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

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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 D₂ 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 describe studies of the heterogeneous platinum-catalyzed reaction of (diolefin)dialkylplatinum(II) [(O₂)PtR₂] 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 (O₂)PtR₂ with dihydrogen. First, which steps in the mechanism are reversible and which are irreversible? Second, what is the stereochemistry of binding of (O₂)PtR₂ 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 (O₂)PtR₂ 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(CD₃)₂ appears in cyclooctane during reduction of this complex. The mode of binding of the (O₂)PtR₂ 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.

Results

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

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Table I. Isotopic Compositions of Methane and Cyclooctane Derived from Reductions of (Diolein)dimethylplatinum(II) Complexes

<table>
<thead>
<tr>
<th>Source of deuterium</th>
<th>Reaction conditions</th>
<th>Methane</th>
<th>Cyclooctane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$d_0$</td>
<td>$d_1$</td>
</tr>
<tr>
<td>n-C₆H₁₄</td>
<td>MTL</td>
<td>96</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>MTL</td>
<td>98</td>
<td>2</td>
</tr>
<tr>
<td>(DCPD-d₁₂)Pt(CH₃)₂</td>
<td>RRL</td>
<td>&gt;80</td>
<td>&lt;2</td>
</tr>
<tr>
<td></td>
<td>RRL</td>
<td>64</td>
<td>10</td>
</tr>
<tr>
<td>CODP(C₂H₅)₂</td>
<td>RRL</td>
<td>96</td>
<td>10</td>
</tr>
<tr>
<td>(DCPD-d₁₂)Pt(CH₃)₂ + CODP(C₂H₅)₂</td>
<td>MTG</td>
<td>34</td>
<td>1</td>
</tr>
</tbody>
</table>

* RRL = reaction rate limited; MTL = mass transport limited; MTG reaction was conducted at 40 °C. *DCPD-d₁₂ = dicyclopentadiene-d₁₂. *Isotopic composition of ethane rather than methane.

There are several difficulties with this method of determining isotopic compositions. The first is the requirement for pure reference samples of isotopically labeled alkanes. We prepared isotopically labeled alkanes with reagents of known, high isotopic purity and estimated the isotopic purity of the product. In the determination of the isotopic compositions of ethanes and propanes, there are also ambiguities as to which isotopically substituted compounds should be used as standards. For instance, should the relative abundances (RAₙ) for alkane-1,1,1-d₄ or alkane-1,1,2,2-d₄ be used in the basis set for reactions involving dipropylplatinum(II) groups? Our choice was dictated by the patterns of isotopic substitution we expected in the product mixture (for example, we used ethane-1,2,2-d₄ rather than ethane-1,1,1-d₄ in analysis of ethane from deuteriation of ethylene) and by availability (e.g., ethane-1,1,1-d₄ is readily prepared whereas ethane-1,1,2,2-d₄ is not). Our mass spectra for methane-d₄ (n = 0–4, Table III) were similar to those in the literature, but our mass spectra for ethane-d₆ (n = 0–3) differed significantly from those in the literature.

A second issue in these analyses concerns the relative sensitivities of our mass spectrometer to different isotopically substituted alkanes. We determined the sensitivity of our mass spectrometer to authentic mixtures of alkane-d₄, alkane-d₅, and alkane-d₆. The trends observed in relative sensitivities for methane-d₄ and ethane-d₄, parallel those in the literature. Details of the calculations of relative sensitivities and isotopic compositions and the synthesis of alkane-d₅ and authentic mixtures of alkane-d₆ are reported in the Experimental Section.

We believe that the isotopic compositions of mixtures of alkane-d₄ have an absolute accuracy of ±5%. Two experiments support our assertion. The largest deviation obtained from theory was 2.2% in analyzing the isotopic compositions of mixed samples of CH₄, C₂H₆, and C₃H₈ from mass spectral data by our method. The second experiment involved examining the sensitivity of the calculated isotopic compositions to random perturbations in the relative abundances of a representative sample of methanes. Random perturbation of these relative abundances by ±4% (absolute) resulted in a change in the isotopic composition of as much as ±5% absolute. Successive mass spectral analyses of a sample of alkane-d₄ yielded mass spectral data that were reproducible to ±2–3% absolute.

