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.

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Registry No. 1, 12266-92-1; COD, 111-78-4; NBD, 121-46-0; DCPD, 77-73-6; DMCOD, 3760-14-3; $\mathrm{COD\overline{PtCH_2(CH_2)_2CH_2}}$, 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.

[3] Miller, T. M.; Izumi, A. N.; Shih, Y.-S.; Whitesides, G. M. *J. Am. Chem. Soc.*, previous paper in this issue.

[4] Miller, T. M.; Whitesides, G. M. *J. Am. Chem. Soc.*, following paper in this issue.

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0002-7863/88/1510-3156$01.50/0

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

		isotopic composition (%, ±5%)										
		methane					cyclooctane					
source of deuterium	reaction conditions[a]	d_0	d_1	d_2	d_3	$\bar{d}$	d_0	d_1	d_2	d_3	d_4	$\bar{d}$
n-C_8D_{18}	MTL[b]	96	1	3		0.066	77	16	5	3		0.34
	MTL	98	2			0.024	92	6	1	0.3		0.09
	RRL	>98	<2			0.0	100	<0.5				0.0
(DCPD-d_{12})Pt$(CH_3)_2$[c]	MTL	64	25	10	2	0.49						
	RRL	96	4			0.047						
CODPt$(CD_3)_2$	MTL						51	33	13	3	1	0.71
	RRL						96	4	0.5			0.048
(DCPD-d_{12})Pt$(CH_3)_2$ + CODPt$(C_2H_5)_2$	MTL	93[d]	3[d]	1	3[d]	0.053[d]	66	14	8	7	5	0.71

[a] RRL = reaction rate limited; MTL = mass transport limited; MTL reactions were conducted at 20 °C unless otherwise noted. [b] Reaction was conducted at 40 °C. [c] DCPD-d_{12} = dicyclopentadiene-d_{12}. [d] Isotopic composition of ethane rather than methane.

was commercial platinum black and had a surface area of 2.8×10^{-4} g-atom/g of catalyst as determined by dihydrogen–dioxygen titration.[3] Reductions were performed with the methods described in the previous paper.[3] The reaction conditions for mass transport limited (MTL) reductions were $P_{H_2} = 0.17$ atm, $T = 20$ °C, $S_{Pt} = 11$ μg-atom (40 mg of catalyst), ω (the rate of rotation of the magnetic stirring bar) = 1800 RPM, and $[(Ol_2)PtR_2]_0$ = 10–20 mM; reaction conditions for reaction rate limited (RRL) reductions were $P_{H_2} = 2.3$ atm, $T = -20$ °C, $S_{Pt} = 8.7$ μg-atom (30 mg of catalyst), ω = 1200 RPM, and $[(Ol_2)PtR_2]_0$ = 10–20 mM.

This work rests on analyzing the isotopic compositions of alkanes containing deuterium. The isotopic compositions were calculated from mass spectra determined by gas chromatography/mass spectroscopy (GC/MS). Determination of the isotopic composition of cyclooctane was straightforward since this molecule yields an abundant molecular ion M^+ with negligible (<1%) $(M - 1)^+$. Isotopic compositions of cyclooctane could therefore be determined directly after correction of the intensity of ions having m/e greater than M^+ for naturally abundant ^{13}C.[6] In some instances measurements of the quantity of deuterium in a sample of cyclooctane containing small amounts of deuterium were desired. The $(M + 1)^+$ ion (m/e 113) of cyclooctane due to naturally abundant ^{13}C was 9.1 ± 0.5% (95% confidence level) that of the M^+ ion on our GC/MS. By examination of authentic samples of 0.5 to 2.0% cyclooctane-d_1 in cyclooctane-d_0, we demonstrated that we are able to detect >0.5% cyclooctane-d_1 in cyclooctane-d_0. Details of the procedures used are described in the Experimental Section.

Determination of the isotopic composition of samples of methane, ethane, and propane was more complex since the mass spectra of methane-d_0, ethane-d_0, and propane-d_0 have significant peaks at $(M - 4)^+$ through $(M - 1)^+$. The isotopic composition of a sample of methane, ethane, or propane containing deuterium was deduced from its mass spectrum by solution of the set of linear equations represented by eq 1 for X_m, where X_m is the fraction of the alkane containing m deuterium atoms. In eq 1, RA_n are the experimental relative abundances of the n ions analyzed (that is, for example, ions m/e = 15–20 for methane) for the alkane whose isotopic composition is desired, and the $RA_{m,n}$ are the experimental relative abundances of the same n ions in the mass spectra of authentic alkane containing m deuteriums. Equation 1 was solved by singular value decomposition.[7] This method minimizes the value of $|[RA_{m,n}][X_m] - [RA_n]|$ and thus provides the best least-squares values of X_m.

$$\begin{bmatrix} RA_1 \\ \vdots \\ RA_n \end{bmatrix} = \begin{bmatrix} RA_{0,1} & \cdots & RA_{m,1} \\ \vdots & & \vdots \\ RA_{0,n} & \cdots & RA_{m,n} \end{bmatrix} \begin{bmatrix} X_0 \\ \vdots \\ X_m \end{bmatrix} \tag{1}$$

$$\bar{d} = 1/100 \sum_{i=1}^{j} i(\%\ \text{alkane-}d_i) \tag{2}$$

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 ($RA_{m,n}$) for alkane-*1,1*-d_2 or alkane-*1,2*-d_2 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*-d_2 rather than ethane-*1,1*-d_2 in analysis of ethane from deuteriogenation of ethylene) and by availability (e.g., ethane-*1,1,1*-d_3 is readily prepared whereas ethane-*1,1,2*-d_3 is not). Our mass spectra for methane-d_n (n = 0–4, Table III) were similar to those in the literature,[8,9] but our mass spectra for ethane-d_n (n = 0–3)[4] differed significantly from those in the literature.[10]

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-d_0, alkane-d_2, and alkane-d_3. The trends observed in relative sensitivities for methane-d_n and ethane-d_n parallel those in the literature.[9,10] Details of the calculations of relative sensitivities and isotopic compositions and the synthesis of alkane-d_n and authentic mixtures of alkane-d_n are reported in the Experimental Section.

