Heterogeneous, Platinum-Catalyzed Hydrogenations of (Diolefin)dialkylplatinum(II) Complexes[1]

T. Randall Lee and George M. Whitesides*

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

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The heterogeneous hydrogenation of olefins is perhaps the most extensively studied reaction in heterogeneous catalysis.[2] Despite intense scrutiny, the mechanism by which this reaction proceeds has not been unambiguously characterized. In 1934, Horiuti and Polanyi proposed the first plausible mechanism (Scheme I).[3] This basic scheme still has wide support, although the individual steps are more complex than those depicted in this simple representation. Questions concerning the structures and reactions of the surface alkyls (e.g., A and B in Scheme I) are particularly complicated. Recent reviews summarize the structures of the many proposed intermediates and the pathways leading to them.[4]

As part of an effort to characterize the reactions of surface alkyls (R*) on platinum, we have developed a new type of heterogeneous reaction that generates R* of known *initial* structure under conditions similar to those employed in organic chemistry for the heterogeneous, catalytic hydrogenation of olefins, viz., the hydrogenation of (diolefin)dialkylplatinum(II) complexes ((DO)PtR₂), using platinum black suspended in organic solvents as catalyst (eq 1; Scheme II).[5-13] Adsorption

$$ \underset{}{} \xrightarrow[\text{Pt(0)}]{3\,H_2} \quad + \quad Pt \quad + \quad 2\,RH \qquad (1) $$
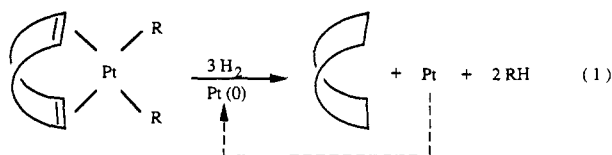
of the components of (DO)PtR₂ onto the surface of platinum generates, as intermediates, surface alkyls (R* and DO*) from the σ-alkyl and π-olefin ligands. The surface alkyls react with surface hydrides to produce alkanes, and the platinum atom in the organometallic complex is incorporated into the surface of the catalyst. The freshly deposited platinum(0) does not alter the bulk morphology of the surface (as determined by SEM) and is catalytically active in subsequent hydrogenations.[5,14]

This reaction is useful for studying the reactivities of alkyl groups on the surface of platinum for five

T. Randall Lee was born in 1962 in Daingerfield, TX. He began his career in research under the guidance of Professor Kenton H. Whitmire at Rice University, where he received his B.A. in 1985. He obtained a Ph.D. from Harvard University in 1991 under the direction of Professor George M. Whitesides. He is currently an NIH postdoctoral fellow at the California Institute of Technology working with Professor Robert H. Grubbs. His research interests include organometallic chemistry, polymer chemistry, surface chemistry, and catalysis.

George M. Whitesides was born in 1939 in Louisville, KY. He received his B.A. from Harvard University in 1960 and his Ph.D. (with J. D. Roberts) from the California Institute of Technology in 1964. He worked at MIT for almost 20 years and is now a member of the Department of Chemistry at Harvard University. His research interests include materials science, surface chemistry, rational drug design, carbohydrate biochemistry, and molecular recognition.

Scheme I
Mechanism Proposed by Horiuti and Polanyi for the Hydrogenation of Ethylene[a,b]
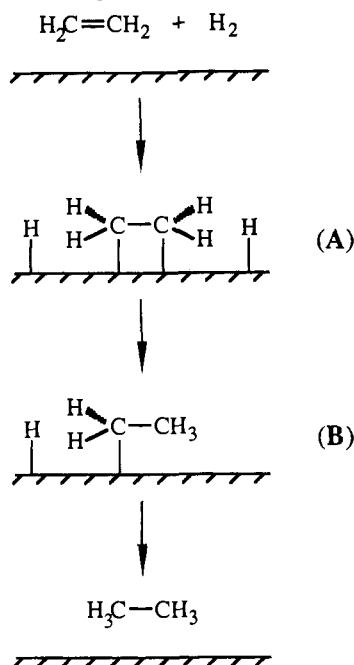
[a] Reference 3. [b] Surface alkyls A ("the initial state") and B ("the half-hydrogenated state") were proposed as intermediates.

reasons. First, because the initial structure of the surface alkyl (R*) is defined by the structure of the R

(2) For pertinent reviews and summaries of heterogeneous hydrogenations of olefins, see: Bartók, M. *Stereochemistry of Heterogeneous Metal Catalysis*; Wiley: New York, 1985. Davis, M. S.; Somorjai, G. A. *Bull. Soc. Chim. Fr.* 1985, 271–287. Burwell, R. L., Jr. *Catal. Rev.* 1972, 7, 25–49. Bond, G. C.; Wells, P. B. *Adv. Catal.* 1964, 15, 92–226. Rylander, P. N. *Hydrogenation Methods*; Academic Press: New York, 1985. Ozaki, A. *Isotopic Studies of Heterogeneous Catalysis*; Kodansha, Ltd.: Tokyo, 1977. Kieboom, A. P. G.; van Rantwijk, F. *Hydrogenation and Hydrogenolysis in Synthetic Organic Chemistry*; Delft University Press: Delft, 1977. For leading references to homogeneous hydrogenations of olefins, see: Brown, J. M. *Angew. Chem., Int. Ed. Engl.* 1987, 26, 190–203. Halpern, J. *Inorg. Chim. Acta* 1981, 50(1), 11–19. James, B. R. *Homogeneous Hydrogenation*; John Wiley & Sons, 1973. McQuillin, F. J. *Homogeneous Hydrogenation in Organic Chemistry*; D. Reidel: Boston, 1976.
(3) Polanyi, M.; Horiuti, J. *Trans. Faraday Soc.* 1934, 30, 1164–1172.
(4) Burwell, R. L., Jr. *Catal. Lett.* 1990, 5, 237–255. Maier, W. F. *Angew. Chem., Int. Ed. Engl.* 1989, 28, 135–145.
(5) Miller, T. M.; Izumi, A. N.; Shih, Y.-S.; Whitesides, G. M. *J. Am. Chem. Soc.* 1988, 110, 3146–3156.
(6) Miller, T. M.; McCarthy, T. J.; Whitesides, G. M. *J. Am. Chem. Soc.* 1988, 110, 3156–3163.
(7) Miller, T. M.; Whitesides, G. M. *J. Am. Chem. Soc.* 1988, 110, 3164–3170.
(8) Lee, T. R.; Whitesides, G. M. *J. Am. Chem. Soc.* 1991, 113, 368–369.
(9) Lee, T. R.; Whitesides, G. M. *J. Am. Chem. Soc.* 1991, 113, 2576–2585.

