursts were also observed. Catalysts from different sources gave varying burst sizes and velocities for a given weight of catalyst. We did not measure S_{Pt} for all of these catalysts, but qualitatively, catalysts with higher activity gave larger bursts. When a reduction of **1** was interrupted by releasing the dihydrogen pressure and purging the vessel first with argon and then (without stirring) with dihydrogen, no burst was seen when the reaction was restarted by resuming stirring. We believe that the catalyst is covered with alkyl groups when the system is allowed to exhaust the supply of dihydrogen in the presence of **1**. We infer that the presence or absence of a burst depends on the species on the surface of the catalyst.

In order to understand these burst kinetics better, we followed the concentration of **1** and cyclooctane simultaneously during the course of a representative reduction. Figure 5 shows a plot of consumption of **1** and production of cyclooctane. The rates of production of cyclooctane and of consumption of **1** were the same within experimental uncertainty. There is a burst both in consumption of **1** and in production of cyclooctane. A plot of the size of the burst in consumption of **1** and in generation of cyclooctane (as determined from plots similar to Figure 5) versus the quantity of catalyst initially present in the reaction showed that both bursts increase with increasing quantity of catalyst and the size of the burst for production of cyclooctane is ~60% of that for consumption of **1**. The observation of a burst in production of cyclooctane indicates that the burst in consumption of **1** is not due simply to adsorption of **1** on the catalyst surface. Irreversible modification of the catalyst can also be ruled out by the data in Figure 2, which show that successive reductions of **1** give rise to successive bursts.

These data are compatible with the hypothesis that the bursts are due to rapid reaction of **1** with dihydrogen adsorbed on the catalyst surface. Another possible explanation is that adsorption of dihydrogen is the slow step in the reaction and that preequilibration of the catalyst with dihydrogen before adding **1** circumvents this rate-limiting step. This explanation is unlikely since other $(Ol_2)PtR_2$ and olefinic substrates react *more* rapidly than does **1** (vide infra); if adsorption of dihydrogen were rate-limiting
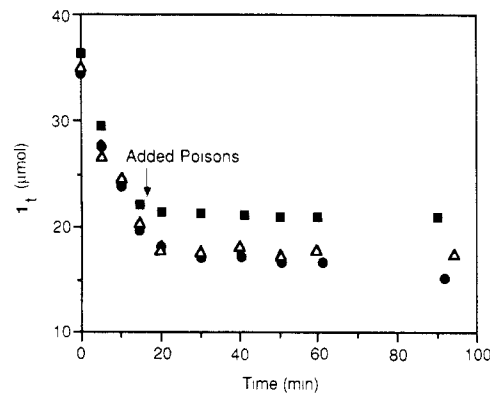
for reaction of **1**, no other substrate should react more rapidly.

We propose that the burst has two components: reaction of **1** with dihydrogen on the catalyst surface, and adsorption of **1** on the catalyst surface *without* reduction. The difference between the quantity of **1** consumed and that of cyclooctane produced gives a qualitative measure of the relative importance of these processes. The difference between the burst in the quantity of **1** consumed and the burst in the quantity of cyclooctane produced is approximately 40% of S_{Pt}, and this suggests that an adsorbed equivalent of **1** or fragments derived from it occupies the area of surface required to adsorb ca. 2.5 hydrogen atoms. We note that the observation of zero-order kinetics in **1** for the steady-state reduction of **1** occurring after the burst implies that the catalyst is saturated with **1** under these conditions. The burst then can be interpreted as an initial, rapid reaction that reduces the surface concentration of hydrogen from its high value in the absence of **1** to a lower value at steady state in solutions containing **1** (eq 4).
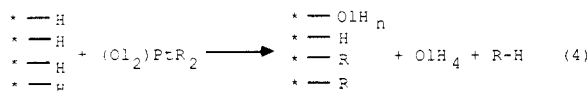

Catalyst Poisoning. As with olefin hydrogenation catalysts, reduction of **1** is subject to poisoning by group V and VI Lewis bases and by mercury compounds as well as by Hg(0) (as was demonstrated previously).[26,32] Figure 6 shows the effect of adding tri-*tert*-butylphosphine, dineopentylmercury, and di-*n*-octyl sulfide on the reduction of **1** under RRL conditions. The velocity of reduction drops dramatically upon addition of all of these poisons. ^{1}H NMR spectra of solutions of **1** and each of these substances demonstrated that they do not react with each other at a significant rate under these conditions.

Mass Transport Limited (MTL) Kinetics. Standard reaction conditions are given in Table II; systematic variation around these conditions established the rate law. Rates measured by following the decrease in concentration of **1** by UV spectroscopy or by the increase in concentration of cyclooctane by GC were indistinguishable.

A plot of 1, versus time with varying initial amounts of **1** under MTL conditions showed that the amount of **1** reduced per unit time is independent of the initial quantity of **1** present and that the kinetic order in **1** is zero. The interpretation of the zero-order dependence on [1] is the same here as under RRL conditions. Figure 7 shows a plot of the surface area (S_{Pt}) of catalyst after single reductions of given quantities of **1** on it under MTL conditions. Over the range of quantities of **1** reduced, S_{Pt} remained constant. No morphological changes from unused catalyst were evident in SEM micrographs of catalyst after reduction of 104 μmol of **1** on its surface.

Figure 8 shows a plot of the velocity of reduction of **1** versus the initial quantity of catalyst present. Increasing the quantity

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(32) Maxted, E. B. *Adv. Catal.* **1951**, *3*, 129–177.
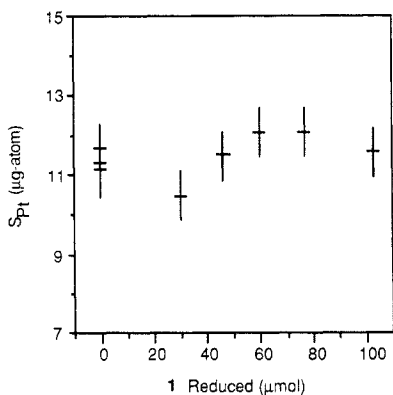
Figure 7. Surface area (S_{Pt}) of the platinum catalyst as measured by dihydrogen–dioxygen titration after reduction of varying quantities of 1 under MTL conditions. The values of S_{Pt} at 1 reduced = 0 are the surface areas of three samples of catalyst (40 mg) as received. S_{Pt} is independent of the quantity of 1 reduced.
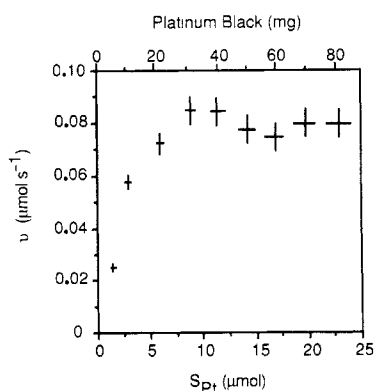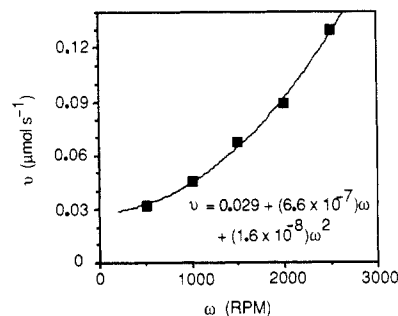