We believe that the isotopic compositions of mixtures of alkane-d_n 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 known mixtures of CH_4, CD_2H_2, and CD_3H 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-d_n yielded mass spectral data that were reproducible to ±2–3% absolute.

Determination of the isotopic composition of mixtures of D_2, HD, and H_2 was straightforward since these substances give clean molecular ions. The D_2 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, $\bar{d}$, 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 (Diolefin)dialkylplatinum Complexes Is Significant under MTL Conditions but Not under RRL Conditions. Platinum-catalyzed reaction of (1,5-cyclooctadiene)dimethylplatinum(II) (**1**) in *n*-

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[6] This calculation ignores the relative sensitivities of the mass spectrometer to the isotopic content of the cyclooctane.

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octane-d_{18} with H_2 at 40 °C under MTL conditions resulted in incorporation into the hydrocarbon products of a total of approximately 0.47 atom equiv of deuterium per equivalent of **1**: 0.13 atom equiv into the methane (2 equiv) and 0.34 atom equiv into the cyclooctane. Under RRL conditions no incorporation of deuterium from solvent resulted. Equation 3 and the first three entries in Table I summarize these results. This activation of solvent by the platinum catalyst under reaction conditions previously 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_{18} into methane and cyclooctane was reduced to 0.14 atom of deuterium per equivalent of **1**. 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.

$$\mathrm{CODPt(CH_3)_2} \xrightarrow[\underline{n}\text{-}C_8D_{18}]{H_2,\ Pt} \text{Cyclooctane-}\underline{d}_n + 2\text{Methane-}\underline{d}_n \qquad (3)$$

$$\begin{array}{l} \text{MTL, 40 °C} \\ \text{MTL, 20 °C} \\ \text{RRL, -20 °C} \end{array} \quad \underbrace{\begin{array}{cccccc} 0.34 & + & 2(0.066) & = & 0.47 \\ 0.09 & + & 2(0.024) & = & 0.14 \\ 0.0 & + & 2(0.0) & = & 0.0 \end{array}}_{\text{Atom equiv of D transferred from } \underline{n}\text{-}C_8D_{18}}$$

Transfer of Deuterium from the Diolefin Moiety into Methane Is Greater under MTL than RRL Conditions. To determine the efficiency of transfer of deuterium originally present in the diolefin 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_{12})dimethylplatinum(II) ((DCPD-d_{12})-$Pt(CH_3)_2$) with H_2 (eq 4; Table I). We used dicyclopentadiene rather than cyclooctadiene because it is more easily obtained in perdeuteriated form. Under MTL conditions, transfer of deuterium from the DCPD-d_{12} moiety to the methyl group was rapid; approximately 1 atom equiv of deuterium was lost from the DCPD-d_{12} group and incorporated into the 2 equiv of methane generated. This reaction also generated significant quantities of methane-d_2 and -d_3. Reduction of (DCPD-d_{12})$Pt(CH_3)_2$ under RRL conditions produced a small quantity of methane-d_1.

$$(\text{DCPD-}\underline{d}_{12})\mathrm{Pt(CH_3)_2} \xrightarrow[\underline{n}\text{-}C_7H_{16}]{H_2,\ Pt} 2\text{Methane-}\underline{d}_n \qquad (4)$$

$$\begin{array}{l} \text{MTL} \\ \text{RRL} \end{array} \qquad \left.\begin{array}{c} 0.98 \\ 0.08 \end{array}\right\} \begin{array}{l} \text{Atom equiv of} \\ \text{D transferred} \\ \text{from DCPD-}\underline{d}_{12} \end{array}$$

The last entry in Table I gives the isotopic composition of the ethane and cyclooctane produced in the reduction of a 1:1 mixture of (DCPD-d_{12})$Pt(CH_3)_2$ and $CODPt(C_2H_5)_2$ 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 diolefin moiety of one molecule of $(Ol_2)PtR_2$ to the alkane derived from the alkyl moiety of a second (eq 5). Deuterium lost from a DCPD-d_{12} moiety can also be captured by incorporation into cyclooctane derived from a second $(Ol_2)PtR_2$ complex (eq 5)

$$(\text{DCPD-}\underline{d}_{12})\mathrm{Pt(CH_3)_2} + \mathrm{CODPt(C_2H_5)_2}$$

$$\Big\downarrow \begin{array}{l} H_2,\ \text{Pt, MTL} \\ \underline{n}\text{-}C_7H_{16} \end{array} \qquad (5)$$

$$\underbrace{\begin{array}{ccc} \text{Cyclooctane-}\underline{d}_n & + & 2\text{Ethane-}\underline{d}_n \\ 0.71 & + & 2(0.053) = 0.82 \end{array}}_{\text{Atom equiv of D transferred from DCPD-}\underline{d}_{12}}$$

