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Isotopic Exchange Reactions Occurring in the Hydrogenation of (1,5-Cyclooctadiene)dialkylplatinum(II) Complexes over Platinum Black[1]

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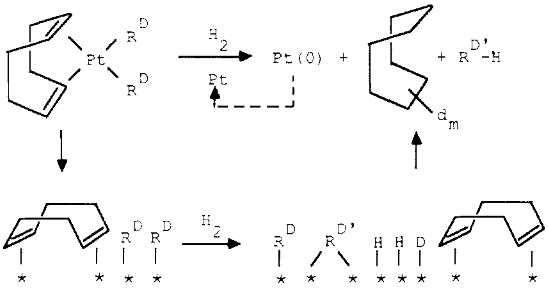
Abstract: This paper analyzes the reactivity of platinum-surface alkyls with two types of deuterium-labeling experiments. In the first, the extent of deuterium incorporation into cyclooctane during reduction of $\mathrm{CODPt(R^D)_2}$ (COD = 1,5-cyclooctadiene; $\mathrm{R^D}$ = a deuterium-labeled alkyl group) complexes with dihydrogen over platinum black is determined as a function of the structure of $\mathrm{R^D}$ and the position of the deuterium label in it. Reduction of $\mathrm{CODPt(CD_2CH_3)_2}$ yields cyclooctane containing substantially more deuterium than that obtained by reduction of $\mathrm{CODPt(CH_2CD_3)_2}$. Reduction of $\mathrm{CODPt(CD_2C(CH_3)_3)_2}$ yields cyclooctane containing less deuterium than that obtained by reduction of $\mathrm{CODPt(CD_2CH_2CH_3)_2}$. The quantity of deuterium incorporated into cyclooctane from reduction of complexes of the type $\mathrm{CODPt(CH_2C(CH_3)_2(CH_2)_{\mathit{n}}CD_3)_2}$ (n = 1-3) decreases from n = 1 to 3. The second type of experiment compares the isotopic compositions of alkanes obtained by reduction of $\mathrm{CODPtR_2}$ complexes with $\mathrm{D_2}$ over platinum black with that of the same alkanes from reduction of the corresponding alkenes with $\mathrm{D_2}$. The relative rates of exchange with surface hydrogen (deuterium) and reductive elimination for the platinum surface ethyl species produced from deuteriogenation of $\mathrm{CODPt(CH_2CH_3)_2}$ and ethylene are similar. Propanes from deuteriogenation of $\mathrm{CODPt(CH_2CH_2CH_3)_2}$ and $\mathrm{CODPt(CH(CH_3)_2)_2}$ contain deuterium principally at C_1 and C_2, respectively. The range of deuteriated isotopomers of cyclopentane obtained from deuteriogenation of $\mathrm{CODPt(\overline{CH(CH_2)_3CH_2})(CH_3)}$ is broader than that from reduction of any other $\mathrm{CODPtR_2}$ complex examined but comparable to that from cyclopentene: β-hydride elimination from platinum surface cyclopentyl groups appears to be more rapid than that from platinum-surface ethyl, *n*-propyl, or isopropyl groups.

(Cyclooctadiene)dialkylplatinum(II) complexes are reduced to cyclooctane, alkane, and platinum(0) on reaction with dihydrogen in the presence of platinum black as catalyst.[2,3] The reaction is heterogeneous: adsorption of the $\mathrm{CODPtR_2}$ complex on the catalyst surface is a prerequisite for reaction, and the platinum(0) generated is incorporated into the surface of the catalyst. The rate-limiting step can be changed from one involving mass transport of dihydrogen to the catalyst surface (the mass transport limited (MTL) regime) to one involving a reaction on the surface of the platinum catalyst (the reaction rate limited (RRL) regime) by changing the pressure of dihydrogen and the temperature of the reaction.

We are developing this reaction as a new method for studying the reactivity of platinum-surface alkyls under conditions representative of those occurring in heterogeneous catalytic reactions, especially the heterogeneous hydrogenation of olefins. The reaction has a number of characteristics that make it attractive for this purpose (eq 1). First, the alkyl groups originally present in the soluble $\mathrm{CODPtR_2}$ complex are transferred intact to the catalyst surface. Thus, it is possible to generate surface alkyls (R*) in which the initial structure of the alkyl moiety is well-defined on a functioning catalyst. Further, when these alkyl groups are isotopically labeled with deuterium ($\mathrm{CODPt(R^D)_2}$), the initial pattern of isotopic labeling in the resulting surface alkyls is determined by the synthesis of the organoplatinum compound. Second, hydrogen (deuterium) atoms (H* or D*) on the surface are mobile. Thus, deuterium lost from $\mathrm{R^D}$ migrates readily to the surface-cyclooctyl moiety, and vice versa.



(1)

Several problems remain to be resolved concerning the mechanism of this reaction. What are the structures and reactivities of the organic moieties on the catalyst surface? How, if at all, do surface alkyls generated with this procedure differ from those generated by hydrogenation of olefins?[4] What influence does the presence of two sets of organic groups (those derived from the COD and Pt-R moieties) have on the course of these reactions?

In this paper we continue to examine this system: in particular, we examine the relative rates with which deuterium is transferred from deuterated alkyls, $\mathrm{R^D}$, into the cyclooctane product (during hydrogenation with $\mathrm{H_2}$) as a function of the structure and position of isotopic substitution of the alkyl moiety (eq 2). These reactions were conducted under MTL conditions.[2] Under these conditions deuterium originally present in the $\mathrm{R^D}$ moiety can be transferred to the surface yielding D*. This D* can be reincorporated into $\mathrm{R^D}$ (either into the original $\mathrm{R^D}$ or into a nearby $\mathrm{R^D}$) at the same position or at a different position, it can be incorporated into cyclooctane, it can combine with H* or with another D* yielding HD or $\mathrm{D_2}$, or it can combine with R′* where R′* is a surface alkyl derived from the solvent. A previous paper demonstrated that H* mediated all of these reactions during the reduction of $\mathrm{(Ol_2)PtR_2}$ complexes.[3] The number of deuterium atoms incor-

$$\mathrm{CODPt(R^D)_2} \xrightarrow[\text{Pt}\atop \underline{n}\text{-Heptane}]{H_2} \text{cyclooctane-}\underline{d}_n \qquad (2)$$

1: $\mathrm{R^D = CD_3}$
2: $\mathrm{R^D = CD_2CH_3}$
3: $\mathrm{R^D = CD_2CH_2CH_3}$
4: $\mathrm{R^D = CD_2C(CH_3)_3}$
5: $\mathrm{R^D = CH_2CD_3}$
6: $\mathrm{R^D = CH_2CH_2CD_3}$
7: $\mathrm{R^D = CH_2C(CD_3)_3}$
8: $\mathrm{R^D = CH_2C(CH_3)_2CH_2CD_3}$
9: $\mathrm{R^D = CH_2C(CH_3)_2CH_2CH_2CD_3}$
10: $\mathrm{R^D = CH_2C(CH_3)_2CH_2CH_2CH_2CD_3}$

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

[3] Miller, T. M.; McCarthy, T. J.; Whitesides, G. M. *J. Am. Chem. Soc.*, previous paper in this issue.