Figure 8. The velocity of reduction of 1 first increases with the quantity of catalyst and then becomes independent of the quantity of catalyst. Standard conditions for MTL reaction involve 40 mg of catalyst (Table II).

of catalyst present caused an increase in the velocity of the reaction until approximately 30 mg (S_{Pt} = 8.5 μg-atom) of catalyst had been used. With more than 30 mg of catalyst, the velocity of reduction became independent of the quantity of catalyst present. The quantity of catalyst used under the standard MTL conditions (Table II) is 40 mg, and it is clearly in the region in which the rate is independent of S_{Pt}. We note that, in Figure 8 as under RRL conditions, the intercept of this plot appears to be zero. This observation indicates that the rate of reaction of 1 with dihydrogen in the absence of catalyst is negligible. Figure 9 shows that the velocity of reaction increased with ω, and a plot of log υ versus log P_{H_2} showed that the velocity of reaction increased with dihydrogen pressure to the first power. A plot of log υ versus log ω was not linear, but a second-order polynomial relating υ and ω given in Figure 9 fits the data quite well. Equation 5 defines the rate law for reduction of 1 under MTL conditions.[31]

$$-d1/dt = 0.086 \pm 0.012 \ (\mu\text{mol s}^{-1} \text{ atm}^{-1.05})(1.0 + 2.3 \times$$
$$10^{-5} \omega + (5.5 \times 10^{-7}\omega^2)(S_{Pt}^{0.0\pm0.2})(P_{H_2}^{1.05\pm0.07})([1]^{0.0\pm0.2}) \quad (5)$$

Heterogeneous catalytic reactions whose velocities depend upon the extent of agitation are generally limited in rate by mass transport of one of the reactants to the catalyst. Here the low pressure of dihydrogen and the dependence of the velocity on the pressure of dihydrogen point to it as the most likely candidate for the species whose supply to the catalyst limits reaction. An additional experiment confirmed that under MTL reaction conditions, mass transport of dihydrogen is the rate-limiting step. Separate measures of the rates of reduction of 1 and 1-octene showed that the rate of reduction of 1-octene is three times that of 1 (eq 6). Since conversion of 1 equiv of 1 to alkane products

$$d(1\text{-octene})/dt = 3(d1/dt) \quad (6)$$

Figure 9. The velocity of reduction of 1 increases with the rate of rotation of the magnetic stirring bar (ω). The line in the figure is described by the given polynomial equation relating υ and ω.
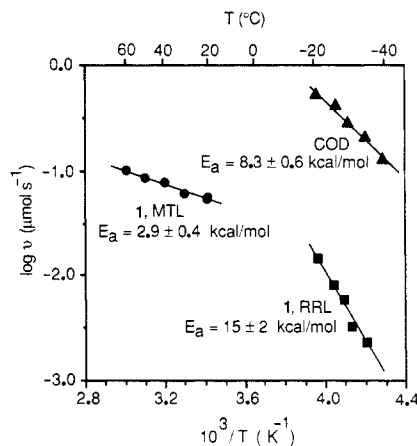
Figure 10. Arrhenius plots of the velocity of reduction of 1 under MTL conditions and of the velocities of reduction of 1 and 1,5-cyclooctadiene under RRL conditions.

requires 3 equiv of dihydrogen, while conversion of 1 equiv of 1-octene to octane requires only 1 equiv, this ratio of rates is compatible with the suggestion that delivery of dihydrogen to the catalyst surface is rate-limiting.

In order to determine whether mass transport of dihydrogen from the vapor phase to the liquid phase or from the liquid phase to the catalyst surface is rate-limiting, we examined the velocity of reduction under MTL conditions as a function of the area of the liquid–vapor interface by performing reductions in vessels of four different inside diameters. The volume of solvent (4 mL) and ω were held constant. The velocity of reduction increased with the area of the liquid–vapor interface. The area of the liquid–vapor interface was that calculated with the liquid at rest. These areas are an approximation because the liquid forms a vortex with stirring thereby increasing the area of the liquid–vapor interface; we believe that the trend is correct, however, and indicates that the rate of reaction under MTL conditions is at least partially determined by the rate of mass transport of dihydrogen from the vapor phase into the liquid phase.

Activation Parameters. Figure 10 shows Arrhenius plots for reductions of 1 under RRL and MTL conditions and for reduction of 1,5-cyclooctadiene under conditions that are RRL for 1. For reduction of 1 in the RRL regime, E_a = 15 ± 2 kcal/mol and log A = 12 ± 2 (A has units of μmol s^{-1} atm$^{-0.38}$ (μg-atom)$^{-1.2}$); for reduction in the MTL regime, E_a = 2.9 ± 0.4 kcal/mol and log A = 0.9 ± 0.3 (A has units of μmol s^{-1} atm$^{-1.05}$); for reduction of COD E_a = 8.3 ± 0.6 kcal/mol.[33]

The importance of these data lies in their ability to characterize these kinetic regimes. Activation energies E_a ≈ 15 kcal/mol

(33) We have obtained similar values of E_a for hydrogenation of Ol₂PtR₂ complexes over a catalyst consisting of platinum supported on controlled pore glass. The value of E_a for reduction of 1 under 1.3 atm of H₂ was 12 ± 1 kcal/mol (−30 to 0 °C), for reduction of CODPt(neopentyl)₂ under 1.3 atm of H₂ it was 12 ± 1 kcal/mol (−3 to 32 °C), and for reduction of 1 under 0.13 atm of H₂ it was 3 ± 1 kcal/mol. Izumi, A. N.; Whitesides, G. M., unpublished results.

Table III. Kinetic Isotope Effect of Substitution of Dideuterium for Dihydrogen

	RRL	MTL
ν_{H_2} (μmol s^{-1})[a]	0.016	0.065
ν_{D_2} (μmol s^{-1})[a]	0.018	0.063
ν_{H_2}/ν_{D_2}	0.9 $\pm$ 0.2	1.0 $\pm$ 0.2

[a] These are noncompetitive rates.

clearly indicate a reaction limited process. Values of $E_a \approx 3$ kcal/mol are characteristic of MTL processes in solvents of normal viscosity and correspond to the "activation energy" for diffusion.[34] Relative rates of reduction of diolefins and platinum complexes derived from them are presented below; however, there are two important points to be made concerning the energy of activation for reduction of COD: first, it differs significantly from the value found for 1 under RRL conditions, and second, it is compatible with other experimentally determined values of E_a for reduction of cyclic olefins over a platinum catalyst under conditions that were shown to be not influenced by mass transport of dihydrogen.[17] Nevertheless, at present we cannot assert unambiguously that the value of E_a is not influenced by mass transport.