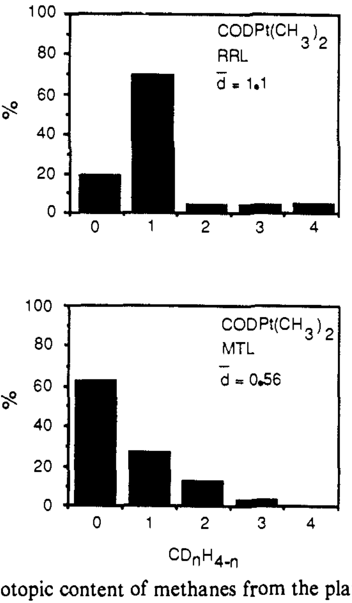

Figure 1. The isotopic content of methanes from the platinum-catalyzed reaction of **1** with D_2 under RRL (upper) and MTL (lower) conditions.

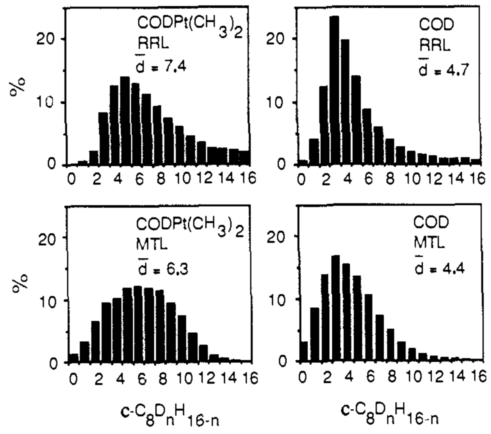

Figure 2. The isotopic content of cyclooctanes from the platinum-catalyzed reaction of **1** with D_2 under RRL (upper left) and MTL (lower left) conditions and of 1,5-cyclooctadiene with D_2 under RRL (upper right) and MTL (lower right) conditions.

Transfer of Deuterium from the $Pt(CD_3)_2$ Moiety into Cyclooctane Is Also Much Greater under MTL than RRL Conditions. The data in Table I 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,

$$\mathrm{CODPt(CD_3)_2} \xrightarrow[\underline{n}\text{-}C_7H_{16}]{H_2,\ Pt} \text{Cyclooctane-}\underline{d}_n \qquad (6)$$

$$\begin{array}{l} \text{MTL} \\ \text{RRL} \end{array} \qquad \left.\begin{array}{c} 0.71 \\ 0.048 \end{array}\right\} \begin{array}{l} \text{Atom equiv of} \\ \text{D transferred} \\ \text{from } CD_3 \end{array}$$

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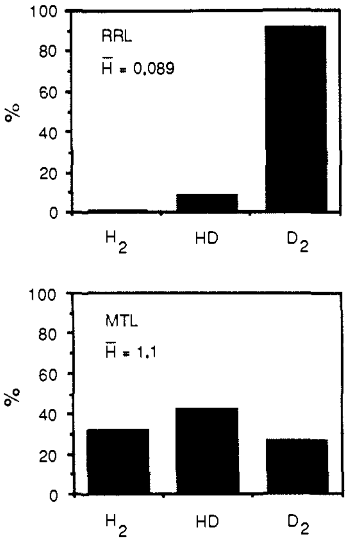

Figure 3. The relative amounts of H_2, HD, and D_2 present after reduction of **1** with D_2 under RRL (upper) and MTL (lower) conditions. The average hydrogen content of the mixture is indicated in the figure by $\bar{H}$. The D_2 used in these experiments was >99.1 atom % D.

for which β-hydride elimination is the predominant reaction.[16-19]

The Distribution of Deuterium in the Products of Platinum-Catalyzed Reaction of 1 and of COD with D_2. Figure 1 shows the isotopic compositions of methane produced in the platinum-catalyzed reaction of **1** with D_2 under both RRL and MTL conditions; Figure 2 shows the isotopic compositions of cyclooctane produced in the platinum-catalyzed reactions of **1** and of 1,5-cyclooctadiene with D_2. The isotopic compositions of methane produced from **1** under MTL and RRL conditions are markedly different. Methane-d_1 predominated under RRL conditions; methane-d_0 predominated under MTL conditions; and the average deuterium content of methane produced under RRL conditions is twice that of methane produced under MTL conditions. It is also of interest to note that the methanes produced from reduction of DCPD-d_{12}Pt(CH_3)$_2$ under MTL conditions with H_2 are nearly identical with those produced from reduction of **1** under MTL conditions with D_2. Reduction of **1** under MTL and RRL conditions yielded cyclooctane with a broader distribution of isotopomers and a higher average deuterium content than reduction of COD. The average deuterium content of cyclooctanes produced in reductions of **1** and COD under RRL conditions was higher than that under MTL conditions.

The high average deuterium content observed for the cyclooctane produced in the reaction of **1** with D_2 was initially puzzling. From the stoichiometry of the reaction, we expected that cyclooctane should incorporate on average four atoms of deuterium. Figure 3 shows that there are significant quantities of H_2 and HD present in the dideuterium remaining after reduction of **1** with D_2 under MTL or RRL conditions. Under MTL conditions the extent of exchange appears to be higher than that under RRL conditions, but the former reaction involved only a threefold molar excess of D_2 (that is, D_2:**1** = 9:1) while the latter used a twelvefold excess (that is, D_2:**1** = 36:1). In addition, in the MTL regime, exchange of hydrogens from the solvent (n-C_7H_{16}) is more rapid than that in the RRL regime, and this reaction introduces hydrogen into the vapor phase that did not originate in **1**. Both effects distort the H_2/HD/D_2 mixture in a way that makes exchange seem more rapid under MTL conditions than under RRL conditions.