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Table I. Isotopic Compositions of Cyclooctane from Hydrogenation of $CODPt(R^D)_2$ Complexes under MTL Conditions (20 °C) in *n*-Heptane

compd	R^D	cyclooctane isotopic composition (%)					
		d_0	d_1	d_2	d_3	d_4	$\bar{d}^a$
1	CD_3	51	33	13	3.3	0.7	0.71
2	CD_2CH_3	52	32	13	2.9	0.6	0.68
3	$CD_2CH_2CH_3$	59	30	9.5	2.0	0.3	0.56
4	$CD_2C(CH_3)_3$	71	24	4.8	0.6	0.1	0.36
5	CH_2CD_3	86	12	1.4	0.1		0.15
6	$CH_2CH_2CD_3$	96	3.8	0.4			0.050
7	$CH_2C(CD_3)_3$	99	0.9				0.009
8	$CH_2C(CH_3)_2CH_2CD_3$	98	1.6				0.016
9	$CH_2C(CH_3)_2CH_2CH_2CD_3$	100	0.0				0.0
10	$CH_2C(CH_3)_2CH_2CH_2CH_2CD_3$	100	0.0				0.0

[a] $\bar{d}$ is the average number of deuterium atoms per cyclooctane.

porated into cyclooctane from R^D is a fraction of the total number of deuterium atoms lost from R^D. We have not attempted to establish this fraction experimentally. We presume, however, that it remains relatively constant for different structures and patterns of isotopic substitution of the $CODPtR_2$ complexes and that the deuterium composition of the cyclooctane-d_n provides a qualitative measure of the facility with which deuterium is lost from R^{D*}. In particular, these studies permit us to assess the relative rates of transfer of deuterium to the surface from the positions α through ζ to the platinum surface bond of R^{D*}, and thus to assess the relative rates of formation of a number of species having multiple bonds from the R moiety to the surface (alkylidenes, olefins, and metallacycles).

This paper also compares the isotopic compositions of alkanes

$$CODPtR_2 \underset{n\text{-Heptane}}{\xrightarrow[Pt]{D_2}} RD_n \underset{n\text{-Heptane}}{\xleftarrow[Pt]{D_2}} \text{Olefin} \quad (3)$$

R = CH_2CH_3; olefin = $CH_2{=}CH_2$
R = $CH_2CH_2CH_3$, $CH(CH_3)_2$; olefin = $CH_2{=}CHCH_3$
R = $\overline{CH(CH_2)_3CH_2}$; olefin = cyclopentene

obtained by deuteriation of corresponding olefins and organoplatinum complexes (eq 3). These experiments allow us to contrast the reactivities of R* generated by different procedures.

Results

Synthetic Methods. The deuterium-containing compounds **1–10** were prepared with conventional synthetic methods: the alkyl bromides (R^DBr) were commercially available or were prepared with literature procedures, and the organoplatinum complexes were prepared by addition of the corresponding Grignard reagent to dichloro(1,5-cyclooctadiene)platinum(II). The isotopic compositions of the R^D groups were assessed by examination of the ^1H NMR spectra of the $CODPt(R^D)_2$ complexes. The isotopic purity was always >96 atom % D in the position indicated.

Isotopic Analysis. Isotopic compositions of cyclooctane, ethane, and propane were determined by analysis of mass spectral data by the methods described previously.[3] Mass spectral data from samples of cyclopentane containing deuterium were analyzed in the same manner as were the data for cyclooctane.[3] We believe, based on the data reported previously, that the isotopic compositions have an absolute accuracy of ±5%.[3]

Procedures for Heterogeneous, Platinum-Catalyzed Hydrogenation of $CODPt(R^D)_2$ Complexes under MTL Conditions. The catalyst was commercial platinum black and had a surface area of 2.8×10^{-4} μg-atom/g of catalyst as determined by dihydrogen–dioxygen titration.[2] Reductions followed the methods described in a previous paper.[2] 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 $[CODPt(R^D)_2]_0$ = 10–20 mM. Reductions were conducted in *n*-heptane solvent (~4 mL) in 20-mL cylindrical reactors.

The standard temperature for reductions under MTL conditions in this work was 20 °C. We used this temperature to minimize the incorporation of hydrogen from the solvent.[3] Platinum black and *n*-heptane were chosen because they were convenient and because this choice facilitated comparison with the work reported in previous papers.[2,3] We chose MTL conditions for these experiments because the data reported in the previous paper indicated that MTL conditions maximized transfer of deuterium from the R^D group to the cyclooctyl moiety.[2] In particular, the quantity of deuterium transferred from CD_3 to cyclooctane during the reduction of $CODPt(CD_3)_2$ was much less under RRL conditions than under MTL conditions; thus, we believe that the quantities of deuterium transferred from many of the alkyl groups would have been too small to measure under RRL conditions.

We reported previously that reduction of $CODPt(CH_3)_2$ under MTL conditions in *n*-octane-d_{18} yielded cyclooctane and methane containing deuterium.[3] To ensure that the deuterium atoms appearing in cyclooctane were coming from activation of a surface-alkyl species and not from a secondary activation of a C–D bond in the free alkane after reductive elimination from the surface, we examined the cycloctane and methane from reduction of $CODPt(CH_3)_2$ in *n*-heptane containing 0.01 M *n*-octane-d_{18}. There was no deuterium detectable in the methane and cyclooctane from this reduction; therefore, we conclude that any deuterium appearing in the cyclooctane during reduction of $COD(R^D)_2$ complexes must be lost from R^D while it is on the surface.