The units of the preexponential A factors are dictated by the form of the rate equations (eq 3 and 5). The complexity of these units makes these values difficult to interpret.

Deuterium Kinetic Isotope Effects. We determined the kinetic isotope effect of substitution of H_2 for D_2 under both RRL and MTL reaction conditions (Table III). Within experimental error, the isotope effects under both reaction conditions did not differ from 1.0. There should not be a significant isotope effect for mass transport of dihydrogen across the vapor–liquid interface or for mass transport in stirred solution. In olefin hydrogenations small normal isotope effects ($\nu_{H_2}/\nu_{D_2} = 1.2$–2.0) have been observed.[20,35] The kinetic isotope effect obtained under RRL reaction conditions is not readily interpreted.

Rates of Reduction of (Diolefin)dialkylplatinum(II) Complexes and Olefins under Conditions That Are RRL for 1. Noncompetitive Experiments. The work described so far has indicated that under the RRL conditions listed in Table II, reduction of 1 is, as claimed, RRL. We have surveyed the rates of reduction of a number of other (Ol_2)PtR$_2$ complexes under these conditions, both to explore the influence of the structure of (Ol_2)PtR$_2$ on its rate of reduction and to confirm further that these conditions *are*, in fact, RRL for CODPt(CH$_3$)$_2$: *if compounds having the same approximate molecular weight, diffusion constant, and number of reducible functional groups as 1 react significantly more rapidly than 1, we can be confident that the rate of reaction of 1 is not limited either by the rate of its mass transport to the catalyst surface or by that of dihydrogen.* We cannot, of course, conclude whether these latter more rapidly reacting compounds react by RRL or MTL processes *without further information.*

Table IV summarizes the results. The velocities of reduction of all (Ol_2)PtR$_2$ complexes were determined by monitoring the disappearance of (Ol_2)PtR$_2$ by UV/vis spectrometry except for NBDPtMe$_2$. NBDPtMe$_2$ reacted autocatalytically with dihydrogen in aliquots withdrawn from reaction mixtures too rapidly to allow measurement of its concentration by UV/vis spectrometry. Thus aliquots from reductions of NBDPtMe$_2$ were withdrawn directly into ethereal solutions of tri-n-butylphosphine whch reacted instantly and quantitatively with unreacted NBDPtMe$_2$ yielding norbornadiene and cis-dimethylbis(tri-n-butylphosphine)plati-num(II). The extent of reaction was determined by analysis of the quantity of norbornadiene in the aliquots by GC. Velocities of reduction of olefins and diolefins were determined by monitoring the disappearance of the starting material by GC.

We did not determine the absolute yields of organic products of these reactions; their identity was, however, established by gas chromatography. In every case except for CODPtPh$_2$, the only

(34) Benson, S. W. *The Foundations of Chemical Kinetics*; McGraw-Hill: New York, 1960; p 499. Shooter, D. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F., Eds.; Elsevier: New York, 1969; Vol. 1, p 253.
(35) Inoue, Y.; Yasumori, I. *J. Phys. Chem.* **1971**, *75*, 880–887.

Table IV. Relative Rates of Reduction of (Diolefin)dialkylplatinum Complexes, Cyclic Diolefins, and Olefins

compound	rel rate[a]
CODPtMe$_2$ (1)	1.0
CODPtCH$_2$(CH$_2$)$_2$CH$_2$	1.0
CODPt(Et)$_2$	1.0
CODPt(Pr)$_2$	0.75
CODPt(i-Pr)$_2$	0.69
CODPt(i-Bu)$_2$	0.40
CODPt(cyclohexylcarbinyl)$_2$	0.42
CODPt(neopentyl)$_2$	0.23
CODPtPh$_2$[b]	0.60
CODPt(CF$_3$)$_2$[b]	0.0
DCPDPtMe$_2$	6.1
DMCODPtMe$_2$	0.48
NBDPtMe$_2$[c,d]	73
COD	42
NBD	84
DCPD	85
DMCOD	25
HMDB	81
norbornene	124
cyclooctene	60

[a] Relative rates were determined in n-heptane under reaction conditions which were RRL for 1 (Table I). The numbers reported are the average of at least two kinetic runs and are relative to the velocity of 1 (0.016 μmol s^{-1}). The error in these values is estimated to be 15%. [b] These complexes were insoluble in n-heptane. The reductions were performed in diethyl ether. [c] NBD = norbornadiene, DCPD = dicyclopentadiene, and DMCOD = 1,5-dimethyl-1,5-cyclooctadiene. [d] The reduction of NBDPtMe$_2$ was performed in n-hexane with approximately 10 mg of catalyst and the resulting velocity multiplied by 3.0.

product obtained from the alkyl moiety of the complexes was the alkane itself. Reduction of CODPtPh$_2$ yielded a mixture of benzene and cyclohexane that became enriched in cyclohexane as the reduction proceeded. After all of the CODPtPh$_2$ was consumed, the remaining benzene was reduced to cyclohexane. No dialkyl coupling products R–R were observed. No olefins derived from alkyl moieties were observed at any time in the course of any of the reductions. The final products derived from the diolefin moieties of the platinum complexes were saturated cyclic alkanes in all cases. 1,5-Dimethylcyclooctene was detected as an intermediate in the reduction of DMCODPtMe$_2$ in yields up to 25%. During reductions of all of the diolefins, monoolefins were major components of the reaction mixture.

Several trends are evident upon examination of the data in Table IV. Increasing the size of the alkyl group attached to (1,5-cyclooctadiene)platinum slows the rate of reduction slightly: the total range in rates from methyl to neopentyl is only a factor of 5. CODPt(CF$_3$)$_2$ does not appear to reduce. The velocity of reduction of DCPDPtMe$_2$ in solution with CODPt(CF$_3$)$_2$ over catalyst that had been stirring with the solution of CODPt(CF$_3$)$_2$ for 0.5 h was the same as the velocity of reduction of DCPDPtMe$_2$ alone. We conclude that CODPt(CF$_3$)$_2$ does not significantly poison the catalyst and presumably does not adsorb on to the catalyst at all.

The number of diolefin complexes of platinum that are amenable to synthesis is limited, but variation in the structure of the diolefin moiety resulted in a far greater range in rates than variation in the structure of the alkyl group. NBDPtMe$_2$ reduced 140 times faster than DMCODPtMe$_2$. The very rapid rate of reduction of NBDPtMe$_2$ is not a result of an increase in the surface area of the catalyst caused by reduction of NBDPtMe$_2$ on it. The surface areas of catalyst samples after having been used for the reduction of NBDPtMe$_2$ were 20–30% smaller than that of the starting catalyst. NBDPtMe$_2$ may reduce even more rapidly than 70-fold faster than 1 in a true RRL regime; its rate in these studies probably reflects the onset of mass-transport limitation; we did not, however, test for this possibility with NBDPtMe$_2$, or with the other rapidly reacting species in Table IV (e.g., norbornene, norbornadiene, dicyclopentadiene). Even the rate of reduction of COD might be influenced by mass transport.