We have used the data for reduction of **1** with D_2 to calculate an isotopic mass balance and, in particular, to estimate the amount of hydrogen (as H_2 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 **1**, and that all the dideuterium 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(CH_3)$_2$ to D_2 of 1:36. Under RRL conditions, the average contents of deuterium in the hydrocarbon products were $\bar{d}_{\mathrm{methane}} = 1.1$ and $\bar{d}_{\mathrm{cyclooctane}} = 7.4$. Thus, eq 7 summarizes the isotopic mass balance for the system. The predicted average hydrogen content ($\bar{H}$, eq 2) from this calculation is 0.109. The experimental value (Figure 3 upper) is $\bar{H}$ = 0.090, and is in reasonable agreement.

$$\mathrm{CODPt(CH_3)_2} + 72\ \mathrm{D} \xrightarrow[\mathrm{RRL},\ \underline{n}\text{-}\mathrm{C_7H_{16}}]{\mathrm{Pt,\ D_2}} \qquad (7)$$

$$\text{Cyclooctane-}\underline{d}_{7.4} + \text{2Methane-}\underline{d}_{1.1} + 62.4\ \mathrm{D} + 3.6\ \mathrm{H}$$

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 D_2. During reductions of olefins with D_2 over heterogeneous metal catalysts, remaining olefin is often found to contain deuterium.[20-22] 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 **1** to react with D_2 under both MTL and RRL conditions, interrupted the reactions after approximately one-half of the **1** had been consumed, and isolated the remaining **1**. We reduced the reisolated **1** with dihydrogen under MTL conditions to ascertain its deuterium content. There was no deuterium detectable in either the methane (<2% CH_3D) or cyclooctane (<0.5% $C_8H_{15}D$) produced from **1** reisolated after partial reduction with D_2 under either MTL or RRL conditions. It thus appears that once the reduction of **1** has progressed sufficiently to form C–D bonds, **1** and fragments derived from it are no longer in equilibrium with **1** in solution.

The Reduction of (Norbornadiene)dimethylplatinum(II) (NBDPt(CH_3)$_2$) with D_2 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 (diolefin)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 NBDPt(CH_3)$_2$ as a substrate. Isotopic exchange involving formation of surface π-allyl complexes is not possible with this compound, and the endo and exo protons of norbornane are easily distinguished with high-field ^{1}H NMR spectroscopy.

Platinum-catalyzed reduction of NBDPt(CH_3)$_2$ with D_2 (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).[23-25] 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 D_2 is clearly predominantly

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(17) McCarthy, T. J.; Nuzzo, R. G.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 3396–3403.

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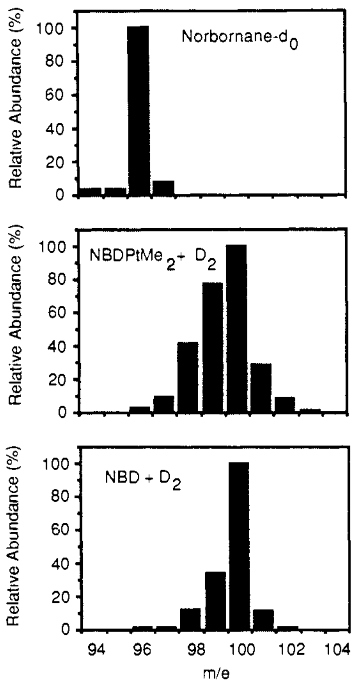
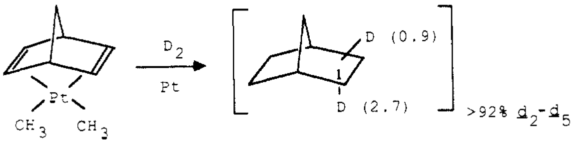
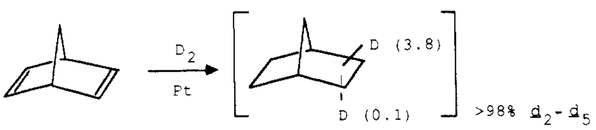


Figure 4. Mass spectra in the molecular ion region of norbornane-d_0 (upper), norbornane obtained by reduction of $NBDPtMe_2$ with D_2 (middle), and norbornane obtained by reduction of norbornadiene with D_2 (lower). The reductions were performed in *n*-pentane at −30 °C under 4 atm of D_2.