Determination of the isotopic composition of mixtures of D₂, HD, and H₂ was straightforward since these substances give clean molecular ions. The D₂ used in this work was checked by mass spectrometry and found to be >99 atom % D.

The average number of deuterium atoms incorporated into a sample of alkane, $d_j$, is defined by eq 2 where $j$ is the maximum number of deuteriums in the sample.

Transfer of Deuterium from Solvent into Alkanes Derived from (Diolein)dialkylplatinum Complexes Is Significant under MTL Conditions but Not under RRL Conditions. Platinum-catalyzed reaction of (1,5-cyclooctadiene)dimethylplatinum(II) (1) in n-

(6) This calculation ignores the relative sensitivities of the mass spectrometer to the isotopic content of the cyclooctane.
previous established to be MTL\(^3\) complicated the interpretation of other isotopic labeling experiments. When the reaction was carried out at lower temperatures (20 °C) but otherwise identical conditions, incorporation of deuterium from \(n\)-octane-\(^{d_8}\) into methane and cyclooctane was reduced to 0.14 atom of deuterium per equivalent of \( I \). Although we have not explicitly investigated the kinetics of the reaction at 20 °C, we believe that it is still safely within the MTL regime. Going to still lower temperature would undoubtedly have reduced the degree of solvent activation further but would have come too close to RRL conditions. Throughout this work we have used 20 °C rather than 40 °C as the standard temperature for MTL reactions.

**Transfer of Deuterium from the Dieolefin Moeity into Methane Is Greater under MTL than RRL Conditions.** To determine the efficiency of transfer of deuterium originally present in the dieolefin moiety into the alkane derived from the alkyl group originally bonded to the platinum atom, we examined the isotopic composition of the methane obtained from platinum-catalyzed reaction of (dicyclopentadiene-\(^{d_9}\))dimethylplatinum(II) ((DCPD-\(^{d_9}\))Pt(CH\(_3\))\(_2\)) with H\(_2\) (eq 4; Table 1). We used dicyclopentadiene rather than cyclooctadiene because it is more easily obtained in perdeuterated form. Under MTL conditions, transfer of deuterium from the DCPD-\(^{d_9}\) moiety to the methyl group was rapid; approximately 1 atom equiv of deuterium was lost from the reaction:

\[
\text{DCPD-}^{\text{d}_12}\text{Pt(}CH_3\text{)}_2 n\cdot C_{6}H_{16} \xrightarrow{H_2, \text{Pt}} 2\text{Methane-}^{\text{d}_7} + \text{DCPD-}^{\text{d}_9}\text{Pt(}CH_3\text{)}_2 n\cdot C_{6}H_{16} \]

DCPD-\(^{d_9}\) group and incorporated into the 2 equiv of methane generated. This reaction also generated significant quantities of methane-\(^{d_1}\) and \(^{d_2}\). Reduction of (DCPD-\(^{d_9}\))Pt(CH\(_3\))\(_2\) under MTL conditions produced a small quantity of methane-\(^{d_1}\).

The last entry in Table 1 gives the isotopic composition of the ethane and cyclooctane produced in the reduction of a 1:1 mixture of DCPD-\(^{d_9}\)Pt(CH\(_3\))\(_2\) and CODPt(CH\(_3\))\(_2\) with H\(_2\) under MTL conditions. The observation of ethane-\(^{d_1}\) and ethane-\(^{d_2}\) as products established that deuterium can be transferred from the dieolefin moiety of one molecule of (O\(_3\))PtR\(_2\) to the alkane derived from the alkyl moiety of a second (eq 5). Deuterium lost from a DCPD-\(^{d_9}\) moiety can also be captured by incorporation into cyclooctane derived from a second (O\(_3\))PtR\(_2\) complex (eq 5):

\[
\text{DCPD-}^{\text{d}_9}\text{Pt(}CH_3\text{)}_2 n\cdot C_{6}H_{16} \xrightarrow{H_2, \text{Pt}, \text{MTL}} \text{Cyclooctane-}^{\text{d}_9} + 2\text{Ethane-}^{\text{d}_9} n\cdot C_{6}H_{16} \]

\[
\text{Atom equiv of } d \text{ transferred from DCPD-}^{\text{d}_9}\]

\[
\text{Transfer of Deuterium from the Pt(CD}_3\text{)}_2 \text{ Moeity into Cyclooctane Is Also Much Greater under MTL than RRL Conditions.}
\]