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Scheme II
Mechanism Proposed for the Heterogeneous Hydrogenation of (Diolefin)dialkylplatinum(II) Complexes
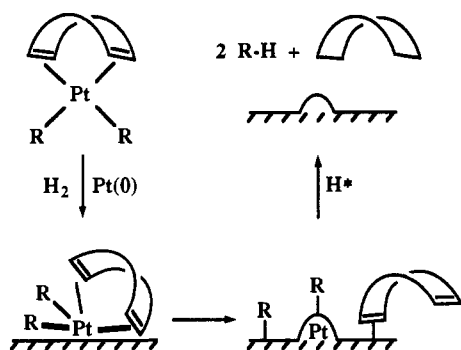
Table I
Standard Conditions for Reductions under MTL and RRL Conditions[a]

parameter	MTL	RRL	remarks
(DO)PtR$_2$ (mg)	10–20	10–20	
solvent (mL)	3–4	3–4	ethyl alcohol or n-heptane
vessel (mL)	20	20	glass pressure tube
P_{H_2} (atm)	0.17	2.4	
T (°C)	40	−20	
catalyst (mg)	40	30–31	platinum black
S_{Pt} (μmol)[b]	11–20	9–15	established by H$_2$/O$_2$ titration
stirring (RPM)	1800	1800	rate of rotation of magnetic stir bar (10 × 6 mm)

[a] MTL = mass transport limited; RRL = reaction rate limited. [b] S_{Pt} is the quantity of platinum surface atoms in a given sample of catalyst.

group in (DO)PtR$_2$, this reaction can generate R* having well-defined patterns of isotopic labeling and known regio- and stereochemistries of bonding to the surface. Second, it can be used to generate surface alkyls (e.g., CH$_3$*, (CH$_3$)$_3$C*, (CH$_3$)$_3$CCH$_2$*) that cannot be generated by the hydrogenation of olefins. Third, this reaction permits entry into the catalytic cycle by generating surface alkyls in the "half-hydrogenated state" (B in Scheme I)[3] and permits these surface alkyls to be compared to those generated by the hydrogenation of olefins. Other routes to surface alkyls corresponding to "half-hydrogenated" olefins (e.g., the hydrogenolysis of carbon–halogen bonds) typically generate R* that cannot be compared directly to those obtained by the hydrogenation of olefins.[15] Fourth, this reaction continually adds fresh platinum atoms to the surface and is thus not readily susceptible to poisoning by small quantities of poisons. Finally, the reaction is convenient to study experimentally because it uses commercially
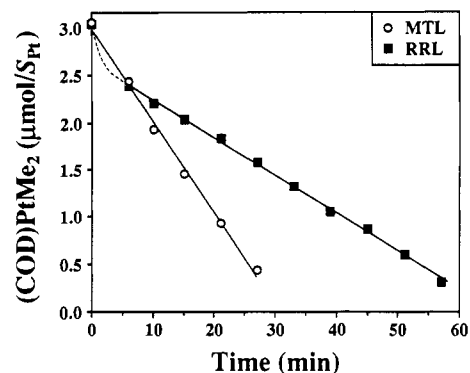
(10) Lee, T. R.; Wierda, D. A.; Whitesides, G. M. *J. Am. Chem. Soc.* 1991, *113*, 8745–8753.

(11) Lee, T. R.; Whitesides, G. M. *Catal. Lett.* 1991, *9*, 461–472.

(12) Lee, T. R.; Laibinis, P. E.; Folkers, J. P.; Whitesides, G. M. *Pure Appl. Chem.* 1991, *63*, 821–828.

(13) McCarthy, T. J.; Shih, Y.-S.; Whitesides, G. M. *Proc. Natl. Acad. Sci. U.S.A.* 1981, *78*, 4649–4651.

(14) For related studies of the chemical vapor deposition of platinum from organoplatinum complexes in the presence of hydrogen, see: Chen, Y. J.; Kaesz, H. D.; Thridandam, H.; Hicks, R. F. *Appl. Phys. Lett.* 1988, *53*, 1591–1592. Xue, Z.; Strouse, M. J.; Shuh, D. K.; Knobler, C. B.; Kaesz, H. D.; Hicks, R. F.; Williams, R. S. *J. Am. Chem. Soc.* 1989, *111*, 8779–8784. Dryden, N. H.; Kumar, R.; Ou, E. C.; Rashidi, M.; Sujit, R.; Norton, P. R.; Puddephatt, R. J.; Scott, J. D. *Chem. Mater.* 1991, *3*, 677–685.

(15) For a notable exception, see: Bent, B. E.; Nuzzo, R. G.; Zegarski, B. R.; Dubois, L. H. *J. Am. Chem. Soc.* 1991, *113*, 1137–1142.

Figure 1. Kinetics of the reductions of (COD)PtMe$_2$ in ethyl alcohol under MTL and RRL conditions. S_{Pt} is the quantity of platinum surface atoms (μmol). Both plots show zero-order dependence on the concentration of the substrate. The rate of disappearance of (COD)PtMe$_2$ observed under MTL conditions is approximately 2 times that observed under RRL conditions. The apparent burst under RRL conditions (— — —) is probably due to experimental artifact.[9]

available catalysts in conventional organic solvents at moderate temperatures (−20 to 40 °C) and pressures of dihydrogen (0.1–3 atm).