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



(8)



(9)

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 isotopomer, significant quantities of nor-bornande-d_2, -d_3, and -d_5 are also produced. Integration of the ^1H 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 isotopomers 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 α-hydride (and perhaps β-hydride) elimination and addition.[4]

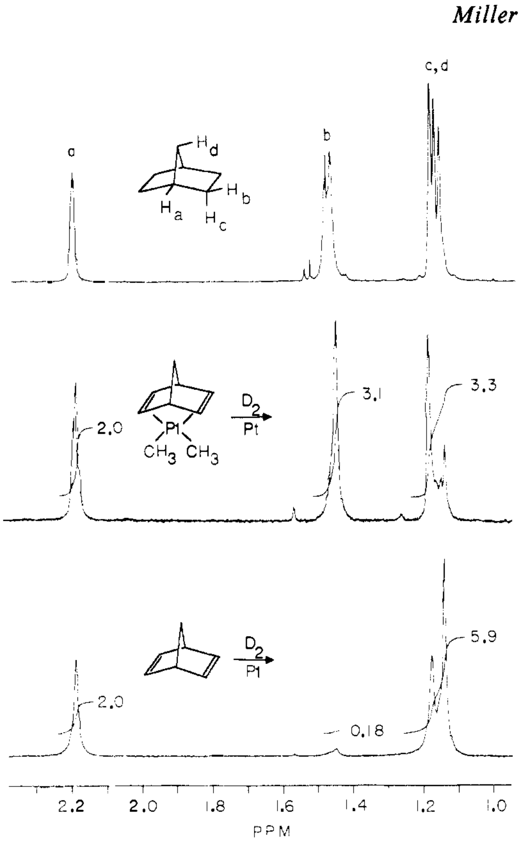


Figure 5. ^1H NMR spectra (500 MHz) in $CDCl_3$ of norbornane-d_0 (upper), norbornane obtained by reduction of $NBDPtMe_2$ with D_2 (middle), and norbornane obtained by reduction of norbornadiene with D_2 (lower). The reductions were performed in *n*-pentane at −30 °C under 4 atm of D_2.

Discussion

Differentiation of the MTL and RRL Regimes with Deuterium Interchange Experiments. Four experimental observations distinguish the RRL and MTL kinetic regimes and/or help to characterize the processes occurring on the catalyst surface. First, more deuterium is transferred from CD_3 to cyclooctane and from DCPD-d_{12} to methane during reductions conducted in the MTL regime than in the RRL regime. Second, the average content of deuterium in methane and cyclooctane is higher from reductions with D_2 run under RRL conditions than under MTL conditions. Third, the average content of deuterium in cyclooctane is higher from reaction of **1** with D_2 than from COD with D_2. Fourth, most of the hydrogen lost from **1** during its reduction with D_2 appears as HD and H_2.

It is plausible that the surface concentration of hydrogen should be higher under RRL conditions than under MTL conditions. As a result, steps that remove hydrogens from surface-alkyl groups should proceed more slowly under RRL conditions. Two experimental observations contrasting the MTL and RRL regimes are in accord with this hypothesis: more deuterium is transferred from CD_3 to cyclooctane under MTL than RRL conditions during reduction of $CODPt(CD_3)_2$ with H_2, and more deuterium is transferred from DCPD-d_{12} to methane during reduction of DCPD-$d_{12}Pt(CH_3)_2$.

The fact that cyclooctane contains less deuterium from reduction of either **1** or COD with D_2 under MTL than RRL conditions is, however, difficult to understand for two reasons. First, the higher incorporation of deuterium in cyclooctane under RRL conditions indicates that hydrogen is removed from surface cyclooctyl more rapidly than under MTL conditions. Clearly, processes which exchange the C–H bonds of surface cyclooctyl are not appreciably slowed by the higher surface concentration of hydrogen or the lower temperature of RRL reductions. Second, this result seems to contradict the observation that less deuterium is transferred under RRL conditions than MTL conditions from DCPD-d_{12} to methane. Evidently surface hydrogen lost from surface cyclooctyl during reduction of **1** with D_2 is trapped more

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(23) Rylander, P. N. *Catalytic Hydrogenation over Platinum Metals*; Academic: New York, 1967; pp 100–101.

(24) Arnold, D. R.; Tucker, D. J.; Whipple, E. B. *J. Am. Chem. Soc.* **1965**, *87*, 2596–2602.

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Table II. Evidence Relevant to the Mechanism of Platinum-Catalyzed Reduction of $(Ol_2)PtR_2$ Complexes with H_2

reaction of $(Ol_2)PtR_2$ with dihydrogen is a heterogeneous platinum-catalyzed reaction[a]
reduction of $NBDPt(CH_3)_2$ with dideuterium yields norbornane having mainly endo C–D bonds[b]
$(Ol_2)PtR_2$ recovered from partial reduction with D_2 contains no deuterium[b]
The kinetic order in $CODPt(CH_3)_2$ is zero under both RRL and MTL conditions[a]
during reduction of $(Ol_2)PtR_2$ 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[b]
reduction of $CODPt(CH_3)_2$ with D_2 yields cyclooctane-d_n containing from 0 to 14 deuterium atoms and methane-d_m containing from 0 to 3 deuterium atoms[b]
the E_a for reduction of **1** under RRL conditions is 15 kcal/mol; E_a for the faster reduction of COD is 8 kcal/mol, but it may be influenced by mass transport[a]
the rate of reduction of a $(Ol_2)PtR_2$ complex is slower than the rate of reduction of its parent diolefin[a]
the kinetic isotope effect of substitution of D_2 for H_2 is not significantly different from 1.0 under either MTL or RRL conditions[a]
the relative rates of reduction of a series of $(Ol_2)PtR_2$ complexes depend strongly on the structure of the diolefin but only weakly on the structure of the alkyl moiety[a]

[a] Reference 3. [b] This paper.

rapidly by surface deuterium yielding HD than by surface methyl yielding methane.