The data in Table 1 establish that transfer of deuterium from the Pt(CD\(_3\))\(_2\) moiety to cyclooctane is surprisingly efficient during reduction of CODPt(CD\(_3\))\(_2\) under MTL conditions (eq 6). Reduction of CODPt(CD\(_3\))\(_2\) under RRL conditions produced only a small quantity of cyclooctane-\(^{d_1}\). The activation of C–D bonds geminal to a C–Pt bond is one qualitative observation strongly supporting the hypothesis that the deuterium interchange reactions observed take place on a platinum surface: α-activation is common in heterogeneous platinum-catalyzed reactions\(^{11-15}\) but is essentially never observed in reactions of soluble platinum(II) alkyl complexes.

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We have used the data for reduction of I with D₂ to calculate an isotopic mass balance and, in particular, to estimate the amount of hydrogen (as H₂ and HD) that should be found in the gas phase at the conclusion of the reaction. We simplify the calculation by assuming that the solvent is not involved in the reaction, that is, all the hydrogen appearing in the vapor phase originates in I, and that the side-deuterium consumed appears in cyclooctane, methane, and HD.

The data for the RRL reductions in Figures 1–3 were obtained by using a molar ratio of CODPt(CH₂)₂ to D₂ of 1:36. Under RRL conditions, the average contents of deuterium in the hydrocarbon products were d_methane = 1.1 and d_cyclooctane = 7.4. Thus, eq 7 summarizes the isotopic mass balance for the system. The predicted average hydrogen content (H, eq 2) from this calculation is 0.109. The experimental value (Figure 3 upper) is H = 0.090, and is in reasonable agreement.

$$\text{CODPt(CH}_2\text{)}_2 + 72 \text{ D} \xrightarrow{\text{RRL, D}_2} \text{Pt}_2 \xrightarrow{\text{RRL, D}_2} \text{C}_16$$

A similar calculation for the MTL data failed to give agreement, because these data (Figures 1–3) were not obtained under strictly comparable conditions, and because solvent clearly participates in isotopic exchange under these conditions.

No Exchange of Deuterium into Soluble 1 Occurs during Platinum-Catalyzed Reaction with D₂. During reductions of olefins with D₂ over heterogeneous metal catalysts, remaining olefin is often found to contain deuterium. This observation establishes that olefin is in equilibrium with alkyl groups on the catalyst surface and is often taken to indicate that the overall rate-determining step in the catalytic process is the final reductive elimination of alkane from the catalyst surface.

We allowed I to react with D₂ under both MTL and RRL conditions, interrupted the reactions after approximately one-half of the I had been consumed, and isolated the remaining I. We reduced the reisolated I with dihydrogen under MTL conditions to ascertain its deuterium content. There was no deuterium detectable in either the methane (<2% CH₃D) or cyclooctane (<5% C₈H₈D) produced from I reisolated after partial reduction with D₂ under either MTL or RRL conditions. It thus appears that once the reduction of I has progressed sufficiently to form C=O bonds, I and fragments derived from it are no longer in equilibrium with I in solution.

The Reduction of (Norborendiene)dimethylplatinum(II) (NB-DP(CH₂)₂) with D₂ Forms Predominantly Endo C-D Bonds. Reduction of Norbornadiene Forms Exo C-D Bonds. As a part of the effort to establish the mechanism of the heterogeneous platinum-catalyzed reduction of (dialkyl)dialkylplatinum(II) complexes, we wished to determine the stereochemistry of the reaction. We chose to examine the stereochemistry of reduction of the diolefin moiety using NBDP(CH₂)₂ as a substrate. Isotopic exchange involving formation of surface σ-allyl complexes is not possible with this compound, and the endo and exo protons of norbornane are easily distinguished with high-field H NMR spectroscopy.

Platinum-catalyzed reduction of NBDP(CH₂)₂ with D₂ (4 atm) at 30 °C resulted predominantly but not exclusively in formation of end C-D bonds; reduction of norbornadiene itself under the same conditions yielded almost exclusively exo C-D bonds (eq 8 and 9). Figures 4 and 5 summarize the data.