Relative Rates of Transfer of Deuterium from R^D to Cyclooctyl Moieties on Hydrogenation of $CODPt(R^D)_2$ Complexes. Table I gives isotopic compositions of the cyclooctane obtained by hydrogenation of $CODPt(R^D)_2$ complexes. The most useful parameter to consider in analyzing these data is $\bar{d}$, the average number of deuterium atoms per cyclooctane. Since there are two R^D groups per cyclooctyl moiety, and since deuterium is almost certainly transferred to other positions of the alkyl groups, to HD, and to the solvent under these conditions, $\bar{d}/2$ is the *minimum* number of deuterium atoms lost from an R^D group.

One interesting feature of these data is the inference that deuterium atoms α to the platinum–carbon bond are transferred to the surface more rapidly than those β (R^D = CD_2CH_3, and R^D = CH_2CD_3). This observation contrasts markedly with observations on organoplatinum compounds in solution, for which α-C–H bond activation is essentially never observed.[5-8]

The observation of deuterium exchange for **1–4** and **7** also differs from results obtained from exchange reactions of methane, neopentane, and 2,2,3,3-tetramethylbutane over platinum with deuterium.[9-11] The major product from all of these alkane exchange reactions was alkane-d_1. Multiple exchange in these compounds can only occur via 1,1-diadsorbed, 1,3-diadsorbed, or 1,4-diadsorbed species. Evidently under the conditions used in these exchange reactions, formation of diadsorbed intermediates

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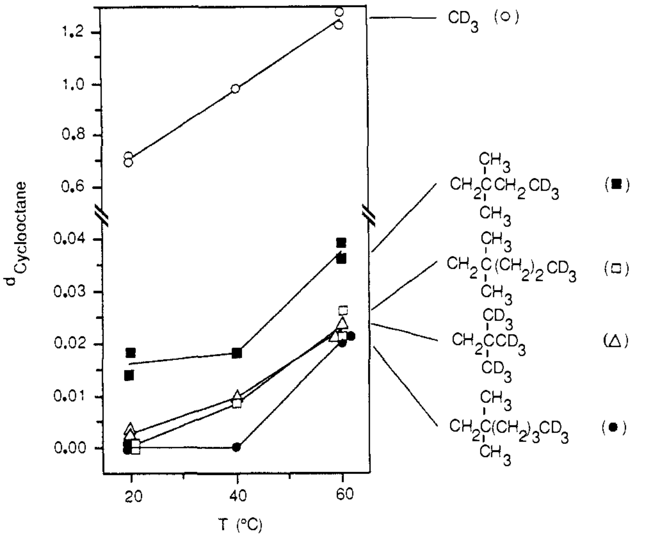
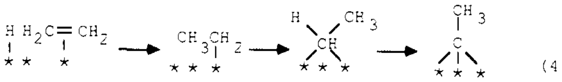


Figure 1. Average number of deuteriums ($\bar{d}$) in cyclooctane produced in the hydrogenation (0.17 atm) of $CODPt(R^D)_2$ complexes versus the temperature of the reaction. The values plotted for **7** ($R^D = CH_2C(CD_3)_3$) are $\bar{d}/3$ to correct for the deuterium content of its R^D. The reactions at 20 and 60 °C were run twice; the two samples of cyclooctane-d_n were analyzed, and the two values of $\bar{d}$ plotted.

was much less rapid than reductive elimination.

Our results are consistent with previous results indicating that ethylidyne is readily formed from ethylene over single crystals of platinum and other metals.[12-16] Rearrangement of surface ethylene to ethylidyne clearly involves some type of α-activation (eq 4).

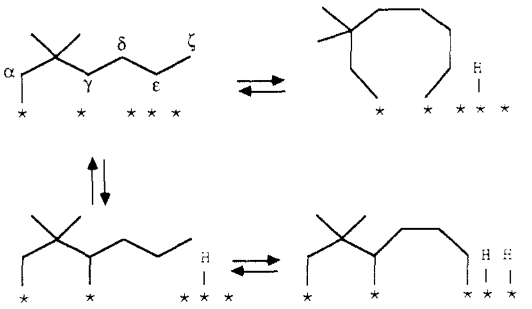

(4)

The quantity of deuterium transferred from the α-carbon of $CODPt(CD_2R)_2$ complexes to cyclooctane decreased as the size of R increased. This result may indicate that for larger surface–alkyl groups, activation of an α-hydrogen (deuterium) is less rapid and/or that irreversible reductive elimination of alkane from the surface is more rapid due to steric repulsion between the alkyl group and the surface.

Less deuterium is transferred to cyclooctane in the reduction of $CODPt(CH_2CH_2CD_3)_2$ than in the reduction of $CODPt(CH_2CD_3)_2$. This result indicates that the sum of the rates of the several processes (including reversible β-hydrogen elimination and addition through surface isopropyl, formation of metallacycles, and formation of π-allyl groups) that would transfer a deuterium from the γ-position of $^*CH_2CH_2CD_3$ to the surface is smaller than the rate of activation of the deuterium β to the platinum in $^*CH_2CD_3$.

Figure 1 demonstrates that $\bar{d}$ increases with temperature. This increase in the quantity of deuterium transferred may reflect an increase in the rate of C–D bond breaking relative to C–H (D) bond formation (that is, of deuterium migration to the surface from R^D relative to reductive elimination of R^D–H from the surface) or an increase in the mobility of D (H) on the platinum surface. We suggest that the former is the more important. The observation of significant quantities of cyclooctane-d_1 through -d_3 in both the deuteriogenation of $CODPt(CH_3)_2$ under MTL (20 °C) and RRL (-20 °C) reaction conditions indicates,[3] as has been found by others,[17,18] that the temperature dependence of the rate of migration of surface hydrogen (deuterium) is small.

Examination of the data in Table I and in Figure 1 shows that more deuterium is transferred to cyclooctane from the δ-position in neopentyl-like $CODPt(R^D)_2$ complexes than from the γ-, ϵ-, or ζ-positions. Activation of C–D bonds γ and δ to platinum in the neopentyl-like $CODPt(R^D)_2$ complexes probably involves direct formation of a surface metallacycle, but activation at more distant positions (ϵ and ζ) might involve either direct cyclometallation forming a large ring or successive reactions involving smaller rings or π-allyl species (eq 5). We have not distinguished between these possibilities. The data in Table I and in Figure 1 make it clear that activation of α-C–D bonds proceeds much more rapidly than activation at any other position. Qualitatively, the rates of activation decrease in the order $\alpha \gg \beta > \delta > \gamma \approx \epsilon \approx \zeta$.



(5)

Studies of the thermal decomposition of complexes having the structure $(PR'_3)_2PtR_2$ have established that the rates of intramolecular activation of C–H bonds decrease in the order $\beta > \delta > \gamma \approx \epsilon \gg \alpha$ (not observed).[5-8] Except for α-activation, the rates of activation of distal C–H bonds in soluble PtR and R* follow the same trend.