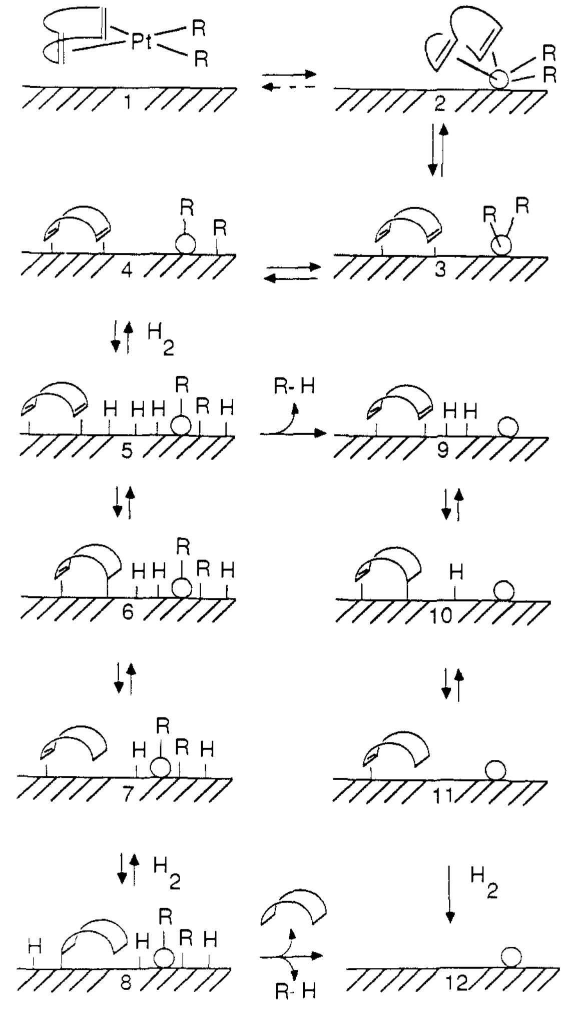
The lower deuterium content of cyclooctane produced under MTL conditions may reflect, in part, activation of solvent (C_7H_{16}) under MTL conditions. We suggest, however, that the major difference between MTL and RRL reductions lies in the reversiblity of dihydrogen addition to the surface. The higher surface concentration of hydrogen under RRL conditions should make loss of $H_2(HD,D_2)$ from the surface more rapid than under MTL conditions. Under RRL conditions surface hydrogen from cyclooctane is thus lost from the surface hydrogen pool to the vapor phase as HD more rapidly than under MTL conditions. The surface concentration of hydrogen is probably lower during reductions of COD than of **1** because reductions of COD may always be close to or in the MTL regime; thus, addition of D_2 to the surface is less reversible and cyclooctanes from reductions of COD have lower deuterium content. Olefins are also known to inhibit exchange of H_2 and D_2 over hydrogenation catalysts.[22,26,27]

The Mechanism of Heterogeneous Platinum-Catalyzed Reduction of $(Ol_2)PtR_2$ Complexes. Table II summarizes the major mechanistic conclusions from this and previous work,[3] and Scheme I presents our hypothesized mechanism.

All of the evidence is consistent with the hypothesis that reaction of $(Ol_2)PtR_2$ with dihydrogen is catalyzed by a platinum surface; thus, we believe we can rule out any mechanism involving *homogeneous* reaction of $(Ol_2)PtR_2$ with dihydrogen. The first step in the catalytic cycle therefore involves adsorption of the $(Ol_2)PtR_2$ complex to the platinum surface. There are two sites in a $(Ol_2)PtR_2$ 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 $(Ol_2)PtR_2$ complex.

The absence of deuterium in **1** recovered from reduction with dideuterium indicates that once surface alkyl groups or diolefins have incorporated deuterium by whatever process (π-allyl formation, α- or β-hydride elimination or addition) they are no longer

Scheme I. Proposed Mechanism for the Platinum-Catalyzed Reaction of $(Ol_2)PtR_2$ with Dihydrogen[a]



[a] This representation of the platinum catalyst is used here rather than the usual "*" convention to make explicit the incorporation of a platinum atom from $(Ol_2)PtR_2$ into the surface. We do not intend to imply any particular morphology for the surface with this representation, nor any geometry for bonding of an R group to a surface platinum atom.

in equilibrium with $(Ol_2)PtR_2$ in solution. It is therefore most economical to postulate that the initial binding of $(Ol_2)PtR_2$ to the surface is irreversible, but we cannot rule out a mechanism in which initial binding of $(Ol_2)PtR_2$ is reversible and a subsequent step, occurring before the C–H(D) bonds in $(Ol_2)PtR_2$ become exchangeable with surface hydrogen, is irreversible. Binding of $(Ol_2)PtR_2$ 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 $[(Ol_2)PtR_2]$.

The final steps in a catalytic cycle of reduction of $(Ol_2)PtR_2$ probably resemble those in the heterogeneous catalytic reduction of olefins. The qualitative similarity in the distribution of isotopomers in the reduction of **1** and COD with dideuterium supports this assertion. The addition of H(D) to the olefins of $(Ol_2)PtR_2$ by β-hydrogen addition is undoubtedly reversible here as well as in the reduction of olefins.[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 $(Ol_2)PtR_2$ complexes, this last statement cannot be strictly correct. The concentration of Ol_2H_4 and RH is, however, very low compared

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with that of the solvent, and the rate constants for addition of Ol_2H_4, RH, and solvent to the catalyst are probably similar. Thus, the rate of the reverse reaction will be negligibly low.