Pt-Catalyzed Hydrogenation of [(Ol₂)PtR₂]

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Time (min)
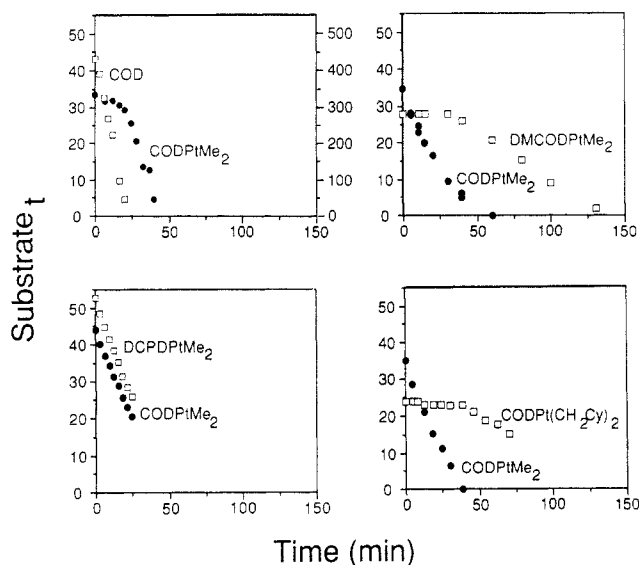
Figure 11. Kinetic plots of the four competition reactions examined. Reactions were run under RRL conditions in heptane except for the reaction of 1 and CODPt(cyclohexylcarbinyl)₂ which was run in hexane. In the experiment with 1 and 1,5-cyclooctadiene, the left scale applies to 1 and the right applies to 1,5-cyclooctadiene.

The rates of reduction of the diolefins used as components of the $(Ol_2)PtR_2$ complexes were also measured, for comparison with the rates of the organoplatinum compounds. The reduction of the $(Ol_2)PtR_2$ was always slower than that of the corresponding diolefin and reduction of the diolefin in the instances examined slower than reduction of the corresponding monoolefin. This observation suggests that reductions of a diolefin and a dialkyl-platinum complex derived from it may not share exactly the same rate-limiting step.

Reductions in the RRL Regime. Competitive Experiments. The relative rates in Table IV were determined by examining the rate of disappearance of a single $(Ol_2)PtMe_2$ complex from solution. The overall rate of this process reflects a combination of rate and equilibrium constants for steps occurring before the rate-limiting step (including physisorption and/or chemisorption from solution) and rates of reaction for surface species. One method of examining a heterogeneous catalytic reaction for the effects of adsorption is to measure competitive rates: that is, rates in experiments in which two compounds whose rates of reaction have been measured independently are allowed to compete for a limited quantity of catalyst.[36] Figure 11 shows data for the disappearance of four pairs of substrates on hydrogenation.

The immediate conclusion from comparison of the relative rates of reaction inferred from the data in Figure 11 with the relative rates reported in Table IV is that these two sets of rates do not parallel each other. The inference from this disagreement is that relative strengths (or more probably, rates) of adsorption play an important role in determining overall reactivities. Thus, in Table IV, CODPtMe₂ reduces less rapidly than DCPDPtMe₂ by a factor of 6; in competitive experiments, the rates are comparable. DMCODPtMe₂ and CODPt(cyclohexylcarbinyl)₂ reduce at approximately one-half the rate of CODPtMe₂ in separate experiments; in competition, DMCODPDtMe₂ and CODPt(cyclohexylcarbinyl)₂ do not react significantly until the CODPtMe₂ is >85% consumed, and the shapes of the curves clearly suggest that the latter is blocking access of the former to the catalyst. We infer from these data that the relative rates of adsorption or strengths of binding to the catalyst surface are COD > CODPtMe₂ > DCPDPtMe₂ > CODPt(CH₂Cy)₂ ≃ DMCODPtMe₂.

Conclusions

We summarize the major experimental conclusions of this work:

1. *The reaction of $(Ol_2)PtR_2$ complexes with dihydrogen is a platinum-catalyzed heterogeneous reaction.* This conclusion

(36) Clark, J. K. A.; Rooney, J. J. *Adv. Catal.* **1976**, *25*, 125–183.

Table V. Comparison of Mechanistic Information for Reduction of **1**

	RRL	MTL
rate law		
[1]	0.0 ± 0.2	0.0 ± 0.2
p_{H_2}	0.38 ± 0.04	1.05 ± 0.07
S_{Pt}, catalyst surface area	1.2 ± 0.2	0.0 ± 0.2
ω, agitation	0.0 ± 0.3	1 + (2.3 × 10⁻⁵)ω + (5.5 × 10⁻⁷)ω²
activation energy (kcal/mol)	15 ± 2	2.9 ± 0.4
burst kinetics	yes	no
ν_{H_2}/ν_{D_2}	0.9 ± 0.2	1.0 ± 0.2
products (%)		
cyclooctane	100	96
bicyclo[3.3.0]octane	0	1.3
methane	200	204
max yield of cyclooctene	0	<5

is based on the previously reported observation that reaction does not occur at a significant rate in the absence of bulk platinum, on the dependence of rates on the quantity of catalyst, and on the observation that the reaction is halted by species that poison platinum catalysts.

2. *The surface area and catalytic activity of the platinum catalyst are sufficiently constant during a reduction to permit interpretable kinetic data to be obtained.*

3. *The platinum-catalyzed reaction of CODPt(CH₃)₂ (1) with dihydrogen falls in two distinct kinetic regimes.* Table V summarizes experimental evidence differentiating these two regimes. The regime whose overall rate is limited by reactions of species present on the catalyst surface (the RRL regime) has an E_a of 15 kcal/mol. The rate in this regime is independent of the degree of agitation of the reaction mixture and depends linearly on the surface area of the catalyst. The regime whose rate is limited by mass transport of hydrogen to the catalyst surface (the MTL regime) has an E_a of 3 kcal/mol. The rate in this regime increases with ω and with the liquid–vapor interfacial area and is independent of the catalyst surface area. Small changes in reaction conditions or substrate structure change the mechanism from one in which the rate-determining step is mass transport of dihydrogen to one in which the rate-determining step occurs on the catalyst surface. Onset of mass transport effects probably influence the kinetics of NBDPtMe₂ and the more rapidly reduced diolefins under conditions that are RRL for **1**.