Surface intermediates that are 1,5-diadsorbed are widely believed to be important in skeletal rearrangements of alkanes over platinum catalysts.[19-23] Our observation that activation of δ-C–H bonds is more rapid than activation of ϵ-C–H bonds is not incompatible with these results. Skeletal-rearrangement reactions are generaly only observed at higher temperatures than the temperatures at which our reactions were conducted, and the participation of 1,5-diadsorbed intermediates is inferred from the identity of products. Product mixtures from skeletal rearrangement reactions reflect the rates of steps that break and form C–C bonds; these steps do not play a role in the C–H bond-activation processes that we are observing.

Procedures for the Heterogeneous, Platinum-Catalyzed Hydrogenation of Organoplatinum Complexes and Alkenes with Deuterium under RRL Conditions. These reductions were carried out with P_{D_2} = 2.3 atm, T = -20 °C, S_{Pt} = 8.7 μg-atom (30 mg of platinum black), ω = 1200 RPM, and $[\text{substrate}]_0$ = 10–20 mM with *n*-heptane (~4 mL) as solvent in 20-mL cylindrical reactors. The hydrogenation of $CODPt(CH_3)_2$ is reaction rate limited under these conditions,[2] and the $CODPtR_2$ and reductions of the CODPtRR′ complexes used here are almost certainly reaction rate limited also. Under these conditions, there is no detectable exchange involving the C–H(D) bonds of the solvent. We do not know whether reductions involving the olefins were influenced by mass transport of dihydrogen. We chose RRL conditions rather than MTL conditions in these experiments in order to generate the simplest possible distribution of deuteri-

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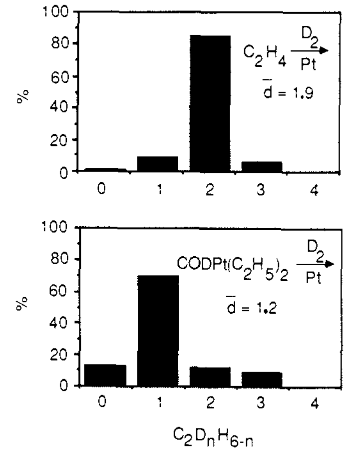
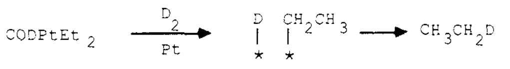


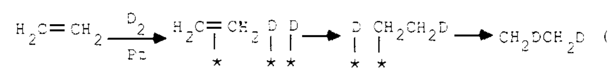
Figure 2. The isotopic composition of ethanes derived from the deuteriogenation (−20 °C, 2.3 atm) of (upper) ethylene and (lower) CODPt(CH$_2$CH$_3$)$_2$.

um-labeled products. MTL conditions prolong the lifetime of the platinum–surface alkyls, and thus increase the opportunity for exchange of hydrogen (deuterium) between the platinum surface and the surface alkyl. MTL conditions were used to obtain the data in Table I, where the exchange was desirable. In these studies, we wished to minimize exchange to simplify interpretation of the data.

Comparison of the Ethane-*d*$_n$ Produced in the Reduction of CODPt(CH$_2$CH$_3$)$_2$ and Ethylene with D$_2$. We compared the catalytic reduction of CODPt(CH$_2$CH$_3$)$_2$ and ethylene with D$_2$ over platinum black as part of our general interest in comparing platinum–surface alkyls formed in these two reactions.[4] At the simplest level of anticipation, we might expect the deuterium content of the ethanes produced in the two reactions to differ by one (eq 6, 7). In reality, several factors will complicate the isotopic compositions. First, surface ethyl groups in both reactions can exchange α- and β-hydrogens with H* (D*). Second, the ratios of surface deuterium to hydrogen (D*/H*) are probably not identical during reduction of CODPt(CH$_2$CH$_3$)$_2$ and ethylene.



$$\mathrm{CODPtEt_2} \xrightarrow[\mathrm{Pt}]{\mathrm{D_2}} \underset{*}{\overset{\mathrm{D}}{|}}\ \underset{*}{|}\!\mathrm{CH_2CH_3} \longrightarrow \mathrm{CH_3CH_2D} \quad (6)$$



$$\mathrm{H_2C{=}CH_2} \xrightarrow[\mathrm{Pt}]{\mathrm{D_2}} \mathrm{H_2C}\underset{*}{\overset{=}{|}}\mathrm{CH_2}\ \underset{*}{\overset{\mathrm{D}}{|}}\ \underset{*}{\overset{\mathrm{D}}{|}} \longrightarrow \underset{*}{\overset{\mathrm{D}}{|}}\ \underset{*}{|}\!\mathrm{CH_2CH_2D} \longrightarrow \mathrm{CH_2DCH_2D} \quad (7)$$

In the previous work we found that the average deuterium content of cyclooctane from the deuteriogenation of CODPt(CH$_3$)$_2$ was substantially higher than that from the deuteriogenation of COD and that the hydrogen lost from cyclooctadiene during the deuteriogenation of CODPt(CH$_3$)$_2$ appears as HD and H$_2$.[3] This result was attributed to greater reversibility of addition of D$_2$ to the surface during reduction of CODPt(CH$_3$)$_2$. Thus, more hydrogen is lost from cyclooctadiene as HD, and D*/H* is probably higher, during the deuteriogenation of CODPt(CH$_3$)$_2$ than of COD.

Isotopic compositions of the ethane-*d*$_n$ produced in these two reactions are summarized in Figure 2. As anticipated, the major product (69 ± 7%) from CODPtEt$_2$ is ethane-*d*$_1$; the major product (85 ± 9%) from ethylene is ethane-*d*$_2$. The ethane from CODPtEt$_2$ shows $\bar{d} = 1.2 \pm 0.1$. Methane from deuteriogenation of CODPt(CH$_3$)$_2$ under these conditions contained on average 1.1 deuterium atoms.[3] We believe that the small excess of deuterium in methane and ethane from deuteriogenation of CODPt(CH$_3$)$_2$ and CODPtEt$_2$ is due to loss of hydrogen atoms in the alkyl group by α-elimination. The average deuterium content of ethane derived from reduction of ethylene with D$_2$ ($\bar{d} = 1.9 \pm 0.2$) is within experimental error of the expected result. The quantities of ethane-*d*$_n$ produced from deuteriogenation of ethylene are comparable to the quantities of ethane-*d*$_{n-1}$ produced from deuteriogenation of CODPtEt$_2$. Thus, the relative rates of reductive elimination as ethane and exchange with D* (H*) for the ethyl groups produced by these two reactions appear to be similar.