The Rate-Limiting Step for RRL Reduction.[30] Under most circumstances in the heterogeneous reduction of olefins, reduction of the surface alkyl by a surface hydrogen and formation of alkane is rate-limiting.[20,21] By analogy, in the conversion of $(Ol_2)PtR_2$ and H_2 to OlH_4 and RH, the reduction of the cycloalkyl moiety or of the alkyl moiety would be expected to be rate-limiting. The observation that the overall rate of reaction of $(Ol_2)PtR_2$ depends strongly on the structure of the Ol_2 group but only weakly on the structure of the R group and that the relative rates of reduction of $(Ol_2)PtR_2$ complexes parallel the relative rates of reduction of their parent diolefins suggests that reduction processes involving the Ol_2 moiety might be the more important. At present, however, two data cloud the identification of alkane elimination from the catalyst surface as overall rate-limiting. First, small positive (1.2–2.0) kinetic isotope effects have been observed for the reduction of olefins, and if this step were rate-limiting in the reduction of $(Ol_2)PtR_2$, we might expect to see a similar isotope effect.[31,32] In fact, we observe $\nu_{H_2}/\nu_{D_2} = 0.9 \pm 0.2$. Second, the Arrhenius activation energies are significantly different for the reduction of COD (E_a = 8 kcal/mol) and $CODPt(CH_3)_2$ (E_a = 15 kcal/mol). If the two starting materials share a common rate-limiting transition state for conversion of the COD moiety to cyclooctane, we must inquire why the activation energies for these processes are not more similar.

The absence of a kinetic isotope effect may not be significant, since the values observed for the reduction of olefins are, in any event, small. The difference in values of E_a is difficult to interpret for two reasons. First, we are not presently confident that the value of E_a = 8 kcal/mol of COD represents a purely RRL reaction. This value of E_a was measured under conditions corresponding to RRL reaction for $CODPt(CH_3)_2$. The rate of reaction of COD under these conditions is approximately 40 times faster than that of $CODPt(CH_3)_2$. Thus, the value of E_a = 8 kcal/mol may represent an apparent activation energy for a process intermediate between RRL and MTL conditions. Second, both the constitution and concentrations of the organic groups on the surrounding surface at the rate-limiting transition state for formation of cyclooctane for COD and $CODPt(CH_3)_2$ are different. We have no way of judging the influence of these differences on E_a. An unambiguous comparison of values of E_a for reduction of an $(Ol_2)PtR_2$ complex and the corresponding Ol_2 will be the subject of a future paper.

Thus, in summary, we cannot presently unambiguously identify the rate-limiting step in the reduction of $CODPt(CH_3)_2$. By analogy with studies of olefin hydrogenation, we would propose $6 \rightarrow 7$, $8 \rightarrow 12$, or a similar step, but we cannot exclude an earlier step, not involving C–H bond formation (for example $2 \rightarrow 3$ or $2 \rightarrow 4$). We believe, however, that we understand the reaction well enough to use it in furthering our understanding of olefin hydrogenation and reforming over platinum catalysts.[4]

Experimental Section

General. The procedures used in preparation of complexes and in conducting reductions were in general the same as in the previous paper.[3] Platinum black was fuel-cell grade purchased from Johnson-Matthey Inc. *n*-Octane-d_{18} (Aldrich) was passed through silica gel and degassed with argon prior to use. Dideuterium was purchased from Airco or Matheson and used without purification.

Preparation of (Diolefin)dialkylplatinum(II) Complexes. (1,5-Cyclooctadiene)dimethylplatinum(II) (**1**)[33] and (1,5-cyclooctadiene)diethylplatinum(II) ($CODPt(C_2H_5)_2$)[34] were prepared by the literature methods. Methyl-d_3-magnesium iodide was prepared from iodomethane-d_3 (Aldrich) in an unexceptional procedure. (Norbornadiene)dimethylplatinum(II) ($NBDPt(CH_3)_2$) and (1,5-cyclooctadiene)bis(methyl-d_3)platinum(II) were prepared by the method described in the previous paper.[3] The preparation of (dicyclopentadiene-d_{12})dimethylplatinum(II) is described in the supplementary material.

Reductions of (Diolefin)dialkylplatinum(II) Complexes for Isotopic Interchange Experiments. The methods for controlling temperature, 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.[3] *n*-Heptane was the usual solvent except when a deuteriated 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 °C rather than 40 °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 μmol, and the initial concentration of substrate was ca. 10 mM.

Mass Spectroscopy of Hydrocarbons. Mass spectra of the hydrocarbon products of reaction and authentic samples of alkane-d_n 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 provided with the instrument. This software continuously monitors up to six ions simultaneously. If more than six isotopomers of a compound were present in a sample, enough separate injections of the sample were made to permit analysis of all of the peaks of interest. Relative abundances were measured for *m/e* 112, 113 and higher *m/e* until they become negligible for samples of cyclooctanes. Relative abundances were measured for *m/e* 15–20 for samples of methanes[35] and *m/e* 94–104 for samples of norbornanes.

Cyclooctane-d_1. To permit determination of the sensitivity of our GC/MS to small quantities of cyclooctane-d_1 in cyclooctane-d_0, an authentic sample of cyclooctane-d_1 was prepared by reaction of lithium triethylborodeuteride (1 M in THF, Super-deuteride, Aldrich) and bromocyclooctane in THF.[36] The cyclooctane-d_1 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% cyclooctane-d_1 in cyclooctane-d_0 were prepared and analyzed by GC/MS.