Although the mass spectrum of norbornane does not lend itself to the same facile quantification of isotopic composition as does that of cyclooctane, the mass spectrum of norbornane obtained from reaction of norbornadiene with D₂ is clearly predominantly

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 (>71%) the $d_4$ isopomer (Figure 5). The virtual absence of a proton signal attributable to the exo C–H bond in the $^1$H NMR spectrum of this material indicates that deuterium is introduced from the endo face of norbornadiene; this inference is in agreement with previous examinations of the stereochemistry of this reaction.$^{23-25}$

Reduction of NBDPt(CH$_3$)$_2$ with D$_2$ is less isotopically clean. The mass spectrum indicates that although norbornane-$d_4$ is the most abundant isopomer, significant quantities of norbornane-$d_3$, $d_2$, and $d_1$ are also produced. Integration of the $^1$H NMR spectrum indicates that there are approximately three exo protons and one endo proton; thus, most of the deuterium was introduced from the endo face of norbornadiene.

The important qualitative conclusion from this experiment is that reduction of NBDPt(CH$_3$)$_2$ takes place with stereochemistry opposite to that of reduction of norbornadiene itself. The generation of a broader mixture of isopomers in the reduction of the NBDPt(CH$_3$)$_2$ probably reflects the same processes described previously: transfer of hydrogen atoms from the Pt–CH$_3$ moiety to the norbornyl group, and exchange of hydrogens and epimerization within norbornyl groups, probably by reversible $\alpha$-hydride (and perhaps $\beta$-hydride) elimination and addition.$^4$

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Table II. Evidence Relevant to the Mechanism of Platinum-Catalyzed Reduction of (O\textsubscript{3}H)PtR\textsubscript{2} Complexes with H\textsubscript{2}

reaction of (O\textsubscript{3}H)PtR\textsubscript{2} with dihydrogen is a heterogeneous platinum-catalyzed reaction

reduction of NBDP(CH\textsubscript{3})\textsubscript{2} with deuterium yields norbornane having mainly endo C-D bonds

(O\textsubscript{3}H)PtR\textsubscript{2} recovered from partial reduction with D\textsubscript{2} contains no deuterium

The kinetic order in CODPt(CH\textsubscript{3})\textsubscript{2} is zero under both RRL and MTL conditions

during reduction of (O\textsubscript{3}H)PtR\textsubscript{2} complexes, deuterium is readily transferred from the alkyl moieties into the cycloalkane product and from the diolefin into the alkane product derived from the alkyl moieties

reduction of CODPt(CH\textsubscript{3})\textsubscript{2} with D\textsubscript{2} yields cyclooctene-d\textsubscript{4} containing from 0 to 14 deuterium atoms and methane-d\textsubscript{4} containing from 0 to 3 deuterium atoms

the E\textsubscript{a} for reduction of I under RRL conditions is 15 kcal/mol; E\textsubscript{a} for the faster reduction of COD is 8 kcal/mol, but it may be influenced by mass transport

the rate of reduction of a (O\textsubscript{3}H)PtR\textsubscript{2} complex is slower than the rate of reduction of its parent diolefin

the kinetic isotope effect of substitution of D\textsubscript{2} for H\textsubscript{2} is not significantly different from 1.0 under either MTL or RRL conditions

the relative rates of reduction of a series of (O\textsubscript{3}H)PtR\textsubscript{2} complexes depend strongly on the structure of the diolefin but only weakly on the structure of the alkyl moiety

*Reference 3. **This paper.

The Mechanism of Heterogeneous Platinum-Catalyzed Reduction of (O\textsubscript{3}H)PtR\textsubscript{2} Complexes. Table II summarizes the major mechanistic conclusions from this and previous work,\textsuperscript{2} and Scheme I presents our hypothesized mechanism.