Experimental Procedures

Reductions were typically performed using the conditions given in Table I. A 20-mL pressure bottle equipped with a magnetic stirring bar was charged with catalyst, capped with a neoprene septum, purged with argon, and placed in a constant-temperature bath. Solvent (ca. 1 mL) was added to the reactor by syringe, stirring was initiated, and the catalyst was exposed to dihydrogen (or dideuterium) for 10 min. Stirring of the catalyst was stopped, the catalyst was allowed to settle to the bottom of the reactor, and the solvent was carefully removed via cannula. The substrate (10–20 mg dissolved in 3–4 mL of solvent) was added to the reactor via cannula, and the reduction was initiated by stirring. During kinetics studies, stirring was stopped periodically to remove aliquots for analysis by UV and/or GC. For isotopic-labeling studies, the reductions were run to completion without interruption, and the products were analyzed for isotopic composition by GC/MS and/or NMR.

Kinetics

The reductions of (DO)PtR$_2$ complexes are characterized by two kinetic regimes: one in which the rate of reaction is limited by the mass transport of hydrogen to the surface of the catalyst (the mass transport limited regime, MTL), and one in which the rate is limited by a reaction on the surface of the catalyst (the reaction rate limited regime, RRL). We have defined these regimes for reductions of (1,5-cyclooctadiene)dimethylplatinum(II) ((COD)PtMe$_2$, 1) in n-heptane and ethyl alcohol.[5,9] The rate laws obtained in the former solvent are given in eqs 2 and 3, where ω is the rate of rotation of a magnetic stir bar, S_{Pt} is the surface area of the platinum catalyst (determined by H$_2$/O$_2$ titration[5]), and P_{H_2} is the pressure of dihydrogen. Either regime can be chosen by adjusting the temperature and the pressure of dihydrogen to appropriate values (Table I).[5,9]

RRL:

$$-\mathrm{d}l/\mathrm{d}t =$$
$$[0.014 \pm 0.003 \ (\mu\mathrm{mol \ s}^{-1} \ \mathrm{atm}^{-0.38} \ \mu\mathrm{mol_{Pt}}^{-1.2})] \times$$
$$([1]^{0.0\pm0.2})(P_{\mathrm{H_2}}^{0.38\pm0.04})(S_{\mathrm{Pt}}^{1.2\pm0.2})(\omega^{0.0\pm0.3}) \quad (2)$$

MTL:

$$-\mathrm{d}l/\mathrm{d}t =$$
$$[0.086 \; \spadesuit \; 0.012 \ (\mu\mathrm{mol \ s}^{-1} \ \mathrm{atm}^{-1.05})]([1]^{0.0\pm0.2}) \times$$
$$(P_{\mathrm{H_2}}^{1.05\pm0.07})(S_{\mathrm{Pt}}^{0.0\pm0.2}) \times$$
$$[1.0 + (2.3 \times 10^{-5})\omega + (5.5 \times 10^{-7})\omega^2] \quad (3)$$

In both regimes, the kinetics are characterized by zero-order dependence on the concentration of the organometallic substrate (Figure 1).[5,9] Zero-order dependence of the rate on the concentration of substrate is usually observed in heterogeneous hydrogenations of olefins and is interpreted to indicate that the surface of the catalyst is saturated with alkyl groups.[16-21] If valid for the reductions of (DO)PtR₂ complexes, this interpretation has special significance: because the rates of reduction are of similar magnitude in both regimes (Figure 1), the rates of reductive elimination (and thus the average residence times of surface alkyls) are of similar magnitude in both regimes. That is, under the conditions employed (Table I), the rates of reductive elimination in the RRL regime (determined by $\Delta G^{\ddagger}$ and T) and in the MTL regime (determined by the rate of diffusion of H₂ to the surface of the catalyst) are coincidentally very similar. This similarity is helpful in comparing the two regimes.

Evidence of Heterogeneity

Five observations strongly suggest that the reaction occurs on the surface of the platinum catalyst. First, the reaction proceeds at a negligible rate in the absence of bulk platinum(0).[5,22] Exposure of a solution of (DO)PtR₂ to H₂ eventually results in reaction, but the process is autocatalytic and is accompanied by the formation of colloidal and bulk Pt(0).[13] Moreover, the dependence of the rates of reduction on the surface area of the catalyst under RRL conditions (eq 2) suggests a heterogeneous process. (Under MTL conditions, diffusion of H₂ to the surface is rate-limiting; thus, the rates of reduction should be independent of the surface area of the catalyst as indicated in eq 3.) Second, the reaction is completely inhibited by strong catalyst poisons (e.g., sulfides, phosphines, Hg(0), organomercury compounds).[5,22] In addition, it is slowed by strongly absorbing olefins (e.g., cyclooctadiene) until they are consumed by hydrogenation.[5] Third, the mass of the catalyst increases in proportion to the amount

of substrate reduced, a result consistent with our proposal that the platinum atom in the complex becomes part of the surface of the catalyst.[5] Fourth, interchange of deuterium occurs between DO* and R* when the catalyst is suspended in *n*-heptane; this interchange undoubtedly occurs on the surface of the catalyst.[6,7,9] Fifth, the rapid introduction of deuterium from deuterated solvents (ROD) into the product alkanes is best rationalized by a surface reaction involving D* (vide infra).[9]

Mechanism of Adsorption

With the heterogeneity of the reaction established, we can formally write the first step in the catalytic cycle as the adsorption of the (DO)PtR₂ complex. There are two distinct sites in the (DO)PtR₂ complex that can plausibly form a bond with the surface: the platinum atom and the exo face of the diolefin (the face to which the platinum atom *is not* coordinated). Adsorption should be preferred at these sites because (1) the platinum atom is the most polarizable part of the molecule and (2) olefins readily coordinate to the surfaces of noble metals.