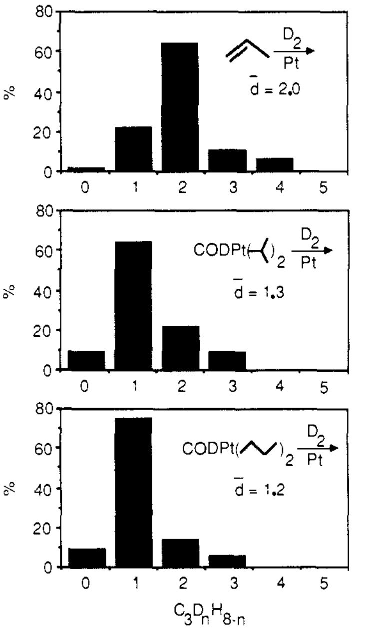


Figure 3. The isotopic composition of propanes from the deuteriogenation (−20 °C, 2.3 atm) of (upper) propene, (middle) CODPt(CH(CH$_3$)$_2$)$_2$, and (lower) CODPt(CH$_2$CH$_2$CH$_3$)$_2$.

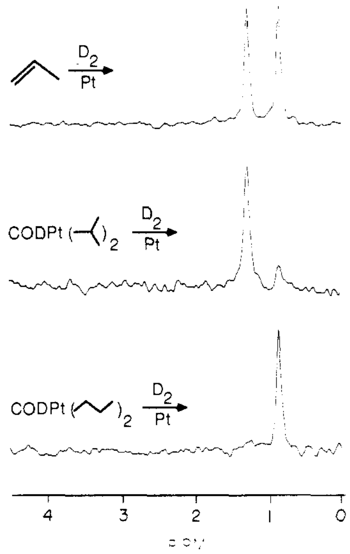


Figure 4. ^{2}H{^{1}H} NMR spectra (46.03 MHz) of propanes obtained by deuteriogenation (−20 °C, 2.3 atm) of (upper) propene, (middle) CODPt(CH(CH$_3$)$_2$)$_2$, and (lower) CODPt(CH$_2$CH$_2$CH$_3$)$_2$. The spectra were measured in CHCl$_3$ and are referenced to ^{2}H present at natural abundance in the CHCl$_3$ (δ = 7.24).

Comparison of the Propane-*d*$_n$ Produced in the Reduction of CODPt(CH$_2$CH$_2$CH$_3$)$_2$, CODPt(CH(CH$_3$)$_2$)$_2$, and Propene with D$_2$. Figure 3 summarizes the isotopic compositions of the propane-*d*$_n$ produced in these three reactions. The propane from CODPt(CH$_2$CH$_2$CH$_3$)$_2$ is relatively cleanly propane-*d*$_1$; that from both CODPt(CH(CH$_3$)$_2$)$_2$ and propene shows broader isotopic distributions.

The observation of approximately 25% propane-*d*$_2$ from reduction of CODPt(CH(CH$_3$)$_2$)$_2$ raised a question concerning the position of the second deuterium. Deuterium NMR spectroscopy indicates that some of this deuterium is introduced at C$_1$ (Figure 4); the peak at δ 0.9 is small but larger than the peak at δ 1.3 for propane derived from CODPt(CH$_2$CH$_2$CH$_3$)$_2$ (if there is a peak at all in this spectrum at δ 1.3). The propane generated from CODPt(CH$_2$CH$_2$CH$_3$)$_2$ appears to be deuteriated only at C$_1$; the approximately 10% *d*$_2$ isotopomer must be predominately CH-

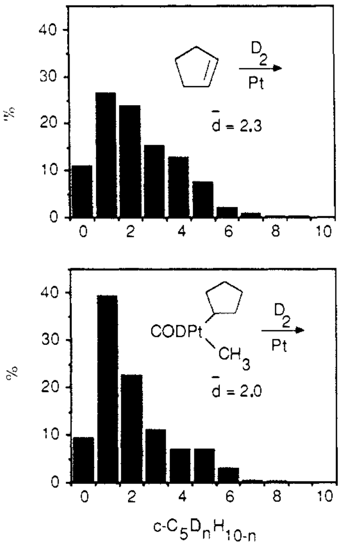


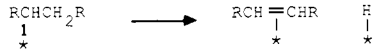
Figure 5. The isotopic composition of cyclopentanes from the deuteriogenation (−20 °C, 2.3 atm) of (upper) cyclopentene and (lower) $\mathrm{CODPt(CH_3)(\overline{CH(CH_2)_3CH_2})}$.

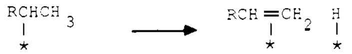
$D_2CH_2CH_3$. The absence of propane-d_4 or more highly deuteriated isotopomers is in accord with the absence of exchange at C_2 indicated by the ^2H NMR spectrum. The ^2H NMR spectrum of the deuteriated propanes generated from propene is of interest primarily in indicating that a 1:1 ratio of deuteriation at $C_{1(3)}$ and C_2 is maintained even though the distribution of isotopomers detected by mass spectroscopy is significantly broad (only approximately 60% of the mixture is propane-d_2).

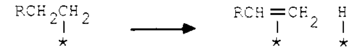
These experiments yield two important conclusions concerning the reduction of $CODPtR_2$ complexes. First, under RRL conditions, the regiochemistry of the platinum–carbon bond of the PtR_2 moiety is maintained when the alkyl groups are transferred to the platinum surface: *n*-propyl and isopropyl do not rapidly interconvert. Second, exchange of hydrogens β to platinum appears to be more rapid for secondary surface alkyls than for primary surface alkyls: there is more deuterium at C_1 in propanes from $\mathrm{CODPt(CH(CH_3)_2)_2}$ than at C_2 in propanes from $\mathrm{CODPt(CH_2CH_2CH_3)_2}$.