All of the evidence is consistent with the hypothesis that reaction of (O\textsubscript{3}H)PtR\textsubscript{2} with dihydrogen is catalyzed by a platinum surface; thus, we believe we can rule out any mechanism involving homogeneous reaction of (O\textsubscript{3}H)PtR\textsubscript{2} with dihydrogen. The first step in the catalytic cycle therefore involves adsorption of the (O\textsubscript{3}H)PtR\textsubscript{2} complex to the platinum surface. There are two sites in a (O\textsubscript{3}H)PtR\textsubscript{2} complex most likely to form a bond with the surface; one is the platinum atom and the second is the face of the olefin to which the dialkylplatinum moiety is not coordinated. The observation that deuterium is transferred to the same face of the olefin in norbornadiene as that to which the dialkylplatinum moiety was coordinated indicates that association with the surface probably occurs via the platinum atom of the (O\textsubscript{3}H)PtR\textsubscript{2} complex.

The absence of deuterium in I recovered from reduction with diuteride indicates that once surface alkyl groups or diolefins have incorporated deuterium by whatever process (π-alkyl formation, α- or β-hydride elimination or addition) they are no longer in equilibrium with (O\textsubscript{3}H)PtR\textsubscript{2} in solution. It is therefore most economical to postulate that the initial binding of (O\textsubscript{3}H)PtR\textsubscript{2} to the surface is irreversible, but we cannot rule out a mechanism in which initial binding of (O\textsubscript{3}H)PtR\textsubscript{2} is reversible and a subsequent step, occurring before the C-H(D) bonds in (O\textsubscript{3}H)PtR\textsubscript{2} become exchangeable with surface hydrogen, is irreversible. Binding of (O\textsubscript{3}H)PtR\textsubscript{2} to the surface cannot, however, be the rate-limiting step in the mechanism, since the rate law would then have to be first order in [(O\textsubscript{3}H)PtR\textsubscript{2}]

The final steps in a catalytic cycle of reduction of (O\textsubscript{3}H)PtR\textsubscript{2} probably resemble those in the heterogeneous catalytic reduction of olefins. The qualitative similarity in the distribution of isomers in the reduction of I and COD with diuteride supports this assertion. The addition of H(D) to the olefins of (O\textsubscript{3}H)PtR\textsubscript{2} by β-hydride addition is undoubtedly reversible here as well as in the reduction of olefins.\textsuperscript{28,29} Reduction of a surface alkyl formed from the alkyl group in the complex by a surface hydrogen yielding alkane is probably a step common to both reactions. Release of alkane from the catalyst surfaces is effectively irreversible in both. Since saturated alkane solvents are slowly activated by addition to the catalyst under MTL conditions in the reduction of (O\textsubscript{3}H)PtR\textsubscript{2} complexes, this last statement cannot be strictly correct. The concentration of O\textsubscript{3}H\textsubscript{2} and RH is, however, very low compared

\textsuperscript{(27)} Smith, G. V.; Burwell, R. L., Jr. J. Am. Chem. Soc. 1962, 84, 925–934.
rich) in an exceptional procedure. (Norborendiine)dimethyl- 
edependent platinum(II) (NBDP(C\(_2\)H\(_3\))\(_2\)) and (1,5-cyclooctadiene)bis(methyl- 
edependent platinum(II) were prepared by the method described in the previous 
paper.\(^3\) The preparation of (cyclopentadiene-d\(_5\))dimethylplatinum(II) 
is described in the supplementary material.

Reductions of (Diolefins)dialkylplatinum(II) Complexes for Isotopic 
Ligand Exchange Methods for Determining Their Reductions. For the 
reduction temperatures, the rate of stirring, and the pressure of H\(_2\) or D\(_2\) and 
for beginning reductions were the same as in the previous work.\(^7\) n-Heptane was 
the usual solvent except when a deuterated solvent was needed, in which case 
-n-octane-d\(_{18}\) was used. The kinetics of these reductions were not usually 
followed, but the reactions were allowed to reach completion assuming the 
correctness of the rates described in the previous work. Reductions under 
MTL conditions were carried out at 20 \(^\circ\)C rather than at 40 \(^\circ\)C in order to 
minimize the incorporation of hydrogen or deuterium from the solvent. 
Because there are not enough H\(_2\) or D\(_2\) in the headspace of the 20-ML 
reactors generally used to complete a reduction under MTL conditions, 
these reactions were provided with a slow (5 mL/min) continuous leak 
permitting a constant pressure of H\(_2\) or D\(_2\) over the solution. The 
quantity of substrate (including COD) reduced was 30-40 \text{\mu}mol, and 
the initial concentration of substrate was ca. 10 \text{mM}.