We used stereochemical information to distinguish between these two possibilities. In one set of experiments, we compared the location and content of deuterium in the product norbornanes from the reductions by dideuterium of norbornadiene (NBD) to those from similar reductions of (norbornadiene)dimethylplatinum(II) ((NBD)PtMe₂).[6] Equation 4 shows that the reduction of NBD adds deuterium predominantly to the exo face of norbornane. Since the reduction of

$$(4)$$

$$(5)$$
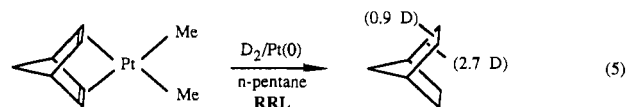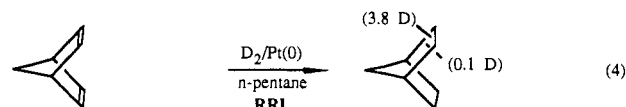
C* bonds proceeds with retention of configuration (vide infra), this result can be rationalized by assuming that free norbornadiene coordinates to the surface via its least hindered exo face. In contrast, the reduction of (NBD)PtMe₂ adds deuterium predominantly to the endo positions of norbornane (eq 5). This result indicates that the norbornadiene moiety in (NBD)PtMe₂ coordinates to the surface via its endo face (the face to which the platinum atom *is* coordinated).

In a second set of experiments, we compared the homohypostrophanes (HOPH) produced from the reductions of homohypostrophene (HOP) to those produced from the reductions of (homohypostrophene)-diethylplatinum(II) ((HOP)PtEt₂).[10] Equations 6 and 7 show that the reduction of HOP incorporates deuterium into the exo positions of HOPH, but the reduction of (HOP)PtEt₂ incorporates deuterium predominantly into the endo positions of HOPH. These results agree qualitatively with those from the experiments involving NBD. Both sets of experiments are consistent with the hypothesis that the adsorption of (DO)PtR₂ complexes occurs at the platinum atom in the organometallic complex.

Formation of R* Occurs with Retention of the Regiochemistry of the Pt–R Bond. In an attempt

(16) Webb, G. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F., Eds.; Elsevier: New York, 19789; Vol 20, pp 1–121.

(17) Hussey, A. S.; Keulks, G. W.; Nowack, G. P.; Baker, R. H. *J. Org. Chem.* 1968, *33*, 610–616.

(18) Kung, H. H.; Pellet, R. G.; Burwell, R. L. *J. Am. Chem. Soc.* 1976, *98*, 5603–5611.

(19) Price, R. H.; Schiewetz, D. B. *Ind. Eng. Chem.* 1957, *49*, 807–812.
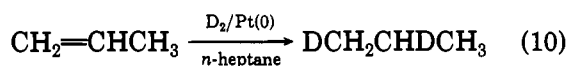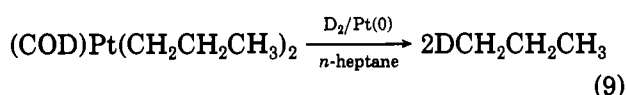
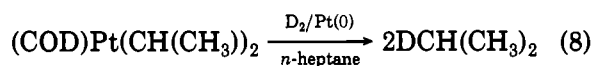(20) Madon, R. J.; O'Connell, J. P.; Boudart, M. *AIChE J.* 1978, *24*, 904–911.

(21) Boudart, M.; Djega-Mariadassou, G. *Kinetics of Heterogeneous Catalytic Reactions*; Princeton University: Princeton, NJ, 1984; pp 180–187.

(22) Whitesides, G. M.; Hackett, M.; Brainard, R. L.; Lavalleye, J.-P. P.; Sowinski, A. F.; Izumi, A. N.; Moore, S. S.; Brown, D. W.; Staudt, E. M. *Organometallics* 1985, *4*, 1819–1830.

$$D_2/Pt(0) \xrightarrow[\text{RRL}]{\text{EtOD}} \quad (6)$$

$$D_2/Pt(0) \xrightarrow[\text{RRL}]{\text{EtOD}} \quad (7)$$
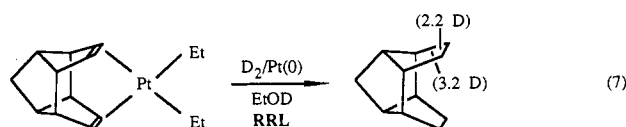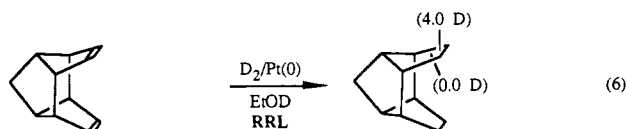
to examine whether the alkyl groups in $(DO)PtR_2$ complexes retain their structural integrity upon transfer to the surface, we compared the propanes obtained by reductions of $(COD)Pt(i\text{-}Pr)_2$ and $(COD)Pt(n\text{-}Pr)_2$ under RRL conditions.[7] Equations 8 and 9 show the major products (>60%) from these reductions; eq 10 shows, for reference, the major product (>60%) from the reduction of propylene. Equations 8 and 9 argue

$$(COD)Pt(CH(CH_3))_2 \xrightarrow[n\text{-heptane}]{D_2/Pt(0)} 2DCH(CH_3)_2 \quad (8)$$

$$(COD)Pt(CH_2CH_2CH_3)_2 \xrightarrow[n\text{-heptane}]{D_2/Pt(0)} 2DCH_2CH_2CH_3 \quad (9)$$

$$CH_2{=}CHCH_3 \xrightarrow[n\text{-heptane}]{D_2/Pt(0)} DCH_2CHDCH_3 \quad (10)$$

that transfer of R groups to the surface of platinum occurs without loss of the regiochemistry initially defined by the bonding of R to platinum in the soluble organometallic complex. Comparison to eq 10 demonstrates one of the advantages of generating surface alkyls from the platinum complexes rather than from olefins: the structures of the surface alkyls derived from the platinum complexes are better defined than those of the surface alkyls derived from olefins.