4. *A rate–structure correlation in the RRL regime showed that changes in the structure of the diolefin moiety of $(Ol_2)Pt(CH_3)_2$ result in significantly larger variations in rate than changes in the size of R in CODPtR₂ complexes; however, the strongly electron withdrawing CF₃ group in CODPt(CF₃)₂ prevented reaction altogether.*

5. *Relative rates of reduction measured in solutions containing only one $(Ol_2)PtR_2$ complex ("noncompetitive" experiments) differ from those measured in solutions containing two $(Ol_2)PtR_2$ complexes ("competitive" experiments).* This difference indicates that adsorption of the organoplatinum complex on the catalyst surface is an important part of the reaction mechanism.

6. *The rate of reduction of diolefins were always larger than the rates of reduction of the $(Ol_2)PtMe_2$ complexes derived from them. The temperature dependence of reduction of 1,5-cyclooctadiene (E_a = 8.2 kcal/mol) is substantially smaller than that of 1 (E_a = 15 kcal/mol).*

We propose that the mechanism of reaction of 1 and other $(Ol_2)PtR_2$ complexes with H₂ proceeds by adsorption of both reactants on the platinum–catalyst surface and reaction on this surface. The experimental evidence described in this paper is largely kinetic and is not sufficient to establish a complete mechanism; the major objective of the work was to define conditions in which physical–organic approaches to mechanism based on structure–reactivity relations would be applicable and interpretable. Thus, detailed discussion of mechanism is deferred to the second paper in this series.

The next level of questions concerning the mechanism of platinum-catalyzed reaction of $(Ol_2)PtR_2$ complexes with di-hydrogen concerns details of the species and their reactions on

the surface. Which steps are reversible in the reduction of $(Ol_2)PtR_2$? What is the step that limits the rate of production of alkane products? To what extent do the surface alkyls generated here resemble those involved as intermediates in the hydrogenation of olefins, and in catalytic reforming? Evidence based on isotopic labeling begins to address these questions and is contained in the following two papers.[2,3]

Experimental Section

General. n-Heptane (Aldrich, 99.9%, HPLC grade, 800 mL) was purified by stirring over 0.5 g of 10% Pt/alumina (Aldrich) under 1.5 atm of dihydrogen for 2–3 days, followed by passing through silica gel and distillation from Na/K alloy immediately prior to use. n-Hexane was treated similarly. Diethyl ether was distilled from Na/benzophenone prior to use. Olefins and diolefins used in hydrogenations were passed through alumina immediately prior to use. Dihydrogen and 10% dihydrogen in argon were purchased from Matheson or Granite State Oxygen and were the highest purity available. They were passed through Ridox and activated molecular sieves prior to use. Dideuterium was purchased from Matheson or Airco and was used as received. A homemade mixture of dideuterium in argon was used to measure the kinetic isotope effect of substitution of D_2 for H_2 under MTL reaction conditions. An empty 10-L gas cylinder was evacuated and charged with 1 atm of dideuterium. The cylinder was then pressurized to 150 PSIG with argon to make a 10% dideuterium in argon mixture. Fuel cell grade platinum black was purchased from Johnson Matthey Inc. and used for all of the kinetics reported here. Platinum black or platinum oxide from Aldrich and Alfa were used for comparison purposes. All other reagents were used as received unless specified otherwise. The yields of Grignard reagents were assessed by titration by the method of Eastham.[37]

Reactors generally used in these studies were 20-mL pressure bottles purchased from Lab Glass. They were cleaned by filling with 2:1 concentrated H_2SO_4:30% aqueous H_2O_2 and heating to ca. 90 °C for 1 h then rinsing with distilled H_2O, absolute ethanol, and ether. The reactors were filled with hexadecane (Aldrich), and 10 drops of octadecyltrichlorosilane (Petrarch) were added. They were allowed to stand for 1 h. Finally, the reactors were washed thoroughly with hexanes, dried in air, and stored in a desiccator. The surface of the glass is quite hydrophobic even after several reactions and washing with soap and water. This treatment reduces the amount of catalyst that sticks to the surface of the glass. By washing with soap and water and rinsing with distilled water, acetone, and hexanes between reactions, the reactors may be successfully used for 6 to 8 reactions before treating again. The septa (Lab Glass) used were neoprene and were extracted for 1 day with toluene in a Soxhlet apparatus and rinsed with hexanes. The septa were then boiled in water, in order to remove the absorbed toluene by azeotropic distillation, followed by washing with methanol and evacuation. Septa were stored under argon prior to use.

^{1}H NMR spectra were measured on CFT 20, Bruker AM 250 or AM 300 spectrometers. SEM's were obtained on a JEOL JSM 35 instrument at 35 kV. Catalyst samples were imbedded in silver paint and coated with ca. 200 Å of gold. Gas chromatographs were run on a Perkin-Elmer 3920 instrument equipped with a Spectra Physics minigrator or a Perkin-Elmer 8300 instrument. UV spectra were measured on a Perkin-Elmer 552 double-beam spectrophotometer in n-heptane, unless the compounds were insoluble in heptane, in which case they were measured in ether. The absorbances of aliquots from kinetic runs were measured on a Gilford 240 single-beam spectrophotometer. Elemental analyses were obtained from Galbraith Labs.

Substrate Synthesis. (1,5-Cyclooctadiene)dimethylplatinum(II) (1),[38] (1,5-cyclooctadiene)diethylplatinum(II) (CODPtEt$_2$),[39] (1,5-cyclooctadiene)diphenylplatinum(II) (CODPtPh$_2$),[38] (1,5-cyclooctadiene)-platinacyclopentane(II),[40] (1,5-cyclooctadiene)bis(trifluoromethyl)platinum(II) (CODPt(CF$_3$)$_2$);[41] (1,5-cyclooctadiene)bis(2,2-dimethylpropyl)platinum(II) (CODPtNp$_2$);[42] (1,5-cyclooctadiene)bis(2-propyl)-platinum(II) (CODPt(i-Pr)$_2$),[43] and dichloro(dicyclopentadiene)platinum(II)[44] were prepared by the literature methods. Dichloro(1,5-di-

methyl-1,5-cyclooctadiene)platinum(II) was prepared by modification of the literature procedure for preparation of dichloro(1,5-cyclooctadiene)platinum(II):[41] mp 174–215 °C dec; ^{1}H NMR (CDCl$_3$) δ 5.41 (br t, J_{H-Pt} = 64 Hz, 2 H), 2.06–3.10 (m, 8 H), 1.94 (t, J_{H-Pt} = 40 Hz, 6 H). Anal. Calcd for C$_{10}$H$_{16}$PtCl$_2$: C, 29.86; H, 4.01; Cl, 17.63. Found: C, 30.14; H, 4.12; Cl, 17.63.