Comparison of the Cyclopentane-d_n Produced in the Reduction of $\mathrm{CODPt(CH_3)(\overline{CH(CH_2)_3CH_2})}$ and Cyclopentene with D_2. We were not able to prepare $\mathrm{CODPt(\overline{CH(CH_2)_3CH_2})_2}$: it, as many other sterically congested derivatives of the CODPt[11] moiety, is not isolable.[7] We were, however, able to prepare a stable platinum(II) derivative of cyclopentane by making the second alkyl group small: viz, $\mathrm{CODPt(CH_3)(\overline{CH(CH_2)_3CH_2})}$. This compound and cyclopentene were reduced catalytically with D_2 (Figure 5). The cyclopentane from both reductions consisted of a much broader range of isotopomers than the ethanes-d_n and propanes-d_n produced from deuteriogenations of ethylene, propene, $\mathrm{CODPt(CH_2CH_3)_2}$, $\mathrm{CODPt(CH_2CH_2CH_3)_2}$, or $\mathrm{CODPt(CH(CH_3)_2)_2}$. The observation that approximately 30% of the cyclopentane generated from the organoplatinum compound contains three or more deuterium atoms indicates that β-C–H exchange must be important in surface cyclopentyl: if only α-C–H exchange occurred, the maximum extent of deuteriation would be d_2.

It is evident that the range of isotopomers of cyclopentane is broader than the range of isotopomers of propane from reduction of either their parent organoplatinum complexes or alkenes. This result could be rationalized in two ways. First, it is possible that β-hydride elimination for a surface cyclopentyl group (eq 8) is indeed faster than that for a surface secondary alkyl of a different structure (isopropyl), perhaps reflecting the greater stability of the dialkyl-substituted olefin. Alternatively, β-hydride elimination from *both* surface secondary alkyl groups (cyclopentyl and isopropyl, eq 8 and 9) might be comparatively fast but β-hydride elimination from surface primary alkyl groups relatively slow (eq 10). In this event, the fact that isotopic exchange observed during conversion of the isopropylplatinum moieties to propane is less than that during conversion of cyclopentylplatinum moieties to cyclopentane would reflect conversion of surface isopropyl to surface *n*-propyl, with "trapping" of these groups in the relatively stable primary alkyl form. In short, it is unclear whether the relatively extensive isotopic exchange observed for cyclopentylplatinum is due primarily to the fact that the alkyl–platinum bond itself is secondary or that the vicinal C–H bond is secondary. Maier has found that activation of a secondary C–H bond over platinum was more likely to lead to multiple exchange than activation of a primary C–H bond, and he has discussed similar rationalizations.[9]


$$\underset{*}{\mathrm{RCH}}\mathrm{CH_2R} \longrightarrow \underset{*}{\mathrm{RCH{=}CHR}} \quad \underset{*}{\mathrm{H}} \qquad (8)$$

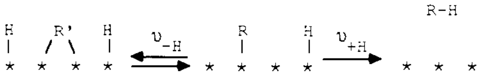

$$\underset{*}{\mathrm{RCH}}\mathrm{CH_3} \longrightarrow \underset{*}{\mathrm{RCH{=}CH_2}} \quad \underset{*}{\mathrm{H}} \qquad (9)$$


$$\mathrm{RCH_2}\underset{*}{\mathrm{CH_2}} \longrightarrow \underset{*}{\mathrm{RCH{=}CH_2}} \quad \underset{*}{\mathrm{H}} \qquad (10)$$

Another purpose of the experiment with $\mathrm{CODPt(CH_3)(\overline{CH(CH_2)_3CH_2})}$ was to determine whether the broad distribution of isotopomers observed in cyclooctane obtained from reduction of either COD or $\mathrm{CODPt(CH_3)_2}$ with D_2 over platinum should be attributed to the fact that these compounds are diolefins (with obvious opportunities for forming surface π-allyl intermediates) or that they are cycloalkanes; the fact that a cyclopentylplatinum moiety yields cyclopentane with a broad range of isotopic composition suggests that the latter explanation is the more important.

Discussion

This work used isotopic labeling experiments to characterize the platinum-surface alkyls (R*) generated by adsorption of $CODPtR_2$ complexes on the surface of a platinum black catalyst. We interpret the results of these experiments—measurements of the isotopic compositions of alkanes in which the deuterium label originated either in D_2 or in a deuteriated PtR^D moiety—in terms of a competition between two reactions (eq 11): irreversible reductive elimination of alkane and reversible transfer of hydrogen


$$\overset{\mathrm{H}}{*}\;\overset{\mathrm{R'}}{*\;*}\;\overset{\mathrm{H}}{*} \underset{}{\overset{\nu_{-\mathrm{H}}}{\rightleftarrows}} \overset{\mathrm{R}}{*}\;*\;\overset{\mathrm{H}}{*} \xrightarrow{\nu_{+\mathrm{H}}} \overset{\mathrm{R-H}}{*\;*\;*\;*} \qquad (11)$$

(deuterium) from the R* group to the surface by cleavage of a C–H bond. When the rate ν_{+H} for the formation of alkane is rapid relative to the rate ν_{-H} for C–H activation, little isotopic exchange occurs; when the magnitudes of these rates are reversed, R* can incorporate deuterium atoms present as mobile D* and deuterium atoms present in R^D can be transferred to the surface.

We infer a number of characteristics of the surface alkyls produced from $CODPtR_2$ based on this mechanistic proposal.

1. The order of decreasing rates ν_{-H} of C–H activation for the platinum–surface system $*(CH)_\alpha(CH)\beta\cdots$ is $\alpha \gg \beta > \delta > \gamma \approx \epsilon \approx \zeta$. The fact that α-C–H activation is significantly faster than β-C–H activation (that is, perhaps five times faster in comparable systems) is especially interesting. Extensive studies of the thermal decomposition of complexes of the structure $(R'_3P)_2PtR_2$ in solution have established the order $\beta > \delta > \gamma \gg \alpha$: in fact, α-elimination has not been observed with soluble complexes.[5-8] More limited data suggest that β-C–H activation is more rapid in surface secondary alkyls: cyclooctyl*, cyclopentyl*, and isopropyl* exchange β-hydrogens more rapidly than do *n*-ethyl* or *n*-propyl*.

2. The rates of α-C–H activation in surface alkyls having the structure RCH_2* appear to decrease with increasing size of R.