Formation of R* Occurs with Retention of the Stereochemistry of the Pt–R Bond. In order to use this system to study the stereochemistry of reactions on the surface, we needed to establish whether the transfer of R to the surface occurred with retention or loss of the stereochemistry at C1 of the R group bonded to platinum in the soluble complex. We used information from two studies to examine this issue. First, since the mechanism for reduction of $(DO)PtR_2$ complexes occurs by initial absorption at platinum,[6,8,10,11] we expect the process of adsorption to leave the stereochemistry of the Pt–R bond unaffected. Second, the similar magnitude of the activation energies for the reduction of $(DO)PtR_2$ complexes $(E_a = 15 \pm 2$ kcal/mol for reduction of $(COD)PtMe_2)$[5] and for inversion at a methyl carbon $(E_a = 15\text{–}20$ kcal/mol for S_N2 displacement on MeI and MeBr)[23] suggests that if inversion at carbon occurs in the reductions of $(DO)PtR_2$ complexes, the rates of these reductions should be influenced by structure in ways similar to those established for S_N2 reactions. For the reduction of a series of $(COD)PtR_2$ complexes under RRL conditions, the relative rates are as follows: R = Me (1.0), Et (1.0), i-Pr (0.69), i-Bu (0.40), Np (0.23), and Ph (0.60); for displacement by Cl⁻ with inversion at carbon, the relative rates are as follows: MeI (1.0), EtI (0.090), i-PrI (0.0029), i-BuI (0.0034), NpI (0.000 001 3), and PhI (0.0). The lack of a correlation between these two sets of data

(23) Streiweiser, A., Jr. *Chem. Rev.* 1956, 56, 571–752.

suggests that S_N2 type inversion at carbon does not occur in reductions of $(DO)PtR_2$ complexes.[10]

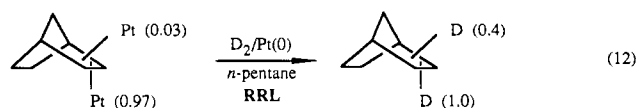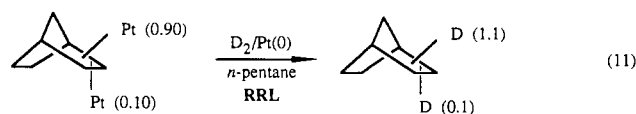## Determination of the Stereochemistry of Reduction of C* Bonds

Defining the stereochemistry of a heterogeneous reaction is a difficult task that usually involves at least one major assumption. In heterogeneous hydrogenations of olefins, for example, the stereochemistry of reduction of the C* bond in the reaction C* → C–H cannot be determined directly because the initial stereochemistry of bonding of the olefin to the surface can only be assumed. We believe that the reductions of $(DO)PtR_2$ complexes, however, generate C* bonds of *well-defined* initial stereochemistry (that is, the stereochemistry present in the $(DO)PtR_2$ complex). These reductions therefore permit a more direct determination of the stereochemistry of the heterogeneous conversion of R* to R–H. This determination depends on our inference that the transfer of the R group in the complex to the surface proceeds with retention of configuration. We believe that this inference is strongly supported by the data (vide supra), but it remains indirect. We do not have a direct, independent measure of the stereochemistry of R*.

Our approach to this problem involved the following.[8,10] We synthesized a mixture containing predominantly (homohypostrophene)neopentyl(*exo*-2-norbornyl)platinum(II) (**Exo**) and one containing predominantly (homohypostrophene)neopentyl(*endo*-2-norbornyl)platinum(II) (**Endo**). The stereochemistries of

Exo   Endo
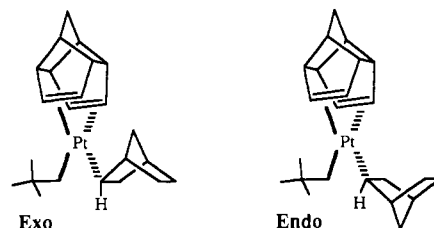
the Pt–norbornyl bonds in these complexes were firmly established by X-ray crystallography.[10] We reduced each mixture with D_2. This process generated, as intermediates, *exo*-2-norbornyl* (from **Exo**) and *endo*-2-norbornyl* (from **Endo**). We examined the location and content of deuterium in the product norbornanes in order to determine the stereochemistry of reduction of the norbornyl* bonds.

Equations 11 and 12 summarize the results of these experiments. Equation 11 describes, for example, the reduction of a mixture of 90% **Exo** and 10% **Endo**.

$$Pt\,(0.90) \quad \xrightarrow[\text{RRL}]{D_2/Pt(0)} \quad \begin{array}{l} D\ (1.1) \\ \\ D\ (0.1) \end{array} \quad (11)$$
$$Pt\,(0.10) \qquad n\text{-pentane}$$

$$Pt\,(0.03) \quad \xrightarrow[\text{RRL}]{D_2/Pt(0)} \quad \begin{array}{l} D\ (0.4) \\ \\ D\ (1.0) \end{array} \quad (12)$$
$$Pt\,(0.97) \qquad n\text{-pentane}$$

These experiments show that the reduction of **Exo** incorporates deuterium only into the exo position of norbornane, while the reduction of **Endo** incorporates deuterium predominantly into the endo position of norbornane. The result from the reduction of *exo*-2-
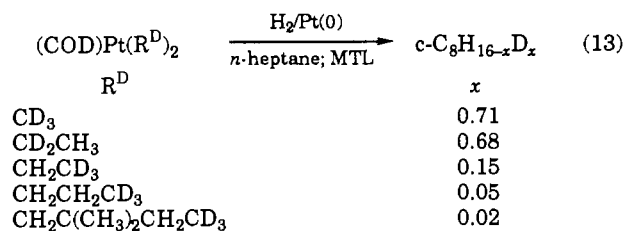
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norbornyl* appears to be stereochemically straightforward, involving simple reductive elimination of *exo*-2-norbornyl* from the surface as the major pathway, and β-hydride activation of the *cis*-C(3)–H (exo) bonds as the only competing reaction. The reduction of *endo*-2-norbornyl* is, however, more complicated. Again, the major pathway appears to be simple reductive elimination. Isomerization of *endo*-2-norbornyl* to *exo*-2-norbornyl* appears to be a competing pathway, probably driven by steric destabilization of the *endo*-2-norbornyl* species. Overall, the results from this study are consistent with a model in which final reductive elimination of C* from the surface occurs with retention of configuration.