New (diolefin)dialkylplatinum complexes were prepared by similar procedures. We give a representative example. A suspension of 1.05 g (2.81 mmol) of CODPtCl$_2$ (Johnson Matthey Inc.) in ether (50 mL) in a 100-mL Schlenk flask under argon was cooled to −78 °C. A solution of cyclohexylcarbinylmagnesium bromide (0.52 M, 12 mL, 6.2 mmol) was added dropwise via cannula. The reaction was stirred and permitted to warm slowly. The reaction was followed by TLC and generally was complete by the time the reaction reached 0 °C. Water was added slowly at first and then more rapidly to quench excess Grignard reagant and to dissolve the salts. The aqueous and organic layers were separated, and the aqueous layer was washed once with ether. The organic solutions were combined, washed with water and brine, and dried over sodium sulfate. The ethereal solution was concentrated by rotary evaporation. (Diolefin)dialkylplatinum complexes were purified by chromatography on silica gel with 10:1 pentane:ether. Yields of (diolefin)dialkylplatinum complexes were generally within 50–70%. After chromatography, 941 mg (67%) of (1,5-cyclooctadiene)bis(cyclohexylcarbinyl)platinum(II) was obtained. This complex and other solid complexes were recrystallized from ether/methanol: mp 89–90 °C; ^{1}H NMR (C$_6$D$_6$) δ 4.58 (br t, J_{H-Pt} = 38 Hz, 4 H), 2.02–2.22 (m, 4 H), 1.60–2.02 (m, 18 H), 1.05–1.60 (m, 12 H). Anal. Calcd for C$_{22}$H$_{38}$Pt: C, 53.10; H, 7.70. Found: C, 53.24; H, 7.84.

Stoichiometry of Reduction of 1. The yields of organic products from 1 were determined by GC. Reactions for these analyses were run in a glass vessel equipped with a $^3/_8$ in. glass-to-metal seal; the vessel was closed with a GC septum held by a Cajon Ultra-torr fitting. The softer rubber of a GC septum prevented minor leaks that were evident especially under RRL conditions when using the usual 20-mL reactors with neoprene septa. Reactions under MTL conditions were conducted in a reactor having a volume of ca. 55 mL thus permitting complete reduction of 50 μmol of 1 without consuming all of the dihydrogen in the reactor. The reactions were otherwise run as described below in heptane under MTL or RRL conditions except that the kinetics were not followed. After completion of the reaction, 0.5 mL (STP) of propane was added via gas-tight syringe and the reactor was allowed to equilibrate at room temperature with stirring for 0.5 h. Analysis by GC of aliquots (100 μL) taken from the headspace with a gas-tight syringe permitted estimation of the relative quantities of methane and propane. A standard solution of n-decane in n-heptane (0.5 mL, 0.01 M) was then added to the reaction. Analysis by GC of the solution permitted determination of the relative quantities of cyclooctane and bicyclo[3.3.0]octane and decane. After correcting for the measured flame-ionization detector response factors for authentic samples of methane, propane, cyclooctane, bicyclooctane, and decane under the same conditions, the yields of products were calculated. The quantity of platinum deposited on the catalyst during reduction of 1 was determined by weighing the catalyst after filtration of the reaction mixture on completion of a reduction.

A 5-mL round-bottomed flask equipped with a magnetic stirring bar was charged with 30 mg of platinum black, capped with a rubber septum, and flushed with argon. n-Heptane (2.0 mL) and a solution of 1 (26.0 mg, 78.0 μmol) in 3.0 mL of n-heptane were added leaving ca. 0.5 mL of headspace. The reaction was maintained at 0 °C and stirred. Every 15 min, measured aliquots of gaseous dihydrogen were added and aliquots of the reaction mixture were removed. The quantity of 1 consumed was determined by monitoring the UV absorbance of the aliquots of the reaction mixture as below.

Kinetic Methods, General. Bath temperatures were maintained with a Neslab Cryocool equipped with a Neslab Cryotrol temperature controller ($T < 0$ °C) and a Fisher circulating bath ($T > 0$ °C). Reactors were immersed to within 1 cm of their metal crown caps. Temperatures were measured with partial immersion, pentane or mercury thermometers and are probably accurate to ±1 °C. Dihydrogen or dihydrogen in argon were introduced to the reactors via a syringe needle soldered to a Swagelok fitting at the end of a coil of $^1/_8$ in. flexible copper tubing. Pressures were controlled with Matheson regulators and measured inside a reactor with use of a pressure gauge equipped with a syringe needle and are probably accurate to ±5%. For dihydrogen pressures of less than 1 atm, a 10% dihydrogen-in-argon mixture was used. Because there was not enough dihydrogen in the headspace of the 20-mL reactors generally used to complete a reduction under MTL conditions, these reactions were run with a continuous slow leak (5 mL/min of gas) permitting a constant

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pressure of dihydrogen over the solution. The leak was maintained by inserting a syringe needle soldered to a micrometer-controlled needle valve into the septum of the reactor. Stirring rates reported are the number of revolutions per minute of the magnetic stirring bar in the reactor in use as measured by a calibrated strobe light.

Kinetics Procedure. A reactor equipped with an egg-shaped magnetic stirring bar (10 × 6 mm) was charged with platinum black, capped, and flushed with argon for at least 10 min. *n*-Heptane (3–4 mL) was added directly from the still via syringe needle. The reactor was placed in the bath and flushed with dihydrogen or dihydrogen in argon and stirring was begun. The platinum black aggregated within 10–20 s after the stirring began. A sample of substrate was weighed into a 1-dram vial equipped with a (7 × 2 mm) magnetic stirring bar, and the vial was capped with a rubber septum. The vial was flushed with argon for at least 10 min and 2–3 mL of heptane was added directly to it from the still. The suspension was stirred until dissolution of the substrate occurred. Stirring was halted inside the reactor, and 2–3 mL of the heptane was removed via cannula. The heptane solution of substrate was then added via cannula under argon pressure. The reactor was again flushed with dihydrogen or dihydrogen in argon for 10–20 s and the first aliquot removed as below. After the first aliquot was removed (t = 0), stirring was begun and a stopwatch started. Aliquots (60–100 μL) of the reaction mixture were withdrawn by stopping the magnetic stirrer and allowing the catalyst to settle for 3–6 s. A 20 cm × 22 gauge cannula was pushed through the septum into the reaction mixture. The other end of the cannula had previously been inserted into a 6 × 50 mm culture tube capped with a NMR tube rubber septum (Aldrich). The volume of gas inside the culture tube was controlled with a 250-μL gas-tight syringe. The plunger of the syringe was withdrawn to a volume of approximately 100 μL, and approximately 100 μL of the solution was drawn into the cannula and culture tube. The cannula was withdrawn from the reaction solution, the magnetic stirrer restarted, the syringe plunger withdrawn to its limit, and the remainder of the aliquot thereby transferred to the culture tube. Typically the stirrer remained stopped for a period of 10–15 s during this procedure. For removing aliquots from reductions with pressures higher than 20 PSIG, a culture tube held by an "O" ring in a Swagelok fitting capped with a GC septum held by a Cajon Ultratorr fitting was used to hold aliquots. Aliquots were diluted under air by a factor of 100 or 40 by measuring 50 μL of the aliquot with use of a 50-μL glass disposable micropipet and diluting to 5.0 or 2.0 mL with *n*-heptane (Aldrich, 99.9%, HPLC grade, used without further purification). This solution was transferred to a 3.0 mL (10 × 10 × 30 mm) quartz cuvette via disposable pipet and its absorbance measured. The amount of substrate (μmol) remaining was calculated by using eq 8 where A_t is the absorbance of the solution removed at time t. Typically, seven aliquots

$$\text{substrate}_t = \text{substrate}_0(A_t/A_0) \quad (7)$$

(average size = 75 μL) were withdrawn over the course of a kinetic run; thus, 10–20% of the total volume of a reaction was removed. Because DCPDPtMe₂ is susceptible to autocatalytic reaction with dihydrogen, aliquots of reactions involving it were cooled to −78 °C immediately after removing them from the reaction.