3. In one case (isopropyl* versus *n*-propyl*) regioisomeric surface alkyls largely retained their separate identities. Examination of the mixture of isotopomers generated on reduction of a cyclopentylplatinum(II) moiety with D_2 indicated, however, that

Table II. Mass Spectral Data for Ethane-d_n (n = 0–3)

compd	m/e						rel sensitivity	basis sets for ethanes	
	28	29	30	31	32	33			
C_2H_6	100	21.3	21.9	0.54			1.00	X[a]	X[b]
CH_2DCH_3	55.2	100	20.2	27.9	0.27		0.781	X	X
CH_2DCH_2D	49.1	93.7	100	25.6	37.4	1.0	0.567	X	
CHD_2CH_3	35.4	100	76.2	22.5	33.7	0.77	0.648		X
CD_3CH_3	20.2	31.8	100	23.1	12.7	26.4	0.937	X	X

[a] The ethane-d_n in this column were used as the basis set for the determination of the isotopic composition of ethanes derived from ethylene. [b] The ethane-d_n in this column were used as the basis set for the determination of the isotopic composition of ethanes derived from CODPt$(CH_2CH_3)_2$.

positional isomerism was more rapid in this system and that it may not always be possible to maintain distinct isomeric surface alkyls interconvertible by β- or α-C–H activation. Even under RRL conditions (−20 °C), it was not possible to suppress α- or β-C–H activation completely. We have not carried out studies at lower temperatures and higher pressures of H_2 (D_2) to see if these conditions can further limit the competition of ν_{-H} with ν_{+H}.

Our studies of the catalytic hydrogenation of $(Ol_2)PtR_2$ complexes are still incomplete, but the available data are compatible with three important mechanistic propositions:

1. The Pt–R groups present in the soluble $(Ol_2)PtR_2$ complexes are converted into platinum–surface alkyls R* by adsorption on the catalyst surface.

2. These surface alkyls R* are similar in their reactions to surface alkyls generated by catalytic hydrogenation of olefins: that is, for example, Et* from CODPtEt$_2$ is similar to Et* from ethylene.

3. The reactivities of R* and soluble RPt differ markedly in their rates of α-activation, but their rates of β- through ϵ-activation parallel each other.

Future work will continue to use the heterogeneous catalytic reduction of $(Ol_2)PtR_2$ complexes over platinum to prepare new R*, to examine the reactivities of R*, and to explore the connections between these reactivities and the reactivities of surface alkyls important in heterogeneous catalytic reactions such as olefin hydrogen and alkane isomerization.

Experimental Section

General. The procedures used for the preparation of complexes and in the conduct of reductions were generally the same as those in the previous two papers.[2,3] Dideuterium was purchased from Airco and ethylene and propene were purchased from Matheson and used as received. Cyclopentene (Aldrich) was passed through alumina prior to its use.

Iodomethane-d_3 (99 atom % D, Aldrich), bromoethane-*1,1*-d_2 (98 atom % D, Cambridge Isotope Lab, CIL), bromoethane-*2,2,2*-d_3 (98 atom % D, CIL), and 1-bromopropane-*3,3,3*-d_3 (98 atom % D, CIL) were purchased from the suppliers listed. 1-Butanol-*4,4,4*-d_3 was prepared in 40% yield from ethylmagnesium-*2,2,2*-d_3 bromide and ethylene oxide.[24] 1-Bromobutane-*4,4,4*-d_3 was prepared by reaction of 1-butanol-*4,4,4*-d_3 with HBr and H_2SO_4.[25] Neopentyl-d_9 bromide and neopentyl-d_2 bromide were prepared by literature procedures.[26] The 1-bromo-2,2-dimethylalkanes were all prepared by the same modification of literature procedures involving alkylation of *tert*-butylisobutyraldimine, hydrolysis, reduction to the alcohol, tosylation, and displacement with lithium bromide.[8,27–30]

Synthesis of (1,5-Cyclooctadiene)dialkylplatinum(II) Complexes. The Grignard reagents from 1-bromo-2,2-dimethylalkanes were prepared in refluxing THF. New CODPtR$_2$ complexes were prepared with the procedure for the preparation of CODPt(cyclohexylmethyl)$_2$ given previously.[2] Chloro(1,5-cyclooctadiene)methylplatinum(II),[31] (1,5-cyclooctadiene)bis(methyl-d_6)(platinum(II)(**1**),[31] (1,5-cyclooctadiene)diethylplatinum,[32] (1,5-cyclooctadiene)bis(ethyl-*1,1*-d_2)platinum(II) (**2**),[32] (1,5-cyclooctadiene)bis(neopentyl-*1,1*-d_2)platinum(II) (**4**),[26] (1,5-cyclooctadiene)bis(ethyl-*2,2,2*-d_3)platinum(II) (**5**),[32] (1,5-cyclooctadiene)bis(neopentyl-d_9)platinum(II) (**7**)[26] and (1,5-cyclooctadiene)bis(2-propyl)platinum(II)[33] were prepared by the literature procedures. All liquid organoplatinum complexes were purified by column chromatography on silica gel with pentane as the eluent. Deuteriated analogues of CODPtR$_2$ complexes were characterized by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra were in all cases consistent with the assigned structure.

Reductions of (1,5-Cyclooctadiene)dialkylplatinum(II) Complexes for Isotopic Interchange Experiments. The methods for controlling the 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 works.[2,3] *n*-Heptane was the usual solvent. The kinetics of these reductions were not usually followed, but the reactions were allowed to reach completion assuming the correctness of the rates described previously.[2] Reductions under mass transport limited (MTL) conditions were carried out at 20 °C rather than 40 °C in order to minimize the incorporation of hydrogen from the solvent. Because there was not enough H_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 as described previously.[2] The quantity of substrate (including olefins) reduced was 30–40 μmol; thus, the initial concentration of substrate was ca. 10 mM.

Mass Spectroscopy of Hydrocarbons. Mass spectra of alkanes were measured on a Hewlett Packard 5992A GC/MS as described previously.[3] Isotopic compositions for cyclooctane were calculated from mass spectral data as described previously.[3] Relative abundances were measured for m/e 28–36 for samples of ethanes, m/e 43–49 for propanes, and m/e 70–80 for samples of cyclopentanes.

Ethane-d_n (n = 0–3) and propane-d_n (n = 0–4) were prepared to permit deconvolution of the mass spectral data for unknown mixtures of deuteriated alkanes by using procedures similar to those described previously for the preparation of methane-d_n.[3] Ethane-d_0 and propane-d_0 were obtained from Matheson. Ethane-d_1 was obtained by treatment of bromoethane (1.0 mmol) with 0.5 mL of Super-deuteride. 1,2-Ethane-d_2 was obtained by addition of 1,2-dibromoethane (1.0 mmol) to 1.5 mL of Super-deuteride. 1,1-Ethane-d_2 was obtained either by addition of 1,1-bromoethane-d_2 (1.0 mmol) to 0.5 mL of Super-hydride or by addition of concentrated HCl to CODPt$(CD_2CH_3)_2$. 1,1,1-Ethane-d_3 was also obtained by either addition of 2,2,2-bromoethane-d_3 to 0.5 mL of Super-hydride or by addition of concentrated HCl to CODPt$(CH_2CD_3)_2$. The mass spectra of samples of ethane-d_2 and ethane-d_3 obtained by these two routes were indistinguishable.