Comparison of the Reactivities of Alkyl Groups in Discrete Platinum(II) Complexes to Those on Platinum Surfaces

A major objective of our work has been to establish the relationship between the reactivities of alkyl groups bonded to platinum in homogeneous platinum(II) complexes and those bonded to the surface of platinum. We conducted research under the following premise: if the reactions observed for alkyl groups in soluble organometallic complexes resemble those on the surface of platinum, we should be able to rationalize the heterogeneous processes in terms of single-center or highly localized chemistry. If, however, the reactions observed for the surface alkyls have no relation to those observed for alkyl groups in the homogeneous complexes, we might consider the proposition that bulk metals possess unique reactivities.

Initial work involving the homogeneous complexes established that the relative rates of carbon–hydrogen bond activation of alkyl groups positioned α, β, γ, δ, and ε to platinum was as follows: β > δ > γ ≈ ε ≫ α (not observed).[24-27]

To measure analogous relative rates for surface alkyls, we used the following strategy.[7] We hydrogenated a series of platinum complexes as described in eq 13 and

$$(COD)Pt(R^D)_2 \xrightarrow[\text{n-heptane; MTL}]{\text{H}_2/\text{Pt}(0)} c\text{-}C_8H_{16-x}D_x \quad (13)$$

R^D	x
CD_3	0.71
CD_2CH_3	0.68
CH_2CD_3	0.15
$CH_2CH_2CD_3$	0.05
$CH_2C(CH_3)_2CH_2CD_3$	0.02

examined the content of deuterium in the product cyclooctanes. From the deuterium content, we inferred the relative rates of C–H bond activation of the surface alkyls: α > β > δ > γ ≈ ε. The relative rates of reaction on the surface and in solution are similar except for α C–H bond activation: α activation is the most facile activation process on the surface; it is the least facile process in solution. Perhaps the most plausible origin of this difference is that facile α activation on platinum requires at least two metal centers.

(24) Foley, P.; Dicosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 6713–6725.

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

(26) McCarthy, T. J.; Nuzzo, R. G.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 3404–3410.

(27) Dicosimo, R.; Moore, S. S.; Sowinski, A. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 124–133.
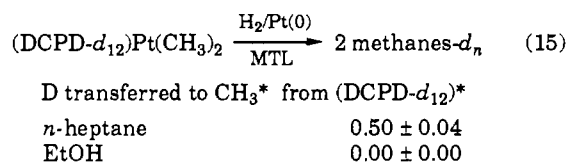
Reductions in Protic Solvents

In our studies of the hydrogenations of olefins and $(DO)PtR_2$ complexes in protic solvents, ROH(D) (where R = H(D) or alkyl), we have found that the exchange of H/D between H(D)* and RO*H*(*D*) is sufficiently rapid that the isotope of hydrogen in the surface hydrides equilibrates essentially completely with the isotope of hydrogen in the solvent (eq 14).[9,28,29] The

$$\text{H}^* + \text{ROD} \rightleftharpoons \text{D}^* + \text{ROH} \quad (14)$$

mechanism of the exchange shown in eq 14 remains unresolved, but we have found that it is independent of the structure of R (where R = D, methyl, ethyl, *n*-propyl, isopropyl, and *tert*-butyl), and it is independent of pH except at very high pH.[29] In addition, it is equally efficient under RRL and MTL conditions.[9,29]

We list here three examples that illustrate the efficiency of this exchange process. First, in reductions of olefins and $(DO)PtR_2$ complexes, the isotope incorporated into the intermediate surface alkyls was largely that present in the solvent (RO*D* or RO*H*) rather than that present in the gas (D_2 or H_2).[9,29] Second, when the hydrogenation of $(COD)Pt(CD_3)_2$ described in eq 13 was carried out in ethyl alcohol (EtOH) instead of *n*-heptane, the cyclooctanes contained only hydrogen.[9] Likewise, in hydrogenations of (dicyclopentadiene-d_{12})dimethylplatinum(II) (($DCPD$-d_{12})PtMe$_2$) in *n*-heptane, deuterium is transferred from $DCPD$-d_{12}* to Me* groups; in hydrogenations of this substrate in EtOH, however, no transfer of deuterium is observed (eq 15).[9] We infer from these results that the inter-

$$(\text{DCPD-}d_{12})\text{Pt}(\text{CH}_3)_2 \xrightarrow[\text{MTL}]{\text{H}_2/\text{Pt}(0)} 2 \text{ methanes-}d_n \quad (15)$$

D transferred to CH_3* from $(DCPD$-$d_{12})$*	
n-heptane	0.50 ± 0.04
EtOH	0.00 ± 0.00

change of deuterium between coadsorbed surface alkyls is completely intercepted by exchange with EtOH. Third, in hydrogenations of *cis*-cyclooctene and $(COD)PtEt_2$ in EtOD under MTL conditions, the major isotopomer of cyclooctane produced is the perdeuterated isotopomer, C_8D_{16}.[9] In order for perdeuteration to occur, the isotopic exchange of hydrogen between EtOD and H* must be faster than the rate of reincorporation of H* into cyclooctyl*.