Determination of Isotopic Compositions of Cyclooctanes. The $(M + 1)^+$ peak in the mass spectrum of cyclooctane-d_0 was 9.1 ± 0.5% (95% confidence) of the M^+ peak (*m/e* 112) and the $(M - 1)^+$ and $(M - 2)^+$ peaks were <1.0% of the M^+ peak. The isotopic content of a sample of cyclooctanes was determined by iteratively subtracting 9.1% of the corrected value for the $(n - 1)$th peak from the *n*th peak and finally normalizing the corrected values.

Preparation of Methane-d_n (n = 0–4). Authentic samples of deuteriated methanes were prepared to permit deconvolution of the mass spectral data for unknown mixtures of deuteriated methanes. Methane-d_0 was obtained from Matheson. Methane-d_1 and methane-d_4 were prepared by slow addition at room temperature of iodomethane (1.0 mmol) and iodomethane-d_3 (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_3 was prepared either by addition of iodomethane-d_3 to 0.5 mL of lithium triethylborohydride (1.0 M in THF, 0.5 mmol, Super-hydride, Aldrich) or by addition of concentrated HCl (1 mL) to $CODPt(CD_3)_2$ (10 mg, 30 μmol) 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_3 were indistinguishable. Methane-d_2 was prepared by addition of diiodomethane (1.0 mmol) to 1.5 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_n. The different isotopically substituted methane-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_3 was claimed by the supplier to be greater than 99 atom % D and the

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

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

(32) Inoue, Y.; Yasumori, I. *J. Phys. Chem.* **1971**, *75*, 880–887.

(33) Kristner, C. R.; Hutchison, J. H.; Doyle, J. R.; Storlie, J. C. *Inorg. 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/e* 21 or *m/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_n cannot be used indiscriminantly for deconvolution of mass spectral data determined on mass spectrometers of other designs.

(36) Brown, H. C.; Krishnamurthy, S. *J. Am. Chem. Soc.* **1973**, *95*, 1669–1671.

Table III. Observed Relative Abundances of Ions in the Region *m/e* 15–20 for Deuteriated Methanes

	m/e						rel
methane-d_n	15	16	17	18	19	20	sensitivity
CH_4	82.7	100	1.1				1.00
CDH_3	19.9	75.0	100	1.3			1.01
CD_2H_2	10.6	35.8	70.4	100	1.2		0.970
CD_3H	5.2	8.0	51.7	41.9	100	1.2	1.08
CD_4	0	11.5	0.1	83.6	0.9	100	1.22

Super-deuteride was 95 atom % D; thus, the product methane-d_4 should be 98 atom % D or consist of 92% methane-d_4 and 8% methane-d_3. The contribution of 8% methane-d_3 was subtracted from the experimental mass spectrum of methane-d_4 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 CODPt(CH$_3$)$_2$ and CODPt(CD$_3$)$_2$ in hexane were reacted with concentrated HCl, and the resulting mixture of CH_4 and CD_3H 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-d_3 and methane-d_0 was obtained when the mass spectrum for the former was multiplied by 1.08. Relative sensitivities for methane-d_1, methane-d_2, and methane-d_4 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-d_0, -d_2, and -d_3 and the number of deuterium atoms in the alkane. Thus, the basis sets (RA$_{m,n}$ 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 isotopomer (X_m). 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 CH_4, CD_2H_2, and CD_3H from their mass spectra. The mixtures were prepared as above by allowing mixtures of CODPt(CH$_3$)$_2$ and CODPt(CD$_3$)$_2$ to react with HCl. The agreement between the isotopic compositions determined from the quantities of platinum complexes and those determined by calculation of X_m 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 as effect on isotopic compositions as those of 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 D_2/HD/H_2. 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 $^3/_8$ 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 spectrum held by a Cajon Ultra-torr fitting. Reactants were introduced through the GC spectrum 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 adaptor 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 reductant. 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 D_2 to partial completion under MTL and RRL 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-d_n 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 NBDPtMe$_2$ and Norbornadiene. The reductions of norbornadiene and NBDPtMe$_2$ 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 D_2.[3] The isotopic distribution of norbornanes was narrower under these reaction conditions than under the standard RRL 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 UCW-98 column at 90 °C. ^{1}H NMR spectra of the norbornanes were recorded at 500 MHz in $CDCl_3$ with a drop of D_2O added to remove the signal due to H_2O.

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Registry No. 1, 12266-92-1; DCPD-d_{12}, 65886-42-2; NBD, 121-46-0; CODPt(C$_2$H$_5$)$_2$, 51192-20-2; NBDPt(CH$_3$)$_2$, 53199-36-3; CODPt(CD$_3$)$_2$, 113451-87-9; (DCPD-d_{12})Pt(CH$_3$)$_2$, 113490-40-7; (DCPD-d_{12})PtCl$_2$, 113490-41-8; *c*-C$_8$H$_{15}$D, 86812-02-4; CH_4, 74-82-8; CDH_3, 676-49-3; CH_2D_2, 676-55-1; CHD_3, 676-80-2; CD_4, 558-20-3; Pt, 7440-06-4; cyclopentadiene, 542-92-7; cyclopentadiene-d_4, 113507-24-7; cyclopentadiene-d_5, 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 cyclooctane-d_1 and the sensitivity to small changes in relative abundances of our algorithm for calculating isotopic compositions of methanes from mass spectra; the synthesis of dicyclopentadiene-d_{12}; and a table comparing known isotopic compositions of CH_4, CD_2H_2, and CDH_3 with those found experimentally with our method (6 pages). Ordering information is given on any current masthead page.