Propane-*1*-d_1, propane-*2*-d_1, and propane-*1,1,1,3*-d_4 were obtained by treatment of 1.0 mmol of 1-bromopropane, 2-bromopropane, and 1-bromopropane-*3,3,3*-d_3, respectively, with 0.5 mL of Super-deuteride. Propane-*1,2*-d_2 was prepared by treatment of 1.0 mmol of 1,2-dibromopropane with 1.5 mL of Super-deuteride. Propane-*1,1,1*-d_3 and propane-*1,1*-d_2 were obtained by treatment of a pentane solution of CODPt$(CH_2CH_2CD_3)_2$ and CODPt$(CD_2CH_2CH_3)_2$ with concentrated HCl.

Mass Spectra and Relative Sensitivities for Ethane-d_n and Propane-d_n. The different isotopically substituted alkane-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 purities of the starting materials in the manner described previously.[3] Mass spectra of ethanes and propanes after correction for isotopic impurities are reported in Tables II and III.

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Table III. Mass Spectral Data for Propanes-d_n (n = 0–4)

compd	*m/e* 43	44	45	46	47	48	rel sensitivity	basis sets for propanes		
C_3H_8	90.8	100	3.4				1.00	X[a]	X[b]	X[c]
$CH_2DCH_2CH_3$	15.0	97.1	100	3.0			0.974			X
CH_3CHDCH_3	22.9	78.2	100	3.2			1.03	X	X	
$CHD_2CH_2CH_3$	38.2	12.0	100	100	3.3		0.884			X
$CH_2DCHDCH_3$	33.7	22.0	75.6	100	4.2		0.951	X	X	
$CD_3CH_2CH_3$	35.7	42.6	25.7	99.1	100	2.6	0.795	X	X	X
$CD_3CH_2CH_2D$	25.6	37.1	37.9	20.2	100	93.3	0.821	X	X	X

[a] The propane-d_n in this column were used as the basis set for the determination of the isotopic composition of propanes derived from propene. [b] The propane-d_n in this column were used as the basis set for the determination of the isotopic composition of propanes derived from $CODPt(CH(CH_3)_2)_2$. [c] The propane-d_n in this column were used as the basis set for the determination of the isotopic composition of propanes derived from $CODPt(CH_2CH_2CH_3)_2$.

Solutions of known quantities of $CODPtR_2$ (R = CH_2CH_3, or $CH_2CH_2CH_3$) and $CODPt(R^D)_2$ (R^D = CD_2CH_3, CH_2CD_3, $CD_2CH_2CH_3$ or $CH_2CH_2CD_3$) in hexane were reacted with concentrated HCl and the resulting mixture of RH and R^DH 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 II and 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. For instance the best fit for the isotopic composition of a mixture of ethane-d_2 and ethane-d_0 was obtained when the mass spectrum for the former was multiplied by 0.648. Relative sensitivities for ethane-d_1, 1,2-ethane-d_2, and ethane-d_4 and propane-d_1, 1,2-propane-d_2, and propane-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 alkane-d_0, -d_2, and -d_3 and the number of deuterium atoms in the alkane. Thus, the basis sets used for the determination of isotopic compositions of mixtures of deuteriated ethanes and propanes are given by the mass spectra in Tables II and III multiplied by the relative sensitivities.

Because the propanes from deuteriogenation of propene, $COD(CH_2CH_2CH_3)_2$, and $CODPt(CH(CH_3)_2)_2$ contain different amounts of deuterium at C_1 and C_2, the ethanes from deuteriogenation of $CODPt(CH_2CH_3)_2$ and ethylene probably contain different amounts of 1,1-ethane-d_2 and 1,2-ethane-d_2, and the mass spectra of these compounds are distinct, different sets of authentic ethane-d_n and propane-d_n were used as basis sets for calculations of isotopic compositions. In the case of ethanes, we chose the isotopomers based on the expected distribution of deuterium, that is, 1,2-ethane-d_2 was used rather than 1,1-ethane-d_2 in analysis of ethane from deuteriogenation of ethylene. In the case of propanes, we chose the isotopomers based on the known (from ^2H NMR spectroscopy) distribution of deuterium (e.g., 1-propane-d_1 was used for propanes from $CODPt(CH_2CH_2CH_3)_2$). The particular sets of isotopomers of ethane-d_n and propane-d_n used as basis sets for each ethane and propane sample are indicated in Tables II and III, respectively.

Determination of the isotopic composition of an unknown sample of ethane or propane was carried out by the method described previously for the calculation of the isotopic composition of an unknown sample of methane.[3]

Isotopic Compositions of Cyclopentanes. Mass spectral data for cyclopentanes were analyzed by the method described previously for cyclooctane.[3] The mass spectrum of cyclopentane has a peak at $(M - 1)^+$ of 4.5% of the value of M^+. No correction was made for the $(M - 1)^+$ peak in the calculation of isotopic abundances and the correction for natural abundance ^{13}C was 5.4%.

^2H NMR Spectroscopy of Propane Samples. After completing a reduction, 0.38 mL (2.9 mmol) of cyclooctene was added to the reactor. The deuterium source was removed, and the reactor was allowed to warm to room temperature and placed under 1 atm of argon. The reaction mixture was stirred vigorously for 1 h. This procedure consumed most of the unreacted D_2. Samples were prepared by closing a 5-mm NMR tube containing $CHCl_3$ and a drop of H_2O with a rubber septum and wiring it on. Five or six 1-mL aliquots of the vapor phase above the liquid of a reduction were injected into the headspace of the NMR tube, and the tube was shaken between additions to facilitate saturation of the solution. The drop of H_2O was added to the NMR sample to exchange the D_2O or HOD present which interfered in the spectra of propanes. ^2H NMR spectra of propane samples were run on a Bruker WM 300 instrument operating at 46.03 MHz with broadband ^1H decoupling and a cycle time of 13.5 s to allow complete relaxation of the deuterium nuclei in the sample ($T_1 < 2.7$ s). The values of T_1 were estimated by the inversion–recovery method for an authentic sample of propane-*1,2*-d_2. The natural abundance deuterium in $CHCl_3$ was used as a chemical-shift reference.

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Supplementary Material Available: Preparation of 1-bromo-2,2-dimethylhexane-*6,6,6*-d_3 and analytical data for new (1,5-cyclooctadiene)dialkylplatinum(II) complexes (2 pages). Ordering information is given on any current masthead page.