The Utility of Conducting Hydrogenations in Protic Solvents

In deuterogenations of $(DO)PtR_2$ complexes in aprotic solvents, interpretation of the isotopic distributions of deuterated alkanes is complicated by three types of H/D exchange: (1) between the surface alkyls derived from the diolefin and the R groups, (2) between H(D)* and H_2 (or D_2), and (3) between the surface alkyls and the solvent via activation of the C–H bonds of the solvent.[6,9] Disentangling the multiple isotopic exchange reactions is difficult. We can, however, simplify the overall process by performing the reductions in protic solvents.[9] Consider, for example, reductions using H_2 and ROD: the reducing species present on the

(28) Lee, T. R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1991**, *113*, 369–370.

(29) Lee, T. R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1991**, *113*, 2568–2576.
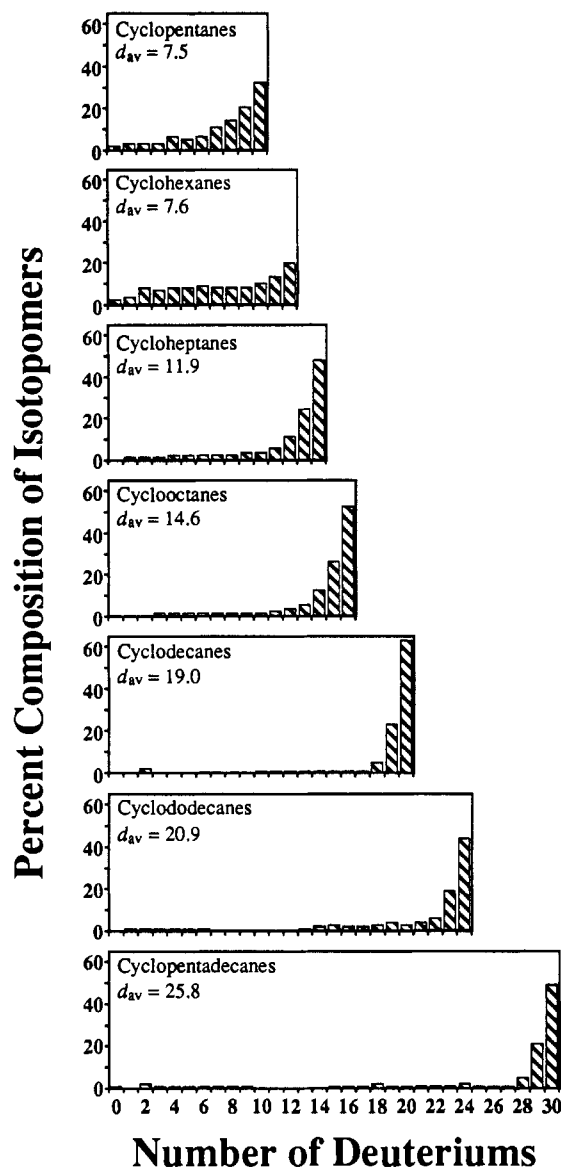
Figure 2. Isotopic distributions and values of d_{av} for the cycloalkanes produced from the reductions of the corresponding cycloolefins (C_nH_{2n-2}) under MTL conditions (75 °C rather than 40 °C) using H_2 and D_2O/THF (1:1, v/v); $pD_{(D_2O)} = 1$.[28]

surface is predominantly (*or exclusively*) D*. The rapid conversion of H* to D* by exchange with ROD simplifies the studies of surface alkyls by intercepting H* generated by any of the three processes of H/D exchange listed above. Moreover, the surface hydrides generated via C–H bond activation of surface alkyls are essentially irreversibly lost from the system into the solvent. For reductions carried out in ROD, therefore, most C* bonds present on the surface of the catalyst become C–D bonds rather than C–H bonds, regardless of the isotopic composition of the reducing agent (H_2 or D_2).

Figure 2 provides a striking example of this phenomenon: we reduced a series of unsubstituted cycloolefins (C_nH_{2n-2}) under MTL conditions (75 °C rather than 40 °C) using H_2 as the reductant and D_2O/THF (1:1, v/v; $pD_{(D_2O)} = 1$) as the solvent.[28] For all cycloolefins, the perdeuterated cycloalkane (C_nD_{2n}) was the major isotopomer produced.

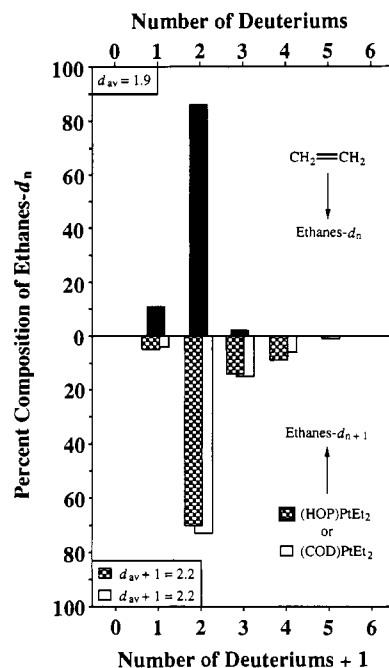The conversion of C–H to C–D by exchange with ROD via the surface provides a useful probe of the

Figure 3. Isotopic distributions of the isotopomers of ethane from the reductions of ethylene (top), and of (COD)PtEt$_2$ and (HOP)PtEt$_2$ (bottom) in EtOD under RRL conditions.[11]

reactivities of surface alkyls. If we examine the isotopic composition of the alkanes produced by the reductions of olefins or (DO)PtR$_2$ complexes in ROD, we can infer the relative rates of the two pathways summarized in eq 16: irreversible reductive elimination of R* groups as alkanes (ν_1), and (formally reversible) exchange of H/D with the surface to generate partially deuterated surface alkyls R^{D*} (ν_2). The rate of exchange (ν_2) reflects the rate of C–H bond activation of the surface alkyls.