Mass Spectroscopy of Hydrocarbons. Mass spectra of the hydrocarbon 
products of reaction and authentic samples of alkane-d\(_6\) were measured 
on a Hewlett Packard 5992A GC/MS with 70-eV electron impact 
ionization. Data were collected and analyzed with use of the 
Selected Ion Monitoring System software previously described. 
This software continuously monitors up to six ions simultaneously. If 
more than six isopropomers of a compound were present in a sample, 
separate injections of the sample were made to permit analysis of 
all of the peaks of interest. Relative abundances were measured for 
m/\(\text{e}=12, 13\) and higher m/\(\text{e}\) until they became negligible for samples of cyclooctane. 
Relative abundances were measured for m/\(\text{e}=14, 15\) for samples of methanes\(^5\) and 
m/\(\text{e}=94-104\) for samples of norbornanes.

Cyclooctane-d\(_6\). To permit determination of the sensitivity of our 
GC/MS to small quantities of cyclooctane-d\(_6\) in cyclooctane-d\(_\infty\), an authentic 
sample of cyclooctane-d\(_6\) was prepared by reaction of 
lithium triethylborohydride (1 M in THF, Super-deuteride, Aldrich) and 
bromocyclooctane in THF.\(^36\) The cyclooctane-d\(_6\) was purified by 
preparative GC and found to be 99% chemically pure (GC) and 93% isotopically 
pure (GC/MS). Four solutions of 2.0%, 1.5%, 1.0%, and 0.5% cyclo-

cocctane-d\(_6\) in cyclooctane-d\(_\infty\) were prepared and analyzed by GC/MS.

Determination of Isotopic Compositions of Cyclooctanes. The (M + 
1)^\* peak in the mass spectrum of cyclooctane-d\(_\infty\) was 9.1 \pm 0.5% (95% 
confidence) of the M^\* peak (m/\(\text{e}=112\)) and the (M + 1)^\* and (M + 2)^\* 
peaks were <1.0% of the M^\* peak. The isotopic content of a sample of 
cyclooctane was determined by iteratively subtracting 9.1% of the 
corrected value for the (n + 1)th peak from the nth peak and finally 
normalizing the corrected values.

Preparation of Methane-d\(_\infty\) (n = 0-4). Authentic samples of deuter-
ated methanes were prepared to permit determination of the mass spectral 
data for unknown mixtures of deuterated methanes. Methane-d\(_6\) was 
determined by Matheson. Methane-d\(_4\) and methane-d\(_2\) were 
prepared by slow addition at room temperature of iodomethane (1.0 
mmol) and iodomethane-d\(_2\) (1.0 mmol, 99 atom % D, Aldrich) to 0.5 mL 
of Super-deuteride (1.0 M in THF, 0.5 mmol, Aldrich) in 25-mL round 
bottomed flasks capped with rubber septa. Methane-d\(_4\) was 
prepared first by addition of iodomethane-d\(_2\) to 0.5 mL of 
lithium tri-
eethylborohydride (1.0 M in THF, 0.5 mmol, Super-hydride, Aldrich) 
or by addition of concentrated HCI (1 mL) to CODP(C\(_2\)H\(_3\))\(_2\) (10 mg, 30 
\text{\mu}mol) in hexanes (1 mL) in a 5-mL round-bottomed flask capped 
with a rubber septum. The mass spectra of these two samples of 
methane-d\(_4\) were indistinguishable. Methane-d\(_2\) was prepared by addition of 
iodomethane (1.0 mmol) of Super-deuteride (1.0 M) in hexanes (1 mL) 
of Super-deuteride. The isotopic purity of the Super-deuteride was ascertained 
by analysis of cyclooctane derived from Super-deuteride and bromocyclooctane. The 
Super-deuteride was 95% d\(_1\).