Rates of reactions were also measured by following the increase in concentration of a nonvolatile organic product. Reactions were performed in the same manner as above except that an internal standard was added to the solution of substrate in heptane prior to adding it to the reactor. Aliquots were withdrawn as usual and analyzed by gas chromatography. The amount of substrate remaining (μmol) was calculated

$$\text{substrate}_t = \text{substrate}_0(1 - ((A_{t,\text{OP}}/A_{\text{IS}})/(A_{\infty,\text{OP}}/A_{\text{IS}}))) \quad (8)$$

by using eq 8 where $A_{t,\text{OP}}$ = area of organic product in an aliquot withdrawn at time t, and A_{IS} = area of internal standard. When following reductions of **1** by GC, *n*-octane or *n*-decane was used as the internal standard.

Catalyst Surface Area Determinations. A Hewlett Packard Model 770 gas chromatograph was modified with two Carle valves. One provided for choosing dihydrogen or dioxygen and the second provided for injecting a pulse of gas of precise volume (116.6 μL) into the carrier gas (argon, UHP) passing over the catalyst. The instrument is equipped with a thermal-conductivity detector, and the gas not absorbed by the catalyst is detected. In principle both dihydrogen and dioxygen could be used to determine the surface area of the catalyst, but with the platinum black used in this study, GC traces for dihydrogen exhibited a great deal of tailing, making integration inaccurate. Consequently, the catalysts were saturated with several (typically 3) pulses of dihydrogen and then the amount of dioxygen required to saturate the catalyst determined. This procedure was repeated three times and the average taken. The number of surface atoms per gram of catalyst was calculated assuming the stoichiometry in eq 9. After completion of a reduction, a reactor was removed from the bath, allowed to attain room temperature, opened, and

$$\begin{array}{ccc} H & & O \\ | & & | \\ 2Pt + {}^3\!/_2 O_2 & \longrightarrow & 2Pt + H_2O \end{array} \quad (9)$$
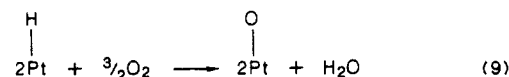
stirred for 10–20 min to permit oxidation of the catalyst surface. **Caution:** Exposure of dry catalyst still covered with hydrogen to air can ignite solvents. The catalyst was then filtered in air and washed with ether prior to determining its surface area. A sample of the catalyst (10–20 mg) was weighed and mixed thoroughly with alumina to adsorb water produced and disperse the catalyst as much as possible. The mixture was placed in a stainless steel tube ($^1\!/_4$ in. tubing) and prevented from moving with a wad of cotton. The tube was mounted in the modified GC with Swagelok fittings. The surface areas (S_{Pt}) of the catalyst samples in Figures 1 and 7 were calculated by multiplying the surface area of the catalyst per gram by the weight of catalyst used in the reaction plus the weight of platinum deposited on it from reduction of **1**. We assumed in this calculation that 100% of the platinum in **1** is deposited on the catalyst during reaction.

Poisoning Experiments. In the poisoning experiments, rates of reduction of **1** were measured by monitoring the increase in the concentration of cyclooctane by GC. Otherwise the reactions were carried out as usual except that at t = 16 min, 20 μmol of tri-*tert*-butylphosphine (Strem), di-*n*-octyl sulfide (Aldrich) or dineopentylmercury were added.[45] *n*-Decane was used for the internal standard. The concentration of cyclooctane could be calculated from the GC ratios of cyclooctane to decane knowing their relative response factors and from this the quantity of **1** remaining. ¹H NMR spectra of equimolar solutions of **1** and tri-*tert*-butylphosphine, dineopentylmercury, and di-*n*-octyl sulfide in C₆D₆ were recorded immediately upon preparation and ca. 0.5 h later to ensure that these compounds did not react homogeneously with **1**.

Variation of the liquid–vapor interfacial area was accomplished by using reactors of three different sizes other than the usual 20-mL reactors. The smallest reactor and the usual reactors are cylindrical. The inside diameter of these vessels was determined from the weight of water required to fill the vessel a known height. The two larger vessels were spherical. The outside diameter of these was measured at the level to which the liquid filled with reactor after completion of reaction, and 2 mm was subtracted from this value yielding an estimate of the inside diameter. The areas were calculated from these diameters by halving the diameter, squaring, and multiplying by π. Kinetics were measured as usual in these vessels.

Relative Rate of Reduction of NBDPtMe₂. Because of the speed of reduction of NBDPtMe₂ and its rapid autocatalytic reaction with dihydrogen, the kinetics of its reduction were measured differently. Aliquots of the reduction of NBDPtMe₂ were withdrawn as above into a culture tube containing 50 μL of 0.5 M tri-*n*-butylphosphine in diethyl ether. NBDPtMe₂ and tri-*n*-butylphosphine react instantly and quantitatively yielding norbornadiene and (bis(tri-*n*-butylphosphine))dimethylplatinum(II). The resulting solutions were analyzed by gas chromatography for norbornadiene and norbornane. The amount of NBDPtMe₂ remaining was calculated using eq 10 where A_{NBD} = area of norbornadiene and A_{NB} = area of norbornane.

$$(\text{NBDPtMe}_2)_t = (\text{NBDPtMe}_2)_0(A_{\text{NBD}}/(A_{\text{NBD}} + A_{\text{NB}})) \quad (10)$$

Relative Rates of Reduction of Olefins and Diolefins. Reductions of olefins and diolefins were performed in the same manner as above except that an internal standard was included. The progress of reaction was monitored by following the decrease in concentration of starting material by GC. The amount of starting material remaining was calculated by using eq 11 where the variables have the same definitions as in eq 8.

$$\text{substrate}_t = \text{substrate}_0((A_{t,\text{OP}}/A_{\text{IS}})/(A_{0,\text{OP}}/A_{\text{IS}})) \quad (11)$$

Product Identification. Methane, ethane, propane, *n*-butane, 2-methylpropane, methylcyclohexane, neopentane, cyclohexane, benzene, cyclooctane, and norbornane were identified by comparison of the GC retention times for the suspected samples with those of authentic commercial samples. Tetrahydrodicyclopentadiene, 1,5-dimethylcyclooctene, and *cis*- and *trans*-1,5-dimethylcyclooctane from reduction of DCPDPtMe₂ and DMCODPtMe₂ were compared with samples of these compounds prepared by reduction of the diolefin itself.