(16)
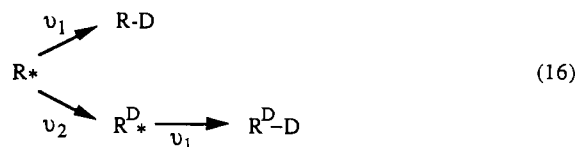
Comparison of Surface Alkyls Derived from (DO)PtR$_2$ Complexes with Those Derived from Olefins

By examining the relative rates of the pathways summarized in eq 16, we can characterize and compare surface alkyls derived from different sources. For example, consider the Et* moieties derived from ethylene, (COD)PtEt$_2$, and (homohypostrophene)diethylplatinum(II) ((HOP)PtEt$_2$). Figure 3 summarizes the isotopic distributions of the ethanes produced from the reductions of these substrates by D_2 in EtOD under RRL conditions.[11] The ethanes obtained from the reduction of ethylene appear similar to those obtained from the reductions of platinum complexes, after correction for one fewer deuterium in the latter. These results suggest that, under RRL conditions, the relative rates of C–H bond activation and reductive elimination as ethane are similar for the Et* moieties derived from each of the substrates.

Under MTL conditions, however, the surface ethyl groups produced from these substrates have markedly different reactivities. Figure 4 summarizes these results.[11] The surface ethyls derived from (COD)PtEt$_2$
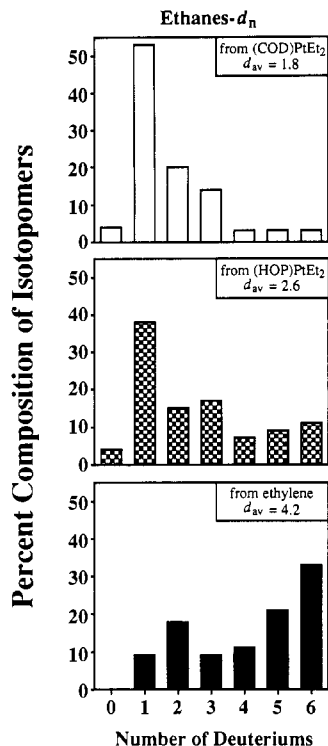
Figure 4. Isotopic distributions of the isotopomers of ethane from the reductions of $(COD)PtEt_2$ (top), $(HOP)PtEt_2$ (middle), and ethylene (bottom) in EtOD under MTL conditions.[11]

have a slower rate of C–H bond activation (relative to the rate of reductive elimination) than those derived from ethylene. This difference is probably largely due to the presence of coadsorbed cyclooctyl* moieties, which readily donate hydrides to the surface of platinum. The excess surface hydrides serve to increase the rate of reductive elimination of the Et* groups from the surface.

The relative rates of exchange and reductive elimination of surface ethyls derived from $(HOP)PtEt_2$ appear intermediate between those derived from ethylene and $(COD)PtEt_2$. The Et* moieties derived from $(HOP)PtEt_2$ more closely model the Et* moieties derived from ethylene than those from $(COD)PtEt_2$, presumably because HOP* is less likely to donate H* to the surface than is COD*. At present, $(HOP)PtR_2$ complexes appear to provide the best precursors for $(DO)PtR_2$-based routes to surface alkyls, and they provide R* most similar to those generated from olefins.

The MTL Regime vs the RRL Regime

In all of the reductions we have studied in ROD, the content of deuterium in the product alkanes was greater

under MTL conditions than under RRL conditions.[9,11,29] Since the rate of reduction (and thus of reductive elimination) is of similar magnitude in both regimes (vide supra), this observation suggests that the rate of C–H bond activation of surface alkyls is faster under MTL conditions than under RRL conditions. Reductions under RRL conditions are typically carried out at –20 °C, and those under MTL conditions at 40 °C. This conclusion is therefore consistent with earlier research, which concluded that rates of C–H bond activation increase with temperature.[30]

Concluding Remarks

Our studies of the heterogeneous hydrogenation of (diolefin)dialkylplatinum(II) complexes demonstrate that by using a combination of organometallic chemistry and catalysis, it is possible to generate structurally well-defined surface alkyls under conditions typically used in organic synthesis. These reactions thus provide a new method of studying surface alkyls using standard physical–organic probes: rate–structure profiles, isotopic labeling, and stereochemistry.

It remains to be established whether this approach can be extended to other reactions and metals. Reactions that require high temperatures run the risk of inducing thermal decomposition or homogeneous reaction of the organometallic species and are thus poor candidates for this approach. Reactions that require specific surface structures or complex surfaces are also poor candidates, and those that do not generate surface alkyls (e.g., the reduction of N_2 or NH_3) are unlikely to benefit from this approach. For reactions that involve surface alkyls and relatively simple metal surfaces (e.g., hydrogenation, hydrogenolysis, isomerization, formation of metal films from OMCVD, Ziegler–Natta polymerization, perhaps Fischer–Tropsch and related reactions), this type of study should be applicable and should provide information complementary to that available from kinetics and vacuum-physics approaches. In addition, the ability of this type of chemistry to form surface organometallic groups should also be preparatively useful in technologies requiring such species, e.g., promotion of adhesion and wetting and control of corrosion and friction.

(30) Anderson, J. R.; Kemball, C. *Proc. R. Soc. London, A* 1954, *226*, 472–489.

Additions and Corrections

R. J. Beuhler, G. Friedlander, and L. Friedman*: Fusion Reactions in Dense Hot Atom Assemblies Generated by Cluster Impact.

Page 198. Recent experiments using crude magnetic analyses of cluster beams after ion acceleration have shown that our original estimates of cluster fusion rates have been overestimated by at least 2 orders of magnitude. These experiments provide direct evidence for artifact beam contamination. Details will be presented in a later publication. Experiments are in progress to determine accurate rates or limits of rates of cluster impact fusion. The new experiments should shed light on the extent to which cluster impacts result in a concentration of energy in a small fraction of atoms in the target.