Mass Spectra and Relative Sensitivities for Methane-d\(_4\). The different 
isotopically substituted methanes-d\(_n\) were not isolated in any case but were 
analyzed directly by GC/MS. The mass spectra were corrected for the 
isotopic impurity containing one fewer deuterium atom by using the 
isotopic purity of the starting materials. For instance, iodomethane-d\(_8\) 
was claimed by the supplier to be greater than 99 atom % D and the

(30) We define the rate-determining step for the purposes of this work as 
the step in which all preceding steps are in quasi-equilibrium.

(31) Ozaki, A. Isotopic Studies of Heterogeneous Catalysis; Kodansha 
Ltd: Tokyo, 1977.


Chem. 1963, 2, 1255-1261.

(34) Brainard, R. L.; Whitesides, G. M. Organometallics 1985, 4, 
1550-1557.

(35) We did not determine relative abundances for ions m/\(\text{e}=21\) or m/\(\text{e}<15\) 
because they are not very abundant and because the software can only 
monitor six ions simultaneously. The relative abundances we report here 
for methane-d\(_4\) cannot be used indiscriminately for deconvolution of mass spectral 
data determined on mass spectrometers of other designs.

1669-1671.
Table III. Observed Relative Abundances of Ions in the Region m/e 15–20 for Deuterated Methanes

<table>
<thead>
<tr>
<th>methane-d₄</th>
<th>15</th>
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<td>75.0</td>
<td>100</td>
<td>1.3</td>
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<td>0.9</td>
<td>100</td>
<td>1.22</td>
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</table>

Super-deuteride was 95 atom % D; thus, the product methane-d₄ should be 98 atom % D or consist of 92% methane-d₄ and 8% methane-d₃. The contribution of 8% methane-d₃ was subtracted from the experimental mass spectrum of methane-d₄ and the spectrum normalized such that the relative abundance of the largest ion in the spectrum was 100. Mass spectra of methanes after correction for isotopic impurities and normalization are reported in Table III.

Solutions of known quantities of CODP(CH₃)₂ and CODPt(CD₃)₂ in hexane were reacted with concentrated HCl, and the resulting mixture of CH₃ and CD₃H was analyzed by GC/MS. The isotopic compositions of the mixtures calculated by the method described below with use of the mass spectra as reported in Tables III did not agree with the known isotopic compositions of the samples. Relative sensitivities were determined by trial and error which made the calculated isotopic compositions agree with the known isotopic compositions. The best fit for the isotopic composition of a mixture of methane-d₄ and methane-d₃ was obtained when the mass spectrum for the former was multiplied by 1.08. Relative sensitivities for methane-d₃, methane-d₂, and methane-d₁ were calculated by fitting the sums of their relative abundances to a straight line determined by the sums of the relative abundances for the methane-d₄, -d₃, and -d₂ and the number of deuterium atoms in the alkane. Thus, the basis set (RAₜₜ in eq 1) used for the determination of isotopic compositions of mixtures of deuteriated methanes are given by the mass spectra in Table III multiplied by the relative sensitivities.

**Determination of the Isotopic Composition of an Unknown Sample of Methane.** The isotopic composition of a sample of methane containing deuterium was determined by solution of the set of linear equations represented by eq 1 for the quantities of each isomer (Xₜₜ). The linear equations were solved with a computerized least-squares fit by singular value decomposition.⁷

**Accuracy of Isotopic Compositions.** We determined the accuracy of our method of analyzing mass spectral data by calculating the isotopic compositions of mixtures of known quantities of CH₃, CD₂H₂, and CD₃H from their mass spectra. The mixtures were prepared as above by allowing mixtures of CODP(CH₃)₂ and CODPt(CD₃)₂ to react with HCl. The agreement between the isotopic compositions determined from the quantities of platinum complexes and those determined by calculation of Xₜₜ from mass spectral data by the method described above is good.

We also established the sensitivity of our deconvolution algorithm to small fluctuations in the mass spectral data. The relative abundances in the mass spectrum of methanes shown in Figure 1 (upper) were modified by randomly adding or subtracting a given absolute percentage (0–6%). An isotopic composition was determined by the method above for this modified spectrum. Modifications of the mass spectrum by only 1 or 2% did not have as large an effect on isotopic compositions of those as 4 and 6%. Random addition or subtraction of 4% caused a change in the isotopic composition of as much as 5%. We therefore believe that our method of deconvolution of mass spectral data has an accuracy of ±5% absolute.