Competitive reductions were carried out in the same manner as above except that two substrates were weighed into a 1-dram vial and added simultaneously. In **1** versus CODPt(cyclohexylmethyl)₂, *n*-hexane was the solvent; in the other three experiments *n*-heptane was the solvent. In the experiments **1** versus 1,5-cyclooctadiene and CODPt(cyclohexylmethyl)₂, *n*-octane was used for the internal standard. For **1** versus

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DCPDPtMe$_2$ and DMCODPtMe$_2$, *n*-decane was used. In **1** versus CODPt(cyclohexylmethyl)$_2$, DCPDPtMe$_2$, and DMCODPtMe$_2$, the extents of reaction were determined by monitoring the increase in concentrations of cyclooctane, methylcyclohexane, tetrahydrodicyclopentadiene, and *cis*- and *trans*-1,5-dimethylcyclooctane by GC. In **1** versus 1,5-cyclooctadiene, the concentration of **1** was determined by measuring the UV absorbance of aliquots, and the concentration of 1,5-cyclooctadiene was determined by following its disappearance as measured by GC.

Registry No. 1, 12266-92-1; COD, 111-78-4; NBD, 121-46-0; DCPD, 77-73-6; DMCOD, 3760-14-3; CODPtCH$_2$(CH$_2$)$_2$CH$_2$, 60161-34-4; CODPt(Et)$_2$, 51192-20-2; CODPt(Pr)$_2$, 113451-83-5; CODPt(*i*-Pr)$_2$, 12130-04-0; CODPt(*i*-Bu)$_2$, 113567-62-7; CODPt(CH$_2$Cy)$_2$, 113567-63-8; CODPt(neopentyl)$_2$, 75101-19-8; CODPtPh$_2$, 12277-88-2; CODPt(CF$_3$)$_2$, 37035-32-8; DCPDPtMe$_2$, 113548-34-8; DMCODPtMe$_2$, 113567-64-9; NBDPtMe$_2$, 53199-36-3; CODPtCl$_2$, 12080-32-9; DCPDPtCl$_2$, 12083-92-0; DMCODPtCl$_2$, 113567-65-0; norbornene, 498-66-8; cyclooctene, 931-88-4; cyclohexylcarbinylmagnesium bromide, 35166-78-0; cyclooctane, 292-64-8; bicyclo[3.3.0]octane, 694-72-4; methane, 74-82-8; dineopentylmercury, 10284-49-8; di-*n*-octyl sulfide, 2690-08-6; tri-*tert*-butylphosphine, 13716-12-6; platinum, 7440-06-4.

Supplementary Material Available: A plot showing the stoichiometry of the reaction of **1** with dihydrogen, UV–vis spectra of (Ol$_2$)PtR$_2$ complexes, UV–vis spectra of aliquots from the reduction of **1** as a function of time, kinetic plots of the reduction of **1** and other (Ol$_2$)PtR$_2$ complexes, scanning electron micrographs of the catalyst with various quantites of **1** reduced on to its surface, a table of UV–vis absorbances and extinction coefficients for (Ol$_2$)PtR$_2$ complexes, and analytical data for new (Ol$_2$)PtR$_2$ complexes (13 pages). Ordering information is given on any current masthead page.

Deuterium-Labeling Experiments Relevant to the Mechanism of Platinum-Catalyzed Hydrogenation of (Diolefin)dialkylplatinum(II) Complexes: Evidence for Isotopic Exchange via Platinum Surface Hydrogen. The Stereochemistry of Reduction[1]

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Abstract: Reduction of (diolefin)dialkylplatinum(II) complexes with dihydrogen over a platinum black catalyst is accompanied by interchange of hydrogen among the organic groups and gaseous dihydrogen. Exchange of hydrogens between an alkane solvent and these organic groups also occurs during the reaction, but only relatively slowly. An examination of the stereochemistry of reduction of (norbornadiene)dimethylplatinum(II) with D$_2$ indicates that the deuterium atoms add predominantly to the same (endo) face of the olefins as that coordinated to the dimethylplatinum moiety. Reduction of uncomplicated norbornadiene under the same conditions yields norbornane having primarily exo C–D bonds. These experiments are compatible with a mechanism for the reduction involving adsorption of the (diolefin)dialkylplatinum(II) complex on the surface of the platinum catalyst via its platinum atom, conversion of the organic moieties of the soluble (diolefin)dialkylplatinum complex to platinum–surface alkyls, and interchange of hydrogen atoms between these surface alkyls via a mobile pool of platinum–surface hydrogen atoms. Combination of the surface alkyls with surface hydrogen yields alkanes in a final irreversible step. Comparison of the evidence from deuterium-interchange experiments conducted under mass transport limited and reaction rate limited conditions is consistent with the hypothesis that the concentration of hydrogen on the platinum surface is lower under mass transport limited conditions.

This and the accompanying papers[3,4] describe studies of the heterogeneous platinum-catalyzed reaction of (diolefin)dialkylplatinum(II) [(Ol$_2$)PtR$_2$] complexes with dihydrogen. We are developing this reaction as a new approach to the preparation of platinum–surface alkyls and to the study of heterogeneous metal-catalyzed reactions, especially olefin hydrogenation.

The work in this paper addresses three questions concerning the mechanism of platinum-catalyzed reaction of (Ol$_2$)PtR$_2$ with dihydrogen. First, which steps in the mechanism are reversible and which are irreversible? Second, what is the stereochemistry of binding of (Ol$_2$)PtR$_2$ to the platinum catalyst? Third, can the mass transport limited (MTL) and the reaction rate limited (RRL)

kinetic regimes be distinguished by other than kinetic means?

We use deuterium-labeling experiments to address these questions. We examine the products of reduction of (Ol$_2$)PtR$_2$ complexes in which deuterium originates in only one component: the diolefin, the alkyl moieties, the solvent, or the reducing species. These experiments permit us to determine, for example, whether any of the deuterium in the methyl group of CODPt(CD$_3$)$_2$ appears in cyclooctane during reduction of this complex. The mode of binding of the (Ol$_2$)PtR$_2$ complex to the catalyst is a more subtle question, which we address by examining the stereochemistry of reduction of (norbornadiene)dimethylplatinum(II). Work in a related system has been the subject of a previous communication.[5]

Results

Methods. The (diolefin)dialkylplatinum(II) complexes used in this study were prepared by conventional methods. The catalyst

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(2) NSF Predoctoral Fellow, 1978–1981.

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