**Analysis of D₄/H₂/H₂.** Mass spectra of isotopes of dihydrogen were measured on a Kratos MS 50 mass spectrometer operating at approximately 100 eV. Reductions in which the remaining deuterium was analyzed were not conducted in the usual 20-mL reactors. These reactions were conducted in a glass vessel equipped with a 1/4 in. glass-to-metal seal; the metal tubing of this seal was connected via Swage-lok fitting to a brass cutoff valve. Reactions were conducted with the valve open, and the assembly was capped with a GC septum held by a Cajon Ultra-torr fitting. Reactants were introduced through the GC septum as described in the previous work.³ Reductions conducted under MTL conditions were run in a vessel having an internal volume of 55 mL, and the slow continuous leak described above was not used. At the conclusion of the reactions, the syringe needle supplying deuterium was removed; the cutoff valve was closed; the adapter holding the GC septum was removed; and the reactor was connected directly to the inlet leak of the MS 50. Examination of the peaks at m/e 4, 3, and 2 yielded the isotopic composition of the remaining deuterium. The deuterium used in this work was checked by mass spectrometry and found to be >99.1% atom % D.

**Deuterium incorporation in remaining 1** was assessed by running reductions of 1 with D₂ to partial completion under MTL and RLR conditions as described previously.³ The progress of these reductions was not followed; they were interrupted by removing the reaction solution via cannula at the time at which we estimated that one-half of the 1 should have been consumed. The catalyst was filtered from the solutions, and the solutions were concentrated by rotary evaporation. Evacuation under vacuum (<10⁻² Torr) overnight removed residual cyclooctane-d₄, and afforded pure 1 which was reduced under MTL conditions with dihydrogen. The resulting methane and cyclooctane were analyzed by GC/MS; neither contained detectable quantities of deuterium.

**Stereochemistry of Reduction of NBDDPMe₂** and Norbornadiene. The reductions of norbornadiene and NBDDPMe₂ were carried out in the same manner as the reductions described in the previous work except that they were conducted in n-pentane at ~30 °C under 4 atm of D₂.³ The isotopic distribution of norbornanes was narrower under these reaction conditions than under the standard RLR conditions. The reaction was conducted in n-pentane to facilitate isolation of norbornane. Norbornanes were isolated after the reduction by preparative GC on a F&M 700 instrument with use of a 1/4 in. × 6 ft UCP-98 column at 90 °C.¹¹ NMR spectra of the norbornanes were recorded at 500 MHz in CDCl₃ with a drop of D₂O added to remove the signal due to H₂O.

**Acknowledgment.** We thank Stephen R. Wasserman for assistance with the computer program to analyze isotopic contents of alkane and Philip Briggs for determining mass spectra of samples of hydrogen. The Bruker AM 300 NMR spectrometer was purchased through the NIH BRS Shared Instrumentation Grant Program 1 S10 RR01748-01A1.

**Registry No.** 1,12266-92-1: DCP-d₄, 65886-42-2; NBD, 121-46-0; CODP(C₃H₇)₂, 51192-20-2; NBDDP(C₃H₇)₂, 53199-36-3; CODP(C₃D₃)₂, 113451-87-9; (DCP-d₄)₂Pt(CH₃)₂, 113490-40-7; (DCP-d₄)₂PtCl₂, 113490-41-8; c-C₄H₅D, 86812-02-4; CH₄, 74-82-8; CD₃H, 676-49-3; CH₂D₃, 676-55-1; CD₂H, 676-80-2; CD₃, 558-20-3; Pt, 74400-06-4; cyclopentadiene, 542-92-7; cyclopentadiene-d₄, 113507-24-7; cyclopentadiene-d₆, 16456-47-6.

**Supplementary Material Available.** Figures showing typical mass spectra of cyclooctane containing small amounts of deuterium; data illustrating the sensitivity of our GC/MS to cycloctane-d₄ and the sensitivity to small changes in relative abundances of our algorithm for calculating isotopic compositions of methanes from mass spectra; the synthesis of bicyclopentadiene-d₁₂; and a table comparing known isotopic compositions of CH₄, CD₂H₂, and CD₃H with those found experimentally with our method (6 pages). Ordering information is given on any current masthead page.